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TRANSLATION

TANTALUM AND NIOBIUM

By G. V. Samsonov and V. I. Konstantinov

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TANTAL I NIOBIY

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PREFACE

The planned development of the national economy of the USSR in the years 1959 - 1965, accepted by the Twenty-First Congress of the KPSS, marks a wide use of materials with improved and special characteristics and properties, such as, corrosion-resisting and heat-resisting metals, light alloys, semiconductor, ferromagnetic and other materials, focusing attention on the industrial application of the facilities of electronic techniques for the mechanization and automatization of the control of production and also on the development of new kinds of equipment for the chemical industry.

Rare metals play a fairly big role in solving these problems, the issue of which must be significantly increased for the seven-year plan.

Niobium and tantalum hold a special place among rare metals, possessing, together with high melting temperatures, high thermoemissivity, the ability to actively absorb gases, corrosion resistance, as well as the ability to yield a number of industrially important alloys.

Information concerning these metals is disseminated according to numerous literary sources, in which exists none of the sufficiently complete surveys of their technology and areas of application. In domestic literatu[illegible] attempts to complete this gap, is the creation of appropriate chapters in books on rare metals by O. A. Sogina,

A. N. Zelikman, G. V. Samsonov and O. Ye. Kreyn, G. A. Meyerson and A. N. Zelikman, which appeared from 1954 to 1956. However, these chapters, according to the very character and purpose of materials cited in them, cannot yet give a full and broad presentation concerning technology, alloys and applications of tantalum and niobium.

In a given monograph the authors made an attempt to generalize the voluminous literary material concerning tantalum and niobium. Special attention was given to the properties of tantalum and niobium in it and to the area of their application, the technology of extraction /6 from concentrates, obtaining metals, and also to the properties and application of alloys. It is natural that such work on the creation, on the nature, of the first monograph concerning such important metals for engineering as tantalum and niobium can not eliminate shortcomings.

The authors will be grateful for all notes and remarks which the readers of the book submit, but they do hope, nevertheless, that in spite of the shortcomings it will be useful to a wide circle of engineers and researchers, working in the most diverse branches of technology and connected, in one way or another, with the production or application of tantalum, niobium and their alloys.

Chapters 2 and 6-9 were written by G. V. Samsonov, chapters 4 and 5 by V. I. Konstantinov and chapters 1 and 3 by G. V. Samsonov and V. I. Konstantinov jointly.

In the writing of chapter 2 the interest of Ye. F. Ziv was rec~~ie~~eived, in the writing of chapter 6 the interest of T. Ya. Kosolapov was rec~~ie~~eived, to whom the authors express thanks.

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Chapter I

General Information on Tantalum and Niobium

The tantalum and niobium constitute elements accompanying each other and endowed with closely related physical and chemical properties.

The history of tantalum and niobium is unique; it is characteristic, at the same time, that the chemists were unable for a long time to distinguish between them, due to a close resemblance of their properties.

In 1801, the English chemist Hatchett reported the discovery of a new chemical element which he named "columbium". The name of "columbite" was chosen by him for the mineral containing this metal. Approximately within a year after the discovery of columbium, Ekeberg detected in one of minerals a new element which he named "tantalum"; this name was meant to symbolize the difficulties experienced by chemists in their attempts to dissolve the isolated oxide of this new element in acids. The mineral containing this new element received the name of "tantalitc".

Basing on researches, primarily those of Wollaston and Berzelius, it was assumed for a long time that columbium and tantalum are identical. However, Wollaston himself found out that the specific weight of columbite (5.2 - 6.4) is considerably lower than the specific weight of tantalite (6.5 - 7.2). The differences were detected also in oxides of these metals, isolated from minerals. Years have passed until Rose (in 1844) and Marignac (in 1866) proved that columbite contains two metals, viz. niobium (named by Rose in honor of the mythical goddess of tears, Niobe, the daughter of Tantalus) and tantalum.

The later researches by German, a Russian chemist, and Blomstrand, a Swedish chemist, confirmed the existence of two element, niobium and tantalum. Thus it was proven that Hatchett's columbium contains two element, namely niobium and tantalum (Bibl. 1). In the USA and England, niobium was called columbium (designated by the symbol Cb) for a long time. Starting with 1952 a single name, viz. niobium, was accepted for this element.

Bolton was the first to obtain tantalum (in 1903) and niobium (in 1907) in form of the pure compact metal. The metallic tantalum was used for filaments of normal illumination lamps, whence it was subsequently replaced by tungsten. The development of industrial methods for derivation of tantalum began, later on, in conjunction with a successful application of tantalum in current rectifiers (1922) and, in particular, in radio tubes (1923 - 1924).

Table 2

Physico-Chemical Constants of Tantalum and Niobium

Constants	Tantalum	Niobium
Index number	73	41
Atomic weight (3)	180.88	92.91
Density at 20°, gm/cm^3 (4)	16.6	8.57
Crystallic structure	body-centered cube	body-centered cube
Parameter of lattice, Å (5)	3.296	3.294
Atomic radius, Å (6)	1.47	1.45
Ionic radius, Å (6):		
Me^{3+}	0.62	0.62
Me^{4+}	-	0.67
Me^{5+}	0.66	0.66

The tables 3, 4 and 5 provide data on mechanical properties of tantalum and niobium. The thermal, electric and other properties are presented in tables 6, 7 and 8.

Table 3

Strength and Expansion of Tantalum, Annealed at 1700° (7)

Testing Temperature °C	Yield Point kg/mm²	Tensile Strength kg/mm²	Uniform Elongation %	Total Elongation %	Relative Contraction %
-195	87.1	-	0	12.4	75
-180	73.5	-	0	13.4	78
-130	58.7	-	0	15	81
-78	42.4	41.3	16.0	37	89
-30	39.7	39.2	20.0	34	86
+25	27.6	35.0	28	45	86
+200	18.4	32.9	24	31	86
+400	15.4	22.6	18	27	84

Being endowed with a good resistance with respect to the action of molten metals, applied as heat-transfer agents in atomic reactors, tantalum and niobium have different values of the thermal-neutron capture cross section, which amount to 20 barn/cm² for tantalum and 1.2 barn/cm² for niobium.

Table 4

<u>Strength and Elongation of Niobium, Annealed at 2000° (8)</u>

Testing Temperature °C	Proportional Limit kg/mm^2	Tensile Strength kg/mm^2	Elongation %
20	16.74	27.28	49
200	10.08	23.25	48
300	9.77	24.03	38
400	10.08	22.94	28
500	10.54	24.64	35
550	7.28	22.32	24

Table 5

<u>Other Mechanical Characteristics of Tantalum and Niobium</u>

Characteristic	Tantalum	Niobium
Compressibility factor, kg/mm^2	21050 (9)	17670 (10)
Elasticity modulus, kg/mm^2	17830 (11)	10600 (12)
Slip ratio, kg/mm^2	7000 (13)	8620 (12)
Poisson's ratio, (11)	0.35	0.39
Brinell hardness, kg/mm^2, of sheet (14):		
for annealed sheet	45-125	[illegible]
for strained sheet	125-350	200-250
for a sheet which absorbed gases while heated in an imperfect vacuum	up to 600	[illegible]
Microhardness of annealed sheet, kg/mm , under load of 30 gm (15)	108	88

Table 6

Thermal Properties of Tantalum and Niobium

Properties	Tantalum	Niobium
Melting point, °C	2996 (14)	2468 ± 10° (16)
Boiling point, °C	5300	3300
Temperature of transition into superconductive state, °C (19)	-268.8	-263.8
Melting heat, cal/gm (19)	37	-
Burning heat, cal/gm (14)	1379	2379
Evaporation rate, $gm/cm^2 \cdot sec$:		
for tantalum according to (17)		
for niobium according to (18)		
2000°K	$1.63 \cdot 12^{-12}$	-
2200	$9.78 \cdot 10^{-11}$	-
2400	$3.04 \cdot 10^{-9}$	-
2467	-	$1.16 \cdot 10^{-7}$
2600	$5.54 \cdot 10^{-8}$	-
2628	-	$1.08 \cdot 10^{-6}$
2800	$6.61 \cdot 10^{-7}$	-
2812	-	$1.06 \cdot 10^{-5}$
3000	$6.79 \cdot 10^{-6}$	-
3200	$3.82 \cdot 10^{-5}$	-
3269	$6.80 \cdot 10^{-5}$	-

Properties	Tantalum	Niobium
Evaporation heat, kilocal/gm-atom at T = 0°K (4)	185.5	170.9
Linear expansion coefficient, cm/cm·degree:		
0 - 100°C (19)	$6.5 \cdot 10^{-6}$	$7.1 \cdot 10^{-6}$
0 - 500	$6.6 \cdot 10^{-6}$ (19)	$7.47 \cdot 10^{-6}$ (5)
0 - 1000	-	$7.88 \cdot 10^{-6}$ (8)
20 - 1500	$8.0 \cdot 10^{-6}$ (19)	-
Specific heat, cal/gm·degree (19):		
0°C	0.03322	0.0645
100	0.03364	-
400	0.03495	0.0682
800	0.03679	0.0724
1200	0.03873	0.0774
1600	0.04078	0.0832
2000	0.044	-
Heat conduction, kilocal/cm.sec.°C:		
for tantalum according to (14)		
for niobium according to (8)		
0°C	-	0.125
20 - 100	0.13	-
100	-	0.130
200	-	0.135

Properties	Tantalum	Niobium
500	-	0.151
1430	0.174	-
1630	0.186	-
1830	0.198	-

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Electric Properties of Tantalum and Niobium

Properties	Tantalum	Niobium
Electric resistance, × 10^6 ohm·cm:		
0°C	-	15.22
20	13.5	-
100	17.2 (3)	19.18 (8)
200	-	23.13
500	35.0	55.00
1000°K (20)	45.0	-
1500	62.4	-
2000	78.9	-
2500	94.4	-
3000	105.6	-
3269	115.5	-
Temperature coefficient of electric resistance, × 10^3 (19):		
20°C	3.1	3.95
0 - 100	3.92	-

Properties	Tantalum	Niobium
Electron emission, a/cm^2 (3):		
1600°K	$9.1 \cdot 10^{-6}$	$2.19 \cdot 10^{-5}$
2000	$6.21 \cdot 10^{-3}$	$1.16 \cdot 10^{-2}$
2400	0.500	0.800
2800	12.53	60.67
3000	45.60	-
Richardson constant, a/cm$^2 \cdot$°K (3)	60	37
Work function, ev (3)	4.12	4.01
Coefficient of secondary emission (3)	1.35	1.18
Positive emission, ev (4)	10.00	5.5
Potential of ionization, v (4)	7.3 ± 0.3	6.77
Radiated power, watt/cm^2 (3):		
1600°K	7.36	6.40
2000	21.6	18.5
2400	51.3	45.3
2800	105.5	130.6
3000	144.4	-
3269	214.5	-
Radiation coefficient at $\lambda = 6650$ Å:		
20°C (23)	0.493	0.37
930 (24)	0.45	-
1730	0.418	-

Properties	Tantalum	Niobium
Specific susceptibility at 18°C	$0.849 \cdot 10^{6}$ (21)	$2.24 \cdot 10^{6}$ (22)

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Corrosion Resistance of Tantalum and Niobium (14, 25 - 30)

Medium	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Inorganic Acids				
Nitrous acid	conc.	150	0.0000	-
Nitric acid	35	200	0.0000	-
	50	200	0.0000	-
	70	200	0.0000	-
	conc.	25	0.0000	0.0000
Nitric acid with admixtures of organic acids	conc.	150	0.0000	-
		175	0.0000	-
		200	0.0000	-
Mixture of nitric and hydrofluoric acids	-	20 - 100	Dissolves rapidly	Dissolves rapidly
Hydrobromic acid	conc.	0 - 150	0.0000	-
Hydrosilicofluoric acid	conc.	0 - 150	Dissolves	-
Orthoarsenous acid	conc.	0 - 150	0.0000	-
Orthophosphoric acid	85	25	0.0000	0.0005

Medium	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Hydrogen peroxide	30	21	0.0000	0.0008
Hydrofluoric acid	40	20 - 100	Dissolves	Dissolves
Sulfuric acid	20	21	0.0000-	0.0000
	25	21	0.0000	0.0000
	98	21	0.0000	0.0004
	conc.	21	0.0000	0.00051
	conc.	50	0.0000	0.0032 (brittle)
	conc.	100	0.0000	0.076 (brittle)
	conc.	150	0.0000	0.852 (brittle)
	conc.	175	0.0004	5.68 (dissolves rapidly)
	conc.	200	0.006	-
	conc.	250	0.116	-
	conc.	300	1.368	-
Fuming sulfuric acid, containing 15% SO_3	-	23	0.0012	-
	-	70	0.368	-
	-	130	15.6	-
Sulfuric acid + CrO_3 (solution for chrome plating)	-	1000	0.0000	0.032

Medium	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Mixture of sulfuric and nitric acids	-	0 - 150	0.0000	-
Hydrochloric acid	20	19 - 26	0.0000	0.0000
	conc.	19 - 26	0.0000	0.0006
	conc.	100	0.0000	0.0234
Mixture of hydrochloric and nitric acids (2:1)	-	19 - 26	0.0000	0.0005
	-	50 - 60	0.0000	0.0254
Phosphoric acid	85	150	0.0000	0.0000
	85	210	0.0008	0.0132
	85	250	20	-
	conc.	20	0.00012	-
	conc.	150	0.10 - 0.15	-
Perchloric acid	conc.	150	0.0000	0.0000
Hypochloric acid	conc.	0 - 150	0.0000	-
Chromic acid	-	0 - 150	0.0000	-
Prussic acid	conc.	0 - 150	0.0000	-
Alkaline Solutions				
Ammonia (aqueous solution)	25	150	0.0000	0.0000
Potassium hydrate	5	20	-	0.1855 (action on surface of liquid)

Medium	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Potassium hydrate	5	100	Stable	Brittle
	40	100	Dissolves rapidly	Dissolves rapidly
Sodium hydrate	5	20	-	0.02815 (action on surface of liquid)
	5	100	Mediocre	Mediocre (brittle)
	40	100	Dissolves rapidly	Dissolves rapidly
Inorganic Salts and Bases				
Potassium alumosulfate	Saturated aqueous solution	0 - 150	0.0000	-
Sodium bromide	Same	0 - 150	0.0000	-
Sodium tungstate	Same	0 - 150	0.0000	-
Barium hydroxide	Same	19 - 26	0.0000	-
Potassium bichromate	Same	0 - 150	0.0000	Corrodes
Potassium carbonate	20	0 - 150	0.0000	-
Ammonium nitrate	Saturated aqueous solution	0 - 150	0.0000	-
Ferric nitrate (with or without admixture of HNO_3)	Same	0 - 150	0.0000	-
Sodium nitrate	Same	0 - 150	0.0000	-
Nickel nitrate	Same	0 - 150	0.0000	-
Silver nitrate	Same	0 - 150	0.0000	-

Medium	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Ammonium sulfate	Saturated aqueous solution	0 - 150	0.0000	-
Iron sulfate	Same	0 - 150	0.0000	-
Nickel sulfate	Same	0 - 150	0.0000	-
Zinc sulfate	Same	0 - 150	0.0000	-
Sodium chlorate	Same	0 - 150	0.0000	-
Aluminum chloride	Same	0 - 150	0.0000	0.0000
Ammonium chloride	Same	0 - 150	0.0000	0.0000
Iron chloride	Same	0 - 150	0.0000	-
Potassium chloride	Same	0 - 150	0.0000	-
Magnesium chloride	Same	0 - 150	0.0000	0.0000
Sodium chloride	Same	0 - 150	0.0000	0.0000
Nickel chloride	Same	0 - 150	0.0000	-
Tin chloride	Same	0 - 150	0.0000	0.0000
Zinc chloride	Same	0 - 150	0.0000	0.0000
	Organic Reagents			
Amylacetate	-	19 - 26	0.0000	-
Aniline (black)	-	19 - 26	0.0000	-
Acetone	-	19 - 26	0.0000	-
Tartaric acid	20	22	-	0.0000
Citric acid	-	19 - 26	0.0000	-

Medium	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Methyl alcohol	-	19 - 26	0.0000	-
Methyl-sulfuric acid	-	19 - 26	0.0000	-
Lactic acid	85	19-- 26	0.0000	0.0000
Nitrobenzene	-	19 - 26	0.0000	-
Nitrosyl-chloride	-	19 - 26	0.0000	-
Acetic anhydride	-	19 - 26	0.0000	-
Acetic acid (ice)	-	19 - 26	0.0000	-
Same, vapors	-	-	0.0000	-
Phenol	Saturated aqueous solution	19 - 26	0.0000	0.0000
Phthaleic anhydride	-	19 - 26	0.0000	-
Methyl chloride	-	19 - 26	0.0000	-
Chlorobenzene	-	19 - 26	0.0000	-
Chloroform	-	19 - 26	0.0000	-
Oxalic acid	Saturated aqueous solution	19 - 26	0.0000	0.01405 (brittle)
	Same	96	0.00252	-
Ethyl alcohol	-	96	0.0000	-
	Molten metals			
Bismuth	-	300	-	Good
	-	600	-	Limited
	-	1000	Corrodes	-

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Media	Concentration %	Temperature °C	Corrosion Resistance mm/yr	
			Tantalum	Niobium
Bismuth-lead	55.5% Bi, 44.5% Pb	1000	dissolves	dissolves
Potassium (with minimum content of oxygen)	-	300	good	good
	-	600	good	good
Calcium	-	300	good	good
	-	600	limited	limited
Magnesium	-	600	good	good
Sodium (with minimum content of oxygen)	-	300	good	good
	-	600	good	good
	-	900	-0.0960 ± 0.01 while tested for 163 hrs	-
Tin	-	1740	dissolves	-
Mercury	-	300	good	good

Behavior of Tantalum and Niobium in Atmosphere of Various Gases

The tantalum and niobium are stable when exposed to cold in the air atmosphere; they begin to oxidize in heating up to a temperature exceeding 300°[1].

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[1] Refer to pp 163 and 199 for information on the dissolvability of oxygen in tantalum and niobium.

While exposed to the atmosphere of hydrogen, tantalum and niobium adsorb the latter (refer to pp 156 and 192); at the same time, the dissolvability of hydrogen in these metals decreases with an increase of the temperature.

The heating of tantalum and niobium in the nitrogen atmosphere at a temperature lower than 600° causes the absorption of nitrogen in a significant amount, as well as the production of TaN and NbN nitrides (refer to pp 151 and 188).

The data, presented in Table 9 (Bibl. 29), make it possible to visualize the behavior of tantalum and niobium in the atmosphere of various gases and the variation in mechanical properties of metals.

Table 9

Action of Various Gases on Tantalum and Niobium at Increased Temperatures

Temperature °C	Tantalum		Niobium	
	Addition in Weight %	Elongation at Indoor Temperature %	Addition in Weight %	Elongation at Indoor Temperature %
		Hydrogen		
200	0.0000	(initial 31.0) 33.0	0.000	(initial 16.1) 16.7
250	0.0000	32.8	0.000	17.0
300	0.0000	32.8	0.000	15.6
350	0.0012	30.6	0.025	14.9
400	0.0017 - 0.0041*	25.8 - 16.0*	0.046 - 0.098*	14.4 - 4.5*
		Nitrogen		
300	0.0000	(initial 31) 28.2	0.000	(initial 16.1) 14.2
400	0.0008	22.0	0.0030	7.8
		Air		
350	0.013	(initial 33.2) 27.1	0.068	(initial 20.1) 13
		Oxygen		
350	0.011	(initial 37.2) 26.6	0.052	(initial 20.1) 22,9

*In dependence on the holding time.

At a high temperature (1200 - 1400°), carbon and carbon-containing gases (e. g., CH_4 and CO) interact with metals and produce carbides of tantalum and niobium (TaC and NbC). At a temperature lower than 600°, CO is absorbed by metals.

Tantalum and niobium yield to the action of fluorine at the indoor temperature; chlorine affects tantalum at the temperature upward of 250°, and niobium - at the temperature upward of 200°; bromine acts upon tantalum at temperatures exceeding 300°, and on niobium - at temperatures exceeding 250°. In relation to the gaseous iodine, tantalum remains inert throughout the entire temperature range up to the red heat (Bibl. 30).

Tantalum is inactive with respect to the gaseous hydrogen chloride up to 400°, and with respect to hydrogen bromide - up to 375° (Bibl. 35). Free SO_3 and sulfur monochloride corrode tantalum.

Technological Properties of Metallic Tantalum and Niobium (Bibl. 19, 36 and 37)*

In the pure form, tantalum is hard, forgeable and ductile. It can be rolled in thin sheets and also drawn into a thin wire. A good mechanical workability in the cold state is combined in tantalum with a good weldability. The welding of tantalum (and niobium) seams should be carried out under the protection of water (or carbon tetrachloride), or else in the neutral atmosphere (argon).

Tantalum and niobium are comparable to nickel as far as their suitability for the die stamping, molding and drawing is concerned.

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*Refer also to Chapter IV.

A high cutting speed is desirable in the working on a lathe. Tantalum is endowed with a good wear- and abrasion resistance, providing that their action is not focused for a long time in one place. The wear resistance can be increased to a significant degree by hardening.

One of the characteristic properties of tantalum consists in its high erosion resistance, even in the annealed state. Upon hardening og the metal its erosion resistance increases to such a degree that the metal is capable of withstanding the effect of a high-speed liquid or vapor stream.

The negative properties of tantalum consist in a very poor stability under load, as well as in its poor welding adhesion to most metals (including tantalum itself); in this respect, tantalum resembles strongly the stainless steel.

The pure niobium yields readily to the pressure treatment (forging, rolling and drawing). It is extremely pliable at the normal temperature and endowed with a negligible tendency to the cold hardening. Niobium is forgeable, ductile and weldable. The pliability of a niobium wire is sufficient for its coiling at the indoor temperature.

In addition to all the above-indicated properties of tantalum and niobium it is necessary to note the fact that these metals are capable of passing the current only in one direction upon their immersion in the acid electrolyte. In live organisms, these metals do not cause any irritation of tissues (Bibl. 30).

Among the properties of tantalum and niobium, analyzed above, the following qualities are particularly interesting: an exceptionally high corrosion resistance of metals, including the resistance to the action of molten metals, combined with a sufficiently high strength and heat conductivity; high pliability;

high melting point; low work function of electrons (attesting to good emission properties) and the gas-absorbing capacity of metals. /19

Regardless of the affinity in properties of tantalum and niobium, they differ from each other in some respects. Thus, for instance, niobium is less corrosion-resistant than tantalum; it has a lower melting and boiling point, and its volatility, by comparison with tantalum, is significantly higher. At the same time, the specific weight of tantalum is twice as high as that of niobium; as a result, niobium is endowed with a higher structural strength. The nuclear properties of niobium differ noticeably from the properties of tantalum; the effective neutron-capture cross section with niobium is much smaller than with tantalum.

2. PROPERTIES OF BASIC TANTALUM AND NIOBIUM COMPOUNDS

Tantalum and niobium are transient elements in the group V of the priodic system; they have therefore a metallic character. In compounds of a higher valence, both metals display, as a rule, the acid nature.

Tantalum and niobium are known to exist in various valent states, such as penta-, tetra-, tri-, di- and even monovalent states.

The valence +5 constitutes the most typical valence of tantalum and niobium in chemical compounds. This valent state is observed in their higher oxides, various tantalates and niobates, as well as in many complex compounds (oxalates, citrates, etc).

The state of tantalum- and niobium oxidation to lower degrees is observed in lower oxides. The tantalum- and niobium oxides of a lower valence are known ordinarily in form of solids; however, in some cases, the multinuclear complex ions, containing these elements, are known to exist in solutions.

The description of most important tantalum- and niobium compounds is provided in the next section.

Tantalum, Niobium and Oxygen[1]

The tantalum pentoxide (Ta_5O_5) and niobium pentoxide (Nb_5O_5) constitute the most frequently encountered technical products. The anhydrous pentoxides are nonvolatile, tasteless and odorless substances of a white or yellowish color (niobium pentoxide).

Pentoxides can be derived by various methods, viz. by oxidation of metal powders, hydrides, nitrides and carbides, as well as by calcination of hydroxides - tantalic and niobic acids, to which the formula $Me_2O_5 \cdot xH_2O$ is ascribed (where Me is Ta and Nb). There are references to the existence /20
of hydrates with a diverse value of x (Bibl. 38 - 45). According to the data in (Bibl. 38 and 363), a complete dehydration of tantalum hydroxide occurs at temperatures exceeding 450°, and that of niobium hydroxide - at temperatures upward of 400°.

The hydroxides of elements can be obtained during the lixiviation by water of products which have been derived in the fusion of their compounds with potassium pyrosulfate; during the neutralization by ammonia of hydrofluoric-acid solutions containing tantalum and niobium; during the treatment by acids of tantalate and niobate solutions, and as a final product in hydrolysis of halide compounds of elements.

The freshly deposited tantalum hydroxide dissoves in water, as well as in hydrochloric and sulfuric acids, to a very negligible extent. The niobic acid dissolves to a slightly higher extent in water, and also in weak hydrochloric and sulfuric acids (Bibl. 38). The niobic acid is dissolvable in concentrated hydrochloric and sulfuric acids; however, it falls out once again upon the dilution of solutions. The tantalum hydroxide produces complexes with tannin, as well as with oxalic, salicylic, citric, tartaric and pyrogallic acids; the niobium hydroxides produces also corresponding complexes with oxalic and tartaric acids.

The hydroxides of tantalum and niobium dissolve readily in oxalic acid and in alkaline solutions of potassium. Corresponding salts of weak tantalic and niobic acids, viz. tantalates and niobates, are produced in the latter case.

Depending on the calcination temperature, pentoxides of tantalum and niobium exist in various crystallic variants (Bibl. 38, 46 - 50). According to Schoenberg (Bibl. 51), the higher oxide of tantalum α-Ta_2O_5 is an isomorph of the low-temperature version α-Nb_2O_5 (Bibl. 49); according to data in (Bibl. 48), the former changes irreversibly into a high-temperature version at $1320 \pm 20^\circ C$. The results of a X-ray diffraction study of α- and β-Ta_2O_5, performed in the research (Bibl. 52), show that α-Ta_2O_5 has the space group I4 (ata) with cell periods $a = 3{,}80$; $c = 56.6$ Å and the density of 8.53 gm/cm^3, while β-Ta_2O_5 has the cell F 2.2.2. with $a = 6.80$; $b = 43.93$; $c = 3.890$ Å and the density of 8.30 gm/cm^3. The specific weight of various versions of tantalum pentoxide changes from 7.35 to 8.71 (Bibl. 53).

According to Zachariasen (Bibl. 49), Nb_2O_5 exists in three versions, viz. α, β and γ, wherein the low-temperature α-version is isomorphous with respect to Ta_2O_5. This is confirmed also by Kiessling (50). Brauer (54) asserts that niobium pentoxide is homogeneous from $NbO_{2.40}$ to $NbO_{2.05}$ and that it exists in three versions, namely the low-temperature version (up to 900 - 950°), medium-temperature version (from 1000 to 1100 - 1150°) and high-temperature version (upward of 1100 - 1150°; formed completely at 1200 - 1250°). Polymorphous transformations of niobium pentoxide are monotropic. The specific weight of niobium pentoxide varies for various versions from 4.37 to 5.02 (Bibl. 53).

The heat of Ta_2O_5 formation from elements constitutes 488.8 ± 0.5 kilocal/mole, while that of Nb_2O_5 formation amounts to 455.2 ± 0.6 kilocal/mole (Bibl. 55). The melting point of Ta_2O_5 equals 1620° (Bibl. 56) and that of Nb_2O_5 - 1532° (Bibl. 57).

The pentoxides of tantalum and niobium are stable substances; however, upon the calcination in vacuo, they decompose liberating oxygen; in particular, Nb_2O_5 breaks down, during the melting in vacuo, producing NbO_2.

The dissolvability of calcined pentoxides in water, acids and alkaline solutions is significantly lower than that of non-calcined pentoxides, and it decreases with the increase of calcination temperature.

In contradistinction to a more stable tantalum pentoxide, niobium pentoxide is reduced by hydrogen to dioxide at 800 - 1200° (Bibl. 58 and 59); niobium nitride is formed during the interaction with NH_3 at 500 - 800°; volatile chloride and oxychloride of niobium are formed during the reaction of Nb_2O_5 with chlorine at the temperature of 1000 - 1050°, or with carbon tertachloride at the temperature of 200 - 225°, while tantalum oxide remains unchanged (Bibl. 61). It should be noted, in passing, that the temperature on the order of 320° is required for the transformation of Ta_2O_5 into a corresponding chloride during the reaction with, e. g., CCl_4 (Bibl. 62).

According to data in (Bibl. 63 and 64), pentoxides of tantalum and niobium produce a continuous series of solid solutions. The specific weight of oxide mixture varies in proportion to the composition (Fig. 1).

Fig. 1. Variation in Specific Weight of Oxide Mixture (Ta_2O_5 and Nb_2O_5 Oxides) in Dependence on Composition.

Legend in Fig. 1: 1 - specific weight; 2 - content, % (by weight).

Tantalates and Niobates

The fusion of tantalum- and niobium pentoxides with oxides of various metals and the treatment of pentoxides by alkaline solutions result in the formation of salts of a complex composition which may be expressed by the general formula $xMeO \cdot yR_2O_5 \cdot zH_2O$, where Me is the corresponding metal; R - Ta or Nb.

Potassium- and sodium tantalates and niobates are most important among various tantalates and niobates. /22

Tantalates and Niobates of Potassium. There exist potassium tantalates with the $K_2O : Ta_2O_5$ ratio from 3 : 7 to 10 : 3 and potassium niobates with the $K_2O : Nb_2O_5$ ratio from 1 : 3 to 5 : 1. Among them, the following tantalates and niobates are dissoluble in water: $4K_2O \cdot 3Ta_2O_5 \cdot 16H_2O$ or $7K_2O \cdot 5Ta_2O_5 \cdot 24H_2O$; $K_2O \cdot Nb_2O_5 \cdot 4H_2O$; $6K_2O \cdot 7Nb_2O_5 \cdot 32H_2O$; $7K_2O \cdot 6Nb_2O_5 \cdot 27H_2O$; $4K_2O \cdot 3Nb_2O_5 \cdot 16H_2O$; $3K_2O \cdot 2Nb_2O_5 \cdot 13H_2O$ and $5K_2O \cdot Nb_2O_5$.

The dissolvability of $K_2O \cdot Nb_2O_5 \cdot 4H_2O$ salt constitutes, at 25°, 59.53% of anhydrous salt; that of $7K_2O \cdot 6Nb_2O_5 \cdot 27H_2O$ constitutes 55.08% of anhydrous salt (the 7:6 salt changes into the 4:3 salt in the aqueous solution of KOH with alkali concentration exceeding 20%; the conversion is reversible); that of $4K_2O \cdot 3Nb_2O_5 \cdot 16H_2O$ constitutes approximately 56% of anhydrous salt (the dissolvability of salt decreases abruptly with a higher concentration of KOH); refer to Bibl. 65). According to Lapitskiy (Bibl. 553), the dissolubility of $KTaO_3$ constitutes $4.87 \cdot 10^{-5}$ mole/l at 25°, while that of $KNbO_3$ amounts to $8.7 \cdot 10^{-4}$ mole/l.

The following stable salts are best known among tantalates and niobates of potassium:

1. $K_2O \cdot Ta_2O_5$ - potassium metatantalate.
2. $4K_2O \cdot 3Ta_2O_5$ - potassium hexatantalate.
3. $K_2O \cdot Nb_2O_5$ - potassium metaniobate.
4. $4K_2O \cdot 3Nb_2O_5$ - potassium hexaniobate.

The salts 1 and 3, as well as 2 and 4, are isomorphous (Bibl. 66); at the same time, salts 2 and 4 are identical with salts having the ratio equal to 7:6, which is conditioned by the possibility of exchange of water molecules for alkali (KOH). These salts can be represented by the general formula, e. g.,

$$K_{16}[Ta_{12}O_{36}](OH)_4 \cdot 30H_2O,$$

where the substitution of O^{2-} ion for OH^-, the loss of water molecules and the addition of K^+ ions are possible (Bibl. 503).

According to data in (Bibl. 554), potassium metaniobate can exist in form of various hydrates, containing 2, 0.4 and 0.2 water molecules per one molecule of salt; hydrates of potassium hexaniobate may have 27, 9, 6 and 4 water molecules and hydrates of hexatantalate - 38, 6, 3 and 1, respectively.

Tantalates and Niobates of Sodium. The fusion of Ta_2O_5 and Nb_2O_5 with caustic soda or caustic potash, followed by the water treatment of the fusion, or the addition of sodium salt to solutions of potassium tantalate and niobate, result in the formation of sodium tantalates and niobates which are endowed, in contradistinction to potassium salts, with a low degree of the dissolvability in water. We are familiar with various sodium tantalates, whose Na_2O : Ta_2O_5 ratios amount to 4:3, 7:5, 1:1, 1:3 and 2:7. For corresponding niobium salts these ratios are equal to 5:1, 3:1, 3:2, 6:5, 8:7, 1:1, 7:8, 3:4 and 2:3. /23
The existence of salts with ratios of 3:1, 3:2, 6:5, 8:7, 3:4 and 2:3 is doubtful.

Best known are the following salts: $NaTaO_3$, Na_5TaO_5, $4Na_2O \cdot 3Ta_2O_5 \cdot 25H_2O$, $NaNbO_3$, Na_5NbO_5 and $Na_2O \cdot 6Nb_2O_5 \cdot 32H_2O$.

According to researches (Bibl. 67 and 69), niobate with the composition of Na_5NbO_5 ($5\ Na_2O \cdot Nb_2O_5$) is produced during the fusion of Nb_2O_5 with NaOH. In aqueous solutions, this salt is subjected to the hydrolysis according to the reaction of $12\ Na_5NbO_5 + 55\ H_2O \rightarrow 7\ Na_2O \cdot 32\ H_2O + 46\ NaOH$. During the fusion of Ta_2O_5 with NaOH we obtain, correspondingly, Na_5TaO_5 salt which is subjected to the hydrolysis in water and yields $Na_7Ta_5O_{16} \cdot 11\ H_2O$ (Bibl. 38). The researches (Bibl. 68) are devoted to studying sodium tantalates.

The following are the values of dissolvability of sodium niobate (7:6 salt) in water and caustic-soda solutions at temperatures of 20 and 90° (Bibl. 69):

Content of NaOH, gm/ml of solution:	-	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Sodium niobate gm/l:	[illegible]	[illegible]									
at 20°	1.60	1.05	0.66	-	-	-	-	-	-	-	-
at 90°	2.60	1.90	1.20	0.75	0.49	0.32	0.24	0.18	0.14	0.12	0.11

When the concentration of NaOH is equal to 1.5 gm/100 ml, 7:6 salt is practically insoluble.

At 13.5°, one part of tantalum salt (4:3) is dissoluble in 493 parts of water.

At 25°, the dissolvability of $NaTaO_3$ salt constitutes $5.5 \cdot 10^{-5}$ mole/l, and that of $NaNbO_3$ - $5.9 \cdot 10^{-4}$ mole/l.

The $5Na_2O \cdot 6Ta_2O_5$ salt can exist in form of hydrates having 52, 7, 5 and 1 water molecules per one molecule of salt; correspondingly, the $7Na_2O \cdot 5Ta_2O_5$ salt is capable of annexing 29, 3, 2 and 1.7 water molecules, niobium salt $7Na_2O \cdot 6Nb_2O_5$ - 32, 6, 4 and 2 water molecules, and $NaNbO_3$ salt - 3.5, 1 and 0.5 water molecules per one salt molecule (Bibl. 554).

According to Lapitskiy, Na_2TaO_5 melts at 1030°, sodium metaniobates at 1250° and Na_5NbO_5 at 980°.

Metatantalates and metaniobates of alkaline and alkali-earth metals are thermally stable and nonvolatile at high temperatures (1200°).

Tantalates and niobates have some common features, which proffers a possibility of proposing a number of structural formules for the clarification of their structure. According to Lapitskiy, for instance, the general structure of aquapolycompounds of tantalum and niobium can be represented by the following formula

$$Me_x[(HЭ_6O_{19})_2 \cdot nH_2O]mH_2O,$$

where Э - Ta and Nb; Me - Li, Na, k and others; n - 1, 2, 3, 4 and 5; x - 14.16; mH_2O - water, coordinated around cations. /24

Tantalum, Niobium and Halogens

Fluorides of Tantalum and Niobium.

The metallic tantalum and niobium, tantalum and niobium oxides, as well as many of their other compounds, dissolve in hydrofluoric acid. The addition of potassium salts to oxalic-acid solutions of tantalum and niobium, containing upward of 7% of the free HF, results in the formation of complex composite compounds, viz. potassium fluotantalate K_2TaF_7 and potassium fluoniobate K_2NbF_7; when the concentration of HF in the solution is less than 7%, the salt K_2NbF_7 hydrolyzes, producing oxy-compounds of $K_2NbOF_5 \cdot H_2O$.

The aforementioned compounds constitute some of the most important tantalum and niobium compounds, and they play an important role in the technology of these elements. In particular, the industrial method for separation of these elements is based on the different dissolvability of K_2TaF_7 and $K_2NbOF_5 \cdot H_2O$ salts (Fig. 2).

Fig. 2. Dissolvability of Complex Fluorides of Tantalum and Niobium in Oxalic Acid of Various Concentration at 25 and 75°. Dissolvabilities Are Determined Separately for Each Salt.

<u>Legend in Fig. 2</u>: 1 - content of K_2NbF_7 and K_2TaF_7, %; 2 - content of HF, %.

<u>Potassium fluotantalate</u>. K_2TaF_7, exists in the form of thin, prismoidal needles which are isomorphous with the corresponding niobium salt, K_2NbF_7. The specific weight of the salt equals 5.24 (Bibl. 30).

The fluotantalate is stable in a dry air. The melting point of the salt constitutes 720±10° (Bibl. 30).

While boiling in water, K_2TaF_7 salt hydrolyzes, producing the insoluble compound of $K_4Ta_4F_{14}O_5$ (Marignac salt) which dissolves again upon an increase in the concentration of HF in the solution.

In contradistinction to potassium fluoniobate, potassium fluotantalate does not hydrolyze in solutions containing an insignificant amount of the oxalic acid (if these solutions are not boiled). Hence, the normal fluotantalate K_2TaF_7 is stable in the solution with all the concentrations of HF (up to 45%). The dissolvability of the salt increases in proportion to the increase in the concentration of HF; roughly from 0.8% (with 1.0% concentration of HF) to 6.5% (with 40% concentration of HF).

Fig. 3. Dissolvability of Potassium Fluotantalate in 1% Solution of HF.

<u>Legend in Fig. 3</u>: 1 - temperature, °C; 2 - dissolvability of K_2TaF_7, %.

The dissolvability of the complex tantalum salt depends also, in a marked manner, on the excess concentration of potassium fluoride added to the solution. According to the data of Savchenko and Tananayev (Bibl. 71), when the excess concentration of KF equals 1%, the dissolvability of K_2TaF_7 decreases by the factor of 10; with 2% concentration of KF it decreases by the factor of 15 - 20 times, and with 5% - by the factor of 35 times.

Fig. 4. Dissolvability of K_2TaF_7 in Relation to Concentration of KF in the Solution. (Concentration of Salt is Expressed Conventionally by Content of TaF_5 in the Solution.

Legend in Fig. 4: 1 - dissolvability of K_2NbF_7 recalculated into TaF_5, %; 2 - concentration of KF, %.

The presence of niobium salt affects also the dissolvability of fluotantalate in oxalic-acid solutions.

According to Meyerson, Zverev and Zubkova (Bibl. 72), the presence of niobium salt decreases strongly the dissolvability of potassium fluotantalate. The presence of niobium salt creates an excess concentration of potassium- and fluorine ions which exert a salting-out effect on the tantalum salt. In order to reduce the dissolvability of K_2TaF_7 to 0.05%, the concentration of niobium salt should constitute 1.5 - 1.7% at 20°, and 3.5 - 3.7% at 60% (Fig. 5).

Fig. 5. Dissolvability of K_2TaF_7 vs Concentration of K_2NbOF_5 in Solution

Legend in Fig. 5: 1 - dissolvability of K_2TaF_7, %; 2 - concentration of K_2NbOF_5, %.

Potassium fluoniobate, K_2NbF_7, exists in the form of small monoclinic crystals which are isomorphous with K_2TaF_7 and K_2ThF_6, but not isomorphous with $K_2TiF_6 \cdot H_2O$. The specific weight of potassium fluoniobate equals 3.21 (Bibl. 53). During a heating in the humid air, K_2NbF_7 changes into $K_2NbOF_5 \cdot H_2O$.

During the dissolution in water and weak solutions of HF, K_2NbF_7 is subjected to hydrolysis terminating in the formation of the dissolvable salt, viz. potassium oxy-fluoniobate, $K_2NbOF_5 \cdot H_2O$.

Consequently, the isotherm of dissolvability of complex niobium salts in oxalic-acid solutions consists of two branches. The first branch corresponds to the equilibrium of the solution with solid-phase crystals of $K_2NbOF_5 \cdot H_2O$ (up to 7% of HF). The second branch corresponds to the equilibrium of the solution with crystals of K_2NbF_7. Depending on the concentration of HF (in excess of 7%), the dissolvability of K_2NbF_7 decreases first (to 26 - 27% of HF) and then increases. The diminishing dissolvability is explained by the suppression of the hydrolysis of K_2NbF_7 in proportion to the increasing concentration of HF. The growing dissolvability upon a further increase in the concentration of HF is explained in the paper of Savchenko and Tananayev (Bibl. 70) by the formation of ions $[NbF_6]^-$:

$$K_2NbF_7 + HF \rightleftarrows KNbF_6 + KHF_2.$$

In the same manner as for potassium fluotantalate, the dissolvability of potassium fluoniobate depends, to a marked degree, on the temperature (Bibl. 71); however, with an increase in the concentration of KF, the dissolvability of the salt decreases to a significantly lower degree than in the case of the complex tantalum salt. Thus, in 10% solution of oxalic acid, the dissolvability of K_2NbF_7 decreases only by the factor of 4.7, when the concentration of KF changes from 0 to 10%.

Potassium oxy-fluoniobate, $K_2NbOF_5 \cdot H_2O$. The normal crystallic version of this salt exists in the form of characteristic crystals of a lamellate shape, which are isomorphous with crystals of $K_2TiF_6 \cdot H_2O$ and $K_2WO_2F_4 \cdot H_2O$. /27 The potassium oxy-fluoniobate is stable in the air at the normal temperature and during the heating. The monohydrate loses water upon heating to a temperature exceeding 100 (Bibl. 73).

The potassium oxy-fluoniobate is stable and readily dissolvable in cold and boiling water, as well as in weak solutions of HF.

The ratio of dissolvabilities of K_2TaF_7 and $K_2NbOF_5 \cdot H_2O$ in weak solutions of HF is presented below.

Temperature, °C	20	40	60	80
Ratio of dissolvabilities	1:11.9	1:11.6	1:10.1	1:11

Pentafluorides of tantalum and niobium, TaF_5 and NbF_5. They are obtained upon the action of fluorine on metals at a temperature on the order of 300°. The tantalum pentafluoride is a colorless, crystallic salt, dissolvable in a mildly acid solution of HF without hydrolysis. The niobium pentafluoride produces colorless, monoclinic prisms during the distillation in vacuo. The salt crystals are very hygroscopic; during the dissolution in water and mildly acid solutions of HF, the salt hydrolyzes, producing free HF and the so-called oxy-fluoniobic acid, H_2NbOF_5. According to the data in (Bibl. 74), the melting point of TaF_5 equals 95.1°; boiling point - 229.2°; $\Delta H_{evap.} = 13.0$ kilocal/mole; lg P mm Hg = 8.524 - 2.834/T; melting point of NbF_5 equals 80.0°; boiling point - 234.9°; $\Delta H_{evap.} = 12.9$ kilocal/mole; lg P mm Hg = 8.439 - 2.824/T.

Apart from fluotantalate, fluoniobate and oxy-fluoniobate of potassium, pentafluorides of tantalum and niobium produce numerous complex compounds with fluorides of alkaline, alkali-earth- and some heavy metals, as well as with ammonium and pyridine.

Chlorides of Tantalum and Niobium

Pentachlorides of tantalum and niobium. Chlorides of Ta (V) and Nb (V) are obtained in the action of chlorine on metals during the heating at roughly 200°, in the action of chlorine on mixtures of oxides of elements with carbon at the temperature of approximately 300°, and also in the action of a dry HCl on the metallic tantalum or niobium at temperatures of 300 - 350° (Bibl. 75).

The tantalum pentachloride is a while or bright-yellow crystallic salt, fuming in the humid air. Tantalum pentachloride hydrolyzes in water, but dissolves in absolute alcohol, carbon bisulfide and carbon tetrachloride (Bibl. 76).

The niobium pentachloride in the solid state is a crystallic, yellow-colored salt; in the melted state, it is a red-colored liquid. Niobium pentachloride fumes in the air and reacts with water vapors. The salt reacts with water very rapidly, producing hydrochloric acid and niobium hydroxide as a result of the hydrolysis. Niobium pentachloride dissolves in concentrated hydrochloric and sulfuric acids; however, the dilution or boiling of solutions results in the hydrolysis with the sedimentation of niobium hydroxide. Niobium pentachloride is dissolvable in sulfur monochloride, carbon tetrachloride and in organic solvents, such as chloroform, alcohol and ether.

Pentachlorides of tantalum and niobium are highly volatile substances. According to (Bibl. 77), the melting point of $TaCl_5$ equals 220.0°; boiling point - - 239.3°; $\Delta H_{evap.\ TaCl_5} = 13.6$ kilocal/mole. The melting point of $NbCl_5$ equals 209.5°; boiling point - 254.0°; $\Delta H_{evap.\ NbCl_5} = 13.2$ kilocal/mole.

$TaCl_5$ and $NbCl_5$ produce a continuous series of solid solutions (Bibl. 78). Refer to Fig. 6. They are endowed with many common properties. Thus, for instance, in contradistinction to pentafluorides, they do not produce any corresponding complex salts with chlorides of various metals; the fusions of pentachlorides do not conduct electric current.

Both tantalum chloride and niobium chloride are thermally unstable at high temperatures; they decompose, producing metals, while in vacuo on surfaces heated up beyond 600°. At high temperatures, pentachlorides are reduced by hydrogen to metals; however, at a temperature of up to 400°, $TaCl_5$ is not reduced, while $NbCl_5$ forms readily the lower chloride, $NbCl_3$ (Bibl. 79). Apart from that, niobium pentachloride can be reduced to tetrachloride both by metallic niobium and tantalum, according to reactions

$$4NbCl_5 + Nb = 5NbCl_4$$ /29

and

$$5NbCl_5 + Ta = 5NbCl_4 + TaCl_5.$$

On the contrary, tantalum pentachloride is not reduced under these conditions (Bibl. 79). The behavior of pentachlorides is also different during the reduction by metallic aluminum.

Niobium oxychloride. In contradistinction to tantalum, niobium tends readily toward the formation of various oxy-compounds with haloids. The niobium oxychloride, $NbOCl_3$, constitutes one of the most important compounds among them; it is derived upon the action of chlorine on niobium pentoxide.

$$2Nb_2O_5 \text{ (solid)} + 6Cl_2 \text{ (gas)} \rightleftarrows 4NbOCl_3 \text{ (gas)} + 3O_2 \text{ (gas)}.$$

In a heavy current of chlorine, the reaction begins at 400°; however, it becomes noticeable at higher temperatures (Bibl. 75). According to Morozov and Korshunov (Bibl. 80), the reaction constant, K_r, constitutes $7.14 \cdot 10^{-13}$ at 1000°. It is also possible to obtain $NbOCl_3$ during the reaction between vapors of HCl and Nb_2O_5 and during the interaction of pentoxide with niobium pentachloride

$$3NbCl_5 + Nb_2O_5 \rightleftarrows 5NbOCl_3.$$

Such a compound is not typical for tantalum (if carbon is absent, chlorine does not act upon tantalum pentoxide up to 1200°; refer to Bibl. 75). Niobium oxychloride sublimates at 400°; at a lower temperature, it precipitates in the form of white, thin needles. $NbOCl_3$ forms complex salts with clorides of alkaline metals and with some organic compounds (Bibl. 30).

The pressure of $NbOCl_3$ vapor is expressed by the following quantities (Bibl. 80):

Temperature, °C	237	240	250	270	280	290	300	330
Vapor pressure, mm Hg	9.1	13.76	20.8	62.0	115.0	206	285	428

$NbOCl_3$ dissolves insignifican ly in the $NbCl_5$ fusion (Bibl. 76). Lower oxides of niobium are formed on the reduction of oxy-compound by hydrogen (Bibl. 81).

Lower chlorides of tantalum and niobium. No chlorides of lower valencies of tantalum and niobium are produced during the direct chlorination of initial products (of tantalum and niobium, or their pentoxides); they can be obtained, in case of tantalum, during the reduction of tantalum pentachloride by aluminum and hydrogen; and, in case of niobium, during the reduction of niobium pentachloride by hydrogen, tantalum and niobium.

$TaCl_4$ is the black-green powder, dissolving in water and in diluted acids (Bibl. 82). $NbCl_4$ is known in the form of small, black-brown needles, isomorphous with $TaCl_4$ (Bibl. 83). $TaCl_3$ is the dark-green powder (Bibl. 81). $NbCl_3$ is described as the black deposit which is stable during the heating up to the temperature of up to 270° in the air and in the oxygen atmosphere (Bibl. 84). Save for $NbCl_3$, these lower chlorides are volatile substances, similarly to penta-compounds. The literature contains references to the existence of tantalum- and niobium chlorides of lower valencies (Bibl. 85).

Bromides of Tantalum and Niobium

The pentabromides of tantalum and niobium, $TaBr_5$ and $NbBr_5$, are obtained either during the action of bromine vapors on metals at temperatures of 300 - 500°, or during the action of bromine on the mixture of pentoxides and carbon blacks at temperatures of 700 - 900°.

$TaBr_5$ exists in the form of beautiful yellow-orange crystals, the salt hydrolyzes while dissolving in water. During the evaporation in vacuo, $TaBr_5$ is stable and does not decompose. $NbBr_5$ is the red powder, dissolvable in water, alcohol and ethyl bromide.

The melting point of $TaBr_5$ (Bibl. 77) equals 280.0°; boiling point - - 348.8 0.1°; $\Delta H_{evap.}$ = 14.9 kilocal/mole. The melting point of $NbBr_5$ equals 265.5°; boiling point - 361.6 0.1°; $\Delta H_{evap.}$ = 18.7 kilocal/mole.

Iodides of Tantalum and Niobium

The pentaiodides of tantalum and niobium can be obtained during the reaction between the iodine vapors and the tantalum- or niobium powder heated up to 800 - 1500°. The tantalum pentaiodide forms black crystals, sublimating without a decomposition; niobium pentaiodide is highly unstable, inasmuch as it liberates iodine even during an insignificant heating-up (Bibl. 86). Both compounds hydrolyze readily in the air.

The melting point of TaJ_5 equals 496°; the boiling point - 543°; $\Delta H_{evap.}$ = 19.7 kilocal/mole (Bibl. 86).

Carbides of Tantalum and Niobium

The carbides of tantalum and niobium belong to some of the most refractory and hard compounds. Tantalum and niobium produce carbides of various composition[1]. TaC and NbC, included in some hard powdered-metal alloys (Bibl. 37), constitute the most important carbides. The tantalum carbide, TaC, is the crystallic dark-brown powder; the niobium carbide, NbC, is the grey-brown powder with a violet hue. Both carbides are insoluble in all the acids, except for the mixture of oxalic and nitric acids. The carbides are resistant against the oxidization in the air during the heating up to 1000 - 1100°; they tend toward the formation of nitrides during the action of nitrogen or ammonia. The hardness of carbides, measured on the Mohs scale, amounts to approximately 10. The melting point of TaC equals 3880°C, and that of NbC - 3900°C. The density of TaC constitutes 14.4 gm/cm^3, and that of NbC -

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[1] Refer to p. 180 - 211 for information on Nb - C and Ta - C systems.

- 7.82 gr/cm^3.

Hydrides of Tantalum and Niobium[1] /31

The hydrides of tantalum and niobium are obtained during the heating of metals in the hydrogen atmosphere. They are highly brittle compounds; this property of hydrides is exploited in processing the waste of these metals. At 800 - 900°, the composition of hydrides may vary in dependence on conditions of the derivation. The hydrides are stable while exposed to the air at the normal temperature; during the heating, they oxidize to pentoxides. As regards the action of chemical reagents, the properties of hydrides are similar to the properties of pure metals. During the heating up to 1000 - 1200°, in high vacuum, the hydrides decompose, separating oxygen.

Complex Organic Compounds of Tantalum and Niobium

The compounds with tannin are most important among the complex organic compounds of tantalum and niobium.

The tantalum complex with tannin has a lemon-yellow coloring, and precipitates upon boiling from a weak-acid solution within the range of pH = 3 - 4. The orange-colored niobium complex falls out from a neutral or a highly weak-acid solution with a surplus of tannin.

The difference in conditions of precipitation of tantalum- and niobium complexes is exploited for the separation of these elements in the quantitative chemical analysis.

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[1] Refer to pp 156 and 192 for information on Nb - H and Ta - H systems.

3. APPLICATION OF TANTALUM AND NIOBIUM, AND THEIR MAIN COMPOUNDS.

At the present time, tantalum, niobium and their compounds are applied widely in the engineering. The Table 10, whose compilation is based on data of the USA industry, makes it possible to gain an understanding of the employment of these elements in various areas (Bibl. 88).

Table 10 /32

Consumption of Tantalum and Niobium in the USA (in 1952)

(% of Total Consumption)

Application Area	Tantalum	Niobium
In the metallurgy:		
stainless steels	26	60
special alloys of nonferrous metals	-	30
hard alloys	16*	5
welding electrodes	-	5
In the chemical industry	20	-
In the production of synthetic rubber	6	-
In the electrotechnical and electro-vacuum industries	25	-
In the medicine	5	-
	100	100

*tantalum carbide

Steels

The tantalum and, in particular, niobium are used extensively as alloying metals in various steels, such as extra strong, corrosion-resistant and red-hard steels.

The diffusion saturation of the carbon steel (with 0.47% of C) with niobium (Bibl. 89) results in the formation of NbC carbide and of another cubic face-centered phase with a 3.83 Å, the nature of which is not clear. The introduction of niobium increases substantially the wear resistance of steel without any noticeable increase of the heat resistance. The niobium-containing steel is distinguished by an increased corrosion resistance in 98% H_2SO_4 and by the normal stability in 50% HNO_3, 37% HCl, 85% $C_2H_4O_2$, 26% H_2O_2 and 10% solution of NaCl.

The addition of niobium (or tantalum) to normal, corrosion-resistant chromium steels, containing 5% of Cr and 0.5% of Mo, increases their strength, reduces to minimum their tendency toward the air hardening, and decreases their brittleness after the hardening and annealing. This action of niobium can be explained by the stabilization of carbon in form of niobium carbide, owing to which the separation of chromium carbides on boundaries of crystals is prevented.

The experiments in additions of tantalum and niobium to the stainless steel (Bibl. 90), containing 0.035 and 0.07% of C, demonstrated that the resistance of steels with niobium admixtures to the intercrystallite corrosion is twice as high as that of steels with tantalum admixtures during 48 hours in the boiling

65% nitric acid; 1 hour in the 10% nitric acid and 3% oxalic acid; 200 hours in the boiling solution of $CuSO_4$.

The higher corrosion resistance is explained in this case as being due to the formation of complex carbides, (Nb, Fe)C and (Nb, Ta)C. It was established, as a result of a detailed research (Bibl. 91), that the corrosion resistance of stainless steels increases most effectively upon addition to these steels of niobium in quantities exceeding by the factor of 8 - 10 the carbon content.

The addition of niobium to widely used austenitic chromium-nickel, /33 stainless "stabilized" steels, containing 18% of Cr and 8% of Ni, reduces also to a significant degree the intercrystallite corrosion and protects the weld seams against breaking. In order to prevent fully the intercrystallite corrosion, the niobium content in these steels should exceed by the factor of 8 - 10 the carbon content.

The niobium improves substantially the creep resistance of steels (Bibl. 92) with 1% of Si, 13% of Ni, 13% of Cr, 2.5% of W, 2% of Mo and 10% of Co, upon addition of 3% of Nb, as well as that of steels with 0.52% of Si, 10.5% of Ni, 19.1% of Cr, 46.6% of Co, 2.2% of Mo and 3% of V, upon addition of 1.4% of Nb (such a steel is also oxidation-resistant up to 800°).

The addition of 0.15 - 2.5% of Nb to the stainless steel with the composition of 0.15% of C, 0.5 - 2.5% of Mn, 0.3 - 3.75% of Si, 17 - 23% of Cr, 21 - 25% of Ni, 1.5 - 5% of Mo and 0.5 - 2.0% of C improves considerably the suitability of steels for the hot rolling, apart from increasing their corrosion resistance, (Bibl. 93).

The niobium exercises a positive effect also upon steels containing a still higher quantity of chromium.

The production of heat-resisting alloys constitutes an extremely important application area of tantalum and niobium. Niobium and tantalum impart the required strength and stability to steels employed for working in the range of high temperatures. Many heat-resisting materials for gas turbines of jet engines, rocket missiles and other similar purposes contain niobium (and tantalum) in their composition.

In this respect, the researchers investigated the effect of niobium- and tantalum additions to the heat-resisting high-chromium steel with 25% of Cr (EI59 or Zh27), endowed with a coarse-grained structure in the cast state (Bibl. 94). The niobium and tantalum were added in quantities exceeding by 8 - 10 times and more the content of carbon (1 - 2%), inasmuch as small admixtures of niobium (0.08%) and tantalum (0.17%) did not exercise any influence whatsoever upon the steel structure. The additions of niobium cause the formation of dispersed eutectic-type separations and the dendritic character of the structure, while tantalum causes the formation of a similar component occurring on junctions and facets of grains. In contradistinction to niobium, tantalum does not cause the dendritic structure of steel. While an intensive growth of grains in a steel without admixtures begins at 900° (with 96-hour holding), the admixtures increase the temperature of recrystallization to 1100 - 1200°.

The minimum content of niobium constitutes herein 0.52, and the additions of 1.2 - 1.7% Nb increase the temperature of grain growth to 1200 - 1300°.

The structural component, decelerating the growth, crystallizes during the heating, resembling in its character small carbide inclusions.

The modifying action of tantalum manifests itself upon addition of 1 - 1.5% /34 of tantalum; the recrystallization temperature increases, at the same time, up to 1100° with prolonged holding periods, and even up to 1200 - 1300° with brief holding periods (up to 4 hours). In addition, mechanical properties of the steel improve to a substantial degree (Table 11).

Table 11

Mechanical Properties of Type EI59 Steel in Relation to the Content of Tantalum- and Niobium Additions and the Moding of Heat Treatment

Addition		800°; 1-hour holding; water hardening			800°; 1-hour holding; water hardening + heating at 1100°; 6-hour holding; water hardening		
Element	Quantity % (by weight)	Tensile Strength kg/mm²	Proportional Limit, kg/mm²	Relative Elongation %	Tensile Strength kg/mm²	Proportional Limit, kg/mm²	Relative Elongation %
without additions		58.3	32.9	18.0	60.3	44.2	6.0
Nb	0.83	54.2	28.0	25.0	61.6	48.2	18.0
Nb	0.52	53.9	39.8	18.7	58.4	42.5	21.6
Nb	1.20	65.0	46.9	25.5	60.5	42.9	24.7
Nb	2.00	60.2	40.1	21.5	51.1	36.0	29.1
Ta	0.17	56.2	38.2	25.0	60.3	46.2	20.7
Ta	1.07	57.4	36.0	23.8	68.8	50.8	20.4
Ta	1.50	57.7	42.4	21.0	61.7	45.0	22.3

The authors of the paper (Bibl. 95) assume that the modifying action of tantalum- and niobium additions is associated with the formation of carbides by these additives; the tantalum and niobium, inhibiting strongly the growth of grains, produce carbides with highest melting points. The niobium, dissolving in the ferrite, hardens the latter to a significant degree and inhibits with a particular intensity the recrystallization and softening during the heating of ferrite steels. The niobium content constitutes herein 0.2 - 0.9%; the phenomena, induced by niobium, are associated with the formation of dispersed inclusions of niobium carbides. It should be noted that niobium additions induce the highest degree of hardening in comparison with other metals, as demonstrated by results of the research (Bibl. 96).

Thus, alloying of the ferrite increases its hardenability in hardening and its tempering resistance. The niobium additions are applied in the production of special steels for parts of gas turbines, such as the steel with 43% of Co, 0.3% of C, 0.8% of Mn, 0.3% of Si, 15% of Fe, 15% of Ni, 19% of Cr, 2.8% of V, 2.0% of Mo and 1.2% of Nb, as well as the steel with 46.5% of Ni, 20.5% of Cr, 2.73% of Mo, 3.33% of Co, 2.92% of Nb, 3.52% of W and 1.1% of Ti. The latter is endowed with a good creep resistance at 650°.

The heat-resisting steels with niobium and tantalum are also produced for parts of gas turbines (Bibl. 97). The ferroniobium with 55% of Nb and 5% of Ta is employed for the production of such a steel, containing, e. g., 20% of Cr, 20% of Ni, 20% of Co, 3% of W, 2% of Mo, 1% of Nb, 0.15% of N and 0.35% of C (Table 12).

Table 12

Lasting Strength of Heat-Resistant Alloy

Composition of Alloy, %				Tensile Strength, kg/mm^2, at 816°C	
Nb	Ta	C	N	in 100 hours	in 1000 hours
1.13	0.08	0.12	0.13	14.5	10.9
0.58	0.64	0.13	0.14	14.5	10.2
0.49	0.64	0.13	0.14	14.9	11.3
-	1.47	0.92	0.14	14.5	10.9

These alloys are endowed with a high strength at 816°C and even at slightly higher temperatures.

The heat-resisting steel, containing 0.25 - 0.35% of C, 16 - 20% of Cr, 12 - 36% of Ni, 1.75 - 2.25% of Mo, 0.8 - 1.2% of W, 0.4 - 0.6% of Si, 1.0 - 1.75% of Mn, 0.7 - 1.1% of Nb, 0.45 - 1.20% of Be and Fe (remnant) are also recommended for the turbine construction (Bibl. 98). The hardness of this steel, R_C equal 40, is preserved up to high temperatures. The tensile strength at the indoor temperature constitutes 123.8 kg/mm^2, and at 820°C - - 45.9 kg/mm^2.

The steels containing 1% of Nb, in addition to cobalt, tungsten, nickel, molybdenum and iron (main component), reveal an excellent heat resistance at 732 - 815° (Bibl. 99).

The patents (Bibl. 100) describe compositions of a number of heat-resisting steels for gas turbines, containing, e. g., 15 - 25% of Cr, 15 - 25% of Ni, 10 - 25% of Co, 7.5 - 15% of W, 2% of Mn, 1% of Si, 0.35% of C, 0.5 - 3% of (Nb Ta Ti) and Fe (remnant).

The niobium is introduced usually into the composition of steels in form of alloys with iron (ferroniobium), containing a small amount of carbon. The ferrotantalum-niobium, viz. the "electromet" alloy (20% of Ta and 40% of Nb), is being recommended recently for introduction into heat-resisting steels in lieu of the ferroniobium (55% of Nb and 5% of Ta); refer to Bibl. 101.

In addition to the above-indicated alloys, niobium is an important component of high-coercivity magnetic alloys (Bibl. 102) and of several other steels.

In bearing steels, e. g. in those containing silicon, niobium forms with the latter $Fe_4Nb_5Si_3$ silicide (detected also in the silicon-rich ferroniobium), which increases abruptly the wear resistance of these steels (Bibl. 103). The wear resistance of the normal carbon-rich steel with 0.3 - 1.5% of C also increases /36
abruptly upon addition of niobium (Bibl. 104).

Upon additions of niobium to steels containing sulfur, phosphorus and carbon, niobium experiences the re-liquation and refines the ingot, reducing the segregation of these elements in the former (Bibl. 105). Upon addition of niobium to steels subjected to nitriding for the purpose of producing a hard surface, their nitriding rate increases significantly, reducing consequently the duration of this process. The action of niobium consists in reducing the content of active carbon, or in eliminating it completely, thus facilitating the hardening of a nitrided steel at a high temperature without risking the formation of quenching cracks. The increase of the initial hardening temperature by 50-100° is permissible for niobic nitrided steels. This enhances the hardness and increases the depth of nitriding, as a result of the transition of niobium excess into the solution (Bibl. 102).

The extensive application of niobium in the composition of welding electrodes for the welding of various steels is based on its pronounced (in comparison with other metals) tendency toward producing complex carbides, which results in the diminishing of the intercrystallite corrosion.

Special Alloys on Nonferric Base

The special alloys of tantalum are used in the industry for employment at high temperatures, for manufacturing of cutters endowed with high cutting speeds and for the production of acid-resistant equipment. The alloys with a high melting point contain from 1 to 40% of Ta in the combination with various amounts of Mo, W, C, Mn, Ni, V and Si. In the above-indicated alloys, tantalum may replace, completely or partly, tungsten and molybdenum (Bibl. 106). In these cases, tantalum is introduced into the alloy in form of pure metal.

Alloys of Nonferrous Metals

The niobium is employed widely, as an important component, in specific aluminum alloys (of duraluminum type). The quantity of niobium, introduced into the alloys, is usually low and constitutes 0.05 - 0.1% (Bibl. 30). Its action consists in modifying alloys and in preventing formation of a brittle ferro-aluminum component.

The niobium is used also as an alloying addition to some cupric alloys. /37_ The addition of niobium in a quantity of up to 1.5% to copper, brass or bronze insures the retention of hardness at high temperatures (Bibl. 106).

Hard Alloys

The tantalum carbide, in addition to tungsten- and titanium carbides, is incorporated in the composition of some brands of hard metal-cutting alloys, and also in the composition of cast tungsten carbides..

We are familiar with hard alloys on the sole base of only tantalum carbide with nickel or cobalt as a carburizing admixture.

The addition of tantalum carbide into the composition of hard alloys improves substantially their cutting properties. Thus, according to the data in (Bibl. 382), the addition of 2% to the hard VK6 alloy makes it possible to increase the rate of pig-iron treatment by 10%, and the addition of 4% of TaC to titanium tungsten--cobalt hard alloys of TK brands increases their rate of steel treatment by 20%. The additions of tantalum carbide to hard titanium-tungsten-cobalt alloys increase also their high-temperature oxidation resistance. Some authors report that cutting tools with tantalum carbide are endowed with a better heat conductivity than the tools of other types, and that their thermal expansion is very insignificant even during the employment under rigid conditions.

The cast alloys with an admixture of tantalum carbide (and niobium carbide) withstand the chemical corrosion and are wear-resistant.

Although a great quantity of tantalum and niobium is employed in form of various alloys, the application of these elements in a pure form is of a tantamount importance. The electro-vacuum engineering and the chemical industry constitute two of the most principal areas of their application.

Electro-Vacuum Engineering

The inception of an extensive employment of the metallic tantalum is linked with the electro-vacuum engineering, and with the manufacture of radiotechnical, radar- and X-ray equipment.

The tantalum was employed first as filaments of electric-illumination lamps, replacing carbon filaments; it was displaced from this area by tungsten. Nevertheless, the electric lamps with tantalum filaments turned out in a number of cases to be more suitable than the lamps with tungsten filaments, for instance, on railroads where more elastic tantalum filaments withstand better the vibrations and bumps. However, these lamps can operate only on DC. A gradual recrystallization of tantalum filaments takes place during the application of AC (Bibl. 107).

In the modern electro-vacuum engineering, tantalum and niobium are used /38 in the form of various parts of vacuum instruments, particularly in oscillating tubes. The capability of tantalum and niobium to absorb and hold gases under low pressures, combined with a high melting point, low pressure of vapors, low coefficient of thermal expansion, plasticity and a good weldability with other metals, renders tantalum and niobium an excellent material for getters and grids in electron tubes, particularly for UHF transmissions. The tantalum and niobium are used for manufacturing of the "hot fittings" (i. e. heated-up parts), such as plates, grids, indirect-heating cathodes and other accessories. However, tantalum is employed for these purposes more extensively than niobium.

The application of tantalum is recommended particularly in electron (oscillation) tubes, operating at high temperatures and voltages with a lasting retention of precision characteristics (Bibl. 107).

The tantalum is not only a "getter" for undesirable gases; in certain types of vacuum tubes it is used also for maintaining the necessary pressure of these gases.

The industrial application of niobium in this area is apparently restricted, at the present time, to its use as a fixed getter in electron tubes. The niobium is preferred to tantalum in this case, because of a favorable combination of the thermionic emission, radiation factor and a good spot-weldability. The gas-absorption properties of niobium, used in rectifier tubes with a high vacuum, are expressed more clearly and encompass lower temperatures than in the case of tantalum; the latter, however, holds absorbed gases at higher temperatures than niobium (Bibl. 14).

The Table 13 presents examples of tantalum application in various fields of the vacuum engineering (Bibl. 23).

Table 13 139

Application of Tantalum in Electro-Vacuum Engineering

Type of Article	Dimensions	Principal Modes of Application
Wire rod	Ø14 - 0.005 mm	Grids in electron tubes, particularly in oscillation tubes. Quartz seal-in. Springs for hot cathodes. Direct-heating cathodes in special vacuum instruments.
Sheets (rough or polished)	0.2 - 0.050 mm thick	Plates in electron tubes, particularly in high-load oscillation tubes. Flanges for the getter on molybdenum- or nickel plates.
Drawn seamless tubes	Ø40 - 0.5 mm; thickness of walls: 2 - 0.1 mm	Plates of oscillation tubes. Indirect-heating cathodes in oscillation tubes.
Powder	fine-grained	Increases the radiation capacity of high-load electrodes. Getter.

The picture of tantalum plates for various electron tubes is shown in Fig. 7.

Fig. 7. A Set of Tantalum Plates for High-Power Electron Tubes, /38
Particularly for Application in Ultrahigh-Frequency Instrumentation.

It should be noted that, in many cases, there is an evident possibility in electronics to replace tantalum, apart from niobium, also by tantalum-niobium alloys with a varying ratio of metals. In addition to the above-indicated application areas, tantalum and niobium are used also in the so-called /40 cryotrons, viz. superconductive elements, e. g., for computers (Bibl. 139). A cryotron is a segment of the cooled tantalum wire (0.2 mm in diameter and 3 cm long), on which one layer of the insulated niobium wire, 80µ in diameter, is coiled. The tantalum wire serves as a superconductor. The current, generating the magnetic field which disrupts the superconductivity of tantalum, is passed periodically through the niobium coil. Thus, it is possible to disconnect the current with the aid of cryotron, regardless of the direction of this current.

Electrolytic Capacitors

When the tantalum (or niobium) is used as an anode material in acid electrolytes, it enters into the reaction with oxygen liberated from solutions, producing a stable oxide film. Consequently, the passage of current discontinues pending the voltage increase, which entails the emergence of a new equilibrium state. This process lasts up to approximately 200 v, whereupon the film begins to break down.

The capability of tantalum to produce stable anodic oxide films, combined with its passivity in relation to acid electrolytes, makes it possible to use this metal in electrolytic rectifiers and capacitors. The tantalum-made peanut capacitors are employed widely for transmitting radio stations, radar sets and various other electronic circuits.

The tantalum rectifiers are used for railroad signals, in telephone switchboards, as well as in fire-fighting and other signal systems (Bibl. 108).

The niobium can be used also as a low-voltage AC rectifier (Bibl. 37).

It is possible to produce tantalum capacitors in two versions, namely with tantalum-sheet spacers and with a porous tantalum. In the first case, it is customary to use acid electrolytes on the glycol base, which are endowed with a high viscosity; in the second case, we use liquid electrolytes, endowed with a high electric conductivity, such as, e. g., an aqueous solution of lithium chloride.

The silver-plated copper bands are employed as cathodes for spacer-type capacitors; in the second case, the vessel itself constitutes the electrode.

The latter is made of silver, or (in case of a nonpolar capacitor) of tantalum (Bibl. 109).

The special feature of tantalum capacitors consists in their small dimensions. We are presenting below comparative dimensions (%) of various types of capacitors (1 F, 150 v); refer to Bibl. 109.

Capacitor, paper, tin foil	100	/41
Capacitor, metallized, paper	40	
Capacitor, aluminum, electrolytic	15	
Capacitor, tantalum, electrolytic	10	

Figs. 8 through 10 present a number of comparative characteristics of tantalum- and aluminum capacitors, attesting to considerably better qualities of tantalum capacitors which are capable of performing at lower temperatures than aluminum capacitors (Bibl. 109).

The tantalum capacitors have a very long life. Their service life may exceed 12 years (Bibl. 36).

Fig. 8. Leakage Resistance of Various Capacitors

Legend in Fig. 8: 1 - leakage resistance, decrease, %; 2 - passivity period (at 50°), hrs; 3 - tantalum; 4 - aluminum.

Fig. 9. Power Factor vs Frequency Curve for Tantalum Capacitor

Legend in Fig. 9: 1 - power factor, %; 2 - frequency, Kc/sec.

Fig. 10. Capacitance vs Temperature Curve for Tantalum and Aluminum Capacitors (1 Kc)

Legend in Fig. 10: 1 - decrease of capacitance, %, from the rated value; 2 - temperature; 3 - tantalum; 4 - aluminum.

Chemical Industry

The tantalum and niobium, combining favorably the corrosion resistance (particularly in acids) with the strength, plasticity and heat conduction, are being used, to an ever-increasing extent, in the chemical industry. The tantalum-made parts have a practically unlimited life time in many chemically aggressive media.

In contradistinction to numerous metals applied in such cases, which lose rapidly their heat conductivity as a result of a corrosion film forming on their surfaces and poorly conducting the heat, no such phenomenon has been observed in case of tantalum (Bibl. 56).

A considerable expansion of the tantalum production, noted recently, is linked mainly in its growing use in the construction of chemical equipment. An ever-increasing number of chemical plants is being equipped with tantalum hardware. Thus, as early as in 1942, 80% of American acid-production plants were outfitted with the tantalum equipment (Bibl. 110).

The tantalum is used for the production of spiral tubes, condensers, pipelines, valves, mixers, aerators and other parts of the chemical equipment (Fig. 11); refer to Bibl. 140 and 141. The tantalum is applied quite often in the chemical industry in combination with plastics and ceramics. Thin sheets of tantalum are used frequently for plating the appropriate parts of equipment, made of conventional metals and alloys; the tantalum coatings are also applied (Fig. 12).

Fig. 11. Quadruple Tantalum-Made Spiral Tube for Heating of Aggressive Media.

Fig. 12. Tantalum-Coated Mixer

The tantalum is used most widely for the production of heaters and condensers. (Fig. 13). The pipelines are made of tantalum less often and only in cases when it is extremely necessary.

The tantalum is employed for the production of equipment subject to the action of hydrochloric, sulfuric, nitric, phosphoric and acetic acids, as well as of chlorine, bromine, hydrogen peroxide, petroleum derivatives, etc. The Table 14 presents examples of industrial operations in which the tantalum is used as a structural material (Bibl. 111 - 115).

Fig. 13. Tantalum-made collector heater for an intensive evaporation of aggressive liquids; the bottom picture shows the welding of tantalum pipes with the collector.

Table 14

Application of Tantalum in Construction of Chemical Equipment

Industrial Product	Equipment	Operation
Hydrochloric acid	Heaters and condensers in separation of fractions.	Distillation of chemically pure hydrogen chloride.

Industrial Product	Equipment	Operation
Ammonium chloride	Heat exchangers	Derivation of pure NH_4Cl in reaction of chlorine with ammonium. Concentration of mother liquors in crystallizers.
Iron chloride	Heaters	Heating of solutions.
Methyl chloride	Condensers and pipes	Pouring of methanol and hydrochloric acids into reactors; elimination of acid from the desiccation equipment.
Ethyl chloride	Heaters	Chlorination of alcohol, ether or ethylene.
Monochlorobenzene	Adsorbers	Condensation of vapors issuing from the reactor for chlorination.
Aliphatic hydrocarbons	Condensers and heaters	Catalytic reactions of chlorination in liquid phase
Amino acids	Heaters and condensers	Treatment of organic products by hydrochloric acid. Evaporation by hydrochloric acid from treated mass; condensation of acid vapors.

Industrial Product	Equipment	Operation
Bromine.	Heater and condenser in separation of fractions	Derivation of bromine from the crude mixture of bromine and chlorine.
Petroleum derivatives	Condensers and heat exchangers.	Heating of ethylene bromide; derivation of monochlorobenzene.
Sulfuric acid	Heaters	Heating of etching solutions.
Ethyl alcohol	Heaters and condensers	Dehydration of alcohol by sulfuric acid.
Nitric acid	Parts of centrifugal pumps; condensers; heat exchangers.	-
Ammonium nitrate	Heat exchangers	Heating-up of nitric acid prior to the reaction of neutralization by ammonia.
Organic nitro-derivatives	Reactors, lined up with tantalum sheets.	Evaporation of large volumes of the mixture consisting of solutions of organic products containing 30% of HNO_3 and up to 5% of HCl.

Industrial Product	Equipment	Operation
Phosphoric acid	Heat exchangers	Heating of phosphoric acid (with a low content of fluorides) in order to eliminate admixtures
Electro-plating operations	Heaters	Heating of solutions
Dry-distillation products of wood pulp	Heaters and condensers	Operations involving mixtures of alcohols with inorganic acids
Pharmaceutical products	Same	Same
Hydrogen peroxide	Heating elements of distillers	Distillation of hydrogen peroxide
Acetic acid	Heaters	Distillation of the technical acetic acid from initial products. Derivation of pure acid from the industrial acid.
Aromatic products for cosmetics, soaps, etc	Heaters and condensers	Evaporation and condensation of high-boiling organic acids

Apart from the metallic tantalum, chromium-nickel steels with an addition of niobium are used in the chemical industry.

The prospects of using metallic niobium in the chemical industry are highly promising; the metallic niobium is endowed with anti-corrosion properties approximating those of tantalum; however, its specific weight is almost 50% lower than that of tantalum, which means that its structural strength is practically twice as high. Apart from that, alloys of tantalum and niobium with various tantalum-to-niobium ratios, preserving valuable properties of both these metals, are important for using in the chemical industry.

However, the application of these two metals in the chemical industry is restricted in several respects, resultant from the lower corrosion resistance of metals to the action of highly concentrated sulfuric and phosphoric acids at a high temperature, as well as to the action of the oxalic acid dissolving rapidly the metals. The tantalum can be used relatively safely in the work involving a concentrated sulfuric acid at temperatures not exceeding 175°, as well as in the work with a concentrated phosphoric acid at temperatures up to 145°. The tantalum is not applied in alkaline solutions, although it is relatively resistant to the action of diluted solutions of alaklis, providing that their action is not focused in one place (Bibl. 36); refer to the Table 8.

The tantalum is highly sensitive to the action of fluorine and its compounds in almost any form at the indoor temperature. In the chemical equipment, where the presence of chlorine is not excluded, tantalum is used at temperatures not exceeding 150°. It is also necessary to avoid the action of a free SO_3 and, particularly, of hydrogen on the tantalum (Bibl. 115).

The use of oils and hot gases as heating media is not recommended in tantalum heaters. The efficiency decreases significantly when other heating media, apart from the vapor, are being used (Bibl. 36).

In addition to instances described above, there are also many other cases of the application of tantalum and niobium as corrosion-resistant materials.

The tantalum is used, for instance, in chemical laboratories for the production of dishes, spatulas, mixers, rods, filters, funnels, etc (110).

The diaphragms for regulating and batching valves are also made of tantalum. The water-purifying stations, e. g., use such valves to control the flow of chlorine (Bibl. 36 and 110).

The tantalum is used as a platinum substitute for the production of standards for high-precision small analytic weights (Bibl. 110).

Atomic Power Engineering

The tantalum and niobium (particularly, the latter) can be used as a structural material for the work with the molten sodium, or the soium-potassium mixture, which are used as coolants in some types of nuclear reactors (Bibl. 116 and 117).

The corrosion resistance of niobium in molten metals, combined with the absence of interaction with uranium up to 900° and a low coefficient of the thermal-neutron capture, proffers the possibility of using niobium as a structural material to produce covers for heat-producing elements employed in nuclear fast- and thermal neutron reactors (Bibl. 118).

Medicine

The tantalum is used for the production of dental and surgical instruments and, particularly extensively, in the restoration surgery. The tantalum is applied in the suturation and also for strengthening the walls of the abdominal cavity which are still weak after an operation (Bibl. 119). The cranial injuries are corrected by means of tantalum plates; the damaged small bones can be replaced by the tantalum wire and narrow strips. A thin wire is spliced so as to render the seam strong and flexible. The tantalum thread and meshwire is used to replace the muscular tissue, as well as the basis for the growth of a new tissue; a thin tantalum wire is applied for the neurosutures. This 147 application of tantalum in the surgery is possible because this metal causes absolutely no irritation of a live issue and remains inactive even after a prolonged action of the liquid medium of a human organism on tantalum (Bibl. 110). A similar application of niobium is also known (Bibl. 30).

Production of Synthetic Silk

The manufacture of drawing dies, used in the production of synthetic-silk yarn, constitutes an important area for the application of tantalum (Bibl. 120). The capability of tantalum for increasing its hardness during a heating in the atmosphere of various gases is particularly useful in this respect for attaining the wear resistance.

Jewelry. Application of Tantalum as a Substitute for Precious Metals.

The tantalum is used in the jewelry as a platinum substitute. The property of tantalum to acquire a coating of the iridescent oxide film facilitates this purpose. The tantalum can be applied also in the manufacture of timepieces, bracelets, etc.

The tantalum is used also as an iridium substitute in the production of tips for fountain pens.

Application of Tantalum- and Niobium Compounds

We have already discussed the application of tantalum- and niobium compounds (see pp 31 and 37). Among other compounds, potassium fluotantalate is used as a catalyst in the production of synthetic rubber, and niobium pentoxide - - in the infrared photography (Bibl. 121).

The tantalum- and niobium oxides are employed as catalysts in some chemical processes (Bibl. 122 and 123), particularly in the derivation of butadiene from ethyl alcohol.(Bibl. 124). They are used also in the manufacture of special optical glasses with a high refraction coefficient (Bibl. 30).

The mixture of tantalum pentoxide with a small amount of iron trioxide is recommended for application in order to speed up the blood coagulation.

The niobium- and tantalum hydrides have found recently an important application area in soldering of contacts on silicon semiconductors (Bibl. 126).

4. Economics of Tantalum and Niobium

The tantalum and niobium are rare, precious metals. The prices for metallic tantalum and niobium in the USA, the main producer of these metals among capitalist countries, constituted, during 1953 - 1955, 130 - 140 dollars per 1 kg. The dynamics of prices for niobium and tantalum in the USA (Bibl. 127), expressed in dollars per 1 kg, is shown below.

Years	Niobium	Tantalum
1940	500* - 560	143 - 160
1948 - 1951	250 - 280	143 - 160
1953	130	-
1955	-	93 - 137

The high prices for these metals are determined primarily by the cost of the raw material, and also by the complexity of technological processes involved in the production of these metals.

The prices for tantalum concentrates remain more or less stable during several years; 1 ton of the tantalite concentrate was quoted in 1939 at 2000 - 3300 dollars, and in 1955 - at 2400 - 2750 dollars.

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*The lower figure refers to the metal in sheets, and the higher one - - to the metal in bars; the price for niobium in 1953 (130 dollars per 1 kg) is related apparently to the metal in sheets.

The prices for niobium concentrates increased abruptly during 1940 - 1955 in conjunction with the expansion of the production of heat-resistant alloys and stainless Cr-Ni steel with niobium for the rocket missiles, jet aircraft, gas turbines, nuclear reactors and the construction of chemical machinery.

The prices for the columbite concentrate, containing 50 - 70% of $Nb_2O_5 + Ta_2O_5$, in the USA (Bibl. 127) are quoted below in dollars per 1 ton:

Years	
1940	210
1948	700
1950	2576
1952	3220
1955	7400**

In 1955, the output of niobium concentrates expanded in many countries and became, on the whole, 1½ times higher than in 1954; at the same time, the procurement for strategic resources of the USA was discontinued. As a result, starting with the second half of 1955, the columbite concentrate became marketable without restrictions, and its prices dropped rapidly, as it is evident from the following figures (dollars per 1 ton):

**This sum includes 100% extra charge, paid by the USA government in addition to the basic price (end of 1954 - beginning of 1955).

	USA	England
Until May 1955	-	5850
June 1955	3575-3250	-
September 1955	3250-2860	2900
November 1955	2860-2500	2730
December 1955	2340-1950	2275
May 1956	1950-1650	-

Nevertheless, the prices for columbite continue to remain high.

In capitalist countries, the production of metallic tantalum, niobium and their alloys is centralized mainly in hands of monopolists of the USA and England (to a lesser degree, of West Germany); at the same time, the production of these metals grows rapidly (Fig. 14).

Fig. 14. Growth in Production of Tantalum and Tantalum-Containing Products during 1947 - 1955.

Legend in Fig. 14: 1 - increase of production, % (1939 assumed for 100%); 2 - year

The production of 60 - 70% tantalite-columbite concentrates in foreign countries is shown in the Table 15 (Bibl. 88, 128 through 134).

Table 15

Production of Tantalite-Columbite Concentrates in Foreign Countries (Tons)

Years	West Australia (tantalite)	USA (columbite and tantalite)	Nigeria (columbite)	Congo (tantalate)	Malaya (columbite)	Total
1905	73	-	-	-	-	73
1920	-	1.81	-	-	-	1.81
1922	5.08	0.27	-	-	-	5.35
1925	19.76	0.9	-	-	-	20.66
1929	24.39	10.03	-	-	-	34.42
1932	10.2	0.18	-	-	-	10.38
1938	27.0	18.0	293.5	61.0	-	399.5
1940	no data	no data	297.5	263.0	-	560.5
1944	-	-	2055	-	-	2055
1945	-	-	1571	-	-	1571
1946	0.4	2	1551	165.0*		1718.4
1950	7	0.5	865	1219.0*	8.1	2099.6
1953	8.1	7.1	1990.3	283.5	52.8	3159.7
1955	no data	no data	no data	2050	240	6200.0

NOTE: All the figures which have not been marked in a special manner designate the total production of tantalite and columbite concentrates.

*The total production of tin-tantalite-columbite concentrates.

Apart from these basic sources (excluding the USA), some amounts of tantalite and columbite concentrates are produced in South Rhodesia, Southwestern Africa, Uganda, South African Union, French Equatorial Africa, Madagascar, Mozambique, Bolivia and Brasil.

The USA, whose own output of tantalite and columbite concentrates is negligible, is the principal importer of these products.

The data relative to the import of columbite concentrates in the USA during 1941 - 1955 are produced below (Bibl. 127 and 134):

Years	Tons	Years	Tons	Years	Tons
1940	-	1945	1909	1950	771
1941	643	1946	1083	1951	-
1942	787	1947	1259	1952	900
1943	1059	1948	881	1953	1722
1944	1645	1949	695	1955	4358

Chapter II

MINERALS, ORES AND CONCENTRATES OF TANTALUM AND NIOBIUM

The atomic Clark number, i. e., the content of Ta and Nb in the earth's crust comprises $2.1 \cdot 10^{-4}$ for Ta and $2.4 \cdot 10^{-3}$ for Nb. The ratio Nb/Ta averages 11.4.

The proximity of the chemical properties and the homogeneous dimensions of the ion radii of Ta and Nb (0.69 Å) conditions their chemical affinity, general participation in geological processes and their combined occurrence in the same minerals.

From the position of Ta and Nb in the periodic system of elements, there also follows their geochemical affinity with many elements, especially with Fe, Ti, rare-earth elements and U, Th and Zr.

Widely distributed in nature are the complex compounds tantalo-niobates and titano-tantalo-niobates with U, Th, TR, where Ta and Nb may be isomorphically displaced by titanium, while U, Th, and rare-earth elements (TR) may be displaced by sodium, potassium, calcium etc.

A large part of the minerals of Ta and Nb are represented mainly by complex, and to a lesser degree, by simple anhydrides, which (in the light of recent crystallo-chemical researches) are regarded as oxides of the type ABX_3, ABX_4, AB_2X_6, $A_2B_2X_7$ and $A_mB_nX_p$, where A = Na, Ca, Sr, Fe, Mn, TR, U, Th, Pb, Bi; B = Nb, Ta, Ti, Fe, Zr; X = O, OH, F.

An inferior significance is possessed by silicates, containing Ta and Nb mainly in the form of admixtures.

In addition (to occurring in minerals proper,) ~~[illegible]~~ Ta and Nb are also found in the form of admixtures in various minerals of Ti, Zr, Sn, W etc, for instance in ilmenite, perovskite, zircon, cassiterite, wolframite and others. The form of the occurrence of Ta and Nb in these minerals is not always clear. Until recently it was considered that Ta and Nb occur in the form of an isomorphic admixture to the crystalline lattice, but researches in recent years have shown that in a number of cases an increased content of Ta and Nb, especially in cassiterites, is connected with microscopic impurities (inclusions) of individualized minerals of these elements.

A significant difference in the geochemical history of Ta and Nb consists in that Ta concentrates in commercial amounts only in granitic pegmatites, whereas niobium deposits are associated with diverse rock types—granites, nepheline /52 syenites, pegmatites, carbonatites and others /134/.

There are more than 130 minerals containing Ta and Nb, but of them only 80 constitute tantalic or niobic minerals; in the remainder, both these elements are present in the form of admixtures.

The most important industrial minerals of tantalum and niobium are: columbite-tantalite, pyrochlore-microlite, and loparite. Euxenite, thorolite, simpsonite, ilmenorutile, as well as tantalum- and niobium-containing minerals—ilmenite, rutile, perovskite (disanalite), titanite, cassiterite and wolframite are also sometimes used.

Columbite $(Fe, Mn)(Nb, Ta) O$ and tantalite $(Mn, Fe) (Ta, Nb) O$ are representatives of a series whose extreme members are purely niobic and purely tantalic variants. The syngony is rhombic, form is lamellated, discoid or short-columnar, rarely acicular and isometric. Tantalite sometimes has spicular and dipyramidal forms. The hardness of columbite is 6.0, and of tantalite 6.0 - 6.5. The specific weight, from 5.2 for columbite to 8.3 for tantalite, is directly dependent upon composition, in particular upon the content of tantalum. Color is black, with greyish (for columbite) and reddish (for tantalite) hue. The glitter is semimetallic, and is pitch-like where broken. In passing light and in thin fragments, the minerals reflect a reddish-brown color.

Both minerals are paramagnetic, wherein, in dependence upon iron content, their magnetic properties vary somewhat.

Columbite and tantalite do not decompose in hydrochloric acid. Upon heating, columbite breaks down in sulfuric acid, while tantalite hardly changes. In hydrofluoric acid, columbite decomposes slowly, and tantalite even more slowly.

Theoretically, the Nb_2O_5 content in columbite may reach as high as 82.7%, while the content of Ta_2O_5 in tantalites can go up to 86.1%. However, in reality the composition of minerals of the group columbite—tantalite is inconstant, even varying within the limits of one deposit.

Below we present the ~~limits~~ range of the contents of oxides in columbite-tantalites, in %

Nb_2O_5	....	5.04—78.06	Fe_2O_3	....	Traces—1.57
Ta_2O_5	....	2.0 —84.0	FeO	....	0.69—18.39
SnO_2	....	To 0.54	MnO	....	2.14—15.0
TiO_2	....	Traces—6.78	MgO	....	0.28—0.72
ZrO_2	....	0.13—0.54	CaO	....	0.31—2.55
SiO_2	....	0.48—7.20	$K_2O + Na_2O$	....	To 0.68
Al_2O_3	....	0.05—4.71	H_2O	....	0.61—0.48

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Iron is invariably accompanied by manganese with predominance of Fe over Mn in columbites, and of Mn over Fe in tantalites. Moreover, in these minerals there are ordinarily encountered admixtures of SnO_2, TiO_2, WO_3, ZrO_2, ThO_2, UO_2, and UO_3, as well as of CaO, MgO, CuO, Ce_2O_3 and Y_2O_3.

The presence of admixtures of other elements is explained by imbedded inclusions of cassiterite, uraninite, cirtolite, zircon, monazite and microlite.

There are two manganiferous variants of columbite and tantalite—namely, mangano-columbite and mangano-tantalite, and one uranic variant of columbite, i. e. toddite, containing up to 10% U content.

The practical importance of minerals of this group is very great. Tantalite constitutes the sole source for obtaining tantalum, and columbite is one of the most important sources for the obtainment of niobium.

Pyrochlore $(Na, Ca)_2 Nb_2O_6F$ and microlite $(Na, Ca)_2 Ta_2O_6F$ comprises the extreme representatives of the series. Syngony is cubic, form is octahedral, rarely in the form of irregular masses and grains. Hardness is 5.0—5.5. Depending upon Ta content, specific weight varies from 4.2 for pyrochlore to 6.42 for microlite. Hydration and other changes lower the specific weight to 3.8, which again increases during calcination.

The color of pyrochlore is black, dark brown, reddish-brown, and various shades of yellow; the color of microlite ranges from light yellow to brown; sometimes hyacinth-red, olive, or green. In thin fragments and in microsections, pyrochlore and microlite are transparent, colorless or faintly colored.

Pyrochlore does not dissolve in hydrochloric acid; at prolonged boiling in concentrated sulfuric acid, it dissolves. Dissolves well in hydrofluoric acid. Easily coalesces with $K_2S_2O_7$ and $KHSO_4$.

Composition is inconstant (Table 16) but the content of Ta O in pyrochlores does not exceed 10%, while the Nb_2O_5 content in microlites does not exceed several percents.

There exist many variants of this group: marignacite, koppite, hatchettolite, tantalohatchettolite, jalmaite, neotantalite, obruchevite (sp ?),* elsworthite (sp ?), mendeleyevite, betafite, titanobetafite, samiresite and blomstrandite.

Pyrochlore is one of the most important industrial sources of niobium.

<u>Loparite</u> (Na, Ce, Ca, Sr) (Nb, Ti) O_3 . Syngony is cubic. Form is cubic-octahedral and octahedral. Hardness is 5.5 —6.0. Specific weight is 4.73—4.99. Color is black, very rarely brownish-red and greenish-brown. In thin fragments and microsections, glitters with a brownish-red color. Slightly paramagnetic and very slightly radioactive. Dissolves in hot concentrated sulfuric and hydrofluoric acids. Becomes identifiable when fused with $KHSO_4$. /54

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* Spelling not confirmed - Translator.

Table 16

Ranges of Content of Oxides in Pyrochlores-Microlites, % (Weight)

Oxide	Pyrochlore	Microlite	Oxide	Pyrochlore	Microlite
Nb_2O_5	37.54—65.60	Traces-7.74	UO_2	0.20—12.90	0—4.21
Ta_2O_5	0—5.86	66.43—77.0	UO_3	0.43—10.65	0—1.99
SiO_2	0.09—3.78	—	FeO	0.02—1.14	0—3.64
TiO_2	0.83—12.25	0—1.58	MgO	0.16—0.55	0.07—0.34
SnO_2	0.25—0.55	0.8—4.0	MnO	Traces—1.16	0.60—7.70
ZrO_2	0.53—4.99	—	CaO	2.82—20.01	10.48—15.03
ThO_2	0.26—9.28	—	SrO	0.04—1.07	—
Fe_2O_3	0.36—4.30	—	Na_2O	2.52—6.93	1.66—5.13
$\sum Ce_2O_3$	0.66—13.33	0.17—4.20	K_2O	0.47—11.55	0.71—5.70
$\sum Y_2O_3$	0.24—11.34	0—0.23	F	0.49—4.31	0-2.85
Bi_2O_3	—	0-3.25			

The composition of loparite is characterized by the constancy, in %: 11.06—11.48 $(Nb, Ta)_2O_5$, 39.22—39.24 TiO_2, 32.30—34.61 $\sum TR$, 0.06—0.72 Fe_2O_3, 0.72 Al_2O_3, 0.27—0.72 SiO_2, 0.53 ThO_2, 4.22—5.76 CaO, 0.26—0.75 K_2O, 7.88—9.06 Na_2O, remaining elements 0.32.

Euxenite (Y, Ca, Ce, U, Th) $(Nb, Ta, Ti)_2O_6$. Syngony is rhombic. The form is thick-tabular, finely prismatic. Hardness is 5.5—6.5. Specific weight is 5.9. Color is dark black, yellowish- and reddish-brown, transparent in thin fragments. Electromagnetic and radioactive. Decomposes slowly in $KHSO_4$ and hot concentrated hydrochloric, hydrofluoric and nitrous acids, more fully in sulfuric acid. Fuses with $KHSO_4$ and $K_2S_2O_7$. Composition is inconstant, %: 3.83—47.43 Nb_2O_5, 0—47.31 Ta_2O_5, 24.17—25.66 TiO_2; 13.20—31.45 $(Y, Er)_2O_3$, 0.44—09.54 $(Ce, La)_2O_3$, 0.67—14.70 UO_2, 0.04—9.08 UO_3, traces—4.96 ThO_2, 0.48—48.6 CaO.

Ratio (Nb - Ta) : Ti - 3:2.

Thorealite $SnTa_2O_7$. Syngony is monoclinic. Form is prismatic, crystals poorly formed. Hardness 6.0. Specific weight 7.6—7.9. Color brownish, ~~[illegible]~~ (is translucent) in thin fragments.

Composition is fairly constant, %: 72.83—77.59 Ta_2O_5, 21.88—22.41 SnO_2, 1.85 SiO_2, 1.02 Al_2O_3, 0.50 Fe_2O_3, 1.28 CaO.

Simpsonite AlTaO . Syngony is hexagonal. Form is tabular or short-prismatic. Hardness 7.0. Specific weight 5.92—6.70. Colorlessto brownish. Transparent, faintly tinted. Composition is subject to great variations, %: 60.01—81.25 Ta_2O_5, 55 0.33—6.05 Nb_2O_5, 0—0.02 TiO_2, 1.0—8.01 SiO_2; 0—2.0 SnO_2, 0.16—0.82 FeO, 0.12—3.48 CaO. Occurs in granitic pegmatites.

- Ilmenorutile (Ti, Fe, Nb)O_2. Syngony is tetragonal. Form is prismatic, often acicular. Hardness 6.0—6.5. Depending on Ta and Nb content, specific weight varies from 4.2 to 5.6. Color black, not transparent in passing light. Not soluble in acids, even in powder form. Difficulty ~~[illegible]~~ detected by fusing with $K_2S_2O_7$.

Composition of ilmenorutile is distinguished by great inconstancy, %: 36.24—66.28 TiO_2, up to 42.66 Nb_2O_5, up to 36.0 Ta_2O_5, up to 2.6 SnO_2, 5.0 Fe_2O_3, up to 15 FeO, 0.44 H_2O.

The nature of ilmenorutile is still obscure—it is hypothesized that this is the product of the disintegration of a solid solution of ilmenite and rutile, or is a mineral of the group of tantalite, or a mixture of minerals, i.e. of rutile with mossite.

Ilmenite $FeTiO_3$ usually contains $(Nb, Ta)_2O_5$ in quantities of the order of hundredths of a percent in the ratio Nb: Ta - 10. In places the content of $(Nb, Ta)_2O_5$ in ilmenite increases to tenths of percents, rarely to whole percents.

Rutile TiO_2 sometimes contains variable quantities of Nb and Ta, forming transitional members to its niobic variants, i. e. to ilmenorutile and to tantalic variant—strüverite.

Perovskite Ca (Ti, Nb)O_3 often contains ~~[illegible]~~ Nb_2O_5 in quantities up to 23%.

The niobic variant of perovskite—i. e., dysanalite (sp?), containing up to 22.73% Nb_2O_5 is especially valuable.

Sphene CaTiSiO usually contains small amounts of Nb and Ta but in certain of its variants, connected with alkali rocks, contains from 0.88 to 1.12% (Nb, Ta) O .

Cassiterite SnO of dark shades always contains (Nb, Ta) O in various amounts, varying (in ~~up~~ dependence upon the genesis of the deposit) ~~up~~ from traces up to 6%.

Wolframite (Fe, Mn) WO from various deposits contains (Nb, Ta) O in amounts ranging from 0.005 to 2.22%.

Deposits of tantalum, relating to but one genetic type—i. e. to granite pegmatites, are known only in several regions in all. The largest deposits of this type, the Pilbara (Australia) and in Brazil, consists of a series of dikes composed of quartz and feldspar, containing a fine impregnation of tantalite, accompanied by columbite-tantalum, cassiterite, and beryllium. In the zones of greisenization (conversion to granite), the tantalite content increases considerably.

The Nb deposits are more variegated in their origin.

Magmatic deposits of Nb, associated with granitoids, are known in Nigeria (Jos Plateau). They are massifs of biotitic and ribekite (sp?) granites, containing as accessories columbite, and also zircon, thorite, cassiterite, ilmenite, more rarely xenotime and monazite. Columbite is very fine, in sizes from 0.074 to 0.15 mm, rarely up to 0.5 mm. The columbite content comprises 0.001—0.01%, and in eroded sectors it increases to 0.2%. Ores of this type, although poor in content, but usually complex, [illegible] are easily beneficiated and represent large reserves.

The pyrochlore granites of No. Nigeria contain fine, of the order of 0.05 mm, impregnation of pyrochlore, rarely topaz and cryolite. In one of the deposits in the Kaffo River valley, the Nb_2O_5 content reaches 0.28% and the reserves are estimated at several tens of millions of tons. An annual extraction of pyrochlore amounting to several tens of thousands of tons [135] is noted.

Loparitic nepheline syenites occur on the Kola Peninsula. Loparite forms a fine (0.05 to 1 mm) but uniform impregnation in various rocks of nepheline syenite complex—in egyrin malignites, lujavrites and urtites, occurring in the form of thin but very enduring sloping strata.

Perovskite ultraxial alkaline rocks refer to the olivinites, pyroxenites, nephelenic pyroxenites etc. in which titano-magnetite and perovskite, containing $(Nb, Ta)_2O_5$ in the ratio Nb : Ta = 39, forms impregnations and pockets. The basic metals are Ti and Fe, while the accessory ones are Nb and rare earths. Deposits of this type have local distribution, being known on the Kola Peninsula.

Pegmatitic deposits of Nb occur widely in nature and are associated mainly with granitic, and to a lesser degree with alkaline, magma. They are known in many regions: in the Transbaikal region, the Sayans, Urals, Turkestan, Kola Peninsula, So. Dakota, New Mexico, SW Manitoba, Norway, Sweden, W. China, Mongolia, W. Australia, etc.

Deposits of this type are veiny- or lens-like bodies with a thickness of over 25 m with a length of up to 1 - 2 km consisting of feldspars, quartz, muscovite with an irregular, in general lean, impregnation of Nb and Ta minerals, including columbite-tantalite, euxenite, microlyte, simpsonite, sometimes being accompanied by the minerals lithium, cesium, tin, beryllium(spodumene, amblygonite, pollucite, cassiterite, beryl).

Tantalo-niobates are usually involved together with other minerals (spodumene, pollucite, beryl) or incidentally in the development of pegmatites in ceramic raw material. At the single deposit called Bare-Baily (USA), where the tantalo-niobic mineral (euxenite) has independent importance, one can extract around 450 tons of niobic concentrate yearly.

Pegmatites of alkaline rocks, associated with nephelinic and biotite-egyrin syenites, contain an impregnation of phyrochlore, zircon, ilmenorutile, accompanied by ilmenite and magnetite. Deposits of this type have local occurrence for instance in the Urals.

Metasomatic deposits are represented mainly by carbonatites, i. e. by coarse- and average-grained rocks, externally resembling marble, as they were mistakenly identified until just recently.

Carbonatites consist mainly of calcite and to a lesser degree of dolomite with an admixture of various micas, vermiculite, olivine, pyroxene, amphibole, magnetite, sulfides—of pyrite, chalcopyrite, and galenite.

The useful components of carbonatites are very diverse: niobic minerals are represented mainly by pyrochlore, less often by hatchettolite, koppite, perovskite and dissnalite. The accessory minerals are zircon, baddeleyite, monazite, uranic thorianite, bastnaesite, apatite, magnetite, titano-magnetite [137].

The content of (Nb, Ta) O in carbonatites usually fluctuates with the range 0.1—0.5%, reaching 1.0% and more, while the ore reserves are reckoned in tens of millions, in places in hundreds of millions, of tonns.

For example, in Mbeya (Tanganyika), the estimated small part of reserves amounts to 9.5 million tons of ore with an average content of 0.6% Nb O .

In Kenya in a recently discovered deposit of carbonatites, about 30 million tons of ore containing 0.7% Nb O was found, but the ore impregnation is very thin, which will obviously create difficulties in beneficiation.

In Sjova (Soeva?) (sp?) (Norway), the surveyed reserves of koppite ores in carbonatites comprise 3 million tons with content of 0.2 - 0.3% of Nb O .

Pneumatolito-hydrothermal deposits are represented by greisens, quartz-feldspars and quartz-vein formations with cassiterite, scheelite, and wolframite. Ta and Nb are found mainly in cassiterite and wolframite in the form of an isomorphic admixture, or possibly in the form of the finest inclusions of individualized minerals.

The content of (Nb, Ta) O in these minerals is measured in tenths, rarely in whole numbers. Of practical interest are the cassiterites from high-temperature formations (of greisens and quartzitic veins, genetically associate (connected) with pegmatites), sometimes containing over 1% of Nb and Ta.

Table 17

Types of Industrial Deposits of Nb and Ta /13/

Genetic type	Useful minerals	
	Main	Accessory
I. Magmatic		
Associated with granitoids	Columbite, pyrochlore	Cassiterite, zircon, malacon (malachon?) (sp?)
Associated with alkaline rocks-nephelinic syenites	Loparite	Cryolite Lomonosovite, murmanite
Associated with ultraxial alkaline rocks	Perovskite	Titano-magnetite
II. Pegmatitic		
Granitic pegmatites	Tantalite	Columbite, tantalite, beryl, cassiterite
	Columbite-tantalite	Cassiterite, beryl, spodumene, lepidolite, pollucite
	Euxenite, fergusonite	Lan-ine, cirtolite (sp?),
Alkaline pegmatites	Pyrochlore, hatchettolite, ilmenorutile	Zircon, ilmenite

(continued on following page)

Table 17 (concluded)

Genetic type	Useful minerals	
	Main	Accessory
III. Metasomatic		
Carbonatites	Pyrochlore, koppite, dysanalite	Magnetite, titano-magnetite, apatite, vermiculite, baddeleyite
IV. Pneumatolito-hydrothermal		
Greisens, quartz-feldspar- and quartzitic veins	Cassiterite, wolframite, scheelite,	—
V. Sedimentary		
Eluvial-deluvial and alluvial	Columbite-tantalite, pyrochlore, samarskite, thorolite	Cassiterite, zircon, wolframite, gold, ilmenite
Bauxites	Ilmenite	—

Sedimentary deposits are represented by placer deposits of various origin— of eluvial, deluvial, and alluvial origins, connected principally with granites and their pegmatites.

From the placer deposits, there are mined columbite, columbite-tantalite, pyrochlore, rarely samarskite and thoralite, usually accompanied by cassiterite (Nigeria, Uganda), by zircon, wolframite, gold (Bynoe Harbor, No. Australia), by monazite (Brazil), zircon and ilmenite (Travancore). Very often cassiterite constitutes the chief component, while columbite-tantalite is extracted incidentally.

The economic significance of placer deposits as a raw material base of tantalic and niobic concentrates is very great. In foreign countries, about 70% of all production of concentrates is furnished by these deposits, especially the Nigerian ones. The content of tantalo-niobates in the deposits varies in broad limits—from 100—200 g/m^3 to 1000 g/m^3.

Among other sources of niobic raw material, one should point out the niobic ilmenite found in the Arkansas bauxites (U. S.), containing 0.8% Nb O (0.0% in the bauxite). In the products of their processing (black sands and brown slime- are concentrated Ta and Nb. The bauxite deposits are evaluated at 44 million tons and they do contain about 22 thousand tons of Nb_2O_5. On the basis of these ores the USA is contemplating the building of a niobium extracting plant.

Foreign literature also carries information about the extraction of Ta and Nb from slags obtained during the reducing smelting process of stannic concentrates (Malaga, Belgian Congo).

The raw materials base for the obtainment of niobium and tantalum concentrates at present time are the alluvial deposits and the basic sources of columbites and tantalites in granites and granite pegmatites and alkaline pegmatites with pyrochlore. Carbonatites with niobium (pyrochlore) contents appear to be highly perspective and promise to become the largest raw materials e for these elements

There are no definite technical conditions for tantalum and niobium ores, use is made of ores with various content of these metals, depending upon the presence of other useful minerals which can be extracted simultaneously with tantalum-niobates.

Industrial importance can be acquired by ores in which the $(Nb, Ta)_2O_5$ content is measured in toto in hundreds of fractions of a percentage.

The low tantalum and niobium content in ordinary ores brings up the need for their concentration (enrichment), which is realized on concentrating tables with subsequent flotation, electromagnetic or electrostatic separation during the obtainment of collective concentrates.

Concentration of tantalite-columbite ores

As an example of concentrating tantalite ore can serve the manufacture of the concentrate at the Black Hills source in the USA [148]. After large scale pulverization of the ore (to - 25 mm) it is subjected to sifting; the top product is recycled for additional pulverization and the lower one is subjected to moderate pulverization in a conical pulverizer (to - 0.12 mm). After pulverization on a roller type grinder the ore is spread into three fractions: - 8 + 14, -14 + 20 and - 20 mesh which are further concentrated on tables with the derivation of types of concentrates in respect to size; 60 The Ta_2O_5 content in the concentrates constitutes from 98.7 to 57% [128].

To further reduce the crude gravitational concentrates many enterprises employ magnetic separators) complex ores of columbite-tantalite, cassiterite and wolframite) and spiral concentrators (ores of the lepidolite-microlite-tantalite) which make it possible to obtain rich concentrates. Later stage enrichment is sometimes done on concentration tables (Nigeria).

As an example of concentrating with magnetic separation is the processing of the tantalite- cassiterite concentrate obtained by gravitational methods from ores of western Australia [149].

This concentrate contains cassiterite ($\sim$ 56.6%), tantalite ($Ta_2O_5 + Nb_2O_5 \sim$ 32.3%) zirconium, tourmaline and a number of admixtures. The separation of cassiterite and columbite by the specific weight is difficult, but their magnetic properties are sufficiently variegated to break up same by magnetic separation.

Magnetic separation is realized on an entirely different separator of the Rapid type at a rate of rotation of the disks of 29 - 42 rpm, DC voltage on the electromagnet of 220 v and amperage of 1.5 amp.

As result of the separation the SnO_2 content in the magnetic fraction drops on the average to 4.33% (amount of fraction is 36.84%) and in the nonmagnetic fraction it increases to 87.23% (63.16% of the weight of the concentrate). In this case the separation does improve with an increase in the fineness of the corresponding fractions: magnetic fractions + 9, + 12, +16 mesh contain 13.33%, and fractions - 200 mesh 2.08% SnO_2.

When magnetic separation is applied to additionally pulverized concentrate - up to 2 - 60 mesh, results were obtained which are shown in table 18.

Table 18. Results of magnetic separation

Product	Yield,%	Content, %	Distribution, %
1-st Magnetic			
2-nd Magnetic			
Nonmagnetic		Values as in original	
Slimes......			

61 Thus, the direct commercial production is 26% of the total concentrate because that part contains 73% $(Ta,Nb)_2O_5$ and 2.6% SnO_2 (less than the permissible 3%) during the extraction of 61% tantalum and niobium.

Further separation (break up) of the nonmagnetic fraction containing also nonmagnetic tantalum minerals (stibiotantalite, microlite and stibiomicrolite) can be done chemically by chlorination, reduction of SnO_2 with hydrogen (a charge requires 27 kg of hydrogen which is passed for 30-35 hours at a rate of 0.34 - 0.40 m³/hr at 750-800° with leaching of reduced tin with hydrochloric acid), calcination with lime or smelting with alkalies or bisulfate, as well as reduction with carbon containing gaseous and solid reducing agents.

The reduction in the latter case is realized in a rotating retort furnace at 950-1000°; the best reducing agent is sawdust. Time of heating during reduction is 9 hours. The beads of reduced tin are sifted and separated on a concentration table and then melted into ingots.

The concentrates from the tables are subjected to contact treatment to separate the metallic tin and the nonmagnetic parts represents a concentrate quite rich in tantalum and niobium.

Fig.15 shows the preliminary technological arrangement for the process of complex magneto-chemical enrichment [149].

The composition of the Nigerian concentrate obtained from alluvial sources usually includes nonmagnetic cassiterite , magnetic cassiterite, ilmenite, magnetite, columbite, monazite , topaz , zirconium, thorite and tantalite.

For its complex enrichment with the obtainment of a series of valuable concentrates mechanical-magnetic-~~electrostatic concentration~~)enrichment) is used [150] the arrangement of which is shown in fig. 16. An analogous method is described by [151] .

Enrichment of pyrochlore and loparite ores [148]

The basic method of enriching these ores is gravitation as result of which is obtained a crude concentrate subjected to final flotation, electromagnetic or electrostatic enrichment. The extraction into commercial production does not exceed 60-70% due to the considerable losses of components in the sludges and the imperfection of the concentrating arrangements.

Enrichment of loppite ores [148]

The enrichment of loppite ores with consideration of the characteristics of their mineralogical composition is done by gravitation on concentrating tables with subsequent removal of the pyrite by flotation, magnetite - by magnetic separation and apatite - by processing the concentrate with nitric acid with the obtainment of calcium nitrate used as a fertilizer.

Fig.15. Technological arrangement of processing cassiterite-columbite concentrate

Fig. 16 (63). Arrangement of combined concentration of Nigerian complex ores.

Use of flotation ~~during~~ the concentration of tantalum-niobium ores [148].

Flotation on initial ores is presently not being employed even though it appears to be perspective; experiments on the flotation of columbite and pyrochlore, carried out at the M.I.Kalinin MITSM and Z have shown, that they do well submit to flotation with sodium oleate and with the cation reagent IM-11. Columbite requires a pulverization size of 200 mesh while pyrochlore needs only - 100 mesh. When sodium oelate is used in the role of collector during the ~~[illegible]~~ flotation of columbite it calls for a weakly acidulous medium, and for pyrochlore - for a weak alkaline medium.

According to [128] the separation of collective concentrates by flotation allows to increase the $Nb_2O_5 + Ta_2O_5$ content from 10 to 45 - 50% and even more; the reagents during flotation are sodium oleate, carboxylic acid, amyl xanthate, pine oil; phosphorus in the form of apatite, is removed by flotation with liquid soap or sodium oleate.

Table 19 [128] shows an ~~[illegible]~~ exemplary composition of tantalite and columbite concentrates manufactured by certain foreign plants.

Table 19. Exemplary chemical composition of tantalite and columbite concentrates manufactured abroad, %

Oxides	West.Australia (tantalite)	Nigeria (columbite)	USA	Congo (tantalite)	Canada

7¾ - 3911 20395
8 - 4085
8 - 4143
8 - 4307
5½ - 2837
6 - 1692

39¼

Chapter III.The Metallurgy of Tantalum and Niobium.

A.Basic Technological Arrangements for the Processing of Ore Concentrates

by

G.V.Samsonov and V.I.Konstantinov

pp. 65-122 from book entitled " TANTAL i NIOBIY " (Tantalum and Niobium) published by Metallurgizdat Moscow 1959.

The discovery of tantalum and niobium minerals can be realized by fusing with alkalies or carbonates, treating with sulfuric or hydrofluoric acids, by chlorination.

The most complicated of all is the revealment of columbites and tantalites; pyrochlore, loparite and certain other minerals are much easier in processing. To discover columbites and tantalites industry employs most frequently the smelting of ores with sodium and potassium hydroxides, soda or potash, with potassium or sodium bisulfates or by processing the concentrates with hydrofluoric acid.

1. Fusing with alkalies

Fusing with NaOH. The principle of the method consists in transforming tantalum and niobium compounds during the fusion with NaOH into sodium tantalate and niobate form. Simultaneously there is the formation of tungstate, stannate, silicate and aluminate of sodium which are removed by leaching with water, as well as ferric and manganic hydroxides, which together with the water-insoluble sodium tantalate, niobate and titanate remain in the residue. When the residue is treated with hydrochloric acid the iron and manganese transform into solution and in the residue remain the hydroxides of tantalum, niobium and titanium (fig.17).

Technologically this principal scheme is realized in the following manner: the concentrate is smelted in iron crucibles or in fire resistant steel crucibles. The weight ratio of the concentrate and alkali during the fusion is usually accepted as equalling 1 : 3.

Instead of NaOH at times is used Na_2CO_3 or a mixture of NaOH (90%) and Na_2CO_3 (10%) [152]. Sodium carbonate is added to reduce the viscosity of the melt. The smelting ceases at a temperature of 850°. The sodium carbonate/alkali mixture is melted at a temperature of ~500°. After its smelting the temperature is raised to 800-850°, and the concentrate pulverized to optimum size (not too thin), so as not to cause waste due
66> to dust elimination, is introduced in small batches during the mixing of the smelt. After a 10-15 minutes exposure at maximum temperature the smelt is either poured into water and granulated, or is poured in a thin layer on iron sheets or pans. The pulverized fusion goes then into the leaching operation.

Fig.17. Schematic drawing of the process of obtaining tantalum and niobium oxides from tantalum (columbite) by smelting the concentrate with sodium hydroxide.

The reactions taking place during the smelting (fusing) were investigated by Spitsin and Lapitskiy [67]. Until this report was made public it was assumed [153, 154] that during the fusion is formed a metaniobate and metatantalate ($NaTaO_3$ and $NaNbO_3$), however already during the processing of tantalo-niobium concentrates it was shown [69] that Nb_2O_5 reacting with the NaOH solution forms a salt of the composition $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$ (a so-called 7 : 6 salt; $7Na_2O$ has $6Nb_2O_5$).

Spitsin and Laitskiy investigated the products obtainable during the fusing of Nb_2O_5, $Na_{14}Nb_{12}O_{37} \cdot 32H_2O$ and $NaNbO_3 \cdot 3.5H_2O$ with sodium hydroxide in molecular ratio of Nb_2O_5 : NaOH = 1 : 33 (weight ratio 1:5.2) within a period of one hour at temperatures of 350, 450 and 650°, whereby it was found that in all instances is formed an anhydrous niobate of the composition Na_5NbO_5 (salt 5 : 1), having a specific weight of 4.405 and melting point of 980°. When exposed to water the salt hydrolyzes with the formation of salt 7:6 and sodium hydroxide. On the basis of these data it was assumed conditionally that tantalum fused with NaOH forms an analogous salt and that the reactions taking place during the fusing (smelting) of tantalite-columbite concentrates with sodium hydroxide or a mixture of $NaOH + Na_2CO_3$ are as follows:

$$(Fe,Mn)[Ta,Nb)O_3]_2 + 10NaOH = 2Na_5(Ta,Nb)O_5 + Fe(Mn)O + 5H_2O$$

Compounds of tungsten, silicon, tin and aluminum form during fusion soluble sodium salts: Na_2WO_4, Na_2SiO_3, Na_2SnO_3, $NaAlO_3$, and an admixture of titanium forms an insoluble titanate. During the leaching of the smelt with water , a job carried out in iron or porcelain reactors at 90-100° and a T : Zh ratio of = 1 : 3-4 [155] salt 5 : 1 hydrolyzes, transforming into 7:6 salt (for niobium) and hard-to-dissolve salt 4:3 (for tantalum): $Na_8Ta_6O_{19} \cdot 25H_2O$; $Na_5TaO_5 + 36H_2O = Na_{14}Nb_{12}O_{37} \cdot 32H_2O + 46NaOH$.

To reduce the solubility of tantalum and niobium salts a surplus of sodium ions (alkalies) is used in the solution during the leaching so that the solubility, for example, of 7:6 salt, according to Lapitskiy and Spitsin [69] decreases (at 90°) already at a concentration of 1% NaOH in solution with 26 to 1.1 g/l, i.e. by more than 20 times In this connection the residue obtained during the leaching is flushed several times with a warmed up [illegible] dilute solution of NaOH after which the sample goes to the acid treating operation.

For this operation is used a 20-% hydrochloric acid and the treatment is carried out by heating the solution to 90-100° with live steam and stirring. The T: Zh ratio in this operation constituted 1 : 4.

During the decomposition of the residue with acid the tantalum and niobium salts transform into their hydroxides:

$$Na_5(Ta,Nb)O_5 + HCl + H_2O \rightarrow (Ta,Nb)_2O_5 \cdot H_2O + NaCl.$$

Oxides of manganese and iron convert into solution in the form of chlorides.

The content of TiO_2 in the hydroxide mixture depends upon its content in the basic concentrate because during the fusion with NaOH, leaching of the melt and hydrochloric acid processing the titanium separates in a very low degree. Calcined oxides contain normally 96-99% of $Ta_2O_5 + Nb_2O_5$, 0.1 - 0.5% SnO_2, to 0.5% SiO_2 and up to 1% $FeO + MnO$ [155].

Fusing with KOH, K_2CO_3 or with a mixture of same. In technological set ups using

68) fusing with KOH or their mixtures, the process is conducted somewhat different because potassium tantalate and niobate are well soluble salts.

Fusion with KOH is realized at 700 - 800°, and with potash - at 900 - 1000°[*]. When analyzing the report [156] recommendation was made to use 1 weighed part of concentrate per 2.25 weighes parts of potash and the fusion itself to be carried out in a slightly reducing atmosphere to prevent the oxidation of the iron and manganese into higher oxides, conversion of titanium parts into potassium titanate, which is soluble in the presence of larger amounts of potassium niobate and conversion of SnO_2 into solluble stannate K_2SnO_3.

To create a reducing atmosphere the iron crucible is placed into a much wider graphite crucible and the space between same is filled up with charcoal powder. The processing time (above melting point) should last about 1 hour.

During the leaching after fusion into solution transform the soluble tantalum and niobium salts as well as K_2SiO_3, K_2WO_4, K_2SnO_3 and so on. From the solution are separated out by the addition of sodium chloride hard-to-dissolve sodium tantalate and niobate [**], or there is immediate deposition of hydroxide by the addition of a surplus of nitric [157], sulfuric [158] or hydrochloric acids. Such acid treatment is applicable

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[*] According to data by Konstantinov the fusion of 1 weighed part of concentrate (tantalite-columbite) with 3 weighed parts of potassium hydroxide should be concluded at a temperature of 750 - 800°.

[**] according to data by Konstantinov the salting out process is best carried out with a saturated solution of sodium hydroxide at room temperature.

only to highly pure concentrates containing a small amount of $WO_3 SiO_2$ and TiO_2. Described is also a method of treating a solution after fusing the concentrate with KOH and immediate leaching with hydrofluoric acid taken in surplus form. This yields a mixture of fluorotantalate and fluorooxyniobate which is then purified of admixtures by repeated recrystallization [159] which considerably increases the tantalum and niobium losses.

In the case of deposition of sodium tantalate and niobate further processing of same is realized by decomposing with hydrochloric or sulfuric acids, as was cited above for the case of fusing the concentrate with NaOH. If fusion with potash is carried out in a highly intensive reducing atmosphere the together with the soluble tantalum and niobium salts are formed insoluble (even in hydrochloric acid) compounds which, apparently, appear to be analogous to tungstic bronzes [155]. To convert same into soluble tantalate and niobate it is necessary to subject same to additional sintering with the potash. That is why during the fusion the atmosphere should by only weakly reducing or even totally neutral. According to data by Konstantinov, as result of fusing tantalite-columbite concentrates, containing a greater amount of titanium silicon admixtures, with potassium hydroxide, leaching of the fusion, salting out the sodium tantalate and niobate with a sodium hydroxide solution and the processing of the residue with hydrochloric acid is obtained an impurity free mixture of niobium and tantalum pentoxides, containing after calcination at 500° no less than 99.2% of $Ta_2O_5+Nb_2O_5$ with the extraction from the concentrate, without consideration of waste processing, of 71.3%. The basic mass of tantalum and niobium wastes is in the residue together with iron, manganese and partially titanium during the leaching of the fusion. After treating with hydrochloric or sulfuric acids these wastes can be restored to industry.

2. Sulfuric Acid Processing

The technology consists in the processing of concentrates with sulfuric acid and the obtainment of soluble sulfates, filtering of the residue, dilution of the solution with a small amount of water for the hydrolysis of alkali-earth sulfates, separation of the solution from the residue and repeated addition to the solution of a larger amount of water for hydrolytic separation of tantalum and niobium (partially also titanium), while the remaining impurities remain in the solution [160]. A greater number of technological variants of this method is known however not even one of these has acquired broad industrial application.

The processing with sulfuric acid was adopted at the IGF plant at Bitterfeld (East Germany) [161]. The ore, containing 0.2 - 0.5% of Nb_2O_5 in the form of koppite ingrained in calcite, was processed with nitric acid with the derivation of calcium nitrate, and the residue containing approximately 5% of Nb_2O_5 was subjected to enrichment (concentration), magnetic separation and gravitational separation on work-benches and derivation of 15-17-% (by Nb_2O_5) concentrate.

The concentrate was treated for 4 hours at 180° with a 75-% sulfuric acid (consumption of acid 40 kg per 1 kg of Nb_2O_5) to transform the niobium pentoxide into solution which was diluted with water to reduce the H_2SO_4 concentration to 55% and to filter same. The filtrate was diluted with water to a 20-% concentration of H_2SO_4 and neutralized with ammonia to preserve in the solution 2% free sulfuric acid. Niobium in the form of hydroxide was transformed into residue, which was filtered and washed. After calcination the product contained 96% of Nb_2O_5, 2% Fe_2O_3 and 0.5% TiO_2. The yield of niobium (from concentrate) constituted ~ 95%. The entire process was carried out in an apparatus coated with acid resistant enamel. To reduction the consumption of acid another IGF plant adopted the treatment of koppite concentrate with 98-% sulfuric acid with transformation of niobium into solution (solubilization of niobium) in the form of a complex oxalate by the action of a diluted oxalic acid solution. During the neutral-
70> ization of the solution with an aqueous ammonia solution the niobium hydroxide deposited on the bottom and the ammonium oxalate was returned for leaching out the product of sulfuric acid treatment.

Sulfuric acid and ammonium sulfate treatment [162]. Using the system of going through the processing with sulfuric acid and ammonium sulfate, the columbite concentrate containing for example 54.2% Nb_2O_5 and 19.9% Ta_2O_5 and an iron and manganese admixture is subjected to oxidizing calcination for a period of 2 - 3 hours until its black color turns brown. Next 50 kg of calcined concentrate is heated for 8 hours at 200-400° with 18½ kg concentrated sulfuric acid and 25 kg of ammonium sulfate; in the final stages of the composition process to the reaction mass are added 500 kg of water so that the mass becomes paste like. The product of the processing is leached out with ~400 kg of water followed by the process of hydrolyzing the sulfates into hydroxides, the pulp is left alone, the residue is filtered out and purified of acids and soluble salts[1]. The hydroxide residue is then treated with a solution of oxalic acid and potassium hydroxide (125 kg acid and 75 kg KOH in 2500 kg of water), after which the pH of the solution is brought up by the addition of hydrochloric acid to 2.2. This reasults in the formation of a complex potassium-niobium oxalate while tantalum does not form such a salt. After this into the solution is introduced a hydrolyzing agent- solution of urea (25 kg urea solution in water at 90°).

In the residue at pH = 4.8 remains chiefly Ta_2O_5. The filtrate is heated up to the point of decomposition of urea and to same are added 40 kg of NH_4OH for the deposition of niobium pentoxide. Into the residue from the concentrate pass over more than 71% of the niobium pentoxide and its content of Nb_2O_5 and Ta_2O_5 constitutes ~ 93.17 and 1.3 (1.3%) respectively. After several repetitions of such treatment the extraction of niobium from the concentrate may reach up to 95%.

Treatment with sulfuric acid and Reducing Agent. By this method the concentrate was treater with sulfuric acid or a sodium bisulfate solution and the solution or pulp are reduced with zinc powder with a final hydrolysis during boiling.

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[1] According to the investigation by Goroshchenko [163] niobium and tantalum in fusions with low water content form the following unstable to moisture binary sulfates with ammonium sulfate: $NH_4NbO(SO_4)_2$, $(NH_4)_6Nb_2O(SO_4)_7$, $(NH_4)_3Nb(SO_4)_4$, $6(NH_4)_2SO_4 \cdot Ta_2(SO_4)_5$ and $(NH_4)_3Ta(SO_4)_4$.

Under the effect of zinc the iron, tin and titanium are reduced to lower valences and remain in the solution, and the tantalum and niobium in the form of hydroxides are in the residue. At times this process is changed into such a way that the niobium is reduced into a 3-rd or fourth valence and separates itself from the tantalum [164]. Upon recommendation of [165] into the solution after sulfuric acid treatment of the concentrate is added a reducing agent, which reduces all metals except tantalum and niobium which precipitates upon hydrolysis in the form of hydroxides. The residue is filtered off, again dissolved in an acid sulfate solution, the niobium is reduced to tetra-valent state while the tantalum deposits upon hydrolysis. The Nb^{4+} is then again oxidized in solution into Nb^{5+} and in the form of a hydroxide is converted into residue by hydrolysis.

7A

Fusing with bisulfates [164]. By this method the finely pulverized concentrate is fused bisulfate (in ration 1:3). The alloy is treated with water which dissolves iron, manganese compounds and a greater part of the titanium. The insoluble residue is washed, treated with ammonium polysulfide to remove the tin and tungstate transforming into solution in the form of thio salts, then subjected to the effect of hydrochloric acid to remove the iron sulfide and other metals. The remaining mixture goes for tantalum and niobium separation.

3. Treatment with Hydrofluoric Acid and Fluoride Salts

This technology belongs to one of the oldest and was preciously used at the Siemens-Schuchart plants [166]. It consists in primary processing of concentrates with hydrofluoric acid during live steam heating, filtration of obtained solution, precipitation of the fluorotantalate by the addition of KF with subsequent 4-5-fold recrystallization of same. When the concentrate is treated with hydrofluoric acid together with tantalum and niobium into the solution pass over iron, manganese and other admixtures which during the recrystallization of K_2TaF_7 remain in the solution where also a larger part of the niobium remains in the form of fluorooxyniobate $K_2NbOF_5 \cdot H_2O$.

The process a greater consumption of hydrofluoric acid and is characterized by low extraction of tantalum. Furthermore the use of this method hamper the simultaneous obtainment of niobium because of the considerable content of admixtures in the mother liquor in which the niobium is situated.

It was suggested to use instead of hydrofluoric acid a mixture of hydrofluoric and oxalic or any other organic carboxylic acid for treateting the concentrate [157]. These acids are capable of binding Ta dn Nb fluorides into complex compounds.

$$H_2TaF_7 + 3H_2C_2O_4 + H_2O = H_3[TaO(C_2O_4)_3] + 7HF;$$

$$H_2NbF_7 + 3H_2C_2O_4 + H_2O = H_3[NbO(C_2O_4)_3] + 7HF.$$

The hydrofluoric acid liberated thereat can be recycled for decomposition of the concentrate. To the described technologies are closely related methods based on the decomposition of concentrates with fluorides of various metals, mostly with fluorspar. 72) The alloy is treated with a mixture of CaF_2, H_2SO_4 and $H_2C_2O_4$ upon heating with live steam with the conversion of tantalum and niobium into solution for subsequent separation of same [168].

In one of the patents a proposal was made to carry out the electrolysis of the obtained fluoride solutions with the formation of insoluble hydroxides with subsequent treatment of same with various methods [169].

These methods found no practical application.

4. Chlorination

One of the most persepective methods of extracting tantalum and niobium from ores are the methods based on chlorination of corresponding concentrates. The principle of technologies based on this method, consists in the fact that Ta, Nb, Ti, Si, Sn and other elements of the concentrate form relatively easily the appropriate chlorides having various vapor pressure, i.e. different boiling points and condensation points, whereby the much higher boiling points of $TaCl_5$, $NbOCl_3$ and $NbCl_5$ offer the possibility by sublimation and fractional condensation to obtain relatively pure chlorides of these elements.

Table 20 lists the characteristics of chlorides of numerous elements most frequently encountered in tantalum-niobium concentrates (data from report [81] with modifications according to reports [77, 82-85, 170] *).

Chlorination of oxides can be realized without reducing agents in accordance with reaction $MeO + Cl_2 \rightleftarrows MeCl_2 + 1/2O_2$, as well as with reducing agents, in the role of which is used carbon, group of CO-phosgene, carbon of carbon tetrachloride and certain other ones.

When chlorinating tantalum-niobium concentrates in the role of reducing agent is normally used carbon in various forms. One of the technological variants of chlorinating loparite concentrate is the method developed in the USSR by Urazov, Morozov, Maksimova and Shmantsar' [171, 172].

Chlorination of tantalum pentoxide without reducing agents begins only at 1200° and niobium pentoxide - at 800° and is concluded by the formation in the case of niobium of a pentachloride/oxychloride mixture.

According to Urazov and others [171,172] in the presence of reducing agent (carbon pure Nb_2O_5 undergoes complete chlorination within 2 hours at 400 - 450° and Ta_2O_5 likewise within 2 hours at 450°. The degree of chlorination of loparite concentrate
73) reaches 100% at 700° and 4-hour exposure. It was established that the rate and thoroughness of chlorination increase upon an increase in time of chlorination, temperature and by increasing the degree of concentrate pulverization.

The entire technological process of chlorinating a loparite concentrate is presented on fig.18 [172] (fig.18).

Pulverization of the concentrate. Loparite concentrate of an approximate composition, % : 6 - 9 $Nb_2O_5 + Ta_2O_5$, 25-40 TiO_2, 18-20 ΣR_2O_3 (oxides of rare earth elements
74) 4-17 $Fe_2O_3 + Al_2O_3$, 7-8 CaO, 4-18 SiO_2, 8 $Na_2O + K_2O$ is pulverized in steel spherical grinders within a period of 5 hours and are sifted through a 60 mesh sieve; weight of 1 cubic meter of dry pulverized concentrate (volume weight) 2.18 t/m³.

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* See also page 27.

Table 20. Properties of Chlorides of certain elements (page 73)

Chloride	Spec.weight g/cm³	Melting point° C	Boiling point°C	Heat of format. kcal/mol	Color, brief characteristic
					Yellow,decomposable in water needles,volatile below boiling point.
					White crystalline substance
					Bright-yellow (white)crystals easily decomposable wit water
					Fuming transparent liquid decomposable by atmospheric moisture.
					Gray to violet crystals decomposable with water.
					Colorless crystals,soluble in water
					Gray-violet-black smelt
					Pinkish flakes soluble in water
					Colorless liquid,decomposable with water.
					Colorless fuming liquid soluble and hydrolizable in water.

Elements and values as in original

Fig.18 (page 74) Technological scheme of processing loparite by chlorination

Briquetting and coking. The batch for briquetting is prepared from pulverized loparite concentrate, charcoal and binding agent, e.g. syrup, gudrone etc. in ratios (by weight) 3:1:1.5. The briquets are pressed under a pressure of ~ 1 t/cm², then kilned to remove moisture and coked for 5 hours at 750-800°. The volumetric weight of the filling of coked briquettes constitutes 0.68 t/m³ and their apparent specific weight 1.5 t/m³

Chlorination of briquettes is carried out at 650-700° using dry chlorine and this lasts for 4-9 jours with a chlorine consumption (on a large scale laboratory installation) 0.1 - 0/2 kg per kg. (1 kg) of briquettes.

The processes taking place during the chlorination of ore raw material are extremely complex and were not thoroughly investigated. As to the mechanism of these processes there are numerous theoretical ideas (Spitsin, Urazov). In its simplest form the process of chlorination can be presented in the following manner.

75 During the chlorination are formed volatile at 650 - 700° chlorides of tantalum, titanium and niobium oxychloride:

$$Ta_2C_5 + 21/2C + 5Cl_2 = 2TaCl_5 + 21/2\ CO_2;$$

$$TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2\ ;$$

$$Nb_2O_5 + 11/2\ C + 3Cl_2 = 2NbOCl_3 + 11/2\ CO_2.$$

evaporating into a condensation system, and also non-volatile chlorides of calcium, rare earth elements etc.which do remain in the residue in the chlorination furnace.

$$2CaO + 2Cl_2 + C = 2CaCl_2 + CO_2;$$

$$\Sigma R_2O_3 + 11/2\ C + 3Cl_2 = 2RCl_3 + 11/2\ CO_2.$$

Fractiobal condensation of chlorides. The volatile chlorides withdrawn from the furnace are guided into the condensation system,consisting of two-three receivers-condensers [172].

In the first receptacle with a temperature of 170-200°, attained by outside hea of same, are collected the chlorides of niobium, tantalum and iron, and the more volati titanium chloride is collected in the second receptacle at room temperature.

The separation of Ta, Nb and Fe chlorides by further distillation is difficult because of the closeness of their boiling points (table 20). They are normally separated by the hydrolysis method,which was thoroughly investigated in report [172].

Hydrolysis. Experiments carried out on synthetic mixtures of $NbOCl_3 + FeCl_3$ showed [172] that during the hydrolysis realizable at ~ 100° with trapping the liberating hydrochloric acid vapors , the niobic acid adsorbs up to 2 - 2.5% Fe_2O_3. The authors of the report recommend a preliminary reduction of trivalent iron into bivalent:

$$2FeCl_3 + 3Na_2SO_3 + 3H_2O \rightarrow 2FeCl_2 + 3Na_2SO_4 + 6HCl.$$

which reduces somewhat the amount of adsorbed iron and mainly promotes the coagulation of the niobium hydroxide residue; recommendation is also made for washing the hydroxide residue with a 2-%HCl with an addition of NH_4Cl. In this case the content of adsorbed Fe_2O_3 drops to 0.2 - 0.4%. Practical hydrolysis is carried out at a ratio T : Zh = 1:13. The pentoxide obtained during the hydrolysis of chlorides from receptacle I (during the chlorination of industrial concentrate) consists of 99.25% $Ta_2O_5 + Nb_2O_5$, 0.5% $Fe_2O_3 + Al_2O_3$ and 0.25% TiO_2. The titanium chloride from receptacle II is also subjected to hydrolysis with the obtainment of TiO_2 or is used directly for the obtainment of titanium by metallothermal reduction.

76) In the experiment by [173] under laboratory conditions were developed methods of deriving pure niobium and tantalum compounds from products of chlorinating ore concentrates. In the role of initial materials they used a product obtained from water processing of chlorides. This product contained 42/14% Nb_2O_5, 1.26% Ta_2O_5, 1.8% TiO_2, 11.55% SiO_2, 6.0% Fe_2O_3, 1.50% P_2O_5 and 25/15% of allied substances. For additional purification from titanium and silicon the hydroxide was calcined, mixed with charcoal and edible syrup. Briquettes prepared from this mass were dried, coked and subjected to chlorination with gaseous chlorine at a temperature of 600°. The chlorides contained (in conversion into oxides) 55.8% Nb_2O_5, 1.30% Ta_2O_5, 0.90% TiO_2, 0.31% SiO_2, 0.80% Fe_2O_5. The chlorides were treated with hydrochloric acid diluted into a ratio of 1:1 at a T:Zh = 1:6 and temperature of 90-95° with subsequent dilution of the solution to to and HCl content of 6-7%. Here was attained an additional purification of titanium amounting to 27-30%. To obtain well settling and filtering residues 10 ml/1 of H_2SO_4 were added to the solution prior to charging the chlorides. In the case where no

additional titanium purification was required the chlorides were treated with water at T:Zh = 1 : 10, temperature of 90-95°; sulfuric acid was also used in the role of coagulator. Losses in ground acids with solutions have not exceeded 0.5%. To separate niobium and tantalum use was made of the fluoride method changed with consideration of the actual Nb:Ta ratio and the titanium and silicon content. In the case when the niobium pentoxide was intended for the derivation of ferroniobium it was necessary to cleanse same from phosphorus. For this purpose the hydroxide obtainable from the chlorides was processed during the heating with a solution containing 3% of NaOH and 10% NaCl. Sodium chloride was added to the solution to reduce niobium losses.

As an example of extracting tantalum and niobium in the form of chlorides may serve the chlorination of tantalite concentrates and slags derived during the processing stannic concentrates from the Belgian Congo [174].

In the experiment [175] to chlorination with gaseous chlorine and carbon tetrachloride were subjected tantalite concentrates containing 50% Ta_2O_5, 14% Nb_2O_5, 4.5% TiO_2, 9.2% FeO, 7% SiO_2, 5% SnO_2, 8% MnO. To chlorinate with chlorine the concentrate was pulverized, mixed with charcoal and palatable syrup, from the mass obtained in such a manner were made up briquettes which were dried and coked at a temperature of 800°. When preparing the briquettes for chlorination with carbon tetrachloride they were calcined in the open air at a temperature of 500°. The chlorination of concentrates was done under laboratory and enlarged-laboratory scales. The basic part of the enlarged
77) laboratory furnace was the quartz tube with a diameter of 110 mm and 1300 mm in height. The condensation system consisted of two condensers made of stainless steel and heated with the aid of an electric coil. This experiment has shown that the use of carbon tetrachloride for the chlorination of tantalite concentrates is unsuitable because it is impossible in this case to considerably reduce the temperature of the process while the cost of carbon tetrachloride is several times higher than the cost of chlorine. To chlorinate concentrates with chlorine the following conditions are recommended: tem-

perature 800°; chlorine consumption 150% of the theoretically needed amount, carbon content in the briquettes 9-10%. The degree of tantalum and niobium chlorination constituted 97% , direct recovery of same in the chlorides ~ 85%. In enlarged-laboratory conditions were obtained chlorides containing 28.34% Ta, 5.6 - 12.5% Nb, 0.09-0.43% Ti, 3.6% Fe , 0.11-0.37% Si, 0.1% Mn, 0.03% Sn. For the processing of chlorides were investigated three methods. According to the first one of these methods the chlorides were processed during heating with weak (diluted) hydrochloric acid using sulfuric acid as coagulator; the final product appeared to be a mixture of tantalum and niobium pentoxide. By the second method the chlorides were run through a filter made of chopped up charcoal at a temperature of 500° for the purpose of cleansing same from iron; the final product in this case was a mixture of tantalum and niobium chlorides. By the third method, the hydroxide mixture obtained during the hydrolysis of chlorides was used to obtain by the fluoride method a mixture of complex fluoride salts of tantalum and niobium with potassium or pure fluoride salts. All these method led to the formation of compounds suitable for the obtainment of tantalum/niobium alloys or pure metallic tantalum and niobium.

In the experiment [174] to chlorination were subjected slags obtained during the smelting of stannic concentrates and containing 7-10% Ta_2O_5, 2-4% Nb_2O_5 and 2-4% TiO_2. the chlorination was carried out in a horizontal tubular furnace (with nickel reaction tube 2.7 m long) with gas heating. The condensation system consisted of four vertical in-series arranged condensers 915 mm long and 101 mm in diameter each. The total area of the entire condensation system constituted 4.65 m^2. Each condenser was equipped with a piston for expulsion of the condensate through the lower haych.

Chlorination of slag treater with acid to remove a greater part of Mg, Ca, Fe, Ti and containing ~ 36.4% of $Ta(Nb)_2O_5$ was carried out in mixture with pulverized graphite (per 4 kg of slag 22.7 kg of graphite). The batch was prepared by subsequent mixing first in a spherical grinder and then in disc type pulverizer.

78) The extraction of $(Ta,Nb)_2O_5$ in the chlorides constitutes 52% and the condensers trapped only 55.4% of the product.

Chlorination of slag not treated with acid was carried out in a batch consisting of 49 kg of powdered slag (containing 7.88% Ta_2O_5 and 11.25% Nb_2O_5) and 22.7 kg of gra-hite at 650°. Chlorine consumption was 73 kg. Chlorination for a period of 28.5 hours led to the derivation of 16.8 kg of product (mean weight yield 0/853 kg/hr). The extraction in this case was 71.4% (according to $(Ta,Nb)_2O_5$) and the effectiveness of condenser action was 73.8%. In this way, at low-temperature chlorination prelimin-acid treatment of slags is not obligatory.

Described is also a number of other variants of the process of chlorinating tantalum and niobium concentrates. And so, the patent [176] proposes the chlorination of a finely pulverized concentrate with sulfur monochloride, in report [177] - chlorination of concentrates containing Nb, Ti and Sn by heating same with carbon tetrachloride and a number of other variants. So far these methods have not found industrial application.

5. Carbidization

Kuznetsov and Kalinina [178] introduced a method of treating loparite ores and concentrates consisting in the carbidization of same in high temperature furnaces with coal or coke taken in amounts sufficient for the conversion of all oxides into carbides, and with the addition of up to 5% Al to improve the crystallization of carbides. The carbide sinter or alloy is pulverized and treated with water and then with acid, whereby from the Ta, Nb and Ti carbides are separated the water-decomposable carbides of alkali earth and rare earth metals.

6. Extraction of Tantalum and Niobium from Stannic Concentrates

One of the additional sources of obtaining tantalum and niobium are stannic concentrates containing these elements. Ordinarily stannic concentrates are subjected to resucing smelting at which are melted out metallic tin and the tantalum and niobium are converted into slag. The method of chlorinating slags is described above. [179] Developed a hydrometallurgical method of extracting tantalum from slag derived during reducing smelting of stannic concentrates. The initial slag contained 4.6-8.55%

$_2O_5$, 1.9% Nb_2O_5, 6.1 - 9.7% Fe_2O_3, 3.5% TiO_2, 22% SiO_2, 14% SnO_2, 0.6% MnO, 7% Al_2O_3, % MgO, 10% CaO, 1.2% WO_3, 8.6% Na_2O. The slag was pulverized and sifted through a 100 mesh sieve, then treated during heating with diluted hydrochloric acid. Almost complete conversion into solution was experiences by iron, aluminum, manganese, magnesium and calcium, approximately 50% conversion was experienced by titanium, tin and tungsten. The residue was then treated with a hot solution of sodium hydroxide as result of which about 85% of the silicon and tungsten converted into solution. The product, obtained after alkaline treatment was subjected to the effect of hydrochloric acid for the destruction (break-up) of sodium salts and then leached out with hydrofluoric acid. From the hydrofluoric acid solution was deposited potassium fluorotantalate followed by recrystallization. Under semi-industrial scales direct extraction of tantalum from slag into commercial potassium fluorotantalate constituted 60-66%.

E. Separation of Tantalum and Niobium

1. Separation in the form of fluorine salts

This method, introduced about a century ago by Marignac [180], is based on the different solubility of binary fluorine salts of niobium and tantalum with potassium. To realize same the tantalum and niobium hydroxides are dissolved in hydrofluoric acid with potassium fluoride or chloride added to the solution.

The residue collects then K_2TaF_7 and partially K_2NbF_7 or $K_2NbOF_5 \cdot H_2O$ depending upon the acidity of the solution ($K_2NbOF_5 \cdot H_2O$ - to a concentration of HF in the solution of ~7% at 25°C). Then, utilizing a considerably higher silubility of $K_2NbOF_5 \cdot H_2O$ as compared with the solubility of K_2TaF_7, by recrystallization from the diluted HF solutions is obtained a relatively pure potassium fluorotantalate which is used for the derivation of tantalum.

From the mother liquors after precipitation and recrystallization of the potassium fluorotantalate is extracted niobium.

The method introduced by Marignac was improved and theoretically based thanks to the experiments of Soviet researchers Meyerson, Zverev and Zhilkova, as well as Savchenko and Tananayeva [70-72].

For practical purposes, the technology of separating tantalum and niobium by the above described method, consists in the following [155]. The tantalum and niobium hydroxide mixture is dissolved in concentrated (35-40-%) hydrofluoric acid taken with a 10% - 15% surplus per the amount necessary for the passing of the reaction:

$$Ta_2O_5(Nb_2O_5) + 14HF = 2H_2[Ta(Nb)]F_7 + 5H_2O.$$

If the HF concentration in the solution after dissolution of the hydroxides is below 7% the fluoroniobic acid hydrolyzes with the formation of H_2NbOF_5.

The dissolution is realized in rubberized ebonite coated or lead-coated reactors upon heating to 70-80°. After settling the solution is decanted and filtered through

80 a cotton or perchlorovinyl fabric. The filtrate is diluted to such a $NbOF_3$ content in it so that by adding KCl the concentration of $K_2NbOF_5 \cdot H_2O$ will be close to saturation (6-8%). Into the heated solution is then added KCl to obtain K_2TaF_7 and K_2NbOF_5:

$$H_2TaF_7 + 2KCl = K_2TaF_7 + 2HCl;$$

$$H_2NbOF_5 + 2KCl = K_2NbOF_5 + 2HCl.$$

To maintain a constant HF concentration in the solution (1-2%), which is more convenient for operation than the concentration optimum for separation, equalling ~ 7%) potash is added to it; Sometimes potash is also used in place of KCl.

The deposition of K_2TaF_7 crystals is filtered off and for additional purification recrystallized from a 1-2% HF solution. The obtained potassium fluorotantalate ordinarily contains 0.1 - 0.3% Nb, ~0.3% Si, 0.2% Fe and 0.01% Ti.

To extract niobium from mother liquors one can employ the following method introduced by Yatsenko and Basse [181]. The acid mother liquor is first treated with potash and then with zinc. At such a neutralization of the solution the tantalum admixture goes into precipitation and the solution evaporates with crystallization of $K_2NbOF_5 \cdot H_2O$ salt which is then recrystallized and treated with hydrofluoric acid for conversion into potassium fluoroniobate K_2NbF_7. However this method, because of its low yield and harmfulness, has not acquired practical application.

The FANSTEEL Co Plants in the USA [159] maintain a complex process in the treating of mother liquors; the solutions boil with small potash additions for the purpose of hydrolyzing tantalum and titanium compounds. The cooled solution is then added to the excess NaOH solution whereby the sodium niobate precipitates in the residue. After its processing with hydrochloric acid is obtained a hydroxide which is dissolved in KOH. From the solution by adding sodium salts is again deposited sodium niobate with practically no titanium content. After alternate solution of sodium niobate in KOH from the solution by adding hydrochloric acid is precipitated high purity niobium hydroxide.

2. Separation by the Hydrolysis of Oxalates [162]

The method is described on page 147.

3. Separation by Fractional Distillation of Volatile Compounds.

Interesting is the Nisel'son [182] method of separating tantalum and niobium by fractional distillation of their pentachloride or even better their pentabrome compounds as having a greater difference between the boiling and melting points.

81)

4. Separation by Selective Reduction of Niobium Compounds

Niobium compounds (chlorides, oxides) in chemical ratio, as a rule, are less durable than analogous tantalum compounds, on what is based a number of assumptions regarding the separation of these elements.

Selective reduction of niobium chloride is based on the fact that niobium pentachloride reduced better with aluminum and hydrogen than tantalum pentachloride [79, 83]. Since aluminum can reduce simultaneously higher chlorides of niobium as well as of tantalum, it is used as a reducing agent in the amount necessary for reducing not more than 80% $NbCl_5$ into $NbCl_4$ (at 270°), which is less volatile than $NbCl_5$, $TaCl_5$ and $AlCl_3$ and remains in solid phase during sublimation of the remaining chlorides at 170°. $NbCl_4$ has a tendency to decompose into $NbCl_3$ and $NbCl_5$, it is stable only in the presence of a sufficient $NbCl_5$ surplus. Yet in the presence of $NbCl_5$, apparently, it is impossib to separate the entire niobium from tantalum by the use of this method. To avoid this it was suggested in this experiment [79] to carry out the reduction with aluminum taken i amount figured for the formation of $NbCl_3$ and not $NbCl_4$. The process of reducing $NbCl_5$ into $NbCl_3$ with aluminum is realized at 280-300°, lasting over a period of several tens of hours.

The composition of the pentoxides, obtained here from the ~~reducing~~ reduction products and not of the sublimated pentachloride compounds, is listed in table 21.

Table 21. Composition of Pentoxides of tantalum and niobium

Basic mixture	Composition of pentoxides, obtained	
	from reduction products	from sublimated pentachloride compounds

Elements and numerical values as in original

An analogous process of selective reducing $NbCl_5$ into lower chlorides, e.g. into

82) $NbCl_3$ is realized during the reduction of an $NbCl_5 + TaCl_5$ mixture with hydrogen. A detailed description of this process is given in reports [183, 184]*.

Another analogous method consists in the reaction of a tantalum and niobium chloride mixture with ammonium chloride at 500° [43]. The ammonium chloride at that temperature dissociates into HCl and NH_3, and the ammonia in turn into nitrogen and hydrogen whereby the nitrogen is capable of reducing Ta and Nb pentachlorides into lower chlorides, the pentoxides - into lower oxides and the oxychlorides - into oxides and chlorides.

Selective reduction of higher niobium oxide was introduced by Kroll and Bacon [185] as well as in numerous other reports of other researchers [186-189].

* see page 96

In accordance with Kroll and Bacon selective reduction of Nb_2O_5 into Nb_2O_4 is realized with dry hydrogen, cleaned of nitrogen, at 900° with subsequent chlorination of the oxide mixture at 400 - 600°. Only the lower niobium oxide is chlorinated; the chloride is sublimated and the tantalum pentoxide remains in residue.

To reduce the possibility of tantalum conversion into chloride to the concentrate prior to sintering are added the basic oxides which together with the tantalum oxide bind themselves into strong tantalates. In the role oxides are used CaO [190], ZnO or carbonates [191]. The extraction of Nb_2O_5 by this method after five-fold processing by reduction and chlorination constitutes only a total of 50-55%.

Total separation of tantalum and niobium pentoxides by this method is hindered by the formation of solid solutions between the Nb_2O_5 and Ta_2O_5 as well as between NbO_2 and TaO_2 and that is why during the reduction is formed a mixture of oxides, which upon chlorination yield niobium chloride with an admixture of tantalum chloride.

[59] suggests to reduce with **moist** hydrogen a mixture of higher tantalum and niobium oxides at a temperature of 1000°. Judging from the reports of the authors reduction yields two products $(Nb,Ta)O_2$- rich in niobium and $(Ta,Nb)_2O_5$- rich in tantalum. When processing the reduction products with 80-% sulfuric acid at 200° niobium dioxide basically transforms into solution.

By this method already after the first reducing prowess the extraction of Nb_2O_5 in the sulfuric acid solution constitutes 85-89%.

According to information by [192] in Arkansas (USA) the selective reduction of niobium pentoxide is done by **sintering** the niobium-tantalum concentrates with carbon (coal) at a temperature of over 1500°.

Methods of separating tantalum and niobium, based on selective reduction of niobium compounds, have so far not attained wide industrial application.

85)

5. Separation with the Aid of Ion-Exchange Resins

Report [193] describes anionite separation of Ta^{5+} and Nb^{5+} from an HCl and HF solution with the aid of Dowex-I resin. The solution was passed through a column 12.5 cm high and cross section of 0.0226 cm^2 at a rate of 0.3 ml/cm^2. min. As result they obtained solutions containing tantalum and niobium of 99% purity.

The researchers under [194] investigated the separation of niobium and tantalum with the aid of anionites in an oxalate medium. The resin Dowex-II with a grain dimension of 200-500 mesh was placed in a 12 cm long column with a diameter of 6 mm; the rate of passing through the column (elutriation) of the solution was 2-3 mm/hr. The use of a solution containing in one liter one mole of HCl and 0.5 moles of oxalic acid, made it possible (at an initial mixture containing equal amounts of both elements) to obtain tantalum with a yield of 95% per one cycle and Nb with a yield of 85-90% with a content of ~ 1% Ta. The process of separating, as in previous experiment, was controlled by tagged Nb^{95} and Ta^{182} atoms.

Chernobrov and Kolonina [195] introduced the following technology for ionexchange separation of tantalum, niobium and titanium.

Complex hydrogen fluoride ions of these metals are absorbed by anionites of medium basicity EDE-10P, the dynamic volumetric capacity of which constitutes for niobium 10 mg/eqiv/g, for tantalum 7 mg-equiv/g and for titanium 6 mg-equiv/g, and then washed out with various solutions, whereby in the dynamic conditions the washing out has the following orders: iron, niobium, titanium and tantalum. Technical hydroxide is dissolved in oxalic acid and the solution is run through a column with anionites up to the point where about 40% of its volume is used up (by the total of Nb, Ta and Ti), after which it is washed out by passing three solutions in sequence: the first solution containing 35 g/l HCl washes out (elutrates) all iron, without niobium, tantalum and titanium, and then niobium (up to 80%), the second solution containing 100 g/m (3-m) HCl washes out the niobium residue and the entire titanium and finally, the third solution containing 175-210 g/l (5-6m) HCl with an addition of 10 g/l (0.5-m) HF washes out the basic part of tantalum without niobium and titanium admixtures. After the wash out (elutration) the anionite is used for further absorption and wash out operations without loss to the

///

interchange properties.

This method offers the possibility of obtaining niobium hydroxide containing less than 0.03% Ta_2O_5 and less than 0.02% of Ti, and also pure tantalum hydroxide.

6. Separation by Extraction

An important factor for separating tantalum and niobium is the method of extracting based on the different solubility of salts of these elements in organic solvents-
24) mixture of xylene and methyldioctylamine, diisopropylketone [196], ketones of aliphatic and aromatic series [197].

The most complete semiindustrial extraction method was developed by [197] by the use of a system consisting of hydrochloric acid-oxalic acid-methylisobutylketone. A drawing of the extraction installation is shown in fig.19. Extraction is by the continuous counterflow method in a pulsating column with sieve plates. The column consist s of a 3.7 m polyethylene tube (resistant with respect to the effect of oxalic and hydrochloric acids as well as organic solvents).

The extraction of tantalum and niobium was investigated with different ketones from a solution of 3.3-n HF and 0.5-n HCl, containing 16 g/l of tantalum and 19.3 g/l of niobium. The results, given in table 22 show, that the best extraction methods are demonstrated by methylisobutylketone and cyclohexanone.

When using methylisobutylketone the degree of niobium and tantalum extraction ~~xxx~~ increases with the increase in HF and HCl concentrations in the solution (fig.20).

Four variants of seperation have been introduced:

1) Extraction of tantalum by multiple periodic or continuous counterflow method from ~~oxalate~~ hydrofluoric acid solutions in the absence of chlorine ~~xxxxx~~ ions in the solution. In this case the amount of extracted niobium is low;

2) extraction of tantalum from ~~an oxalate~~ hydrofluoric acid solution in presence of hydrochloric acid in one or two stages, in this case a part of the niobium is extracted with the tantalum, the niobium remaining in the aqueous phase contains practically no tantalum;

3) extraction of niobium with hydrofluoric acid from solutions of anhydrous tantalum and niobium chlorides in methyliso butylketone;

4) single-stage extraction of tantalum from hydrofluoric-hydrochloric acid solution , adhering to the optimum separation conditions.

In accordance to the first variant as result of five-fold periodic extraction at an Nb: Ta ratio perior to extraction equalling 57.8, the extraction amounts to 75.6% Ta and 0.68% Nb.

The results of continuous counterflow (counter current) extraction are shown in table 23.

Tantalum hydroxide precipitates from the organic phase with a 25-% ammonia solution, after which the organic phase is separated by decantation and the hydroxide residue is filtered off from the equous phase.

In the tantalum containing residue after desiccation and calcination are detected 0.001% Al, 0.005% Cu, 0.05% Si, 0.0001% Mg. 0.001% Fe and 0.1-1.0% Nb.

55)

Fig.19. Drawing of the extracting installation. 1- Reverse control arm; 2- refinate; 3- initial aqueous solution; 4- feeding pumps; 5- discharge, 6- pulsating pump; 7- extract; 8- initial organic solution.

Table [illegible]. Extractional effectiveness of ketones

Solvent	Extracted in %		Coofficient of separation
	Ta	Nb	
Methylisobutylketone			
Diisobutylketone			
N-butylethylketone			
Methyl-n-hexylketone			
Methyl-n-amylketone			
Diisopropylketone			
Cyclohexanone			

Fig.20. Degree of extraction of tantalum and niobium with methylisobutylketone from hydrofluoric acid solutions (equal volumes of phases; 16 g/1 Ta; 19.2 g/1 Nb).

6) Table 23. Results of continuous counterflow extraction of Tantalum

	Composition, g/1			Yield coefficient g/hr.inch^2	Ta	Nb
	Ta	Nb	Fe			
Initial aqueous solution						
Extract						
Refinate						
Initial aqueous solution after restoring to it the first batch of refinate.				Values as in original		
Extract						
Refinate....						

When an additional extraction of tantalum from the refinate is made it yields a product containing %: 99.9 Nb_2O_5, 0.05 Al, 0.05 Cu, up to 0.37 Fe, 0.009 Si and 0.1 Ti

According to the information by the authors, during the xtraction is possible the purification of niobium from titanium and silicon, but at high concentrations of hydrofluoric acid this may result in technological difficulties.

The employment of extraction at maximum acidity, speed of circulation and other conditions allows to obtain 99.85%-tantalum oxide and 99.97-% niobium tetroxide.

XXXXXX Report [198] proposes extractional separation of tantalum and niobium in the form of sulfates of oxalate complexes with the aid of amines, e.g. tribenzylamine in chloroform or methylene chloride in the presence of hydrochloric acid of 10-11-n concentration.

Good results are also attained by separating tantalum and niobium by the method of preferential extraction of Ta with 12-n hydrochloric acid from a mixture of methylaisobutylketone and diisobutylketone solutions containing anhydrous tantalum and niobium pentachlorides [199, 200].

[201] Investigated of cyclohexanone to extract complex fluorides of tantalum, niobium and titanium. It was estabiched that the most fully extracted is tantalum, in considerably lesser amounts niobium and in even smaller quantities titanium. The presence of niobium in the initial solution aids in a more complete extraction of tantalum into the organic phase. An analogous effect is exerted by titanium on the
87 extraction of niobium. An increase in the acidity in the initial hydrofluoride solution and the introduction into it of sulfuric, hydrochloric and nitric acid additions aid in increasing the extraction of tantalum and niobium. The most perfect extraction of tantalum and niobium is in organic phase and they separate from titanium when the initial solution contains 125 g/l HF and 225-300 g/l H_2SO_4. The presence of iron and silicon in the initial solution does not reduce the extraction of niobium into the organic phase. The presence of sulfuric acid is responsible for the reduction in iron and silicon extraction. Experiments were carried out under laboratory conditions to obtain pure niobium and tantalum compounds from a product containing 2.9% Ta_2O_5, 60.84% Nb_2O_5, 1.23% TiO_2. During double consumption of cyclohexanone, as compared with the initial aqueous solution, the extraction in organic phase constituted: 96% Nb, 99.9% Ta, 12% Ti. To cleans it from titanium the organic phase was washed with diluted sulfuric acid. Nibium from organic phase was reextracted with water, tantalum with an ammonium fluoride solution. The niobium penoxide obtained from the reextract contained ~ 0.080% Ta_2O_5 and 0.002% TiO_2.

C. Recovery of tantalum and niobium from their compounds.

Tantalum and niobium in the form of compact metals can be obtained from metallic powders and directly as result of reducing or thermal dissociation of certain compounds. In the first instance are employed ceramet (powder metallurgy) methods, arc, or induction smelting (for niobium).

In the second instance are ~~xx~~ used methods of reducing in vacuum (derivation of niobium by recovering its pentoxide with carbon or from a mixture of Nb_2O_5+ 5NbC) or the volatile chlorides are reduced with hydrogen (DURING the obtainment of tantalum and niobium coatings).

Tantalum and niobium powders are derived from proper compounds by methods of metallothermy or by electrolyzing the smelted media. In the role of initial products are used tantalum and niobium chlorides , complex fluorides and oxides.

Table 24 offers a listing of all the known methods of recovering tantalum and niobium including also the ones which yielded negative results.

The industrial methods used at present time for the manufacture of above indicated metals are: electrolysis of the smelted K_2TaF_7+ Ta_2O_5, KCl and KF mixtures, sodium-thermal reduction of K_2TaF_7 and K_2NbF_7, reduction of niobium (recovary of Nb) from the mixture of its pentoxide and carbide in vacum.

88 Table 24. Listing of methods of recovering tantalum and niobium

Process	Researchers	Remarks
Reduction of K_2TaF_7, K_2NbF_7, K_2NbOF_5 with alkali metals (Na,K)	Berzelius (1824), Rose (1856,1858). German (1872), Marignac (1868), Siemens (1909), Pennington (1896) Spitsym and Kashtanov [202] (1929) Dikson -Dukes [203], 1958. Zverev [263] (1937), Kolchin and associates [264-266] (1957-1958).	Metallic Ta and Nb powders are obtained
Reduction of $TaCl_5$, $NbCl_5$ and $NbOCl_3$ with metallic sodium or amalgam of alkali metals.	Rose (1856), Marden (1927), Morozov, belozerskiy, urazov [204] 1938 Glyazer [205] (1955).	
Reduction of $TaCl_5$ & $NbCl_5$ with metallic magnesium	Priyeto-Isasa, Cebaler, Wolf [206] (1947) Johansen, May [207] (1954)	
Reduction of $TaCl_5$, $NbCl_5$ & $NbCl_3$ with hydrogen	Pirani [208] (1908), Ebers [209] (1934), Cambell, Powell, Conser [210-213] (1948-1951), McIntosh Broadly [183] (1957), Steele Geldard [184] (1957)	Used in obtaining metal Ta and Nb coatings on various bases and for the obtainment of Metallic Nb powder.

Table 24 continued

1	2	3
Thermal decomposition of $TaCl_5$ and $NbCl_5$	Van Arkel [214] (1934) Burgers, Basart [215] (1934)	
Electrolysis of smelted mixture of K_2TaF_7, Ta_2O_5, KCl and KF	Weintraub [216-217] (1906-1910) Balke [218] (1931), Driggs [219-221] (1930-1932); Driggs, Lilliendahl [222-223] (1931-1932); Kirk, Brandt [224] (1935); Myers [225,226] (1946) Ma [227] (1952); Drossbach [228,229] (1953) Konstantinov, Suzdal'tsev, Sklyarenko [267] (1957).	Metallic tantalum powder obtained
Electrolysis of smelted mixture of K_2NbOF_5, K_2NbF_7, KCl & KF.	Balke [230] (1932), Ma [227] (1952); Drossbach [228,229] (1953-1954); Gurovitch [538] (1949).	Metallic niobium powder obtained
Electrolysis of melted mixture of Na_3PO_4, $NaPO_3$ and NaCl containing Nb_2O_5 or Ta_2O_5	Hartmann, Ebert and Dreitschneider [231] (1931); Sklyarenko, Druzhinina [232] (1940); Hartmann - Massing [233] (1951)	NbP or TaP deposits on cathode.
Electrolysis of solutions containing tantalum chloride	Plotnikov, Gratsiyanskiy [234] (1935.	
89 Electrolysis of aqueous and organic media containing Ta and Nb.	Droughall [235] (1928); Peirce [236] (1931); Izgaryshev, Prede [237-242] (1932-1934); Izgaryshev-Kaplan [243] (1934); Grenagle [244] (1933) Pokorny, Schneider [245] (1934) Armstrong, Menefee [246] (1937), Holt [247] (1935); Sein & Holt [248] (1949)	Negative results
Recovery of Ta and Nb from oxides with carbon and from their oxide and carbide mixtures	Berzelius (1825), Joliot (1876) Bolton (1907), Slade - Higson [249] (1919); Rohn [250] (1934-1935); Balke [251,252] (1940,1944), Kroll Schlechten [253] (1948); Kolchin and assoc. [264, 275] (1957, 1958).	Industrial method of obtaining Nb.
Reduction of Tantalum and Niobium oxides with metallic calcium and calcium hydride.	Cachemille [254] (1924), Meyerson, Kats, Kohlhaas [255] (1940); Gardner [256] (1950)	
Reduction of tantalum and niobium oxides with silicon	Zintl, Morawietz [257] (1942)	
Reduction of tantalum and niobium oxides with Al, Mg and rare earth mixture	Goldsmith, Bautin (1898), Smith, Maas (1894); Bolton (1905-1906) Weise, Achel, Nutman (1904-1907) Hagen (1910).	During reduction with Al are formed its alloys with Ta and Nb.
Reduction of tantalum and niobium oxides with hydrogen	Wartenberg, Broy, Reinicke [272] (1923), Grube, Kubashewski, Zwianer [258] (1938); Abrikosov [259] (1938).	Reduction with H_2 yields lower oxides.

1. Obtainment of powderous tantalum and niobium

Reduction of tantalum and niobium halide compounds.

Sodium-thermal method of manufacturing powderous tantalum and niobium

Sodium-thermal reduction of potassium fluorotantalate which is done in accordance with the following process

$$K_2TaF_7 + 5Na = Ta + 2KF + 5NaF$$

appears to be one of the first investigated tantalum obtainment methods which has been adopted by industry; it is based on a relatively low chemical strength of complex fluorides.

From the view point of energy the problem of separating metallic tantalum from potassium fluorotantalate, which can be represented as a product of combining $2KF + TaF_5 = K_2TaF_7$ or $TaF_5 \cdot 2KF$, consists mainly in breaking the bond between the tantalum and fluorine atoms, because the loss of time needed for the destruction of the $TaF_5 \cdot 2KF$ complex is comparatively small in comparison with the strength of TaF_5.

The isobaric thermodynamic potential TaF_5 $\Delta F^{\circ}_{298} = -56$ kcal/g-atom F. With a rise in temperature this value decreases correspondingly (fig.21 and 22).

The isobaric thermodynamic potential od NaF constitutes 129.2 kcal/g-atom F. Thus, during the reduction of TaF_5 with sodium:

$$TaF_5 + 5Na = Ta + 5NaF$$

are liberated about 70 kcal per 1 g-atom of fluorine in conversion by 1000° (approximate reducing temperature [155]). If we should take into consideration the heat of that reaction (+ 360 kcal) and convert same per 1 g of the $K_2TaF_7 + 5Na$ batch, then the specific thermal effect of the reduction reaction of K_2TaF_7 with sodium will be 713 cal/g, which is perfectly sufficient for spontaneous reaction without external heating [260].

In the role of reducing agent is used sodium rather than potassium (potassium less often). Calcium, magnesium and aluminum are noy used because calcium and magnesium fluorides are practically insoluble in water and aluminum forms a fusion with tantalum.

Under industrial conditions prior to activating the sodium-thermal reduction process the potassium fluorotantalate is dried at a temperature of approximately 125° and the cut up sodium pieces are thoroughly washed with gasoline and exposed to air to the point of absolute evaporation of the gasoline. The reducing reaction is carried out normally at a sodium surplus of not less than 15%.

The reduction is realized in iron conical crucibles in which the sodium pieces and the potassium flurotantalete are placed in layers. First of all, before placing the potassium fluorotantalete into the crucible the bottom of it is covered with a sodium chloride layer. Over the charge is placed a protective layer consisting of and old, already used and well calcined sodium chloride.

The crucible plus charge are heated at 120-130° in a drying cabinet. Prior to reduction it is covered with a lid with a weight to prevent ejection of the mass.

To begin the reaction the crucible is heated with a gas burner in one place (near the bottom) until it is heated to redness.After rapid passing of the reaction the crucible is again thoroughly heated by the burner.

9A

Fig.21.Dependence of the isobaric thermodynamic potential of fluorides of certain element upon temperature.

Fig.22.Dependence of isobaric thermodynamic potential of chlorides of certain elements upon temperature.

92> According to Sanderson [158] the crucible during reduction is being heated at a slow temperature rise in a shaft furnace. Thanks to this arrangement the entire charge is heated uniformly at a higher temperature and full reaction of these reagents (all their reagents) is warranted, and the sodium surplus is also utilized more effectively. [155]. Better results are obtained when the reducing operation is realized in a steel or nickel bomb from which the air is removed at first. [120]. However in accordance with Miller [261] this is not necessarily so because the sodium vapors form a protective atmosphere.

When the operation is carried out as result of batch-heating to high temperature (above 800°) the sodium is to a greter extent in vaporous state thus providing fine contact between the sodium and all the crystals of the potassium fluorotantalate up to the moment when parts of the charge become smelted. The termination of the reduction of potassium fluorotantalate, which is at high temperature in smelted state in the mixture with sodium chloride and fluoride and potassium fluoride, is secured by the high solubility of sodium in the melted salts [155].

After the reduced mass cooled off the tantalum powder is in form of very small particles ingrained in the solidified salt fusion which also contains the remains of the unused sodium surplus.

After the reduved mass is taken out from the crucible and after pulverization is carried out the so-called" quenching ". The pulverized mass in small portions during mixing is submerged into an iron water filled vat. Some industries use methyl alcohol instead of water for this operation [262].

After numerous water flushings the tantalum powder, containing admixtures of chlorides and fluorides of alkali metals, are pulverized in steel spherical grinders and finally washed several times with cold and hot water. If during the flushing the fine tantalum powder settles slowly, the addition of a 5-% NH_4Cl or NaCl solution and the flushing continues up to the point of totel separation from the fluoride salts [262].

After the water flushing the tantalum powder is processed with diluted hydrochloric acid. During the hydrochloric treatment there is the solution of the iron mixture, which for some reason or another has falln into the tantalum powder (from the iron crucible during reduction, during the pulverization in spherical steel grinders etc.) and to partial solution are also subjected the surface tantalum oxide films. The flushing with hydrochloric acid partially reduces also the content of titanium admixture.

93) Next the powder is washed with hot distilled water, diluted aqueous solution of ammonia and then desiccated at a temperature of 100-120°.

The powder, thanks to its greater specific surface, contains up to 2 - 5% of oxygen in the form of oxide films. A certain reduction in the oxide content can be attained if after the hydrochloric flushing we apply an additional flushing with cold diluted hydrofluoric acid [155, 262].

Besides oxygen the tantalum powder contains a certain amount of hydrogen adsorbed during the primary flushing of the reduction product by water. Furthermore, during an insufficient qualitative flushing the tantalum powder may still contain admixtures of sodium and potassium salts, constituting in conversion into the sum of alkali metals up to 0.1 - 0.2%.

According to Zrubin and Koptsik [154] the tantalum powder obtained by the sodium-thermal method, contains 97% Ta, 2.5% O_2, 0.20% C, 0.15% Na + K, 0.15% H and has the following grain selection: 86 (weight) % to 1 μ, 14% from 1.1 to 2 μ. According to Titterington [262] the powder contains 0.004% Fe, 0.15% C, 0/03% Si,).01% CaO, 0.10% Nb and has a grain selection as shown in table 25.

Table 25. Dimensions of tantalum powder grains obtained by sodium-thermal method

Grain dimension μ, not more than	Content %		Grain dimension μ, not more than	Content %	
	weight	number		weight	number

Numerical values as in original

Niobium powder can be obtained by an analogous method during the reduction of potassium fluoro fluoroniobate with sodium [203, 263-265]. According to [203] the reaction of reducing potassium fluoroniobate is realized ~~[illegible]~~ at 1100° with subsequent pulverization, leaching, filtration, flushing and vacuum desiccation of the obtained powder.

According to [264] the reduction of potassium fluoroniobate with sodium is carried out under a layer of sodium chloride in open vessel in the open air at 1000°. As result of reducing of larger amounts of potassium fluoroniobate, flushing and desiccation is obtained a metal powder containing 98.9 - 99.2% Nb + Ta (the amount of tantalum is determined by its content in the initial salt and ordinarily does not exceed 0.5%), 0.02 - 0.06% Ti, 0.04 - 0.07% Fe, 0.03 - 0.06% Si, 0.1-0.3% Pb, 0/09 -0.15% C and about 0.5% O_2. Direct extraction of niobium amounts to about 90% [265].

Powderous niobium can be obtained also by reducing potassium oxyfluoroniobate K_2NbOF_5 with sodium [266] (after the water molecule is removed from same by desiccation at 200°). The reducing conditions are analogous to the ones described for the reduction of potassium fluoroniobate.

Derivation of powderous tantalum and niobium by reducing their halide compounds with magnesium.

In addition to the above described methods of obtaining tantalum and niobium powders from halide compounds there is still another interesting method of reducing tantalum chloride (niobium chloride) with magnesium [206,207]. This method is analogous to the widely employed method of obtaining titanium and zirconium. The reducing reaction is exothermal:

$$2TaCl_5 + 5Mg = 2Ta + 5MgCl_2 + 38 \text{ kcal.}$$

and it takes place at a temperature of about 450°, i.e. below the melting point of magnesium. Prieto-Isaza conducted the process at 750° [206]. At this temperature the isobaric thermodynamic potential $-\Delta F^{\circ}_{1023} \approx 42$ kcal/g-atom which secures the passing of the reduction reaction to its conclusion. The reduction of $TaCl_5$ at such a temperature is realized in vaporous state.

The process consists of belnding a tantalum pentachloride powder with magnesium chips taken in a 10% surplus, and with any kind of substance which at a corresponding temperature forms a liquid bath with magnesium chloride, obtainable as result of reduction, particularly with potassium chloride. The mixture is entered into an iron or Pyrex tube one end of which is hermetically sealed. The tube is heated gradually, beginning with the bottom, Until the reaction starts it isneccessary to raise the temperature at any given point of the mixture above 450°. A more simple method for such heating is the lowering of the tube with mixture into the furnace at rate of approximately 250 mm/min. The furnace should be heated to a temperature of about 750°. When equal amounts of KCl (or NaCl) and tantalum salts are used the reaction discontinues if the heating of the tube by submerging same in the furnace is discontinued.

After the reaction is completed the salt ingot with the tantalum contained in it is treated with water. Then is added a small amount of hydrochloric acid to dissolve the magnesium surplus, as well as the iron and titanium, the powder is filtered off, flushed 6)
with water and alcohol and desiccated in vacuum at 70° (upon heating the tantalum or niobium powder obtained by a similar method, there may be a spontaneous combustion when
95) exposed to air at a temperature of about 60°). Niobium powder can be obtained by a similar method.

Tantalum and niobium powders consist of very small crystals having an acute-angled dendritic suructure (fig.23). The distribution of tantalum particles by dimensions is approximately the following: 100% less than 8 μ, 90% less than 5 μ, 1% less than 1 μ and 7.4% less than 0.6 μ. Particles of niobium powder had a dimension of less than 10 μ whereby 50% of them were less than 5 μ, 22%-less than 1 μ.

Fig.23. Thin particles of tantalum powder obtained by reducing tantalum pentachloride with magnesium. Electronmicroscopic picture X 13000

In the powder, obtained by reducing the chlorination products of ore concentrates, was detected the presence of from 0.10 to 0.54% of Mg, 0.30% Fe and 0.12% Ti.

Johansen and May [207] modified this process somewhat by reducing tantalum pentachloride vapors over smelted magnesium. In accordance with their description the tantalum chloride is placed in a quartz shuttle situated in the horizontal tube made of borosilicate glass with three zones of heating. The process is carried out in a protective helium atmosphere with perfect control of the degree of pentachloride evaporation to complete reduction of same. In one of the experiments the extraction of tantalum from $TaCl_5$ amounted 77.5%.

From the magnesiumthermal tantalum powder was obtained , by the arc smelting method, a tantalum ingot which was later rolled into sheets. In the sheet tantalum was found the following content of admixtures: 0.01% Al, 0.001% Mg, 0.1% Si, 0.016% C, 6 no iron has been detected. With a similar method was also obtained a nibium -tantalum alloy.

In a number of recent experiments [184.184] to obtain metallic powder recommendation was made to employ the method of reducing chlorides, particularly that of niobium, with hydrogen. It is assumed that this method- is one of the most economical ones. According to this method the mixture of tantalum and niobium chlorides, cleansed of all iron, is first heated at 500-550° in a hydrogen current (hydrogen stream), as result of which the niobium pentachloride reduces to an air-stable niobium trichloride, which condenses during the reducing process, while tantalum pentachloride remains unchaged.

Next the niobium trichloride is reduced with hydrogen at above 600° with the derivation of a niobium powder.

The unfavorable factor in the process is this that $NbCl_3$ is thermalyy unstable an during the reaction forms Nb and $NbCl_5$ thus reducing the effectiveness of reduction.

Electrolytic methods of obtaining tantalum and niobium powders

Electrolysis of smelted fluorides.

Derivation of electrolytic tantalum powder. Method of electrolyzing smalted fluoride media to obtain tantalum powder- is at present time the most widely employed industrial method. Using a similar method, but on smaller scale, for a period of many years was obtained also niobium. With this method it is possible to obtain also tantalum-niobium alloys [267].

As result of long lasting experimentation Balke in the 30-ties took out a patent for the derivation of tantalum by the electrolysis of smelted fluorotantalate in mixture with tantalum pentoxide and potassium fluoride [218].

Almost simultaneously with Balke, Driggs and Lilliendahl have also proposed to obtain metallic tantalum powder by electrolyzing the melt of tantalum fluoride in mixture with its pentoxide, whereby the authors pointed toward the need of adding potassium chloride and fluoride to the bath. In report [223] published by these authors, is described a number of experiments with the object of obtaining electrolytic tantalum powder with recommendations for the following composition of the initial bath, % (weight):

K_2TaF_7	8.5	
Ta_2O_5	8.5	
KCl	55.9	83.0
KF	27.1	

97〉 and additions in the electrolysis process:

K_2TaF_7	16.0	
Ta_2O_5	12.7	
KCl	59.7	71.3
KF	11.6	

Condition for carrying out the electrolysis: temperature of the process 750°, Current density on the cathode 90 amp/dm^2, cathode- nickel bar, anode - graphite crucible. The obtained powder after water flushing and pulverization was again processed with a nitric/hydrochloric acid mixture during boiling to remove traces of metal impurities and finally with a mixture of concentrated nitric and sulfuric acids during boiling to discontinue the liberation SO_3 vapors for the purpose of removing carbon residues.

It contained 0.05% C, 0.02% Fe, 0.01% Ni, 0.002% Mn.

Fig.24. Distribution curves showing the sizes of particles of electrolytic tantalum powder (according to Driggs and Lilliendahl):
● -KF; o-KCl; - KCl + KF.

Concerning the dimensions of particles of the obtained tantalum powder it is possible to evaluate same by the distribution curves of the powder particles, shown in fig.24. The calculated, according to information of the authors, tantalum extraction constituted , considering also the basic bath and the additions during the process, 86.7%.

It is mentioned that potassium chloride increases the yield in flow and dimension of the deposited metal particles, tantalum pentoxide nullifies the anodic effect and increase the yield in flow with the potassium fluorotantalate acting as solvent for the tantalum pentoxide.

The authors assume that tantalum is obtained during electrolytic reduction of its pentoxide.

However with respect to what compound decomposes during the obtainment of metallic tantalum there is also another opinion. And so, Kirk and Brandt 224 having determined the decomposition potentials of salt mixtures containing tantalum, arrived at a conclusion that the metal is obtained during electrolytic decomposition of potassium fluorotantalate.

The authors, having investigated the intensity of decomposition of tantalum pentoxide mixtures with 14 different salts: KCl, NaCl, $CaCl_2$, $KHSO_4$, KB_2, KF, $ZnCl_2$, NaB_2, NaF, KOH, $KC_2H_3O_2$, KF, $Na_2B_2O_7$ and $Na_4P_2O_7$, have not detected on the J - V-curves any other inflection points corresponding to the intensity of decomposition of tantalum pentoxide. They assume that either Ta_2O_5 does not submit to the effect of current in the melts of these salts or its decimposition intensity is higher than that of the corresponding salt, i.e. metallic tantalum can be obtained during the electrolysis of mixtures containing only Ta_2O_5.

On the J-V curve for the mixture, containing $KTaF_7$, Ta_2O_5 and KCL, were noticed two inflections, corresponding to two values of decomposition tensions; one, apparently, corresponding to the decomposition of K_2TaF_7 (1.46 v), the second one - to the decomposition of Ta_2O_5 (2.47 v). (The determinations were made at a temperature of 800° with a platinum cathode and graphite anote).

According to Drossbach [228, 229] who studied the phenomenon of polarization during the electrolysis of mixtures K_7TaF_7 with Ta_2O_5, at first there is the decomposition of K_2TaF_7 with the formation of Ta, KF and CF_4, whereby this process has a corresponding polarization intensity value of 1.68 v. The addition of Ta_2O_5 into the electrolyte, according to the observations of the author, causes no depolarization.

However the presently available experimental material does not offer the provisions of making definite statements regarding the mechanism of the process.

Under industrial conditions tantalum is obtained during the feeding of tantalum pentoxidide into the bath, whereby a periodic feeding of same into the bath prevents the appearance of the anodic effect.

The Myers reports [225, 226] published back in the forties. added new data concerning the conditions of conducting the process of obtaining electrolytic tantalum powder.

According to Myers the composition of the electrolyzing bath is as follows: a mixture of 86% KCl-KF of eutectic composition, 10% K_2TaF_7, 4% Ta_2O_5.

The solubility li it of Ta_2O_5 in the bath at a 10% content of K_2TaF_7, constitutes 5%. In the eutectic mixture of KCl-KF are contained 49.2 weight % of KCl and 50.8% KF.

Consequently, the total composition of the bath was in %:

K_2TaF_7	10.0	
Ta_2O_5	4.0	
KCl	42.4	86.0
KF	43.6	

The optimum temperature of the process was 750°. It is reported that an increase in temperature or in cathodic current density leads to an increase in the dimensions of particles of the metallic tantalum powder.

However, according to the investigation by Ma [227] the increase in current density produces an inverse effect on the dimension of particles of the tantalum powder (fig. 25, 26 and 27).

Fig.25. Dimensions of tantalum powder particles and their dependence upon the cathodic current density (amp/dm^2) (by data of Ma) (Bath composition: 1 p. K_2TaF_7, 1 p. KCl and 0.1 p. Ta_2O_5).

Fig.26, Dimensions of tantalum powder particles and their dependence upon the temperature of the process at 20 amp/dm^2 (by data of Ma). (Composition of bath: 1 p. K_2TaF_7; 1 p KCl, 0.1 p. Ta_2O_5)

Fig.27. Dimension of tantalum powder particles and their dependence upon the temperature of the process at 30 amp/dm^2 (according to Ma) (Composition of bath the same as in fig.26)

According to Ma an increase in electrolysis temperature from 800 to 950° leads to a reduction in dispersity of the tantalum powder; an increase in cathodic current density from 10 to 40 amp/dm^2 leads to a reduction in the dimensions of the crystalline particles of the tantalum powder.

The author remarks that by exactly controlling the conditions ol the process it is possible to obtain a coarse of fine powder suitable for any exceptional case.

In industry electrolytic tantalum powder is obtained with a medium grain size of the order of 50 μ [268].

Industrial derivation of electrolytic tantalum powder at American plants is 100) realized in iron baths (vats) with the application of iron cathodes and graphite anodes [159], or in iron crucibles serving as a cathode with graphite anode, submerged in the fluorotantalate smelt in mixture with proper salts [1, 269, 270]. Tantalum pentoxide is being added periodically to the smelt. Electrolysis is carried on to the point until the volume of the remaining smelt appears too small for the continuation of the process. Ordinarily the electrolysis is realized in the following manner: [155] a steel crucible (cathode) is filled u p with a mixture consisting of potassium fluorotantalate with potassium chloride and fluoride. The salt mixture is melted when passing alternate current through an auxiliary electrode, especially introduced into the bath, from which the alternating current is short-circuited on the graphide bar, in the center of the bath in the (anode). In order that during this stage of preparing the bath the steel crucible should not be attached by the smelted electrolyte , it is cooled externally by a stream of cold air or water jacket, which produces on the walls and bottom of the vat a protective lining crust of the cooled off salts. After the electrolyte has melted tantalum pentoxide is submerged in the melt, alternating current is connected, the auxiliary electrode is pulled out and DC current is cut in. From this moment on the external cooling of the crucible is cut off, because the steel crucible servesas cathode, and as long as DC currenr runs the crucible will not be attached (corroded) by the electrolyte.

As the cathodic deposition accumulates on the bottom and walls of the crucible the anode is being raiced gradually.

Judging by the electrolysis process into the crucible is being added regularly tantalum pentoxide.

After conclusion of the electrolysis the cooled mass is extracted from the crucible, it is lumped and then pulverized into a powder in a spherical grinder in a closed cycle with air separation.

Due to the greater differences in the specific weights of the metal (16.6) and in the component parts of the electrolyte (the heaviest of these - Ta_2O_5 - has a specific weight of 8.71), as well as in the particle sizes of easily reground electrolyte salts and large viscous not submitting to pulverization metal particles, the latter are easily distinguishable from the powder of the cooled off electrolyte during the separation of mixtures in the rising air stream. After separation the mixture consisting of component parts of the electrolyte can be used directly for charging the electrolytic bath [1].

The metallic powder goes then for treatment on a concentrating table where the electrolyte deposits and graphite particles are separated, these particles penetrate into the cathodic product as result of disturbance of the graphite anode. (Losses in

101 weight of the graphite anode amount approximately 16% of the total weight of the settled tantalum [262]. After final water flushing of all salt traces and iron impurities etc. with acids the powder is desiccated in ceramic steam heated pans [269, 270]. In some instances the powder is subjected to additional purification and the fluoride traces are removed when the powder is heated in vacuo up to 1200-1600° [14].

Fig.28. Schematic drawing of the process of obtaining electrolytic tantalum powder. 1-drying furnaces; 2- charging K_2TaF_7; 3- iron crucibles for electrolysis; 4- cake containing fluorides and metal; 5- Raymond pulverizer; 6- dust catcher; 7- mixture

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[1] To extract tantalum from cathodic deposition it is expedient to use the method of smelting-

Footnote continued: the electrolyte in argon and vacuum distillation [267].

Fig.28, continued

of powderous fluorides and metal; 8- fluoride ; 9- metallic tantalum; 10- concentration table; 11- heating coil; 12- ceramic pans for desiccation; 13- pure metallic tantalum powder.

fig.29, General view of electrolytic installation

The schematic of the described process used by the FANSTEEL Corp in the USA is shown in fig.28, the place where the electrolysis operations are carried out - in fig.29

In German factories the process of obtaining electrolytic tantalum powder is realized somewhat different [271].

The electrolysis is carried out in a bath containing 8.5% K_2TaF_7, 8.5% Ta_2O_5, 25.5% KCl, 57.5% KF.

102 As cathode material are used molybdenum strips with a dimension 0.8 X 20 X 30 mm. the anode is made of graphite. Yield of the metal is about 85%, whereby for the derivation of 1100 g of tantalum powder are consumed 1000 amp/hr. The purity of the obtained powder 99.8 - 99.9% Ta.

* Comparison of electrolytic and sodiumthermal methods of obtaining tantalum powder, acc in liter [153] p.241

Because of the considerably larger grain size electrolytic tantalum contains much less oxide films than finely-pulverized sodiumthermal powder. It normally contains 0.1-0.2% O_2, 0.01% F, 0.003-0.1% C, 0.1 - 0.5% Fe+ Ni 0.002% Nb and up to 99.8-99.9% Ta [155].

Fig.30.The Balke apparatus for obtaining electrolytic niobium powder.
1-graphite anode; 2-steel crucible;
3-plate; 4-anode raising mechanism;
5-powder deposition; 6-electrolyte.

Fig.31,Dimensions of particles of electrolytic niobium powder and their dependence upon the cathodic current density (amp/dm²) by Ma(.(bath compositional parts K₂NbOF₅, 1 p. KCl)

Derivation of electrolytic niobium powder. The first patent on the manufacture of electrolytic niobium powder was taken out by Balke [230] in 1933.

The patent spoke about the derivation of metallic niobium powder durin g the electrolysis of a potassium hydroxyfluoroniobate smelt in an iron crucible with external water cooling, with the crucible serving as cathode and graphite bar as anode. Fig 30 gives a schematic description of the apparatus.

Ma [227] investigated the effect of cathodic current density on the dimensions of crystalline niobium particles during the electrolysis of the smelt consisting of 1 p. K_2NbOF_5 and 1 p. KCl. The temperature of the process was 800°. The experimental conditions were the same as for tantalum. The data obtained by Ma are given in fig. 31.

10 According to the description by Goetzel [14] the process of obtaining electrolytic niobium powder, with the exception of few changes, is the same as the one used for tantalum. The purified salts is melted in a nickel crucible, which also serves as the cathode; a graphite serves a anode. To prevent anodic polarization they add regularly chlorides of alkali metals, fluorides and Nb_2O_5. This yields a quite coarsely grained residue, which is important, because after converting same into powder it should be flushed with with diluted acids. If the particles are too small they may transform into colloidal solutions of niobic acid [140].

However, according to Balke reports [32] the process of obtaining niobium powder during the electrolysis of potassium hydroxyfluoroniobate has a series of shortcomings: it calls for the consumption of more time and energy and the yield of the metal is unsatisfactory and for the obtainment of a comparatively small amount of powder it is necessary to operate with a greater amount of salt. This method in industrial scale was replaced by the method of recovering the niobium from mixture of niobium pentoxide and niobium carbide in vacuum at a proper temperature.

Electrolysis of other media.

We know of numerous efforts of obtaining tantalum and especially niobium by electrolyzing various aqueous and organic media [235-246], as well as from smelted phosphate [231] and chloride [234] baths.

Thorough experiments have shown, however, the impossibility of obtaining electrolytic tantalum depositions according to Izgaryshev and Prede [247] and also in accordance with other similar proposals [248]. During the electrolysi of phosphate melts over a cathode, as was found by [232], there is the separation (formation) not of metallic tantalum and niobium, but their phosphides.

Reduction of tantalum and niobium oxides with calcium hydride.

The reduction of tantalum and niobium pentoxides with calcium hydride in a hydrogen atmosphere was investigated by Meyerson and associates [255]. Heating the mixture of oxides and calcium hydride in iron cylindrical cartriges in electric tubular furnaces in a hydrogen stream at atmospheric pressure they obtained tantalum and niobium hydrides. The hydride powders contained up to 99% of the total metal + hydrogen including up to 0.8% of H in tantalum hydride and 1 - 1.4% H in niobium hydride. The main mass of hydride grains had a dimension of up to 1 μ and washed off easily from the calcium oxide diluted with hydrochloric acid. It was found that the best conditions for reducing Ta_2O_5 is the temperature of 1025 - 1100° and a one hour exposure; for Nb_2O_5 950-1035°
104) and an exposure of from 45 min to 1 hr.

A patent for such reduction in 1950 was obtained by Gardner [256] who points out that the obtained hydrides can be converted into metallic powders by heating to 1850° in vacuum. The reduction of CaH_2 can be combined with $CaSi_2$ or with magnesium and aluminum silicides with subsequent obtainment of pure metals by heating the derived products to 2300° for the distillation of silicon. 10

The method of reducing oxides of various metals, including that of tantalum and niobium, directly with calcium in a cylinder (bomb) with the addition of alkali halides or rare earth metals was introduced back in 1924 by [254]. This method found no practical application.

Reduction of tantalum and niobium oxides with silicon, magnesium, rare earth elements and hydrogen.

There are numerous other methods of obtaining tantalum and niobium and their alloys from oxides, which nevertheless, found no industrial application. These also include the proposal of reducing metal oxides with silicon at temperatures sufficient to remove the forming silicon monoxides [257], method of reducing tantalum and niobium oxides with rare earth elements and magnesium [73].

Experiments were made to reduce tantalum and niobium oxides with hydrogen at various temperatures and pressures. During its action are formed lower tantalum and niobium oxides [258, 272]. According to A. Kosov metallic niobium can be obtained from pentoxide by employing atomic hydrogen for the reduction [259].

Reduction of tantalum and niobium oxides with carbon

One of the methods presently used in industry for the obtainment of niobium is the carbothermal method. In view of the closeness of the properties of tantalum and niobium oxides, ~~atmx~~ with this method it is, apparently, possible to obtain also tantalum (and tantalum/niobium alloys). In this case compact metal are obtained directly. Theoretically the process is based on the following reactions:

$$Ta_2O_5 + 5C = 2Ta + 5CO; \quad (1)$$
$$Nb_2O_5 + 5C = 2Nb + 5CO. \quad (2)$$

Carbon reduces tantalum and niobium pentoxides at temperatures of 1500-1900° at atmospheric pressure; in vacuum this temperature decreases. Since tantalum and niobium 105> possess great affinity to carbon then in the presence of carbon-containing gases and at a greater rate of diffusion in the solid phase, which take place at such high temperature, the metal appear to be contaminated with carbides and to eliminate this it is necessary to have an oxide surplus in the charge. The first experiments to obtain tantalum by reducing its pentoxide with carbon were made by Berzelius. In 1907 to obtain tantalum the Siemens Halske Comp. [273] recommended to heat the mixture of tantalum oxide with carbon in stoichiometric amounts at white heat in a hydrogen atmosphere with subsequent removal of the sorbed (sorption) hydrogen by heating the metal in vacuo.

Equilibrium reactions (1) at 1000 - 1270° were investigated by Slade and Higson [249]. The first efforts to obtain niobium by a similar methods were made by Deville [73] who having heated the niobium pentoxide mixture with carbon and sodium carbonate obtained a mixture of carbides and niobium nitride. Muasan obtained niobium containing 2,3-2.4% of carbon in form of carbide, by heating the niobium pentoxide mixture in carbon black in vacuum in an electric furnace at high temperature [73]

In the 1930-ties Rohn proposed to obtain certain metals, including also niobium, by recovering same from a carbide/oxide mixture in vacuo [250]. The I.G.Farbenindustry Co patented a similar method for obtaining metals from the II to VII groups, character- ized by the fact that the recovery is done in an insufficient vacuum in the presence of a certain amount of hydrogen [278].

In the 1940-ties Balke patented a method of obtaining tantalum, niobium and their alloys by reducing in the mixtures their oxides and carbides in vacuo [251,252] .

According to Balke [252] the process of obtaining niobium consists in the follow- ings high purity niobium oxide is prepared from niobium wastes remaining during the derivation of tantalum. A part of the oxide is carbonized by heating its mixture with lamp black at a temperature of 1800 - 1900° in a graphite-tubular furnace in a protec- tive atmosphere (hydrogen, argon) or in vacuum at 1600° until the separation of CO ceases. Carbide is mixed with oxide in the amount warranting equal atomic ratio bet- ween the oxygen and carbon. The mixture is pressed into blocks or into bars under a pressure of from 15 to 80 kg/mm^2. The reduction is carried out in a protective gas atmo- sphere (hydrogen, Argon, Helium etc) or still better in vacuum. The pressed little bars are suspended in the interior of the graphite resistance tube, attached in the vacuum furnace between the cooling water clamps. When reaching the necessary degree of vacuum through the graphite tube is passed an electric current sufficient for heating the tube to a temperature exceeding 1600°.

Separation of the carbon monoxide according to reaction

$$Nb_2O_5 + 5NbC = 7Nb + 5CO \qquad (3)$$

is very rapid whereby a greater part of it is being removed by pumps within a period of several minutes. Toward the end of the process the rate of reaction decreases and the pumping continues up to the point of attaining good vacuum. After cooling the metal is taken out from the furnace in the form of a porous forged mass having an initial form of of small pressed bars but of somewhat smaller dimensions. After hydrogen tion the metal is pulverized into powder in a spherical grinder. The powder is again pressed into small bars under a pressure of 80 kg/mm², then heated in vacuo by xx running an electric current through same. In addition to sintering the metal it also reduces the carbon content and removes the oxygen. To seal up the pores and to obtain a consistent metal the bars after sintering are forged together to reduce the thickness by approximately 20%. They are then returned into the sintering furnace and again heated to high temperatures. This cycle is repeated once more and the obtained metal is compact and free of pores/.

According to data of [264,275] niobium, recovered from a $Nb_2O_5 + 5NbC$ mixture at 1700° in vacuum, is not pulverized, but immediately after recovery is subjected to sintering at 2350° in vacuum as result of which is obtained a lamellar high purity niobium which easily submits to cold pressure treatment. Direct extraction of niobium from its pentoxide into pure metal exceeds 96%. In the experiments of [264,275] were investigated the technological factors and the mechanism of recovering niobium from its pentoxide by the carbide (carbide-thermal) methods is explained. It was established in particular that the total reaction (3) is realized through the following intermediate reactions:

$$Nb_2O_5 + 5NbC \xrightarrow{\sim 1200^\circ} 2NbO_2 + 5\text{"NbC"}\ (NbC_{0.8}] + CO\uparrow \qquad (4)$$

(Because yhe "NbC" phase is homogeneous within limits of from $NbC_{1.00}$ to $NbC_{0.72}$)

<u>insert formulas 5</u>, 6, and 7.(page 106)

One of the important phases of the niobium and tantalum reducing mechanism in the formation of lower oxides of these elements, characterized by considerable vapor pressure

107 already at 1700°, and the reaction of these oxides in vaporous state with the solid carbides or with carbon black (during direct reduction).

Niobium, recovered by the carbide method contains after sintering in vacuo at 2350° no less than 99.98% of Nb+Ta (the tantalum amount is determined by its content in the initial niobium pentoxide and may amount to < 0.1%). $(2.5 - 7)\cdot 10^{-3}\%$ O, $(3-10(\cdot 10^{-3}\%$ C, $4\cdot10^{-3}\%$ Sn, less than $1\cdot10^{-3}\%$ Si, S, P, As, Cu, Ca, Mg each, less than $1\cdot10^{-4}\%$ H, Pb, Bi, Cd, $3\cdot10^{-3}\%$ Ni, $< 2\cdot10^{-3}\%$ Fe, $<1\cdot10^{-6}\%$ Sb. Tantalum and its alloys with niobium are derived of the same high purity [275].

It would have been possible to obtain metallic niobium in a vacuum furnace by ~~xxxx~~ direct reaction of the pentoxide with the carbon black with a small surplus of Nb_2O_5 in the charge. However when charging a vacuum furnace with an $Nb_2O_5 + 5NbC$ mixture the yield of the furnace increases considerably as compared with the charge of the $Nb_2O_5 + 5C$ mixture during direct reduction because the $Nb_2O_5 + 5NbC$ mixture contains niobium (~~xxxx~~ 82.4%) which is 1.5 times greater than the $Nb_2O_5 + 5C$ mixture (57.2%). Furthermore, the first mixture has an additive specific weight by 1.7 times greater than the second mixture (6.25 and 3.7 respectively).

In addition it is necessary to take into consideration the fact that niobium carbide, constituing a predominant part of the $Nb_2O_5 + 5NbC$ mixture is more coarse-grained than the dispersion Nb_2O_5 powders and carbon black, and this serves as an additional reason for greater volumetric weight of the $Nb_2O_5 + 5NbC$ mixture than that of the $Nb_2O_5 +$ 5C mixture. As result of this a unit of working volume of the vacuum furnace can hold 2.5 to 3 times more material (figuring the niobium content) in the former briquettes made of the $Nb_2O_5 + 5NbC$ mixture than from the $Nb_2O_5 + 5C$ mixture [155]. Furthermore, the deficiency of direct reduction appears to be the obtainment of a metal of very high porosity which makes its further processing quite difficult.

With the carbide-thermal (carbide) method is possible to obtain compact tantalum and niobium and their alloys not only from pure finely pulverized oxides but also directly from concentrates [251.]

In the case when concentrates or other contaminated materials are used we first obtain course carbide. It ordinarily contains a certain amount of titanium and silicon which only partially volatilize in the process of carbidization and also iron and manganese in form of metals or compounds easily submitting to the effect of mineral acids.

Since admixture in course carbide do not form chemical compounds with niobium and tantalum carbides, and are only blended with same, (with the exception of dissolved TiC) then during the processing of the product, e.g. with hydrochloric acid, and
108 then with aqua regia and again with hydrochloric acid the iron, manganese, silicon and other admixtures (with the exception of titanium) are removed and a pure niobium or tantalum carbide is obtained, which can be converted into oxide by calcining in open air. From then on the order of operations is analogous to the one explained.

D. Derivation of compact metals

Of the known methods of obtaining compact metals as result of the high melting point of tantalum and niobium only the following ones can find possible applications: the powder metallurgy (cermet) method, vacuum arc or induction melting.

Obtainment of compact tantalum and niobium by the Cermet method.

The powder metallurgy (Cermet) method, which includes pressing and sintering operations, appears to be the conventional method for the obtainment of compact tantalum and niobium.

Pressing (Extrusion). Depending upon the designation of the of the billet it is pressed in form of rectangular plates, if it is intended for rolling into sheets or in the form of small square bars if it is intended for wire drawing. At present time the weight of small tantalum bars goes up to 2.5 - 10 kg. Maximum dimensions of such small bars: length 760 mm, width 64 mm and thickness 32 mm [14]. The most conventional dimensions of small niobium bars (moldings) is [illegible] X 67 X 16 mm at a weight of 750 g [276] and 457 X63.5 X 25 mm at a weight of about 2 kg [277].

To press such small bars detachable steel die casting molds are used in which vertical and lateral pressure is produced. For the purpose of pressing is usually used a mixture of initial metal powders with their hydrides (from wastes) and with special additions (Ta_2O_5 or carbon black).

The finely-grained powder, obtained by metallothermal reduction, thanks to its larger specific surface is pressed into sufficiently durable billets under a pressure of 2.0 - 2.5 t/cm^2 (tantalum) and 1.0 - 3.5 t/cm^2 (niobium) [266]; in some instances for a niobium powder are used somewhat higher pressing pressures.

Coarse-grained tantalum and niobium powders, obtained by electrolysis, are pressed at a much higher pressure (up to 8 t/cm^2).

The porosity of pressed moldings (small bars) constitutes for metallothermal tantalum and niobium powders about 25 - 30%, for electrolytic tantalum powder about 20% (by volume) [155].

Sometimes a lubricant is used during the pressing - a solution of glycerin in
109> alcohol or paraffin in gasoline. During the pressing, to avoid stratification, it is highly important to reduce the pressure gradually and uniformly.

Sintering. When sintering tantalum and niobium moldings in vacuum a number of complex physico-chemical phenomena takes place : evaporation of liquid residues used for moistening the powder during the pressing, adsorbed water vapors; liberation of the hydrogen absorbed by the powder during its hydrometallurgical processing; decomposition and evaporation of the admixtures, which may also react between themselves and with the tantalum and niobium (oxides of tantalum and niobium, silicon, titanium, iron carbon, residues of salts of alkali metals); growth of metal crystals; shrinkage of briquettes and conversion of the reported porosity into closed pores with simultaneous reduction in the entire volume.

Because of the difference in the sintering temperatures of niobium (about 2350°) and tantalum (2600°) the admixtures during the sintering of niobium are removed with lesser effectiveness.

The processes taking place during the sintering of tantalum are as follows [355 ,262 258]: first of all up to a temperature of 100 - 150° there is the evaporation of the liquid residue used during the pressing as well as adsorption of water and gases. It should be mentioned at this point that the tension of evaporation of the adsorbed films of admixtures, included in the thin microscopic and submicroscopic cracks and pores, particularly on surfaces, coated with porous oxide films, is below normal. At this stage of sintering there is a noticeable increase in pressure in the vacuum apparatus.

The following considerable pressure rise in the apparatus is observed at a temperature of 600-650°, which is connected with the intensive liberation of the hydrogen absorbed by the metal.

During further sintering at 110 - 1600° the alkali metal and carbon monoxide compounds experience intensive volatilization caused by the reaction of the carbon with tantalum oxides.

If during the first two stages the gaseous admixtures are being eliminated quite rapidly then this stage is characterized by a relatively slow expulsion of gases. During this stage is also observed a noticeable growth in the grains, increase in dimensions in interparticle contacts and the development of process of exchanging nonmetallic contacts into metallic ones.

Up to 1600° in vaccum takes place a thermal dissociation of the tantalum pentoxide with the formation of lower oxides accompanied by the liberation of oxygen. It is possible that lower tantalum oxides dissolve to a certain extent in metallic tantalum. Above 1600° there is a gradual volatilization of the lower tantalum oxides with simultaneous decomposition of the solid solution. The volatilization of tantalum oxides continues all the way up to the final sintering temperatures.

110) When the vacuum apparatus contains certain amounts of oxygen and nitrogen in the temperature range of between 1600-1900° a reverse absorption of these gases by the metal may take place.

Analogous processes, but at somewhat different temperatures, take place also during the sintering of niobium [278].

When tantalum is sintered at temperatures of 1600-1900° and over there is also the separation of silicon and certain other admixtures; here the silicon volatilizes basically in the form of a lower oxide SiO (a part of it can also be removed in the form of metallic silicon).

At a temperature of plus 2000° the evaporation of also other admixtures comes to a halt, this includes for example iron and nickel. As it draws closer to the melting point of tantalum a small evaporation of the metal itself begins. At above 2000° there is the most intensive shrinkage in connection with the development of the grain growing process.

It was established that the defivation of qualitative tantalum, practically free of any admixtures, is possible only in the case when the initial powder has a specific ratio between the content of admixtures, especially carbon and oxygen. It is assumed, for example, that to remove the admixtures from tantalum oxides of volatile metals are added (oxides of Mg, Li or Be [279]). The admixtures are removed in form of oxygen compounds and the volatile metals condence on the cool parts of the vacuum apparatus. The best thing in this respect is to add Ta_2O_5 directly. At an oxygen surplus in the initial powder it is necessary to add a certain amount of carbon (carbon black). It is assumed that tantalum and niobium admixtures at high temperature sintering are elimin in the form of lower oxides, e.g. CO, SiO etc.

When sintering niobium moldings the process may be divided into the following three stages [278 Up to 800-1000° a greater amount of hydrogen is liberated; its content from approximately 0.27% (weight) in the initial powders- drops to < 0.001% (weight); during the second stage of the process at temperature ranges of 1000-2000° is removed the carbon and the basic amount of oxygen in the form of CO, and in the case of an oxygen surplus the initial niobium powder is boosted by a certain amount of carbon (2/3 of the calculated for removal oxygen in form of carbon monoxide).

The reactions between carbon and oxygen take place at substantial rate at 1600 - 1700°. The decisive factor in this stage of the process, as well as during all other stages, is the rate of solution and diffusion of admixtures, especially oxygen and carbon, in niobium, presence of apparent porosity, which is attained by using for the sintering a mixture of thin and more coarse (from hydride) powders and a general size of the molding surface and rate of temperature rising. To avoid the formation of cavities and blisters within the molding (bar) the rate of temperature rise at this sintering stage should be low. At this stage we also have the separation of a considerable amount of silicon, probably in the form of SiO.

The third stage of sintering (temperature 2000-2300°) is characterized by relatively slow removal of oxygen remains in the form of lower niobium and nitrogen oxides.

According to [278] in the sintering of niobium a greater role is assumed by the processes of absorbing and dissolving gases (oxygen, nitrogen) in the metal at temperatures of up to 1780°, leading to an increase in the electric resistance and hardness of the sintered briquettes.

The numbers, characterizing the content of admixtures in the initial powder and compact niobium molding, are listed in table 26.

Table 26. Content of admixtures in niobium powder and in compact molding [276,277]

Tested material	Content of admixtures, % (weight)
Metallic niobium powder	Elements and numerical values as in original
Compact niobium molding	

Judging by the behavior of the admixtures and by the change in the properties of the moldings, the maximum temperature of tantalum sintering should be 2600° and that of niobium 2250 - 2350°. The change in properties of tantalum moldings during heating and long lasting exposure at maximum sintering temperature is presented in fig. 32 and 33, and the change in the properties of niobium during the sintering process - in fig. 34-36.

According to Myers [268], when heating tantalum moldings during their sintering it calls for the following conditions (data given for the molding with dimensions of 127 X 6.3 X 3.2 mm):

Temperature °C	1150	2000	2600
Voltage per one cm of length of the molding	0.118	0.256	0.319 v.
Amperage, amp.	200	550	1000

The sintering of tantalum and niobium moldings (bars) is ordinarily realized in one - sometimes- in two stages. In the first stage of sintering is eliminated the lubricant which was added during the pressing[1].

Fig.32. Change in properties of tantalum molding during its sintering in vacuum (according to Myers); 1- density; 2- electric resistance; 3-weight

Fig.33. Curves indicating the effect of heating duration in vacuum at 2600° on the density (1) specific electric resistance (2) and weight losses (3) of tantalum molding (according to Myers).

113⟩ If the process is carried out in two stages then the first stage of sintering is carried out ordinarily in a horizontal tubular vacuum furnace with alundum tube heated by a spiral molybdenum wire coil. The furnace is placed in a hermetically sealed metallic jacket to which vacuum pumps are connected. The sintering takes in several moldings at one time at a remnant pressure in the furnace of 1. 10^{-2} mm of mercury column and a final temperature of 1000-1200°.

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[1] Two stage sintering appears to be undesirable and superfluous in the process of obtaining compact tantalum and niobium [278]

Fig.34. Change in specific electric resistance, hardness, density, weight and quality (of surface layers) of niobium moldings during two-hour heating at various temperatures (according to Kolchin and others).

After the first sintering the molding goes for high temperature sintering.

114) Pressed moldings or moldings after the first sintering are clamped in the tongs of the vacuum sinter furnace ("welding apparatus"). After the apparatus has been provided with the necessary vacuum (about 1. 10^{-3} mm of mercury column) electric current is cut in and at continuously operating vacuum pumps the amperage is raised gradually and correspondingly also the temperature of the molding.

Fig.35. Change in electric resistance of niobium moldings upon sintering (accord. to Williams)

Fig.36. Change in density and ultimate strength of niobium moldings upon sintering (accord. to Williams)
X ----X - density; 0-----0-ultimate strength.

In the case the indirect heating method is employed the pressed moldings are placed in high temperature sintering furnaces: induction or resistance furnaces.

The construction of vacuum welding devices of direct heating for tantalum and niobium is similar to the construction of ordinary devices for the sintering of tungsten and molybdenum moldings (fig.37, 38). The basic difference lies in the fact that the interior area of the dome should be under high rarefaction (vacuum up to 1 - $3 \cdot 10^{-5}$ mm. of mercury column). In induction furnaces the molding is placed in the interior of a heated cylinder with the induction coil surrounding same.

In high temperature vacuum resistance furnaces, usde for the sintering of shaped objects and having approximately equiaxial dimensions, verically arranged tungsten rods serve as heating elements (fig.39). 16)

115) In conformity with the described stages of the sintering process and changes in the properties of moldings are set up the tantalum and niobium sintering processes. The rate of discharging the gases liberated during the sintering appears to be the basic value establishing the duration of the high temperature sintering processes.

According to Titterington [262], for the sintering of two tantalum moldings weighing a total of 3 kg is used a vacuum welding apparatus, equipped with an 8-inch oil diffusion pump with an output of 500 liters/sec at a pressure of 1· 10^{-3} mm of mercury column in combination with a single chamber mechanical pump with a delivery of 98 m^3/min. The pumps offer the possibility of obtaining rarefaction in the apparatus of up to 10^{-4} mm of mercury column.

Fig.37. Construction of a vacuum apparatus for tantalum welding (accord.to I.M.Suzdal'tsev); 1-block; 2-steel dome; 3-slides; 4-upper stationary contact; 5-copper props supplying current to upper contact; 6-carbon screen; 7-lower movable contact; 8-rubber rings 9-flexible cable; 10- load; 11-mount prop 12-current feeding busbars; 13- water intake and outlet. 14- flexible water hose; 15-nozzle leading to pump.

Fig.38. Vacuum apparatus for sintering niobium moldings (United Kingdom Atomic Energy Athority, Springfields, Laboratory); 1-vapor-oil diffusion pump; 2- rotary pump; 3-fasteners; 4- air intake; 5- screen ; 6-quartz port; 7- rubber packing; 8- Wilson packing; 9-electrote lifting motor; 10-current conducting busbars. 11- power transformer; 12-control transformer

The " MUREX " Comp. employs tantalum sintering devices, equipped also with 8 inch

117) oil pumps with a delivery of 500 liters/sec at a pressure of 10^{-4} - 10^{-5} mm of mercury column in combination with a rotary mechanical pump [261].

Fig.39. Construction of a vacuum electric furnace with tungsten incandescence rods for high temperature sintering by radiation:

1- tungsten incandescence rods; 2- molybdenum screens; 3- upper cooling plate; 4- current delivery; 5- lower mobile contact ; 6- sylphon; 7- nozzle to vacuum-pump.

Fig.40. Sintering of electrolytic tantalum moldings(accord.to Myers)

Fig.41. Sintering of tantalum moldings (accord.to Titterington).Total weight of sintered moldings 3200 g.

Fig.40 shows the sintering ~~the~~ of electrolytic tantalum moldings [258].Fig.41 shows according to [262] a typical process of sintering two tantalum moldings, each with dimensions of 350 X 32 X 15 mm and weighing 1600 g.

Fig.42. Density of tantalum in carious stages of processing (accord. to Myers).

Moldings of such dimensions are used for the manufacture of sheets. Billets which should be used for the manufacture of wire and rods have square cross section; the dimensions of basic moldings in this case equal 350 X 20 X 20 mm and the weight is 1400 grams. The energy necessary for heating two such moldings to maximum sintering temperature is 78 kvamp.

According to recommendations by [264, 278] the first small exposure during the sintering of pressed moldings of niobium should be made at a temperature of not less than 1750° because at much lower temperatures the niobium may absorb a considerable amount of gases (especially when no deep vacuum is used), the purification from which requires an additional increase in sintering time at maximum temperature.

118) The second, long lasting exposure is necessary at maximum sintering temperature which should be possibly close to the melting point of the metal. For moldings with a profile of 10 X 10 mm such exposure can be made for example for a period of 3-4 hours at 2250° or even better for a period o one (1) hour at 2250° at 2 hours at 2300-2350°. In this case we have a most intensive purification from oxygen, nitrogen and carbon admixtures and purification from certain other impurities; the process of collective recrystallization is much more intensive, the metal softenes and becomes plastic.

To itensify the process of sintering is possible by a relatively rapid rise in temperature from 1750° to maximum sintering temperature.

Sintering of niobium in conditions, recommended by [264, 278], under laboratory conditions it requires 4.5 to 5 hours, in factory conditions 8 hours and it leads to the derivation of pliable (plastic) metal containing 99% Nb ~0.5% Ta, 0.03% Ti, 0.05% Si, 0.05% Fe, 0.02% S, < 0.01% P, < 10^{-4} % Pb, < 0.01% C, ~ 0.03% O_2 and ~ 0.03% N_2.

According to Williams [277] the sintering of niobium moldings weighing 2 kg (157 X 63.5 X 25 mm) is carried out in a welding apparatus (see fig.38) the dome and water-cooled walls of which have about 610 mm in diameter and are 915 mm in height . The vacuum system consists of two 14-inch vapor-oil pumps with a delivery rate of 6500 liters/sec. at a pressure of $1 \cdot 10^{-4}$ mm of mercury column and rotational pumps. The ultimate vacuum reached in the system is of the magnitude $1 \cdot 10^{-5}$ mm of mercury column.

Fig.49, Process of sintering niobium moldings
(by Kolchin and others).

19) The electric power supply is controlled by a transformer (4000 amp at 30 v or 8000 amp at 15 v).

The pressed niobium molding is clamped in tongs of the welding apperatus and after the system attains minimum pressure the current is cut in. The temperature is raised rapidly to 300 - 400°, short exposure is made, within which time the hydrogen is eliminated. The temperature is then raised gradually up to 2300° ; the total heating time is about 40 minutes. Maximum shrinkage takes place at 1600 - 2000° and it is compensated by proper maneuvering the electrode. The time of soaking (exposure at 2300° varies from 2 to 10 hrs depending upon the weight of the sintered metal. The molding is then cooled to 200° prior to cutting off the vacuum.

During induction sintering of niobium moldings [275], the preference of which is the economy of metal, because in this case the tips of the moldings are heated just as well as their center, the operation of heating is carried out in a reservoir with a capacity (volume) of 200 liters. The furnace is pumped out with the aid of pumps offering the possibility of obtaining a pressure of $1 \cdot 10^{-5}$ mm of mercury column. The high frequency part of the furnace has a power generator with maximum capacity at the output of 50 kw at a frequency of 10 cps. The system is operated at 2-4 cps and voltage not higher than 250 v to prevent the origination of discharges. Temperature control is normally realized by the consumed power, at times measuring the temperature of the sample by an optical pyrometer.

The process of sintering niobium moldings weighing 750 g in an induction furnace is set up in such a manner that a 1700° temperature is attained within 40 minutes the molding is then exposed (soaked) for two hours between 1700 and 1900° until the basic mass of carbon ~~monoxide~~ and silicon is ~~[illegible]~~ removed. The heating power is then increased gradually for a period of 6 hours until a temperature of 2300° is reached. During the 6 hours of soaking at this temperature the oxygen, which has not separated in the form of CO, is separated in form of volatile lower niobium oxides, xx and the molding becomes free of admixtures. During the sintering operation the pressure changes from $4 \cdot 10^{-4}$ mm of mercury column, during the removal of CO, to $2 \cdot 10^{-5}$ mm of mercury column at the end of the operation.

Together with controlling the vacuum durnh the sintering process it is important to control the temperature whereby it is necessary to take into consideration the changes in the emissivity of the molding (fig.44).

The shrinkage of tantalum and niobium moldings during the sintering constitutes ordinarily 12-15%.

Losses in weight during the sintering of moldings depend upon the admixture content in the initial powder and they amount to 5-8% for sodium thermal tantalum powder and less when an electrolytic powder of greater purity is used.

120) After the sintering the moldings have a remanent porosity of 7-15%, which for tantalum corresponds to a density of 14-15 g/cm³; for niobium 7.25 - 8.00 g/cm³. Sintered tantalum and niobium moldings are cold-hammered (peened) to reduce their profile by 15-25%, in consequence of which the pores become sealed (closed) up. Then is carried out the second sintering (tempering) in a vacuum welding apparatus, for a short period this time (~ 1 hr) by heating the molding at a temperature somewhat lower than the sintering temperature. As result of the tempering we have recrystallization with corresponding growth in grain size and reduction in porosity. Sometimes a second stage of hammering i carried out with a 25% reduction followed by a second tempering in vacuo.

Fig.44. Change in coefficient of emissivity of the surface of the niobium molding during sintering (by Williams) 149

The result of hammering and tempering yields a billet with compact polyhedral structure. The hardness of such tempered billet constitutes by Brinell 45 - 125 kg/mm^2.

Employing oridinary cold-pressure treating methods the billet is further converted into sheets and wire[1].

Derivation of compact tantalum and niobium by arc and induction smelting

The first compact tantalum was obtained by Bolton [281] using the arc smelting method. At the Siemens Halske plant this method was used to approximately the 1930 for the obtainment of tantalum [282] with subsequent replacement of this method with sintering the pressed briquettes in indirect heating furnaces.

Fig.45 shows a schematic representation of a vacuum apparatus used for arc smelting. For smelting they used pressed and presintered tantalum moldings (smelting done with an expendible electrode). The smelting was carried out with a DC-arc with the tantalum electrode (positive pole) attached freely. The tantalum melted in form of a small ingot on a cooled copper plate.

The derivation of small tantalum ingots by the arc smelting method from a magnesium thermal powder has been reported by Isaa and other [206]. They obtained ingots with a hardness according to H_B of about 70 kg/mm^2. Casted tantalum was easily rolled into thin sheets. According to [283] tantalum was obtained by the arc smelting method in vacum at the following conditions: the area of the transverse section of the expendable tantalum electrode was 194 mm^2, diameter of operation crucible 51 mm, amperage of AC-current 2000 amp, arc voltage 36 v, expendable power 1.85 kw-hr•kg, operational vacuum $2.5 \cdot 10^{-2}$ mm of mercury column. When the arc smelting method is used in larger scales the following difficulties may originate: a) during smelting with nonconsumable electrode the metals may become contaminated by the electrode materials b) the metal

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[1] A study of tantalum sintering process and a detailed description of the process of preparing compact tantalum according to data by Czech researchers are also listed in the reports by Vacek [260, 496]

may become infiltrated by gaseous Argon admixtures, a gas which must be used to produce a stable arc; furthermore, in the presence of this gas admixtures of the melted out metal are being removed with lesser effectiveness; c) when smelting with an expendable electrode the purification of the metal is also not as effective because of the fact that the evaporizing admixtures (particularly oxides of various metals) condense on the cold walls of the furnace and are then again adsorbed by the metal; d) when smelting ordinary industrial tantalum and niobium powders, containing x specific amounts of oxygen, carbon and other admixtures, it is practically impossible to provide a pumping rate necessary for the elimination of same. And so for example, when removing oxygen in form of CO during the smelting of niobium, containing 0.3% C, at a smelting rate of 2 kg/min the rate of pumping out should be of the order of 10^4 liters/sec at a sufficiently high vacuum.

Fig. 45. Schematic representation of the apparatus for arc smelting of Ta (according to Bolton)

1- filter-asbestos texture; 2- cooled copper plate; 3- metallic regulus of melt; 4- rubber plug; 5- glass cap; 6- Ta-packing.

The arc smelting method in the given case can be suitable either during the founding of tantalum and niobium ingots from highly pure powders, or for the obtainment of larger metal ingots by resmelting moldings which are already sintered and free of metal impurities [277].

During induction smelting of tantalum and niobium the problem involves the selection of a suitable crucible material. In this respect attention should be devoted to the method of induction smelting of metals in vacuo or in an inert gas atmosphere in suspended state [284].

It is necessary to mention here also tge smelting method by bombardment with electrons; with this method on laboratory scale was derived niobium of ultra-high puri [277].

Reprocessing of metallic tantalum and niobium wastes.

Tantalum and niobium have this advantage that their wastes, including the tips of the moldings after sintering, wastes from rolling sheet material or from wire drawing (cut offs, defective sheets etc), wastes obtainable during the manufacture of goods and, finally, return of parts of shipments from the user, after the corresponding component goes out of commission(this group includes tantalum and niobium components of faulty radio tubes, transmitting tubes, components of chemical devices etc) can be fully reclaimed and returned back to industry.

The most suitable method of reprocessing such tantalum and niobium wastes is the method of hydrogenating same [285,286] by heating (to 800-900°) in purified and desiccated hydrogen . The obtained hydrides are pulverized into powder in a stell annular grinder. To flush off the iron impurities, which penterate during the pulverization of the hydrides, the powder is sometimes subjected to magnetic separation and treatment with diluted hydrochloric acid or simply to treatment with hydrochloric acid followed by water flushing. Ordinarily the hydrides are added into the powder going directly for sintering, but the most proper thing is first to subject same to degasification in vacuo upon heating to 800-900°.

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Chapter IV

Mechanical Working and Heat Treatment of Tantalum and Niobium

Manufacture of Products. Welding

1. Mechanical Working

The mechanical working of tantalum and niobium, in order to obtain rods, wire, thin sheets and shaped articles, is a cold working. Tantalum and niobium are notable for high plasticity and are coldhardened very slowly in the process (fig.46).

Pressure Treatment

Obtaining sheets. Forged and annealed plates of tantalum and niobium are the initial blanks for obtainingsheets of various thicknesses. Rolling is accomplished by customary methods. In rolling, high degrees of deformation are possible without intermediate annealing. So, for example, a sheet with 0.05 mm and less thickness can be obtained from an 8 to 9 mm thick blank without intermediate annealing.

Fine-grained metal must be used in the strip in order to obtain better results in the rolling of plates. If the metal is annealed before the rolling process, then it is necessary that annealing be accomplished at not too high a temperature as long as, in this case, increased metal volatility is observed from boundaries of the grains, and this in turn leads to the fact that a strip with dented edges (287)[1] is obtained as a result of rolling.

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[1] This was shown to be true for the working of small size moldings.

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The texture of tantalum rolling is the same as that for metals with body-centered cube space lattice (288). This texture can be designated by orientations {100} <011> , {112} <011> and {111} <112> . The last two are double textures which are arranged so that they form a symmetry correspondingly in the cross direction of the rolling. Intensity peaks, related to the orientations {112} <011> , are not all centered exactly on this orientation. Components, having the highest intensity, digress approximately 12° from {112} and correspond roughly to orientation {223} <011> .

1124

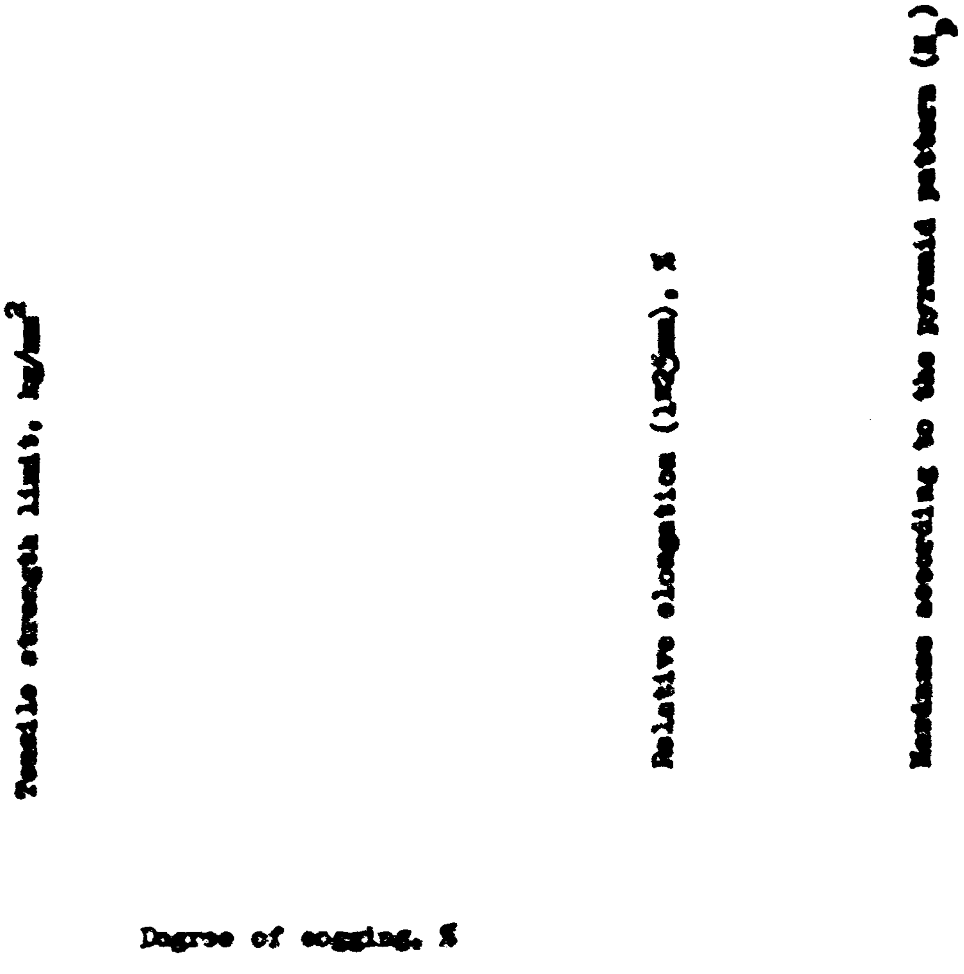

Fig. 46. Curves showing the effect of deformation on the hardness, tensile strength limit and tantalum's relative elongation (according to Myers).

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Obtaining rods and wire. Forging square section blanks on a rotary forging machine is done to obtain rods. According to Myers (287), it is best to forge a sintered molding of a square section of tantalum into a round rod for one passage (Myers studied the treatment of moldings having the dimensions 6.3 x (6.3 - 9.5) x (76 x 178) mm). This allows avoiding the rolling of material by reason of the circular flow of ribs proceeding in the case of utilizing lesser primary compression ratios. In greater compressions, the general decrease of the cross-section area of the specimen made up 50% for three passages and the metal density increased to that of the theoretical value.

After such treatment, annealing was needed which was carried on in a vacuum 10^{-3} to 10^{-4} mm Mercury column in vacuum welding equipment at heating to 2600° an hour.

The molding edges, ordinarily not thick, are not trimmed in the first forging. They are removed after annealing (and are afterwards treated as waste material). The rod obtained is cold worked to a diameter of 2 to 3 mm, and is given over to wire drawing. In the forging process, it is recommended that forged threading dies with possibly longer operating parts be used and which provides better quality in the treated surface of the forged metal. In forging tantalum, it is possible to use dies with long working parts which are five times as large, and in that way obtain smooth, level samples of metal without the use of special finishing dies.

In order to carry out the wire drawing of tantalum and niobium wire, wire-drawing dies of tungsten carbide are used (for the wire drawing of 2.54 to 0.38 mm diameters) with a groove at an angle of 16° and

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diamond dies for the drawing of wire thinner than 0.38 mm (287). As a lubricant, it is recommended that a cutting lubricant containing 5% soft soap and 5% lard oil be used. The rod or wire is passed through the lubricant, after which it is quickly dried in the air at the expense of its own heat. Such a method of lubrication guarantees the complete coating of the material. However, the lubricant does not take hold on an unprepared surface. An oxide layer on the wire surface is needed in order to make the lubricant adhere. This is done either by heating the wire in air to 580° or by electrical anode oxidation in a 1% solution of H_2SO_4 and Na_2SO_4. The wire, covered with an oxide film at a voltage of 110 to 115 volts (maximum voltage), can be brooched by using a cutting lubricant of soap and lard oil as lubrication through several wire-drawing dies without renewing the film. The renewal process is very simple and doesnot require a great loss of energy. A good oxide film is obtained in only 1 to 2 sec., in relation to the area of the tantalum surface which undergoes anodic treatment and to the characteristics of the power source. In anodic oxidation, the wire can be passed through a groove, provided on the edges with rubber disks having grooves and filled with 1% solution of sodium sulfate, whereby the wire is the anode and the groove — the cathode. In order that the continuity of the wire-drawing process is not disturbed, it is possible to set up in front of the wire-drawing die a vat for anodic oxidation and a vat containing the lubricant, having connected the wire to the current source in front of the vat.

The tantalum and niobium wires in an annealed state are very soft and plastic. The wires can easily be bent at an angle of 180°;

and it is possible to wind a core of a diameter equal to that of the wire's diameter. In operations utilizing wires, ordinary productional processes are used where the instruments are made from aluminum bronze (289).

Obtaining pipes. As a rule, pipes of various diameters from tantalum and niobium are obtained by the method of deep drawing (from a hood blank) and the consequent wire drawing.

The operation begins with a blank of disks from annealed metal of suitable thickness, whereby the results of the operation are better at the application of a thick, rather than thin blank (289).

Diminution of the cross-section area of the drawing operation, for example, for niobium makes up 47.5 to 51%, on the basis of the formula

$$\left(\frac{D_{blank} - D_{stamp}}{D_{blank}}\right) \cdot 100\%,$$

where D_{blank} and D_{stamp} are the diameters of the blank and a stamp respectively (277).

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Tantalum and niobium in drawing process are not cold worked as quickly as the majority of metals, and the drawing begins on the upper portions of the detail part earlier than in its lower portions. For one operation, the drawing is possible for no more than that of the diameter. If the carrying out of several operations is needed, then ordinarily in the first operation the depth of drawing is given and constitutes 40 to 50% of the detail part diameter. The thicker the material, the more possible is a great depth of drawing. Practically, in the drawing of tantalum and niobium, the wall thickness can be decreased

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80% or more.

In carrying out this operation, instruments made of aluminum bronze are ordinarily used, although it is also possible to use steel instruments. As a lubricant: lard, paraffin lubricant or other similar lubrication composition can be used (289).

As a result of wire drawing, the cross-section area can be reduced to 35%, with an overall decrease of pipe size 60 to 80%, before roasting is required (277). In the roastingprocess, the sizes of the metal grains are carefully controlled in avoiding the development of scores and burrs. A paraffin lubricant or lard (289) are also lubricating composition in wire drawing. Wires can be of aluminum bronze which is hard-alloy ~~or chromium-plated~~; aluminum bronze is the most effective material (277).

Obtaining products from tantalum and niobium by extrusion. In obtaining products from tantalum or niobium by extrusion, aluminum bronze is also usually used as material of instruments. In this instance also, the above-mentioned lubricants are effective (289).

Pressworking. Pressworking of a product from tantalum and niobium are obtained in the same way, as for example from low-carbon soft steel, with the exception of the fack that precautionery measures against the sticking of metals on the stamp part are enforced. The dies are manufactured of common steel or better from aluminum bronze or beryllium copper. A mixture of light oil and kerosene are used in pressworking as a lubricant(289).

The clearance (gap) between the punch and the matrix used equals 6% of the stamped product metal thickness.

The operation of drilling holes in tantalum and niobium is done without any special difficulties, but to prevent the formation of cracks, wear and separation of peices, we usually amply dies having smooth suffaces (289).

CUTTING PROCESS

The cutting of tantalum and niobium with high-speed steel cutting tools is accomplished entirely with satisfaction; this requires that the cutting tool is sufficiently sharpened. In almost all cases of cutting operations, 1127 it is tentative during the cutting of soft copper, and applicable even to tantalum and niobium. Lateral and rear angles of cutting should amount to 15°. The peripheral speed of cutting may reach 90 meters per minute, and should reach 30 meters per minute. The cutting tool made of carbide tungsten does not provide a good quality of mechanical cutting of tantalum and niobium which welds itself to the edge of such cutting tools.

The cooling liquid, which eliminates wear and rupture of the metal pieces, appears to be carbon-tetra-choloride.

During the cutting of tantalum and niobium cutters are used, the blades of which are spaced in a staggered order with a large foreward angle and considerable gap. Standard drills with large angles of cutting (118°) are set in such a way so that they do not rub against the wall of bore holes.

The thread on large diameter details are usually cut by cutting tools with a narrow cutting edge, but not by dies; on small diameter details the threads are cut by die tips. Knurls are often used and not threaded.

Use is often made of knurling and by notching; in this case they often use a paraffenic lubricant. The taps and threading heads in the process of tantalum and niobium treatment are cleaned periodically of any metal shavings. Final threading is carried out at low transverse feed, sufficient however for the purpose that the cutting bit of the tool is sunk into the metal of

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the treated part. The passages of the cutting tool during plate treatment are done within one operation. The maximum rate of transverse feed is 0.127mm per revolution during the machining on a lathe and 0.127mm per tooth during milling (289).

2. CLEANING TANTALUM AND NIOBIUM SURFACES

For cleaning the surfaces of tantalum and niobium surfaces, regular methods are used, as used for cleaning steel products, with the exception of cleaning by hot alkaline solutions and annealing by hydrogen flame (289).

Chemical Cleaning is performed by hot chromic acid solution, similar to that adaptable for cleaning glass; dual-chromic acid of potassium is also useful, however, traces of salt can remain on the metal. After cleaning in a vat the products are rinsed in distilled water and dried in a warm air current free from dust. The cleaning of the products is done by hand in order not to allow any contact between the material and paper (24, 289).

Polishing tantalum and niobium is performed with large difficulty and sometimes generally impracticably, if the metal is found to be in a tempered state. Raw metal can be polished by means of carborundum polishing wheels. The /128 pressure (load) of a polishing wheel on polishing products is accomplished by an acceleration method, but less than polishing copper products. In the process of polishing tantalum and niobium it is often demanded to guide the polishing wheel and to cool it with vegetable oil (289).

Grinding tantalum and niobium for roughtsurfaces (in the electric vacuum industry) is conducted in several seconds by the use of steel filings, directing them under small wheels to the surface of the metal from a nozzle under 8 to 16 lbs pressure. The shot is used with a pointed edge; using a blunt shot produces only formations of hollows on a cleaned surface. Sand, carborundum or alundum should not be used owing to the impurities of tantalum and niobium and the difficulty of the following cleaning. After processing metals with steel filings, the surface of the tantalum and niobium is washed-off ordinarily with hot hydrocholric acid with subsequent flushing with running water (24, 289)

Polishing tantalum and niobium products is possible, but not to secure a mirror-like glass. Polishing begins with emery cloth 0000 moistened with carbon tetrachloride, and ends with paste of aqueous solution of elutriated aluminum oxide applied on a cloth. For creating a mirror-like surface on tantalum or niobium it can be done by electric polishing.

Wensch, Bruckhart, and Conolly (290) suggest the following electrolyte composition for electro-polishing tantalum: 90 volumetric parts of concentrated H_2SO_4 and 10 parts of concentrated (48%) HF. The process is carried out at a temperature of 35 to 40° with the use of graphite or platinum anode. The current density is 0.10 amperes/cm^2 (during the etching the current density should be 0.02 amp/cm^2).

Gall and Miller (291) introduce a somewhat different composition of the electrolyte and a process of introducing of electro polishing of tantalum: the electrolyte is aqueous solution with a content of 2-7% HF and 32-38% H_2SO_4 or 2-7% HF and 75-98% H_2SO_4. The current density during electro polishing over tantalum anode is 40-160 ma/cm^2.

THERMAL PROCESSING OF TANTALUM AND NIOBIUM

During the mechanical processing of tantalum and niobium (forging, rolling, broaching) demands periodical tempering of metal.

The tempering is necessary to be done in a high vaccum of not less than 10^{-4} mm mercury column. According to Titterington (292), the tempering of tantalum stripe is done in a vaccum 10^{-6} mm mercury column at 1400° for 15 minutes, whereupon if the increasing hardness of the metal appears to be the result of the presence of admixtures of oxygen or nitrogen, then the tempering temperature is increased to 2000 - 2200°. /129

Cole reports that during the tempering of tantalum it is necessary to heat it to at least 2000° (24). The Temperature of tempering Niobium builds up to 1300-1400° (143). The tempering is conducted by inductive heating in quartz-like tubes, lined inside with tantalum sheets. Before tempering products (strips), they are rinsed in chromium mixtures by heating to 110° and then in distilled water.

Hardness of an imprint pyramid (H_p)

Temperature in °C.

Figure 47. Curve, indicating the increase of the hardness of tantalum in the resultant tempering (according to Mayers)

According to Mayers (293), during the heating of tantalum samples in a vaccum of 10^{-3}mm mecury column in the pemperature limits is 1100 to 2200°; in such cases, if the samples are not inserted in a closed tantalum cylinder, the hardness of the samples will not decrease, and even to the contrary, will increase (see figure 47). This is related to the absorption of metal of gaseous admixtures, especially oxygen whereupon better gas absorption takes place in the temperature limits of 1700 to 1800° (the absorption of gases can be removed from metal by heating to a temperature higher than 2200°). The absorption of gases by tantalum is accompanied by increased parameter of the lattice, by increased hardness and electrical resistance. During the tempering of the samples located in a closed tantalum cylinder, similar effects are not observed.

According to Cole (24), the following effect occurs during the tempering of tantalum: occluded gases is removed during temperatures lower than 1100°. /130 To 1600° specific seperation of gas does not occur. At temperatures of 1600 to 1800° the tendency of the metal to gas absorption does not occur. During heating to higher temperatures (higher than 2000°) complete seperation of the gases and decomposition of oxides is observed.

During the tempering of tantalum and niobium it is necessary to take the degree of deformation into consideration. The greater the deformation of the metal, the earlies it will begin to relieve the pressure, the result of which appears to be a reduction in hardness. An so at a 20% compression of tantalum, the hardness begins decreasing between 600 and 650°; and at an 80% the hardness begins to decrease at 400 to 450° (see fig. 48). The begining of the vaccum etching is noticed at a temperature of about 1750°, but a substantial value is aquired at approximately 2400°.

According the Meyers data, recrystallisation of tantalum during tempering occurs during the temperature range of 1200 to 1800° in relationship to the degree of deformation (fig. 49). According to Wensch, Bruckhart and Deibler (294), complete recrystallisation of tantalum, rolled in the cold with 40% reduction (see fig. 50) sets in at 1520, 1570, 1620, and 1670° at 140, 35, 14 and 3.5 minutes.

The texture of deformations of sheet tantalum rolled in cold during tempering varies by the following method (288): for materials, tempered at 1100, 1200, 1300, 1400, and 2500°, a gradual reversal is observed of the grain of cold rolling to the textures of recrystallisation. Complete recrystallisation is observed during tempering at 1400°. The texture has only orientation /132

{11} <112> The texture of the material, tempered at 2500°, is similar to the texture of the material tempered at 1400°, except more distinctly expressed.

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Hardness of an Imprint Pyramid (H_p)

Temperature in °C.

Figure 48. The hardness of deformed tantalum after tempering in a vaccum for 30 minutes during various temperatures (according to Meyers); figures and curves denote the degree of reduction, %.

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Average Amount of Grain Across the Longitudinal Section.

Grain Elongation

Grain Equilibrium

Indefinite Zone

Temperature in °C.

Figure 49. Diagrammatic representation of microstructures of deformed tantalum after tempering in a vaccum.

The Duration of Complete Recrystallization in Minutes.

The Inverse Value of Absolute Temperature

Figure 50. Curve relationship of the duration of tempering to the temperature during recrystallization of tantalus, rolled in the cold with 40% reduction.

The sequence of variations during tempering is as follows: During the time fo collective recrystallisation the grain is more abruptly expressed $\{112\}\langle 110\rangle$; during the time of recrystallisation the orientation becomes increased $\{111\}\langle 112\rangle$ which prevails after crystallisation and finally increases after the growth of the grain. Recrystallization of tantalum has a preeminant selective mechanism of development. Orientation $\{111\}\langle 112\rangle$ already present in cold-rolled material apparently increases during the decomposition of others, which gives proof about the intentional formation of nuclei.

4. WELDING

Niobium welds well with niobium and other metals; tantalum can be qualitively welded only with tantalum, niobium, ans such metals as molybdenum, tungsten, and nickle. For binding tantalum and niobium electro-welding or arc-welding is used. Acetylene welding and atomic-hydrogen welding is not suitable for such metals.

Welding by resistance is conducted by usual method, with the exception that welding with roller-type electrodes is conducted under water for averting oxidation. The point of welding is ductile and has the very same strength as the basic metal. Single point welding is carried out in the open air, but triple and ten-fold point welding is done under water.(289).

The most favorable impenetrability of the current during welding by resistance appears to be 132amp/mm^2 on the surface of the electrode at the point of contact with tantalum or niobium. Using copper electrodes however, are only short-lifed; it is more useful to use tungsten electrodes.

Welding by resistance is not conducted in the present case during large compression (289).

For tantalum and niobium carbon-arc welding with the aid of a graphite rod is possible. It is conducted under carbon tetrachloride.

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For welding objects 0.38mm thick, 3.9mm electrodes are used; welding is performed by 20 ampere 40 volt direct current (for welding much thiner objects the listed indices are decreased correspondingly). Welding rods for arc welding with carbon electrodes are not being used (289).

Arc-welding of tantalum and niobium with the use of tungsten electrodes /133 is conducted in atmosphere of pure helium or argon (142-144, 295). The gas current must be suffieient for preventing oxidation of the details upon which specific gases of standard quality additionally purifies from the admixtures for improving the quality of the welded seam. The gas protecting medium is maintained on both sides of a welded seam till the tantalum is cooled (to a temperatures of 200°) (277, 289). The consumption of gas is in a majority of cases approximately 5 liters per minute. Argon-arc welding of tantalum and niobium products is often done in special protective chambers (295) (Fig. 52). No flux, fillers, or even welding rods are used.

pipe flange

Figure 51. Diagrammatic representation of carbon-arc welding of tantalum and niobium by using graphite rods. Graphite rods are securely fastened at the time when rubber compression makes it possible to rotate the object, while undergoing the welding: 1-container; 2-rubber seal; 3-carbon tetrachloride; 4-exhaust ventilating pipe; 5-graphite rod; 6-tantalum pipe; 7-extensible part of the container wall.

Prior to welding the surfaces of the welded joints are washed off with acetone; any other material is trapped by the heated tantalum and niobium.

Principly, both alternating and direct current is used for welding; however, direct current is preferable during direct polarity: welded detail - anode, electrode - cathode. During this, greater heat exchange is concentrated on the welded metal, which is important because the difference of melting points of the tungsten electrodes, which may contaminate the welded seam, and that of tantalum and niobium is relatively low. During welding by direct current the initial ignition is carried out with high frequency current.

In table 27-28 is brought general applicabel significance of the current /134 and voltage during the argon-arc welding of tantalum and niobium details with a tungsten electrode (295).

helium intake

Figure 52. Diagrammatic representation of welding tantalum and niobium details by arc-welding in a helium atmosphere with the use of a tungsten electrode; 1-tantalum pipe; 2-steel chuck; 3-rotary chuck; 4-tantalum flange; 5-tungsten electrode; 6-steel cover; 7-electrode holder.

Table 27

DATA ON ARGON-ARC WELDING OF TANTALUM SHEETS

(DC current of direct polarity, welding with a non-fusible electrode without a welding rod)

Thickness of sheet in mm	Diameter of Tungsten electrode in mm	Diameter of the opening for feeding the argon stream in mm	Consumption of Argon in cubic meters per hr		Amperage during welding in amperes	Rate of welding in mm/min	Remarks
			Burner	Blasting			
							Machine Weld
							Machine Weld
							Machine Wel
							Manual Weld
							Machine Weld
							Machine Weld
							Machine Weld
							Manual Weld
							Machine Weld

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Table 28 /135

DATA ON ARGON-ARC WELDING OF SHEET NIOBIUM

(DC current of direct polarity, machine welding with a non-fusible electrode without a welding rod)

Thickness of sheet in mm	Diameter of Tungsten electrode in mm	Diameter of the opening for feeding argon stream in mm	Consumption of argon in cubic meters per hr		Amperage during welding in amps	Rate of welding in mm/min
			Burner	Blasting		

The microstructure of a welded seam of tantalum and niobium appears to be characteristic for puremetals. During welding of raw metals, the typical hammering structure changes into a structure of recrystallized metal in the thermal welding zone and into the structure of a welded metal in the zone of the seam (295). The high grade seam possesses such a ductibility as the base metal; its durability is similar to tempered metal, but less than the durability of raw samples (table 29) (295).

Table 29

STRENGTH OF SEAMS OBTAINED DURING ARGON-ARC WELDING OF A 5mm TANTALUM SHEET

(Butt welding without welding rod DC Current of direct polarity)

Conditions of welding	State of Metal	Tensile strength in kilos per kilos/m^{-2}
W/O protective chamber	Not sintered	
W/O protective chamber	Sintered	
In chamber	Not sintered	
In chamber	Sintered	
W/O protective chamber	Sintered, rolled to 0.4mm, not sintered	
W/O protective chamber	Sintered, rolled to 0.4mm, sintered	
In chamber	Sintered, rolled to 0.4mm, not sintered	
In chamber	Sintered, rolled to 0.4mm, sintered	
----	Unwelded, unsintered	
----	Unwelded, sintered	

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The hardness of the seam is less hard than the hardness of a non-sintered metal, but greater than the hardness of a sintered metal. This is demonstrated by the diffusion of oxygen in metal from surface oxides coatings, formed on the welded seams and adjacent zone during the cooling following welding.

These oxides should be removed, for example, by the processing with abrasives and subsequent etching in a hydrofluoric acid solution, otherwise sintering in a vaccum the oxygen will diffuse into the base metal.

There are very scant data regarding the corrosion resistance of welded tantalum and niobium seams, but up to cettain tests, they prove to be no less corrosive resistant than the base metal. And So, for example, when testing in potassium hydroxide solutions a lesser effect on the seam was observed than on the base metal (295).

5. METALLOGRAPHY OF TANTALUM AND NIOBIUM

For the purpose of metallographic studies, tantalum and niobium are first polished with emery with the addition of carbon tetrachloride as a humidifier, and then by the suspension of aluminum oxides in water on a rotating felt cloth. The etching for exposing the grain limit must be conducted by fluoric acid with the addition of ammonium fluoride (4).

According to Meyers (293), the best etching for tantalum appears to be cold concentration of nitric acid with 5% addition of 40% hydrofluoric acid.

Chapter V

Coatings of Tantalum and Niobium on Base Materials

Coatings of tantalum and niobium on various base materials, such as metalic and even non-metallic materials, is of great interest, and opens new possibilities for using these metals. The use of these coating permits the economy of metal and to use it in conditions where it otherwise could not be easily used owing to the difficulty of processing.

The coating of tantalum and niobium can be accomplished by various methods including cathodic dispersion.

Very thin tantalum and niobium coatings could be obtained by electrolysis from molten mediums, however, the process of obtaining tantalum and niobium coating by this method has not yet been developed.

Coatings generally build-up by means of decomposition of haloid compounds of tantalum and niobium, volatile during relatively low temperatures and thinly decomposing on surfaces intended for applying the coating with the formation of comparatively thick dense layers of metal. The decomposition of haloid compounds may produce thermic dissociation or restoration of hydrogen. As a rule, it conforms to restoration of chlorides by hydrogen, in so far as it occurs during lower temperature.

The first time a high melting tantalum wire coating was used by the reduction of same by $TaCl_5$ with hydrogen was realized by Mr. Pirani (208).

g Van-Arkel' (5), Burgers and Bazart (215) obtained plastic coating, by subjecting pentachloride of tantalum and niobium to thermal decomposition in a vaccum on tungsten filament, heating to 1800-2000°.

Moyers (209) ascertained that plastic deposits of tantalum can be extracted from hydrogen mixtures with pentachloride of tantalum on tungsten filament heating 1200-1450°. He obtained on a tungsten core having a diameter of 0.05 mm tantalum strips having a diameter of up to 3.5mm at a rate of deposition of 3.9mm per hour. Niobium coatings were also obtained, however, niobium precipitated at these conditions was not as pliable as tantalum. It became more pliable after heating in a vacuum.

The original coating of tantalum and niobium was applied only for /138 tungsten filaments, then the process of deoxidising Tantalum with hydrogen was used for coating large size objects (pipes, blast pipes of rockets, melting pots, plates, rods, and wires) and from other materials (iron, copper, nickel, molybdenum quartz, aluminum oxide, graphite) (296).

Campbell, Powell, and Gonser (210-213) investigated in detail the process of obtaining coating on various base materials.

Although the formation and condition being applied by coating various aspects of samples, may differ between themselves, the basic process in all cases is the same.

Purified hydrogen in passed over the powder or chloride briquette, heated to a temperature sufficient for obtaining the necessary value of partial vapor pressure of chlorides. The mixture is then passed over heated sample for obtaining the coating.

During the application of a coating on a metal the deposition often takes two stages:

a.) The formation of a thick layer (generally thicker than 0.0001mm) as the result of reaction of transformation between the coating of metal and vapors of haloid composition of metal;

b.) Deposition of a basic layer of coating at the expense of deoxidisation of hydrogen.

On inactive base materials such as glass, porcelain; coating is obtained only at the expense of deoxidisation of hydrogen.

Niobium and tantalum are deposited in the same conditions and can be easily deposited in the form of alloys from mixtures of vapors of pentachlorides of both elements.

The composition of the coating may be changed in relation to the ratio of the quality of volatile salts.

The temperature of the sample, on which the coating builds up, the velocity of the flow of gas and its pressure, the state and form of the coated sample, and finally, the method of its heating, influences the process of obtaining tantalum and niobium coatings.

THE EFFECT OF TEMPERATURE

Usually the process of obtaining a coating is brought about in the temperature range of 800 to 1200°, during which the process increases, with increased temperature. During 600° the deposit occurs with very low velocity, at 1400° it occurs very rapidly. The velocity of process, during optimum temperatures, lies in the limits of 7.5 to 65 microns per minute.

Selecting the process temperature depends on the nature of the undergoing coating of metal and on the character of the required coating. On copper objects, in view of low temperature smelting of copper, the coating must be performed at temperatures lower than 1100° (usually 800 to 1000°). On the other hand, nickel can be coated with tantalum at temperature to 1400°, /140 that is higher temperatures of fusion of intermediate ision of nickel with tantalum (in the case of forming alloys between metal coating and base metal, for example in the case of Ta and Ni, the size of intermediate layer of fusion appears to be the function of temperature). On iron the coating builds-up at temperatures higher than 1200°, and on molybdenum at temperatures to 1500°.

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Figure 53. Device for continuous coating of wire during the reduction of chlorides of tantalum or niobium by hydrogen: 1- coated filament; 2.- insulation; 3- heater; 4- halide; 5- thermocouple.

Figure 54. Device for coating details with tantalum and niobium during the reduction of chlorides by hydrogen: 1- hydrogen inlet; 2- thermocouple;

3- heating spiral; 4- chloride of Ta or Nb; 5- insulation; 6- heater; 7- asbestos insulation; 8- rubber seal; 9- watee-cooled base; 10- supporting hook; 11- non-conducting current screen; 12- inductor; 13- coating detail (nozzle); 14- pyrex-type tank; 15- heater; 16- condensating vessel; 17- outlet; 18- mineral oil.

The temperature of the sample affects also the character and stability §140 of the deposition. At low temperatures the coating result as very fine grain, almost amorphous. Increasing the temperature will result in the formation of more coarse-grained coatings..

At very high temperatures monocrystallised or pseudomonocrystallized deposition can be obtained if the coating is built-up on monocrystal of base metal.

At increased temperatures a reduction or decomposition of less stable compounds up to the point of attaining a heated surface is possible. This leads to the formation of a continuous powderess deposition which fill up the deposition surface faster than the metal becomes coated.

THE EFFECT OF GAS PRESSURE AND VELOCITY OF ITS FLOW

The concentration of reagents in gas mixtures affects the velocity and crystallized structure of coatings being formed. The higher the concentration of chloride in the mixture, the greater will be the speed of deposition. The lower the pressure of gas mixtures in the apparatus, the more coarse will be the resultant crystalls in the deposition of metal layers. Thermal decomposition in a vaccum very coarse crystalls. Conducting a process by atmospheric pressure mixture leads to the formation of microcrystallic coatings.

The velocity of the gas and the character of its passage over the specimen (laminar or turbulent) is affected on the external appearance of the coating, of its similarity, and the efficiency of the deposition process. During the steady flow of gas and low rate (<10 CM^3/per second) of extraction of tantalum during the coating of wire attains 60 o/o. Increase of the rate of gas permits

permits the obtaining of a more even and uniform coating, however, with the lower extraction of tantalum (at the rate of gas flow > 20 cm^3/per second it is less than 25%).

THE EFFECT OF FORM AND SURFACE CONDITION OF THE SAMPLE

In cases when the sample contains sharp angles, protrusions or surfaces of greater curvature, the coatings are non-uniform because in such points the deposition of the metal is much faster. But the surplus of metal can be easily removed by grinding or polishing. More uniform covering of samples /141 of irregular shapes can be obtained using turbulent flow of gas or by rotating the the coating component.

Apparently, there is no limitation of the size and shape of articles (from large pipes to thin filaments) on which an industrial method of coating may be obtained, however, in very large articles with powerfully developed surfaces (especially during the coating of external surfaces of long pipes) the tendency increases (at increased temperatures) on the formation of loose adjacent powder-like coating.

Surface conditions of samples affects the structure of the deposition. At high temperatures monocrystallic surfaces leads to the obtaining of even an monocrystallic coating. At moderate temperatures the surface conditions does not affect the structure of the deposition.

EFFECT OF THE METHOD OF HEATING

The sample becomes heated either by an induction or a passing current. It is possible also to use external heating but the effectiveness of the process in this case is low and depositions are formed on the walls of the working chamber, which is ordinarily taken into consideration when constructing such machines (298)

THE EFFECT OF THE QUALITY OF CHLORIDES, CARRIER GAS, AND COATED SURFACES

In addition the relation to the conditions of conducting the process, the properties of the coatings depend also on the purity of the tantalum and niobium chlorides, obtained either by direct reaction between metal and chlorine with subsequent purifying distillation, or by the reaction of chlorine with Ta_2O_5, Nb_2O_5+C with the obtainment of a mixture of haloids and hydroxyhaloids which is then thoroughly seperated.

Traces of oxygen and hydroxychlorides present in the mixture of gases, do affect the form of deposition and its properties. Oxides and nitrides form corresponding compounds in coating, making the obtainment of uniform surfaces highly difficult. These mixtures normally produce a brittleness in the tantalum and niobium coatings.

The pliability and density of the adjoining tantalum coating could deteriorate even owing to the absorption of a small amount of hydrogen in the prodess of forming coatings and its condensation (in hydrogen) especially in the conditions when the coatingforms during low temperature and prolonged condensation, in particular owing to the absorption of hydrogen or other gases, contained in a base metal, and subsequently seperated by them in the coating process (brittle and loosely adjoining coating resulting on iron, pre-heated to redness /14/ and cooled in the atmosphere of hydrogen).

In certain conditions the quality of the coating material affects the process of coating. So during the obtainment of a coating on copper, it must not contain oxygen if it is desired to avoid brittleness.

In such conditions when high mechanical durability is demanded, coating of 0.1-0.2mm thickness is applied. Thicker coatings can be obtained at once or successive applications of thick layers one on another.

For the protection of corrosion in a chemical agent, a coating of 0.1-0.6mm thickness is generally required, because with a smaller thickness it is difficult to avoid a porous coating.

The reduction in the porosity of coatings is attained by the application of two or three layers, and polishing each of these layers prior to the application of the following layers and shifting the sample in the apparatus for better deposition so that the applied layer covers the pores and evens the existing non-uniformities. In this waycoatings were obtained offering perfect protection of the copper and steel samples against the effects of nitric and hydrochlorine acids when testing same for a period of 2-3 months.

Coating thickness to 0.1mm safely adheres to objects and possesses good pliability during which, from the point of view of these properties, the best coating appear to be 0.04 to 0.06 thickness. A steel rod with a diameter of 3mm with a coating of 0.04 to 0.06 thickness was bent several times to an angle of 30°, but the coating did not split not flake off.

By Brinell test, the hardness of tantalum coatings is 180-220 kg/mm^2, at the same time as the hardness of technical tantalum in the form of tempered rods or sheets ranges in the limits of 50 to 80 kg/mm^2.

The pliability of these coatings changes with certainity, in conformity with the changes of their hardness, inasmuch as certain samples having less hardness can be more brittle. Greater hardness of coating is indicated on the presence of impurities whcih were not removed in the tempering process.

X-ray investigation of samples of tantalum coatings on copper, iron, and molybdenum, obtained by the reduction of hydrogen TaCl$_5$ during mild temperatures, indicated that, for example, the parameter of crystalline lattice of deposited metal is always more or less enlarged in comparison with the lattice of polished tantalum. This deformation is caused, by appearance, by the formation of solid solutions of introduced hydrogen in the metal, it is not removed even by tempering in a vacuum during a temperature of 1200°. [1, 2]

Tantalum coatings, obtained by low temperature, have strongly deformed [14] lattice of tantalum and possess fine-grained structure (essentially "amorphous").

Such a sharp distortion in the lattice was caused, apparently, by considerable hydrogen absorption which takes place at much lower temperatures. Hydrogen can be partially removed by tempering in a vaccum at a temperature of 1200°, that simultaneously leads to the growth of the grain of the coating. Tantalum coatings obtained during higher temperatures have less distortion of crystalline lattice and more coarse-grain structure. Tempering in a vaccum at a temperature of 1200° does not affect the properties of these coatings.

By x-ray investigation of samples, there was no detection of the formation of alloys or solid solutions bycoating iron and molybdenum with tantalum.

A relatively thick alloy layer is located between nickle and tantalum. This alloy is very hard and stable against corrosion and forms a very strong bond between coating and base.

It is also possible to obtain metal coatings of tantalum and niobium on different bases; copper, nickle, iron, molybdenum, tungsten.steel, graphite, porcellan, quartz, alumium, pyrex, and carbide compounds; but depending upon the basic products it is also possible to obtain carbides, nitrides, borides, and silicides of tantalum and niobium.

CHAPTER VI

BRIEF ANALYTICAL CHARACTERISTICS OF TANTALUM AND NIOBIUM

The analysis of materials containing niobium and tantalum is one of the /144 most difficult sections of analytical chemistry, since these elements have no reaction characteristics and make up few of the colored compounds [299].

Qualitative identification of niobium and tantalum is usually conducted with the aid of organic agents, chiefly tannic acid, which, with niobium, makes an orange colored compound, and with tantalum, makes a yellow color.

A number of other organic phenol type substances, such as pyrogallol, pyrocatechin and gallic acid, are also being used for the qualitative development of niobium and tantalum.

Tantalum in a solution can be developed with the aid of rhodamine B (tetraethylrhodamine), making up, with tantalum, a violet-colored compound. This reaction does not hinder the presence of niobium and tantalum ions. Iron, mercury, antimony, gold, copper, tungstate and molybdate ions also produce colored compounds [299, 300].

Kuznetsov [301] offered a number of organic agents with sudden color changes in the presence of niobium and gave the principle deliberation on the discovery of new color selective reactions.

A number of rough qualitative indications of the content of niobium and tantalum in minerals is shown in the work of Abramov [302].

A. The Separation and Qualitative Determination of Niobium and Tantalum

The work of the English chemist Schoeller, in the school Alimarin, is in the basic qualitative method of determining niobium and tantalum

The most complete summary of methods of qualitative determination is prepared by Chernikhov and Goryushina [304]. The systematization proposed by them is discussed in the given summary

1. Separating Tantalum and Niobium

The capability of mineral acids to easily undergo hydrolysis in acid surroundings makes it possible to separate them in such a way from many elements.

Along with the basic methods q separating tantalum and niobium (especially from titanium) are: tannic acid, pyrogallic, phenylarsenate and others.

The tannic acid method. The gravimetric method of hydrolytic precipitation of niobium and tantalum in the presence of tannic received the greatest expansion. [299, 303, 305, 306]

The role of tannic boils down to the depression of the adsorbability of tantalum and niobium hydroxides, which permits them to separate from many elements, from tilanium in particular. This method was first suggested by Schoeller and received the designation "pyrosulfate - tannic acid" method in view of the fact that the tannic acid 545L separation precedes the separation of the analysed material by melting with potassium pyrosulfate.

During separation by melting with pyrosulfate, as shown by Chernikhov and Uspenskaya [307], the completeness of separating niobium from a solution containing sulfates of alkali metals, less than in the case of the recommended separation of a hydrofluoric and sulfuric acid mixture. However, in this case there is a large content of titanium in the samples, there is a complete separation of niobium in the residue, and a decrease in the large quantity of titanium converted into residue.

For complete separation one is obliged to repeat many times the resedimentation, which leads to the disappearance of niobium. The separation of tantalum from titanium passes much easier.

Alimarin and Frid suggested replacing tannic acid with pyrogallic acid, based on the fact that titanium with pyrogallic acid forms in an acid medium a more stable and better soluble compound than with tannic acid [308,309]. For some time past, the tannic acid method has improved at the expense of the use of complex-forming reagents which permit separating tantalum, niobium and titanium from all elements, with the exception of tin and antimony [310].

The pyrogallic acid method [306, 308, 309, 311, 312]. Alimarin and Frid [308,309] found that pyrogallic acid forms complex compounds of the R_2-H[NbO($C_6H_4O_3)_3$] - xH20; R_3-H [$T2_2$ O ($C_6H_4O_3)_6$] - xH20 type.

As for a similar compound with titanium in an acid solution, it is a more stable and more soluble complex compound than the compound with tantalum and niobium.

Thus, during the acidification of alkaline solutions containing complex compounds of niobium, tantalum and titanium with pyrogallic acid, the mineral acids quantitatively separate in the residue, during which the residue of niobium is colored brownish-red, and tantalum is colored lemon yellow. With this method it is possible to separate niobium and tantalum from titanium, aluminum, iron, zirconium and others.

The hydrolytic method of separating niobium from titanium was worked out by Syrokomskiy and Klimenko and set up on the fact that pH started the sedimentation of pentavalent and trivalent niobium hydroxides, from one side, and titanium hydroxides from the other, are sharply distinguished. So, for concentrating niobium from 0.003 to 0.013 g-atom/liter of pH sedimentation of its hydroxide changes to from 0.35 to 0.27, Ti^{4+} hydroxide in pH = 1.5 and Ti^{3+} in pH = 4. Titanium in a solution is reduced by zinc amalgam [315] or electrolytically to Ti^{3+}, after which differential hydrolysis is conducted during sharp dilution with water and boiling.

During the first sedimentation the employment of this method already succeeded in obtaining a residue of pentoxides, containing up to 3% TiO_2; in a repeated sedimentation the quantity of TiO_2 in the residue became 1% less.

The presence of tartrates, oxalates, fluorides and greater quantities of sulfates prevent separation.

The introduction of 20-30 ml of a 1% gelatin solution into the solution speeds up considerably the coagulation of the residue.

Golubtsova [316] determined that hydrolytic separation of niobium in a 2% hydrochloric acid solution, which passes unsatisfactorily in the presence of titanium, reaches completeness in the presence of iron. Titanium was not discovered in the residues of Nb_2O_5, hydrolytically separated in the presence of a large quantity of titanium and iron.

The phenylarsenic method [317] is based on the sedimentation of phenylarsenic acid in the highly acid medium (0.3 - 3-n) of mineral acids in the form of the $H_2[Me_2O_4(C_6H_5AsO_3)_2]$ Compound, where Me = Ta^{+5}, Nb^{+5}. The residue does not dissolve in tartaric, oxalic, citric, hydrochloric and nitric acids. We shall now dissolve in alkalis, hydrofluoric acid, concentrated sulfuric and phosphoric acids. From the sulfuric acid solution, containing hydrogen peroxide, the phenylarsenic acid deposits only tantalum, and niobium remains in the solution in the form of a peroxide compound.

The theory of the complex formation of arsenic acid in application to chemical analytical goals is brought out in the work of Portnov [318].

2. Distribution of Tantalum and Niobium.

The next stage of chemical analysis - the separation of tantalum and niobium from their collective precipitate - represents the most difficulty, as was pointed out in the technological section; here these difficulties aggravate the need for quantitative distribution.

The Marin'yak method, based on the dissimilar solubility of $K_2T_2F_7$ fluoro-tantalate and $K_2\,NbOF_5$ fluorohydroxyniobate, permits carrying out fractional crystallization of these salts (see page 79). However, owing to the complexity of this method, he will not make practical use of it for analytical goals at present.

The Schoeller method [305, 319] results in the fractional distribution of tantalum and niobium with tannic acid in an oxalic acid medium in the presence of ammonium chloride. The physico-chemical basis of this method is given in the works [306, 312], in which the pH hydrolytic sedimentation of niobium and tantalum with tannic acid was investigated in an oxalic acid medium and it was established that their complete distribution in this is impossible owing to the nearness of pH at the beginning of their sedimentation (2 for tantalum and 3 for niobium); for completeness of distribution, repeated resedimentation of tantalum is necessary with its gradual separation from niobium.

Cunningham [311] suggested conducting separation in two fractions, conduct control according to the bromophenol blue indicator and determine the niobium in the tantalum fraction by the volumetric method, but Chernikhov suggested dividing into two fractions according to color and determining the niobium in the tantalum fraction by the colorimetric method.

Phenylarsenic distribution [309, 317] is based on the separation of tantalum from the acid solution of phenylarsenic acid by retaining the niobium in the solution with the aid of hydrogen peroxide (see page 146). This indicates the difficulty of practical application of this method for mass analyses.

Hypophosphite distribution [320] is based on the formation of a low-soluble complex of a compound a tantalum with hydrophosphorous acid in the oxalate medium. The method consists of tantalum and niobium oxides in melting with potassium pyrosulfate, dissolving pig iron in ammonium oxalate and the sedimentation of tantalum in sodium pyrophosphite in the form of a wall coagulating white precipitate $(PO_2H_2)(Ta_2O_5)$. The quantitative separation of tantalum requires double sedimentation.

The reaction with hypophosphite is very sensitive and permits the discovery of the presence of tantalum in a solution with a concentration of 1: 1000000 [312].

The iodate method of distribution Chernikhov and Uspenskaya [321] suggested the iodate method of distributing niobium and tantalum, based on the dissimilar stability of their oxalate complexes. Tantalum, with iodate in acid solutions containing oxalate, produces an insoluble compound, the exact composition of which is not established. They complete the determination with iodometric titration of the resulting compound, emerging from the empirical factor, obtained on the basis of the results of titration, according to which the ratio is: $T_2 : IO_3^- = 1:2$.

The extraction and ion-exchange methods of distribution, discussed in detail in the technological section, at present are also developing a very large application in analytical practice.

B. Volumetric Methods of Detecting Tantalum and Niobium [304]

The volumetric methods of detection (oxidimetry and electrolytic reduction) were worked out chiefly for niobium.

Oxidimetric detection is based on the ability of niobium to produce a variable valence compound and can be used only in the absence of titanium and other elements, also possessing variable valence. Reduction of niobium can be performed with amalgomated zinc in the presence of succinic acid, with zinc in the presence of fluorides or phosphoric acid with subsequent oxidizing titration with permanganate. However, all these methods of oxidimetric detection are unreliable, since niobium reduces to different degrees of valence, which makes the exact calculation of the results of the analysis practically impossible.

Electrolytic reduction of niobium is performed on lead, platinum and mercury cathodes with subsequent oxidimetric titration.

Volumetric methods of detecting tantalum are unknown (in connection with the fact that it does not possess variable valance in solutions), except the iodate method.

V. Colorimetric Methods of Detection

Colorimetric methods are also worked out chiefly for niobium, since tantalum produces comparatively little selectivity of colored compounds.

One of the better methods of colorimetric detection of niobium is the method worked out by Alimarin and Podval'naya [322]. It results in the formation of a yellow complex compound of $H[NbO(SCN)_4]$ extractable with oxygen-containing organic substances: alcohol, esters and others. In this, tantalum produces the colorless $H_2 [T_2O(SCN)_5]$ complex.

Titanium also produces a yellow-colored rhodanide complex, but the sensitivity of the reaction on titanium is considerably less than on niobium, both in the ratio Nb: Ti = 1:30 and the concentration of TiO_2 in a solution of not more 0.3 mg in 10 ml q titanium have U42 no noticeable influence on the detection of niobium. As was shown above, niobium and tantalum produce complex compounds with pyrogallic acid. In an acid medium, containing oxalates, tantalum produces a yellow colored soluble complex, at the same time, niobium in an acid medium does not form a colored compound. Niobium, in contrast to tantalum, produces a colored complex only in an alkaline or neutral medium. This permits detecting niobium in the presence of tantalum and, on the other hand, permits detecting tantalum in the presence of niobium [323, 324]. The disadvantage of this method results in the necessity of predétecting almost all associated elements, chiefly titanium, which produce an intensive yellow color in these conditions.

Dirnin's investigation [325] showed that if detection is carried out in a 4-N. hydrochloric acid medium and if measurements are made of the optical density in the ultraviolet region of the spectrum then titanium and a majority of the other elements hinder detection very little and it can be carried out without preseparation from the associated elements.

In sulfuric acid solutions, niobium with hydrogen peroxide produces a yellow colored per acid [319]. The intensity of the residue reaches maximum in 100% sulfuric acid. In these conditions the residue is very insignificant at the expense of titanium. Tantalum does not produce a residue.

The influence of titanium on this reaction is removed by the fact that colorimeterings originate in a mixture of 60% H_2SO_4 and 40% H_3PO_4.

Langmyhr [326] and Pallila, Adler and Hiskey [327] studied the absorption spectra of the per acids $HNbO_2 [O_2]$ and $HT2O_2 [O_2]$, which are formed in an acid medium with hydrogen peroxide [327]. They worked out a method of detecting niobium and tantalum based on spectrophotometering their peroxide compounds in sulfuric acid solutions.

The observed absorption maximum for niobium is 2 = 365 Å, for tantalum, 2 = 285 Å. The absorption maximum for titanium is 2 = 410 Å, in which the absorption of niobium and tantalum is negligible [328].

A colorimetric method of detecting tantalum in the presence of niobium was worked out resulting in the fact that a fluoride complex of tantalum with methylviolet forms a blue-violet colored compound in pH = 1.9 - 2.3 which is extracted by toluene. The light absorption maximums are 2 = 600 Å and 2 = 550 Å. By this method one can detect from 0.025 to 1.5% of the tantalum in metallic niobium. Titanium does not hinder the sensitivity of the reaction on pure salts in 0.2 v/ml [329].

Colorimetric detection of niobium, based on the reaction of the formation of phosphomolybdic blue (heteropoly acids), suggested in the work [330], did not receive wide application wide application.

Chlorination methods, used early for the analytical separation of niobium and tantalum from titanium, are being developed anew. So, in the work [331], a method of separating niobium and tantalum with chlorinotion with octachloropropane at 300°.

Niobium can be separated from tantalum by leaching the mixture of oxides with selenium oxychloride [331], in this case the niobium together with titanium change into solution, and the tantalum is in all 100% in the residue, which is calcined and suspended in the form of Ta_2O_5.

G. Physical Methods of Analyzing

When it becomes necessary to determine small amounts of tantalum in mixture with niobium or vice versa, we use physical analysis methods such as spectral, roentgenospectral and other methods. Spectral determination of niobium has been most thoroughly developed by Charles [332], rapid roentgenospectral of niobium in steel was developed by Cordovi [333]. Beydon and Fisher [334] introduced a method for quantitative determination of niobium, tantalum and titanium from the sum of their oxides, it is based on the fact that from these oxides only tantalum gives a radioactive isotope with long period of half-life, which in turn offers the possibility of measuring its radioactivity.

Titanium in that mixture of oxides is determined colometrically, and niobium —— by the difference.

Chapter VII

TWO-COMPONENT ALLOYS OF TANTALUM AND NIOBIUM

Many alloys of tantalum and noibium with other metals and also with nonmetals possess a number of valuable properties-- acid resistance, heat stability and corrosion resistance, high mechanical properties at ordinary temperatures, hardness and thermal emission properties.

However, these alloys are not widely used in industry because they still have not been fully studied and in a number of cases there is a complete absence of data on phase diagrams of systems of tantalum and niobium with other elements.

In this and the following chapters we will examine the data published in literature both on tantalum and niobium alloy systems and also on individual phases in these systems, which are of practical and scientific interest.

For convenient use an outline is constructed in alphabetical order, whereby the binary systems of tantalum and niobium are examined and then the ternary and quaterrary and quinary systems with participation of these alloys.

Niobium-nitrogen. Niobium nitrides can be produced by direct synthesis, i.e., by treating the niobium powder in a current of nitrogen or ammonia /335, 336/.

Nitriding of niobium shavings for 4-5 hrs at 1300° permits obtaining the high^er^ nitride of niobium $NbN_{1.00}$, and at 1450° the nitride $NbN_{0.93}$. By heating these nitrides in a high vacuum at 1300-1400° for 3-6 hrs (in order to remove a part of the nitrogen) nitrides are obtained which are more nitrogen-impoverished, (from $NbN_{0.88}$ to $NbN_{0.70}$).

Finally, when heating mixtures of nitrogen-rich nitrides with niobium shavings at 1450° (3 hrs) in an argon atmosphere, low nitrides are obtained (down to $NbN_{0.05}$).

The kinetics of the reaction of nitriding niobium and tantalum were studied by Gulbransen and Andrew /337/.

The energy ~~of~~ activation for ~~during~~ reactive diffusion of nitrogen in niobium is about 25.4 and in tantalum 39.4 kcal/mole, i.e., nitriding niobium is easier than nitriding tantalum.

Niobium nitride can be produced also by nitriding a mixtures of Nb_2O_5 or Nb_2O_3 with carbon in a stream of nitrogen.

A list and the results of the old studies on the properties and conditions ~~conditions of~~ for obtaining ~~producing and the properties of~~ niobium nitrides are given in ref. ~~study~~ /87/.

In 1940 Umanskiy studied (by means of X-ray diffraction) niobium nitride which was produced by Babich by roasting for three hours a mixture of niobium with its hydride in a stream of nitrogen at 1100-and 1300° .

while ~~When~~ nitriding a 0.25-mm diameter niobium wire with ammonia for one hour at 1400-1800° the authors of study /339/ discovered by means of an electron microscope the presence of an external layer of NbN and an internal layer of Nb_2N.

Fig. 55. Phase diagram of niobium-nitrog system.

KEY:
    1) content, at.%.

Well crystallized deposits of niobium nitride are obtained /340/ by precipitation on a tungsten wire with a diameter of 200 microns at 1340-1350° as a result of the reaction between the gaseous $NbCl_5$ (at a pressure of its vapors of 40-50 mm Hg) and the mixture of equimolecular volumes of $N_2 + H_2$ (total pressure of the gases to 600 mm Hg).

A complete X-ray investigation of the Nb-N system was made by Brauer and Jander /335/ and then by Schoenberg /336/ which mainly confirmed the results of Brauer that there are two nitride phases in the area of $NbN_{0.75}-NbN_{0.98}$.

Figure 55 gives the diagram of the location and width of the phase area in the Nb-N system.

The solubility of nitrogen in niobium is very small, less than 4.~~[illegible]~~ at.% ~~percent~~, because the alloy corresponding to the formula $NbN_{0.05}$ already contains the phase Nb_2N. The ~~alpha~~ α-solid solution of nitrogen in niobium has a body-centered cubic lattice with a period which differs very little from the period of pure niobium (3.2948 ± 0.0002 A). An investigation of the solubility of nitrogen in niobium was also made in study /341/ on specimens prepared by nitriding niobium wire. For this purpose, ~~diameter~~ wire 30μ in diameter was annealed at 2000° in a vacuum of 10^{-5} mm Hg (for 5 min) and then nitrided by N_2 or NH_3 at 1100° and a part of the nitrogen removed by heating in a vacuum at 2000°. By measuring the electrical conductivity of the nitrided wires and also their hardness it was determined that the coefficient of diffusion of nitrogen into niobium with the formation of a solid solution is $D \cong 1.71\, e^{-\frac{2900}{T}}$; the electrical conductivity is directly proportional to the nitrogen content and the limit of solubility of nitrogen in niobium, although it is very small, is nevertheless greater than 0.063 wt %.

Niobium nitride (NbN) with 13.1% N in powdered form is light-grey in color with yellowish ~~haze~~ tinge. It is very resistant to the attack of hydrochloric, sulfuric and nitric acids, and even of (aqua regia - boiling) /342/. When heated with NaOH or boiled in strong alkalis it decomposes with liberation of ammonia. Nb_2N is also resistant to the effects of acids, and when heated with strong alkalis, or during fusion with them, there is a liberation not of ammonia but of nitrogen /341/. Nb_2O_5 is formed ~~when~~ NbN is heated in the air to 500-800°.

An important property of niobium nitride (NbN) is its ability to ~~trans-~~ become ~~form into a~~ superconductive state at a rather high temperature -- about 15.6°K /331/.

Figure 56 shows the results of investigating the heat capacity of NbN at low temperatures /344/. The anomaly on the curve of heat-capacity at about 15°K shows the transition of niobium nitride to the superconductive state. The critical magnitude of the magnetic field determining the transformation temperature to a superconductive state is 257 gauss/deg.

Fig. 56. Heat capacity of niobium nitride NbN at low temperatures.

KEY:
1) C_p, cal/deg · mole
2) Temperature, °K

Niobium nitrides have great perspectives for use in radio engineering and automation. NbN is used as a detector for radio waves /345, 346/, in construction of tubes for transmitting images /347/ and also for superconducting bolometers /348 -- 350/. In many cases the ability of niobium nitride to become a superconductor at a relatively high temperature, about 15.6°K is put to use /351/.

<u>Niobium--Aluminum.</u> This system is practically unstudied. Marignac /352/ obtained the compound Al_3Nb (53.6% Nb) during aluminothermic reduction of K_2NbF_7. The ~~region~~ range of solubility of aluminum in niobium was not exactly determined /353/.

In ~~study~~ ref. /354/ the alloys of niobium with aluminum were prepared by introducing compacts of pressed 98% niobium and aluminum powders into the fused aluminum at 1200-1300° (with a $BeCl_2$ flux).

Two phases were revealed on the microsection of an alloy with 2.8% Nb-- hypothetically a solid solution on a base of aluminum and a compound $NbAl_3$, the crystals of which have a brown color when examined in polarized light.

The microhardness of the α-solid solution and the compound $NbAl_3$ (under a load of 5 g) is respectively 78 and 375 kg/mm^2.

Brauer /355/ repeated the experiments of Marignac by reducing ~~calcium~~ potassium fluoxniobate with aluminum at 1200° with subsequent cooling at a rate of 33 deg/hr.

no ¶ → In order to separate the compound $NbAl_3$, the product of reduction was treated ~~for 1 hr in~~ with 1 N hydrochloric acid, which did not effect the intermetallide in contrast to the alkalis which decomposed the $NbAl_3$ with the formation of a white-colored product.

$NbAl_3$ is stable against oxidation in the air; during the action of acid it is passive. X-ray studies showed the presence in this compound of a tetragonal lattice with ~~periods~~ spacings: a = 5.427 Å, c = 8.584 Å, c/a = 1.582, sp.gravity - 4.54 (in comparison with 4.52 which Marignac ~~determined~~ established in his study).

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spacings of the tetragonal body-centered lattice are: $a = 7.357 \pm 0.004$ A; $c = 4.247 \pm 0.002$ A; $c/a = 0.577$ A; the mean distance of Nb-Be is 2.28 kX.

Niobium-Boron. During investigation of the system /358/ in the region to 10 at.% B, in addition to the α-phase (solid solution of boron in niobium, the boundaries of which were not established) the phases β- and β'- were discovered, whereby the β-phase proved to be stable at room temperature and the β'-phase at a high temperature. According to the data of /358/ the β'-phase has a cubic lattice with a spacing of 4.21 A. In the region between 25 and 25 at.% B THE β' PHASE WAS FOUND ONLY IN ALLOYS COOLED FROM HIGH TEMPERATURES. Together with NbB_2 there forms a compounds of an indeterminate composition NbB_m and NbB_n of a bertollid type/359/ in ALLOYS CONTAINING BETWEEN 25 AND 50 AT.% B.

The compound NbB_m is unstable at high temperatures; with an increase in the content of boron in the alloys the degree of stability of this bertollid is reduced. The phases ζ and NbB_n correspond apparently to the compound Nb_3B with 25 at.% B, which are stable in the temperature regions of the order of 20-1500°. This phase is an isomorph of Ta_3B.

The phase NbB_m probably is Nb_2B, a boride somewhat more stable than Nb_2B. This phase is not an isomorph of Ta_2B. The γ-phase of NbB is an isomorph of CrB and TaB. It has a rhombic structure with spacings $a = 3.298$ A, $b = 8.724$ A, $c = 3.166$ A.

The δ-phase of Nb_3B_4 is an isomorph of Ta_3B_4, Cr_3B_4, and Mn_3B_4, with a rhombic cell the spacings of which are: a = 3.305 A, b = 14.08 A, c = 3.137 A.

~~Thus~~ The ε-phase of NbB_2 has an AlB_2-type hexagonal lattice with spacings a = 3.089 A, c = 3.303 A, c/a = 1.07. This phase has a region of homogeneity extending along both sides of the stochiometric composition, but not was not precisely determined.

NbB_2 has a density of 6.60 g/cm^3, a microhardness (30 g) of 2595 kg/mm^2, resistivity of 32 μohm · cm, and its heat of formation is about 36 kcal/mole. The melting ~~temperature~~ point of NbB_2 is 3000 ± 50°C.

Niobium diboride is rapidly decomposed by ~~molten~~ fused alkalis and carbonates. Oxidation in the air to a rather considerable degree begins even at 500-600°C. It is stable against the effects of mineral acids, is easily decomposed by mixtures of acids during heating.

Table 30 gives the data /360/ for the degree of stability of niobium boride in various reagents.

Niobium-Vanadium. This system was studied by Wilhelm, Carlson and Dickenson /361/. The specimens of alloys were prepared by mixing powders of niobium and (?) vanadium produced by calcium-thermic reduction of its pentoxide, and pressing compacts with their subsequent reheating in an arc-furnace with a tungsten cathode and a copper anode. After preparation the alloys are subjected to homogenizing annealing at 1600° (4 hrs) and studied by metallographic, X-ray, and thermal methods. The thermal method consisted in determining the melting temperature according to Pirani and Alterthum /362/. The results show the presence in the Nb-V system of a continuous series of solid solutions (Fig. 57) with periods of the lattice varying additively (Fig. 58), and a hardness, the shape of which is characterized by a flat maximum at 75-80 R_A (as compared with 50 R_A for vanadium and 43 R_A for niobium) (Fig. 59).

The corrosion resistance of alloys with 5.10 and 50% Nb is approximately the same as for stainless steel; after remaining for 375 hrs in contact with water vapor at 178° no substantial changes of the specimens were noted. The alloys prepared from niobium powders proved to be more brittle than alloys prepared from niobium shavings, which is explained by the greater content of impurities in the powders.

According to the data in /8/, niobium containing 2 wt.%V has a limit of proportionality of 29.7 kg/mm², rupture strength of 39.1 kg/mm², elongation of 11% and a Vickers hardness of 123 kg/mm².

Niobium-Hydrogen. Muthman, Weiss, and Ridelbach in 1907 obtained niobium hydride with 1.12% H by heating powders of metallic niobium in a hydrogen atmosphere. They assigned the formula NbH to the hydride (1.07% H by calculation) at atmospheric pressure and room temperature [illegible] absorbs hydrogen in an amount corresponding to the ratio. atomic %

H : Nb = 0.46. At the same pressure and 1000°C the solubility of hydrogen and niobium is 50 times less.

Table 30

The Stability of Niobium and Tantalum Borides in Various Acids and Acid Mixtures.

KEY:
1) Reagent
2) *conditions for dissolving*
3) Degree of stability (% of undissolved boride)
4) niobium boride
5) tantalum boride
6) 24 hrs at 20°
7) heated to boiling, 2 hrs
8) concentrated
9) saturated solution
10) Aqua regia.
11) hrs

Fig. 57. Diagram of the Niobium-Vanadium system

KEY:
1) content niobium, at.%
2) Temperature, °C
3) content Nb, wt%

Fig. 58. Dependence of the lattice spacing on the composition of alloys of niobium-vanadium.

KEY:
1) lattice spacing, A; 2) content, at.%

The solubility of hydrogen in 98.5% niobium is as follows /364/:

Temperature, °C	900	800	700	660	550	500
Solubility of hydrogen, cm^3/g	4.0	6.1	9.7	18.5	29.7	74.4
Temperature, °C.......	450	400	350	300	200	20
Solubility of hydrogen, cm^3/g......	65.6	76.8	83.6	88.0	93.3	104

Fig. 59. Hardness of niobium and vanadium alloys:

○ – annealed alloys of niobium powder; □ – fused alloys of niobium alloys;

⊖ – annealed alloy of niobium shavings; △ – fused alloys of niobium shavings.

Key:
1) Hardness, R_A
2) Content, wt. %

Fig. 60. Change in the weight of niobium during the reaction with hydrogen relative to temperature and time.

KEY:
1) Change in weight, mg/cm^2; 2) time, min; 3) temperature, °C

At temperatures of 450–500° the solubility of hydrogen in niobium is proportional to $\sqrt{p}$.

For the solubility of deuterium in 98% niobium values are obtained which are close to these figures, but equilibrium, especially at temperatures below 500°,xxxxxxx is reached more slowly.

According to the data of Gulbransen and Andrews /365/ the reaction of niobium with hydrogen begins at 250°, wherein the content of hydrogen is rapidly increased to 360° and then decreases to 560°, apparently due to the decomposition of the lower-temperature hydride, and from 560° to 900° the hydrogen content in niobium again increases (Fig. 60). This indicates the existance of two hydrides of niobium with different temperature ranges of stability.

According to Umanskiy's data /338/, the atoms of niobium form in its hydride a lattice which differs only a little from the face-centered cubic lattice with a spacing of a = 3.42 A. It is possible to assume that this lattice is rhombically or tetragonally distorted. Such an assumption satisfactorily explains the severe blurring of all lines except (222) on the x-ray diffraction pattern of niobium hydride. This explains the considerable divergence of the values of its lattice spacing obtained from measuring the lines with various indices.

Fig. 61. The intervals of transition to a superconductive state relative to the content of hydrogen in niobium:

1) Nb; 2) Nb + 5.06% H; 3) Nb + 9.89% H; 4) Nb + 32.76% H

Key: a - induction reading, %
b - temperature, °K.

Ya.S. Umanskiy established that the content of hydrogen in niobium hydride is ~~equal to~~ 44 at.%, which approximately corresponds to the formula NbH.* The specific gravity of NbH is 6.0-6.6.** The hydride NbH at 15°K transforms to the superconductive state /342/. According to the data in /365/ hydrides containing less than 50 at.% H also ~~transform to a superconductive state~~ become superconducting (in the study, hydrides were used which were obtained by treating 99% niobium in hydrogen at 800°; cf. Fig. 61).

A detailed study of the systems niobium-hydrogen and niobium-deuterium was made in ~~study~~ ref. /147/, where the coorresponding alloys were produced by hydrogenation or deuteration of niobium sheet preliminarily degassed by heating in a high vacuum at 1000°. It was established that the rate the alloys form with deuterium is less than for hydrides. The nitrogen prevents hydrogenation due to the formation of the nitride Nb_2N.

According to the results of the X-ray investigation, niobium dissolves hydrogen to a composition of the α-phase $NbH_{0.11}$ with an increase of the ~~face~~-centered cubic lattice spacing of niobium to a = 3.295 kX, and the solution of deuterium passes to $NbD_{0.08}$ ... [? - ms. illegible in text]

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* In study /356/ the existence of NbH_2 with a = 4.56 kX was also revealed.

** For the properties of NbH see also pp. 31 and 47 [page nos. refer to original text].

Thus the boundary of the α-phase exactly coincides with that which was cited in study /366/ 9.89 at.%. From $NbH_{0.11}$ to $NbH_{0.7}$ (and from $NbD_{0.09}$ to $NbD_{0.7}$) there is a two-phase region ($\alpha + \beta$), and further from $NbH_{0.7}$ to $NbH_{0.89}$ there is a β-phase with a rhombic face-centered lattice with spacings for $NbH_{0.89}$ of: $a = 4.83$ A, $b = 4.89$ A, $c = 3.44$ kX (such a phase also occurs for the system Nb-D) These data do not agree with the structural data in ~~study~~ ref /366/, where the β-phase is ascribed as a cubic body-centered lattice and, apparently, these data are more correct. Brauer and Hermann determined the region of the beta-niobium hydride between 41 and 47.1 at.% H /147/.

Niobium-Tungsten. According to the data in /15, 465, 367/, the niobium-tungsten alloys are a continuous series of solid solutions.

A detailed investigation of the alloys of this system was made by Mikheyev and Pevtsov /369/ by the methods of determining the hardness, microstructure and electrical conductivity. The alloys were prepared by reheating compacts pressed from powders in an arc furnace in a helium atmosphere.

This investigation did not confirm the existence of a continuous series of solid solutions since in the range of 0 to 7.5-10% W a significant increase in the melting point of the alloys was revealed; in addition [illegible] the alloy with 4.6 at.% W quenched from 1800° has a two-phase structure [illegible] alloys with a content of 7.9-30 at.% W are also two-phase [illegible] increase in the tungsten content in the alloys from 18-80 at. %, the amount of one of the phases is decreases. The alloys containing between 80-100 at. % are single-phase both in the sintered and in the annealed states,

The hardness of the alloys reaches 350-470 H_{BR} with 10-50 wt. % W; the resistivity is 0.3-0.4 ohm · mm^2/m.

According to the data in /8/, niobium containing to 10 wt. % W has the following properties:

W content, wt. %	Limit of proportionality, kg/mm^2	Rupture strength, kg/mm^2	Elongation %	Vickers Hardness kg/mm^2	Electric conductivity μohm·cm
0	22.6	28.9	29	87	16.2
5	20.6	31.2	8.9	111	-
7.5	39.9	52.9	10	119	-
10	40.6	46.6	9.9	191	21.2

Niobium-Hafnium. In Duwez' study /370/ the alloys of niobium with hafnium, containing 10, 20, 23.5, 30, 43.5, 47, 55, 66, and 77 at. % Nb were prepared by fusion in an arc furnaces in a helium atmosphere, and after fusion were homogenized in a quartz, evacuated tube for 48 hrs at 1000° and quenched from this temperature. An X-ray investigation of the alloys showed that between 100 and 30% Nb the alloys are single-phase and have a face-centered cubic lattice with a spacing varying strictly along a straight line from 3.30 to 3.44 Å, i.e., they are a solid solution of hafnium in niobium.

Alloys containing less than 30 at. % Nb are two-phase and are a mixture of the solid solution of Hf and a hexagonal phase on a hafnium base.

Niobium-Germanium. According to Wallbaum's data /371/, in the system Nb-Ge there is a compound $NbGe_2$ with a structure of the $CrSi_2$ type and lattice spacings: a = 4.957 A, c = 6.770 A. The existence of this compound is confirmed by study /372/ where the same type of lattice is given, but with somewhat different lattice spacings a = 4.966, c = 6.781 A. Besides this niobium germanide in this solution there are also the compounds $NbGe_{0.67}$, $NbGe_{0.54}$ and Nb_3Ge. The first of these is stable only to 1650° and the other two up to 1910°.

Nb_3Ge has a β-W type structure with a lattice spacing of 5.165 A. Niobium germanides actively react with ~~fused fused~~ fused soda and sodium hydroxide, and also in the cold with hydrofluoric acid, and with a solution of sodium hydroxide and hydrogen peroxide. Hydrochloric acid acts only on the germanide $NbGe_{0.54}$, and concentrated sulfuric acid on $NbGe_2$ and Nb_3Ge.

Niobium-Iron. Wever /373/ established the presence in the closed field system α — γ-Fe — a solid solution with a two-way conversion α (δ) ⇄ γ.

Voronov /374/ investigated the system niobium-iron by the thermal, microscopic and hardness methods, by measurements of electrical conductivity and by X-ray analysis. He established that the maximum solubility of niobium in iron is at a eutectic temperature (1360°) about 2.5 at. % (~ 5.0 wt.%)

and the content of niobium in the eutectic is 9.8 at.% . (15.5% wt. %). With a reduction in temperature to 20° the solubility drops to about 1 at.%. The region of the γ-solid solution is to 1.5 at.% Nb. The chemical compound Fe_3Nb_2 was revealed in the system. With a solution of niobium in iron the hardness of the annealed alloys is increased ~~as~~ from 54 H_B to more than 80 H_B . and the hardness of the alloys containing 15-25 at.% Nb is 175-250 H_B. The resistivity increases with an increase in the niobium content from 0 to 5.55 at.% to 9.92 to 13.66 μohm·cm (at 25°) and from 14.08 to 16.68 μohm · cm (at 100°)

Reference /375/ investigated the aluminum-thermic method of preparing alloys of niobium with iron, thus assuring ag admixture of aluminum not exceeding 0.10-0.33%. The compound Fe_3Nb_2, to which in this study is ascribed the composition Fe_2Nb, is resistant to the action of acids, is brittle and nonmagnetic.

The original method of investigation—the diffusion of niobium in iron /376/—confirms the closed condition of the γ-field.

The phase diagram of Nb-Fe has repeatedly been had more accurate /377-379/ and its most complete form is shown in Fig. 62.

Fig. 62. Phase diagram of Nb-Fe.

Key: 1) Temperature ; 2) [Content, wt.%] ;

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The USSR has developed an industrial production of ferroniobium with a content of not less than 50% Ta+ Nb, not more than 0.12 C, 10-11.5% Si, 7% Al 0.15-0.17% P, 0.03-0.05% S, and 7% Ti by the alumino-thermic reduction of loparite concentrate /380-381/; in Germany ferroniobium with 60-65% Nb, 1-2% Si, 0.1% S, 0.1% P, and 0.2% C is produced also by the ~~aluminum~~ alumino- thermic reduction of technical niobium pentoxide containing 70% Nb_2O_5 and 25-30% Fe_2O_3. Such ferroniobium of the IGF firm is used at the Krupp plants for manufacturing certain types of heat-resistant steels of the following approximate composition: 17-19% Cr, 13-16% Ni, 1.8-2.5% Mo, and 0.8-1.4% Nb/161/. (?)

In the USA large-scale production of ferroniobium-tantalum is realized on the basis of Oregon ores (N.W. USA) /383/.

In England, ferroniobium with 60.6% Nb+Ta and 27% Fe is produced by ~~the~~ alumino thermic reduction in the presence of fluxing and ~~catalyzing~~ catalyzing additives BaO and $NaOCl_3$ /384/.

<u>Niobium Oxygen.</u> An investigation of the sytem Nb-O conducted by Brauer /54/ showed that oxygen is dissolved in niobium to 0.86 wt% (4.76 at.%); the investigation established the existence, apart from the high-oxygen phase Nb_2O_5 (*) of intermediate oxides of NbO_2 or Nb_2O_4 and NbO.

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* For Nb_2O_5 see also p. 19.

The oxide NbO_2 according to Goldschmidt has a rutile structure with a = 4.77 A and c = 2.96 A; however the X-ray study by Brauer shows only a small relation of the NbO_2 structure to the rutile structure, but not identical. This phase is homogeneous from $NbO_{1.94}$ to $NbO_{2.09}$.

The data on the existence of the oxides Nb_2O, Nb_2O_3 and Nb_3O_5 is not confirmed.

The solubility of oxygen in niobium was closely studied by Seibolt /385/ on specimens obtained by oxidation of niobium containing 99.5% Nb, 0.1% C, 0.5% Ta, 0.04% Ti (0.2% Si and 0.01% Fe. Measurement of the lattice spacings) and the investigation of the microstructure of the alloys containing to 6 wt.% O enabled plotting the section of the curve of the dependence of solubility on temperature (Fig. 63). With an increase in the oxygen content in the solid solution to 0.8 wt.% the hardness of niobium is increased from about 100 to 350 (Vickers hardness) and the lattice spacing from 3.3002 A, 0.014 wt.% O to 3.319 A (3.76% O).

Fig. 63. Curve ~~of the~~ solubility of oxygen in niobium.
KEY: 1) Temperature, °C; 2) content ~~of~~ oxygen wt. %; 3) solid solution

The heat of solution of oxygen in niobium calculated from the solubility curve is 12.5 kcal/mole.

Seibolt also made a series of indices on the dependence of solubility of oxygen in niobium on the pressure and the possibilty of purifying the metal from oxygen which are of practical importance.

Ang /386/ determined the energy of activation for diffusion of oxygen in niobium and it was 27.6 kcal/mole.

The dissociation pressure of the solid solution of oxygen in niobium at 1000° was considerable less than 10^{-3} - 10^{-4} mm Hg. At higher temperatures the dissociation pressure rapidly increases and the oxygen can be completely removed from the metal. Thus, Ang and Wert /387/ while heating a niobium wire to 2000° at 10^{-5} mm Hg reduced the content of oxygen in niobium to 0.002%.

Niobium dioxide NbO_2 is a black-blue powder with a heat of formation of 193.5 ± 5 kcal/mole. A number of properties of niobium oxides are given in handbooks /53, 342/.

Fig. 64. Diagram of the system Nb-Co (after Pogodin and Veniaminov).
Key: 1) temperature; 2) content of Nb, %.

Niobium-Cobalt. The very first systems were studied by Koster and Muhlfinger /384/ who investigated the phase diagram to the first intermetallic constituent, which was given the formula $CoNb_2$, i.e. to a content of in the alloy of 38.8% Nb. According to the data of these authors the saturated solid solution of niobium in cobalt forms with the intermetallic compound a eutectic at 21% Nb. The eutectic temperature is 1235°. The solubility of niobium in cobalt at the eutectic temperature is about 7%, and at room temperature it is less than 4%.

A measurement of the hardness of the alloys after appropriate heat treatment indicates their ability to age. Thus, the alloys with 3,4, and 8% Nb will be hardened with a temperature of 1200°, with subsequent holding for 30 minutes at 700-800° the hardness increases on the average of 30%.

The very incomplete study of Koster and Muhlfinger was checked and added to by Pogodin and Veniaminov (1939) who prepared alloys of the system Nb-Co by aluminothermic reduction of mixtures of $Nb_2O_5 + Co_3O_4$, whereby the content of the impurity of aluminum in the niobium-poor alloys was reduced to 0.2-0.35%, and in niobium-rich alloys to 0.02-0.3%. An investigation of the microstructure, hardness, and random X-ray analysis permitted establishing the presence in the system of a intermetallic compound Co_2Nb (and not Co_5Nb_2) containing 44.1% Nb, and to plot the cobalt of the phase diagram of the Nb-Co system, which is shown in Fig. 64. The Vickers hardness of the compound is more than 500 kg/mm^2; the alloy of this composition is very brittle and cracks when measuring hardness.

The aging of alloys of the system Nb-Co containing to 5.9% Nb was confirmed by the study of Pogodin and Veniaminov. They found that the solubility of niobium in cobalt at 20° is 0.1 wt %, at 500° is 2.6%, at 1000° is 5.4% and at 1250° (the eutectic temperature) is 6.6%.

Niobium - Silicon. Wallbaum /389/ by sintering a mixture of Nb and Si powders in a corundum crucible under argon prepared the silicide $NbSi_2$. Breuer and Sheele established that less than 5.41 % Si is dissolve in niobium with the preservation of the completely unchanged niobium lattice and that the compounds Nb_2Si (two modification, α and β) and $NbSi_2$ are present in the system. The density of the α - modification of Nb_2Si is 7.75 and the β- modification 7.3 g/cm³.

$NbSi_2$ has a hexagonal lattice of the $CrSi_2$ type with spacings: a ≈ 7.785 ± 0.005 A, c ≈ 6.576 ± 0.005 A, c/a ≈ 1.374; its density is 5.29 g/cm³, microhardness under a 100 g load is 1050 kg/mm², melting temperature 1950-2000°, resistivity 6.3 μohm · cm. $NbSi_2$ transforms to a superconductive state at a temperature of < 1.2°K. It is stable against oxidation to 800-1000°C /211/.

Schachner, Cerwenka, and Nowotny /391/ uncovered in this system a phase Nb_5Si_3 having a structure of the type $D8_8$ with spacings: a ≈ 7.52 kX, c ≈ 5.25 kX, c/a ≈ 0.698.

A further study by Parthe, Schachner, and Nowotny /392/ established the existence of another phase Nb_5Si_3 having a structure D^{18}_{4h} with spacings: a ≈ 9.95 kX, c ≈ 5.07 kX, c/a ≈ 0.51. The presence of this phase is confirmed also by ref. /393/.

In 1955 Krantons /394/ studied the system Nb-Si in more detail by the methods of determining the melting point, of X-ray and metallographic investigation of alloys prepared by fusion in an arc furnace under argon. ~~Ex~~ As a result of this study three phases were revealed in the system: Nb_4Si, Nb_5Si_3 and $NbSi_2$, but the existence of α -and β -Nb_2Si was not confirmed. The compound Nb_4Si is formed peritectically at 1950°C from Nb_5Si_3 and the liquid phase. This compound is an isomorph of Ta_4Si, but has a space group differing from $D0_{19}$ which is indicated for Ta_4Si in ref /395/.

The phase Nb_5Si_3 fuses congruently at 2480° and exists in two modifications, α (low temperature) and β (high temperature) with α → β transformation between 1900 and 2100°. With the addition of small amounts of carbon to this phase a ternary compound system forms, Nb-Si-C with a structure of $D8_8$. The melting point of $NbSi_2$ is 1930°, the eutectic $NbSi_2$-Nb_5Si_3 fuses at 1550° and lies at 58 at.% Si. The eutectic Nb-Nb_4Si fuses at about 1880°. Lupton's observed increase in the lattice spacing during solution of silicon in niobium from 3.289 to 3.300 kX indicated the possibility of low solubility of silicon in niobium.

A subsequent investigation of alloys of this system by Kieffer and associates /396/ on specimens prepared by sintering by the method of hot pressing and also by sintering prepressed compacts under argon made it possible to construct the diagram shown in Fig. 65.

Fig. 65. Diagram ofthe system Nb-Si (after Kieffer and associated).

KEY: 1) Content Si, Wt. % ; 2) temperature, °C; 3) Content Si, at. %; 4) appx. transformation temperature.

In contrast to Knapton's data this study did not reveal the compound Nb_4Si, the existence of the other phases ($\alpha \equiv Nb_5Si_3$, $\beta \equiv Nb_5Si_3$ and $NbSi_2$) was confirmed.

In study /397/ by the methods of determining the melting point, microhardness, resistivity and metallographic and X-ray analysis of specimens prepared by hot pressing mixtures of powders of pure niobium and 99.9% silicon with subsequent annealing, there was revealed an individual X-ray for Nb_4Si indicating a hexagonal system, and also the presence of the compounds Nb_5Si_3

and $NbSi_2$ was confirmed. In this investigation it was established that Nb_4Si does not have a latent, as Kempton indicates, but an open maximum of the melting point. It is evident that α-and β-Nb_2Si, as earlier indicated by Brauer and Scheele /390/ are actually α- and β modifications of Nb_5Si_3.

Fig. 66. Diagram of the system Nb-Si (after Samsonov, Yermakova and Neshpor)

KEY: 1) Content Si, wt. % ; 2) Temperature, °C ; 3) Content Si, at. %.

The final view of the phase diagram of the system Nb - Si can be described in the following way (Fig. 66).

The solubility of silicon in niobium, according to /394/ is less than 1 at.%, the solid solution forms a eutectic with Nb_4Si — a compound that fuses congruently at 2600°; this compound forms a eutectic with the phase Nb_5Si_3 which exists in two modifications with the point α → β transformation at about 2000°. Nb_5Si_3 forms with $NbSi_2$ the third eutectic of the system at at 1900°. The last eutectic $NbSi_2$ with Si or the solid solution of niobium in silicon is formed at 4-5% Nb and has a melting point of about 1300°.

The chemical stability of the niobium silicide $NbSi_2$ in the cold was studied in Ref /398/. During the course of one hour it did not dissolve in HCl (concentrated and 1 : 1), HNO_3 (concentrated and 1 : 1), in a solution of NaOH, for 3 hrs in H_2SO_4 (concentrated 1:1 and 1:10), for 5 hrs it did not decompose in $KHSO_4$ and 8.5 hrs in $KHSO_4 + KHF_2 + SeOCl_2$. It dissolved completely after 30 min in a mixture of $HF + HNO_3$, after 1 hr the greatest part is dissolved in a mixture of $KHSO_4 + KHF_2 + H_2SO_4$, and after 3 hrs in HF and in a mixture of $HF + H_2SO_4$. It is completely decomposed by fused Na_2CO_3 and NaOH.

Fig. 67. Lattice spacings in alloys Ta-Nb, [illegible] Ta-Mo; Mo-Nb; Mo-W; W-Nb (after Buckle) KEY: 1) lattice spacing, A ; 2) at.% .

Niobium-molybdenum. According to the data in /263, 367/ Nb and Mo form a continuous series of solid solutions. The alloys of this system were investigated by Buckle /15/ on specimens prepared by pressing powder mixtures of molybdenum and niobium with subsequent sintering of the compact in a vacuum [illegible] of 10^{-5} - 10^{-6} mm Hg. A measurement of the lattice spacings of the alloys, and also their microhardness and an investigation of microstructure showed the presence in the system of a continuous series of solid solutions (Fig. 67).

A more detailed study of the system Nb-Mo was made by Yeremenko /399/. The alloys were prepared by pressing mixtures of niobium powders (containing 0.7% Ca and 0.7% Fe) and pure molybdenum (traces of Fe and Ni were found spectrally) into 6x6x50 mm molds and by their sintering in a induction furnace in a vacuum of $4 \cdot 10^{-} - 5 \cdot 10^{-5}$ mm Hg at a temperature of 1850°.

A measurement of the lattice spacing, microhardness (with a load of 50-100 g on a PMT-3 instrument) and a dilatometric study of the alloys confirmed the presence in the system of a continuous series of solid solutions.

Recently this system was studied in detail by Korniloy and Polyakova /400/. The alloy specimens were prepared from powders of 98.7% Nb and 99.9% Mo by pressing their mixture, with subsequent sintering of the molds in a vacuum. The measurement of the melting point, microhardness, specific gravities, resistivity and its temperature coefficient yielded the results shown in Table 31.

Table 31

Certain Properties of Nb-Mo aloys

Alloy composition, wt. %	Melting point, °C	Microhardness, kg/mm²	Specific gravity	Resistivity (25°) μohm · cm	Thermal coefficient of resistivity (25-100°) $\alpha \cdot 10^{5}$

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Additions of niobium to molybdenum greatly increase the recrystallization temperature of molybdenum /401/ and increase its hardness /8/ (Fig. 68). In Table 32 are the mechanical properties of niobium with additions of molybdenum /8/.

Table 32

Mo content, wt. %	Limit of proportionality kg/mm	Rupture strength, kg/mm^2	Elongation, %	Vickers hardness, kg/mm^2	Resistivity, μohm · cm

In Ref /402/ the alloys of niobium with molybdenum were prepared by sintering the molds (10x10x290 mm) in a vacuum at 2280° with a direct passage of a current through them. The sintered molds were rolled into sheets 1.5 mm thick, which were annealed one hour at 1400°, after which their hardness was measured in a vacuum at a temperature to 800°C by means of a Vickers pyramid under a load of 30 kg (Fig. 69).

Fig. 68. The effect of additions of niobium on the hardness of alloys Mo-Nb after annealing. KEY: 1) Vickers hardness, 30 kg load ; 2) annealing temperature, °C

Fig. 69. Hardness of alloys Mo-Ta and Mo-Nb with a temperature increase.

KEY: 1) None; 2) Temperature, °C

The alloys of molybdenum with niobium containing more than 85% Mo, 10-10.25% Nb and admixtures of 0.009 -0.4% Al, 0-0.02% C and less than 0.02 % O_2 are patented. The alloys can be treated by pressure at elevated temperatures and retain cold working after holding an hour at 1200° /409/.

Fig. 70. Diagram of the system Nb-Ni (after Pogodin and Zelikman)

KEY: 1) Temperature, °C ; 2) Content Nb, wt.%; 3) Content Nb, at. %.

Niobium-Nickel. The phase diagram of alloys of this system were constructed by Pogodin and Zelikman /407/ (they also cite the results of important, previous studies) on the basis of the results of thermal, X-ray, and microscopic analyses, and also on the basis of measuring the hardness (Fig. 70).

The existence of the chemical compound Ni_3Nb /405/ having a region of homogeneity with a content between 32.5 and 36% Nb was confirmed in the system as well as the assumed phase NiNb.

The solid solution on a base of Ni_3Nb forms two eutectics— with α -solid solution of niobium in nickel at 23.5 wt.% Nb and 1275° and with the assumed phase NiNb (γ -phase) at 51.6 wt.% Nb and 1175°. The solubility of niobium in nickel is 20.3 wt.% at 1258°; 18% at 1200° ; 15.0% at 1100° and 10.7% at 900°.

Kubaschewski and Schneider /407/ found that the solubility of niobium in nickel is less than that which was established by Pogoin and Zelikman and is 15% at the exactly determined eutectic temperature of 1265°. The solubility of nickel in niobium is about 5%.

Alloys Nb-Ni are relatively ductile. Their hardness with 33% Nb is 340 H_B as compared with 145 H_B with 3% Nb. The greatest resistance to oxidation are the alloys containing 5-15% Nb (i.e., solid solutions of niobium in nickel) /406/. In a heterogeneous field (α + Ni_3Nb) the resistance to oxidation is decreased and with 35% Nb the alloys are less resistant than pure nickel. The alloys of niobium-nickel are very resistant to acid corrosion /15/. Alloys in the zone of the solid solution of niobium in nickel are the most resistant to corrosion by hydrochloric acid, and alloys in the two-phase zone, the solid solution and Ni_3Nb, are especially [illegible] to . the effect of of nitric acid, which, according to the postulation in /155/, should be considered as due to the formation of an inhibiting film.

Niobium-Tin. According to the data in /407/ the Nb-Sn system contains the compound Nb_3Sn which has a β -W structure. The alloys in this study were obtained by fusing tin on niobium powder in a sealed quartz tube at 1200°. Nb_3Sn is formed by a peritectic reaction at a temperature between 1200 and 1500°.

The compound Nb_3Sn is a superconductor at 18.05 ± 0.1°K -- at the highest temperature of transition of all those known for intermetallides.

An X-ray diffraction study /408/ confirmed the presence of a β -W cubic lattice for the compound Nb_3Sn with a spacing 5.289 ± 0.002 A with a X-ray density of 8.92 g/cm^3.

Niobium-osmium and niobium-iridium /409/. In the system Nb-Os and Nb-Ir was found the phases Nb_3Os and Nb_3Ir with a β -W structure and spacings respectively of: $a = 5.121$ A and $a = 5.131$ A.

The X-ray density of Nb_3Os is 11.59 and Nb_3Ir is 11.52 g/cm^3.

According to the data in /408/, Nb_3Os transforms to the superconductive state at a temperature < 1°K, and Nb_3Ir at 1.7°K.

Niobium-Palladium /409/. Niobium forms with palladium only one intermediate σ -phase (Sbfd) with spacings $a = 9.$[illegible] A, $c = 5.11$ A, c/a = .

Niobium-Platinum. Wallbaum /410/ discovered in this system a Laves phase, but did not prove it. In ref /409/ the phase Nb_3Pt was revealed with with a β-W structure and spacing a = 5.11 A.

The X-ray density is 11.59 g/cm³. According to the data in /408/, Nb_3Pt transforms to the superconductive state at 9.2°K.

Niobium-Rhenium. According to the data of an X-ray analysis a series of intermediate phases were revealed in the system. The alloy containing 37% (atomic) Nb at 1200° is a phase with an α-Mn-type lattice with a spacing of a = 9.670 Å.

Annealing the alloys containing 37-65 at. % Nb at 1000° causes the appearance of the σ-phase (ReNb) which is in equilibrium with the α-Mn-type phase and the phase of the niobium-base solid solution. The compound ReNb has a hexagonal lattice with spacings a = 9.72 Å, c = 5.07 Å c/a = 0.52, the niobium-base solid solution has a face-centered cubic lattice.

Up to 40 at. % Re dissolves in niobium at 1000° (see also p. 247).

Niobium-Rhodium. According to the data in /409/ two phases were revealed in the system at 1000°: $RhNb_3$ with a β-W structure and a spacing of a = 5.115 Å and the so-called σ-phase (RhNb) with a = 9.774 Å, c = 5.054, and c/a = 0.517. In equilibrium with the σ-phase is still another unidentified phase which is rich in rhodium.

The solubility of rhodium in niobium is high, but not exactly determined.

Niobium-ruthenium. A number of intermediate phases were revealed in the system at 1200° /409/: with 48 at. % Nb a niobium-base solid solution phase, with 57-52 at.% Nb a tetragonal phase with spacings: a = 3.00 A, c = 9.38 A, c/a = 1.13; with 32-42 and 22 at. % Nb two more phases were found whose structures were not determined.

Up to 22 at. % Nb dissolves in ruthenium.

Niobium-Sulfur. In Ref /411/ the sulfide $NbS_{1.74}$ was revealed. In Ref /412/ Biltz and Kocher obtained niobium sulfides by synthesis of the elements under pressure, and also by removing the sulfur from the higher niobium sulfides. Tensimetric analysis of the sulfides showed that the preparations with S :1.6 to 1.8 ($NbS_{1.6-1.8}$) are compounds which are slightly decomposed at a temperature of red heat (700-800°) and even at 1070°. Niobium forms two sulfides: Nb_2S_3 which is homogeneous to the composition NbS_4, and the mono-sulfide NbS which dissolves to one atom of Niobium, i.e., to a composition $NbS_{0.5}$. The specific gravity of $NbS_{0.5}$ is 6.66; NbS is 5.77, Nb_2S_3 is 5.14 and $NbS_{2.72}$ is 3.86.

HCl and NaOH does not affect NbS; but H_2SO_4 easily dissolves it, but HNO_3 and bromine water convert to niobium acid (completely in the case when NbS is finely pulverized); hydrogen peroxide decomposes NbS with the formation of perniobium acid and the precipitation of sulfur.

The chemical properties of $NbS_{1.7}$ are analogous except that HCl and NaOH slowly dissolve it.

Niobium-Tantalum. From the results of an X-ray and metallographic investigation it was found that niobium and tantalum form a continuous series of solid solutions /120, 15, 567/; their alloys are noted for their high corrosion resistance and the same strength as tantalum and niobium. Pogodin and associates investigated the tantalum-niobium system by method of determining the temperature at the beginning of melting of the specimens which were sintered from a mixture of powders, and by determining the electrical conductivity. Their data are presented in Fig. 71. Teymer, on specimens of electrolytic alloys prepared by Constantinov, determined the tensile strength, specific elongation, the microhardness under load of 200 g and the ductility by the Erichsen test when testing with a punch diameter of 8 mm. Determination was made on 0.1 mm thick sheet materials after annealing at 1500° in a high vacuum.

Her data are as follows:

	σ_b, kg/mm²	δ %	H_{V200}	Depth of Erichsen cupping, mm
Electrolytic Nb	24.0	[illegible]	[illegible]	3.35
Electrolytic alloys:				

cont'd on next page

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	σ_b, kg/mm	δ %	H_{V200}	Depth of Erichsen cupping, mm
83 wt. % Ta + 17 wt. % Nb	39.0	—	117	3.22
70 wt.% Ta + 30 wt.% Nb	35.0	13	119	3.15
35 wt.% Ta + 65 wt.% Nb	39.0	13	116	3.28

According to /8/ the alloy of niobium with 10 wt % tantalum has a rupture strength of 42-45.1 kg/mm², a limit of proportionality of 31.0-32.7 kg/mm², elongation of 10.7-19.8%, Vickers hardness of 111-74 kg/mm². Nefedova and Konstantinov studied the corrosion resistance of electrolytic alloys of tantalum with niobium. Their data are given in Fig Table 33 (for Ta-Nb see also /565/).

Niobium-Titanium. The sytem was studied in detail by Hansen et al /413/. The alloys were prepared on base of magnesium thermic (99.75%) and iodide (99.9%) titanium and niobium containing to 0.2% Si, fused in an arc furnace with a tungsten electrode in an inert-gas atmosphere, homogenised by annealing for 20-40 hrs at 1250° and subjected to metallographic and X-ray examination, on the basis of the results of which a phase diagram was constructed and is shown in Fig. 72. The solubility of niobium in α -Ti decreases with an increase in temperature, reaching to 4% at 600°. The region α+β expands with a reduction in temperature. Niobium with β -Ti forms a continuous series of solid solutions.

Further investigation of this diagram, which was done by Yelyutin, Bernshteyn and Pavlova /414/ yielded additional results.

Fig. 71. The system Ta-Ni; a) diagram of fusibility; b) constitution diagram. Resistivity (after Pogodin etc al.).

Key: 1) Temperature by pyrometer, °C; 2) content, wt.%; 3) resistivity, ohm^{-1} cm^{-1}; 4) content, wt.% ; 5) temperature coefficient, %

Fig. 72. Diagram of the system Ni-Ti (after Hansen etc al.).

Key: 1) Content Nb, at.% ; 2) temperature, °C; 3) content Nb, wt.%; 4) fusion

Fig. 73. Diagram of the system Ni-Ti (after Yelyutin et al.).

KEY: 1) Content Nb, at. %; 2) Temperature, °C ; 3) Content, wt.%

Table 53

Corrosion Resistance of alloys of tantalum with niobium.

Media	Temp., °C	Losses, g/m². hrs
Nitric acid		
30%		
30%		
55%		
75%		
75%		
Sulfuric acid,		
92%		
Acetic acid, ice cold		
Aqua regia		

The alloys in this study were prepared in a graphite crucible by vacuum fusion and they contained between 1.5 and 80.4% Nb with a content of 0.7-0.9% C. The specimens after casting were homogenized in a vacuum at 1000°. A phase of the approximate composition of TiNb, with a dissociation temperature of 1100° was found while investigating the alloys by the method of ultra-violet microscopy. The data obtained enabled plotting the diagram shown in Fig. 7[illegible].

Grum-Grzhimaylo's study /415/ of the diffusion of activated titanium containing radioactive scandium, revealed in the alloys Ti-Nb a sharp increase

[illegible]

in the coefficient of diffusion for scandium for alloys with 90% Nb and 10% Ti and still another maximum D_{Nb} for alloys with 20-30% Nb. The presence of the first of these maximum confirms the existence in the system Nb-Ti of the compound established in ref /414/, to which Grum-Grzhimaylo ascribed the formula Ti_2Nb_3; the second maximum indicates the existence of the compound Nb_3Ti, which is improbable.

The mechanical properties of the alloys of niobium with titanium were investigated by Gross /416/ on specimens prepared by powder metallurgy methods. The results (Fig. 74) show that with an increase in the niobium content to 20% the tensile strength continuously increases and elongation decreases from 1[illegible]% to about 2%.

During pressure treating in the cold /417/ the rupture strength of the alloy with 7.5% Nb, as compared with alloys hot-rolled at 900°, increases 1.5 times, but the elongation is decreased from 22 to 5%. Greater additions of niobium to titanium insignificantly decrease the ductility of the alloys /418/.

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According to the data of Ermilova, Druzhinina, and Mal'tsev /419/, additions of 1 to 10% of Nb to titanium increase the strength of titanium at room and elevated temperatures without lowering the resilience; these alloys have an increased modulus of elasticity at high temperatures and high rupture strength; they may be used as heat-resistant alloys.

(1) Content in %; (2) kg/mm^2

Fig. 74 Mechanical properties of niobium-titanium alloys.

According to the authors of work /414/, it is generally difficult to strengthen alloys on the Ti base because the solubility in the high temperature modification of titanium (β-Ti body-centered cubic lattice) is less than in the low temperature modification (α-Ti close packed); due to ~~MK~~ this, it is impossible to strengthen the alloy during cooling because there is no formation of the saturated state on the α-Ti base. Niobium, on the other hand, helps to fix the high temperature modification of titanium and is capable of increasing its strength considerably. This is confirmed by the data available in the literature on measurements of physical properties of these alloys.

Table 34 gives the mechanical properties of niobium with additions of titanium according to data /8/. Kroll proposes anti-corrosion alloys of niobium-tantalum (10-60%) with titanium /[illegible]/.

Table 34

Mechanical Properties of Niobium with Additions of Titanium

Content of titanium in wt. %	Proportional limit, kg/mm^2	Breaking point, kg/mm^2	Strain	Vickers hardness kg/mm^2	Electrical resistance μ ohm . cm

Studies /421/ of the electrical resistance of Nb-β-Ti alloys in the temperature range between 88 and 1173° K have shown that an increase in the titanium content causes a continuous increase in the electrical resistance, and a decrease in the temperature coefficient right up to the β-alloys, which contain less than 25 at.% Nb when the temperature coefficient is negative. 179 The extrapolation of isotherms electrical resistance-concentration against the content of Nb when Nb→0 shows that at temperatures very close to absolute zero β-Ti manifests the properties of a semiconductor. (It should be noted that alloys containing less than 20% Nb are unstable at low temperatures.)

Fig. 75 Diagram of the system niobium-thorium

(1) Content of Nb in at.%; (11) Temperature in °C; (111) Content in wt. %.

Niobium-thorium. The system ~~of~~ niobium-thorium was studied in works /422, 423/. The alloys were prepared by arc-fusion of compacts composed of compressed thorium (purity 99.9%) and niobium, which contained about 1% of impurities, including 0.05% C. The fusions were performed in a neutral atmosphere in a water-cooled copper crucible with the utilisation of a tungsten electrode. The obtained alloys were investigated by the metallographic and x-ray methods of analysis, by visual determination of the fusion points, by recording of the cooling curves, and by measurements of the electrical resistance. The resulting state diagram is shown in the plot of Fig. 75. In the region of β -thorium-niobium alloys the state diagram has a simple eutectic character with a eutectic line at 1,435°, and a eutectic with 8% of Nb. The solubilities of components have not been investigated in practice; /80 if we do not consider the directions of Chiotti /434/, according to whose data the addition of niobium to thorium lowers the temperature of its transformation from the face-centered cubic lattice to the cubic base-centered modification ~~at~~ from 1,450 to 1,375°. This lowering is related to the solubility of niobium in the base-centered modification of thorium. Generally speaking this solubility is very small.

Niobium-carbon. Niobium carbide, the same as tantalum carbide, was first

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obtained in 1876 by Jolie, who reduced and carburised the pentoxide of niobium.

In 1925 Friedrich and Zitting obtained niobium carbide by the Smith and Massa method /425/, by reducing and carburizing the trioxide of niobium at a temperature of 1,200-1,800°. The carbide contained 11.37% C, which corresponds approximately to the formula NbC; the carbide also had a lattice structure of the NaCl type and lattice spacing of 4.40 Å /426/.

McKenna /427/ also obtained niobium with 11.37% C by crystallising fused aluminum, which leached out of the melt on cooling. X-ray investigation of carbide confirmed the data in /426/ on its type of crystalline lattice, however the lattice spacing turned out to be much greater, 4.4578 instead of 4.40 Å. Specific density of carbide 7.80 g/cm³ as obtained experimentally by McKenna is very close to the theoretical value.

Maurer and others /446/ assumed that the niobium carbide formula is Nb_4C_3.

A similar x-ray diffraction study of niobium carbides with different carbon content was conducted in 1940 by Umanskiy /428/, who obtained carbide by heating a mixture of powdered niobium (with a large admixture of niobium hydride) with carbon black. Of the 11 investigated carbide specimens containing 2.5 to 10.6 wt. % /17-47 at %/ of combined carbon, 7 were prepared at 1,200° C by holding from 4 to 5 hours in a vacuum furnace at a pressure of 0.01-0.001 mm Hg, while the remaining 4 specimens were prepared in the graphite-tube furnace in the atmosphere tube furnace in the atmosphere of carbon monoxide or in the hydrogen stream at a temperature of 1,400-1,500°.

The quantity of the carbon content attained in all the specimens prepared by Umanskiy did not correspond to the formula NbC (11.47% C). The carbides had a brownish-grey color, at the same time the brown shade was brighter when the carbon content in the carbide was richer.

At 1,500° the carburization reaction of niobium was practically completed in a period of 1 hour, while at 1,200° after a period of 3 to 4 hours (evidently, carburization of powders of other grain structures neccessitates different periods of holding). Carburization in an alundum furnace in the hydrogen stream was accompanied by the "burn out" of carbon. Niobium in the hydrogen stream of the graphite tube furnace was intensely carburized by the gaseous medium, and the CO atmosphere at 1,500° evidently remained practically neutral. No nitration of niobium mixed with 16 1
carbon black at the expense of nitrogen, which was present in the graphite tube furnace, was observed. According to Preston's x-ray pictures, lines of only one phase were present in the majority of cases - of niobium carbide phase whose metallic atoms form a face-centered cubic lattice. Carbide lattice spacing, according to the x-ray pictures, depends on the content of carbon (Fig. 76).

X-ray pictures of specimens containing 6.4 and 7.2% C /35 and 37 at %/, showed a simultaneous presence of two carbide lines with 4.434 and 4.450 Å lattice spacing, whereas on the otherhand , single phase alloys of these compositions according to Fig. 76, should have had lattice spacings of 4.436 and 4.440 Å. Hence, we can conclude that the state diagram of niobium-carbon alloys at 1,200° possess two regions in which the same carbides exist, and are divided by a two phase region: niobium forms at 1,200° two carbides of different composition, but with exactly the same arrangement of metallic atoms. The first of these carbides, containing 33 at % C was designated by formula Nb_4C or Nb_3C, the second, containing between 41 and 48 % C was designated by formula NbC or Nb_4C_3.

Fig. 76 Lattice spacing of niobium carbide (according to Umanskiy)

(1) Content of C in at %.

Additional data on the system were obtained by Umanskiy during x-ray investigation of the phenomena of diffusion of carbon in niobium. A study was made of the process of carburization of a niobium plate, covered with carbon black and heated in the hydrogen stream of the graphite tube furnace at 1,900°. During the twelve hour period the surface of the plate showed a growth of the carbide layer, which attained 0.1mm. From the x-ray analysis of the layers, lying at different depths, it was possible to conclude that the lattice spacing at a depth of 0.15mm varies between 4.22 and 4.45 Å, and that at 1,900° carbon is absent in the two phase region of the niobium diagram.

For checking purposes Umanskiy roasted a two phase specimen containing 7.2% C in vacuum at 1,500 and 1,800°. After annealing at 1,500° the alloy still showed two phases, however the x-ray pictures taken after annealing at 1,800°, showed only the presence of carbide lines with a lattice spacing of 4.439 Å, which is in good agreement with the length $a(Å) = f(C)$. Thus the break in the single 182 phase carbide region on the diagram of niobium-carbide at 1,800° disappears, because in any case its value sharply decreases.

Fig. 77. Arrangement of atoms in the plane (100) of a crystalline lattice of niobium carbide: a) is the ideal lattice; b) is the carbide lattice containing small amounts of carbon. (1) niobium; (11) carbon.

Niobium carbide NbC, when saturated with carbon up to the limit, must have a crystal structure of the NaCl type / Fig. 77., a and b depict a schematic distribution of atoms on the plane (100) of such a crystal/. If carbides containing small amounts of carbon represented solutions of niobium in niobium carbide NbC, constructed on the basis of the displacement type of structure, then their lattice spacing should increase with decreasing content of carbon, whereas in reality the lattice spacing decreases. Hence, it is necessary to assume that in the crystal lattice of niobium carbides, containing small amounts of carbon, there are vacant (in comparison to the ideal NbC lattice, depicted in Fig. 77, a) sites. This assumption is confirmed in comparison of the x-ray data analysis and in measurements of density of the carbide specimens with 2.5, 8.8 and 10.6% C and with lattice spacing corresponding to 4.402, 4.454 $\overset{s}{\text{Å}}$ and 4.461 Å.

Tretiakov (see /429/) obtained niobium carbide by reducing niobium pentoxide with carbon black in a graphite tube furnace at a temperature of 1,600° for a period of 2 hours, i.e., analogous to the operation of obtaining TaC in work /430/. Here, the content of carbon combined with carbide did not exceed 8-9.5%.

In reducing Nb_2O_5 in vacuum at a temperature of 1,500-[illegible] 1550° in vacuum Samsonov /429/ obtained niobium carbide which contained 11.0 % C; he established that the optimum temperature of the process for obtaining carbide in the graphite tube furnace is 1,800°; the carbide contained up to 10.7% C_{bound} and 0.2-0.8 % C_{free} /429/.

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Table 35

Densities of Niobium Carbide Specimens with Different Contents of Carbon

(1) Carbon content; (11) wt. %; (111) at %; (1V) measured density g/cm^2; (V) Calculated density; (Vl) it was assumed that there were vacant sites in the lattice (Fig. 77, b); (Vll) it was assumed that the carbon atoms were displaced by niobium atoms (Fig. 77 a)

Fig. 78. Phase diagram of the niobium-carbon system.

A detailed investigation of the niobium-carbon system was conducted by Brauer and others /431/. Alloy specimens were prepared from sheet and powdered niobium (with purity corresponding to 99.9 and 99.6%) and niobium carbide, which was obtained by heating two times the Nb_2O mixture with carbon black in vacuum at 1,600°

for periods of two hours each time, the roasting of Nb+NbC powder mixtures were performed in the graphite tube vacuum furnace three times, also for periods of 2 hours each time. X-ray investigation of these specimens containing from 0.68 to 11.40% C showed the presence of two phases - Nb_2C and NbC.

The phase diagram of the system Nb-C is shown in Fig. 78.

The solubility of carbon in Nb is very small, and microscopic investigations established it to be equal to 0.02 at % C. In the region Nb up to $NbC_{0.35}$ there is a two phase field of ~~mx~~ mixtures of α-solid solution with carbide Nb_2C; the region in which it exists extends from $NbC_{0.35}$ to $NbC_{0.50}$ / i.e., from 26 to 33 at % C/. The Nb_2C phase has a hexagonal lattice structure with lattice spacing varying from a = 3.1116 Å, c = 4.946 Å (at the lower phase boundary) to a = 3.1191 Å and c = 4.953 Å (at the upper boundary). Evidently, the Nb_4C phase discovered earlier by Umanskiy actually represents the Nb_2C carbide with a defficiency of carbon atoms.

The NbC phase is homogeneous within the limits of the compositions which correspond to formulas $NbC_{0.72}$ to $NbC_{1.00}$ /442-538/, and coincide with the data obtained earlier by Umanskiy.

Since all these specimens were prepared at a temperature between 1,600 to 1,700°, the question of the disappearance or the decrease in the break of the phase regions as observed by Umanskiy at temperatures on the order of 1,800°, remained unsettled until the present time, and an experimental state diagram constructed by Umanskiy (Fig. 79), may be still used without any substantial changes. In any case the eutectic diagram of the section Nb-NbC as proposed by Goldschmidt /432/ must be rejected.

Fig. 79. Experimental state diagram of niobium-carbon (according to Umanskiy, and with more precise data of the latest works): ○ are the single phase specimens; ● are the two phase specimens.

(1) Temperature in °C; (11) Content of C in at %.

Niobium-phosphorous. Heinrath and Bilts /433/ obtained a compound of NbP (24.9% P) by heating niobium with an excess of phosphorous at a temperature of 500°.

According to the data in /434, 435/ the phosphides of niobium are isomorphous to the phosphides of tantalum.

Schonberg /436/ discovered in the system two phases α- and β-NbP (see the description of the system Ta-P for the method of preparing the Nb-P alloys).

The α-NbP phase of the composition $NbP_{0.95}$ has a face-centered tetragonal lattice structure (Z = 4) with lattice spacings of a = 3.325 Å, c = 5.69 Å, c/a = 1.71; x-ray density 6.40 g/cm³. Distance Nb-Nb = 2.68 Å, P-P = 3.1 Å.

The NbP phase also has a face-centered cubic lattice structure with 4 atoms of niobium and 4 atoms of phosphorous in each elementary lattice space; the lattice spacings are: a = 3.325 Å; c = 11.38 Å; c/a = 1.71; x-ray density 6.54. pycnometric density 6.15 g/cm³.

Besides the NbP phase, work /437/ shows the NbP_2 phase which was obtained in a sealed tube at 750°; the phase decomposes in vacuum at 650° with the formation of NbP. The NbP_2 phase has a black color and is isomorphous to TaP_2.

Phosphides of niobium are quite stable against the action of reagents, with the exception of hot concentrated H_2SO_4, which quickly decompose them.

Niobium-chromium. According to the data in /406, 409, 438/, as a result of thermic, x-ray, and microscopic analyses the Cr_2Nb compound was discovered.

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* Footnote- On the properties of niobium carbide NbC, see page 38. 125

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The solubility of niobium in chromium is on the order of 8 to 10%, and the solubility is accompanied by an insignificant expansion of the chromium lattice. Intermetallide Cr_3Nb_2 appears when the Nb content is 20%. This compound containing 50 to 60% Nb is formed by the peritectic reaction; the temperature for its complete fusion is between 1,750 and 1,960° (for the alloy of ~50% Nb). Alloys containing more than 40% Nb are so brittle that it is impossible to prepare their slides for microscopic analysis. In work /406/ studies were made of the strength of alloys of this system against oxidation at 1,250° (Fig. 80). The alloys containing more than 40% Nb, i.e., in the region where Cr_3Nb_2 is present, are most resistant to oxidation.

According to the data in /439/, the system Nb-Cr possesses a Cr_2Nb phase, the low temperature modification of which possesses a face-centered cubic lattice structure with a spacing of a = 6.795 KX, and interatomic distances Nb-Cr = 2.892 KX; Nb-Nb = 3.[illegible]1 KX and Cr-Cr = 2.466 KX. No transformation of the Cr_2Nb phase into the high temperature modification was observed.

In the work of Yelyutin and Funke /440/ investigations were made of the high temperature region A of the state diagram of the system Nb-Cr. Electrolytic chromium powder containing 99.9% Cr, 0.1% Fe, 0.01% Si, and niobium in powdered form and pressed moldings which contained 99.5% Nb, 0.06% Fe, 0.01% C, and 0.02% Si served as basic materials.

Alloys containing 70 to 100 at % Nb were prepared by the powder metallurgy methods, while alloys containing up to 70 at % Nb were prepared by fusion. At the same time it was noticed that the cast alloys are brittle and do not subject themselves to mechanical treatment. The temperatures of melting (solidus) and total fusion (liquidus) were determined by the optical method by indirect heating of the specimens, and also by heating them in a stream.

The investigation of the phase composition by the metallographic and x-ray methods and measurements of the macro- and microhardness established that three phases existed in the system: α -solid solution of niobium in chromium, β -phase, having a lattice structure of the MgCu$_2$ type with a lattice spacing of a 6.95-6.96 Å and a compound of Cr$_2$Nb, and γ -solid solution of chromium in niobium. The system contained two eutectic regions β + γ at 21-22 at % Nb (1,600°) and α + γ at 39 at % Nb (1,660°). Limits of solubility (in the region of α and γ phases), which were established from the determination of microhardness and the study of microstructure, comprised: 10-11 at % niobium in chromium at 1660° 5-7.5 at % 186 at 1,550°; 4.25 at % at 1,500°; 3.24 at % at 1,400°, and about 20 at % of chromium in niobium at 1,660°, and 12-13 at % at 1,500°.

Fig. 80. Resistance to oxidation of alloys of niobium with tantalum and chromium:

X – Cr-Nb; ⊕ – Cr-Ta.

(1) Pressure decrease in mm of Kg/cm^2 ; (11) Ta or Nb content in at wt. %.

Fig. 81. Diagram of the system niobium-chromium (according to V. I. Yeremenko, G. V. Zudilova and L. A. Gayevskaya)

(1) Temperature in °C; (11) Nb content in wt. %.

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From the diagram data of the system niobium-chromium, obtained by Yeremenko and his coworkers /441/, in principle substantiate the results of Yelyutin and Funke, however the location of the lattice points on the diagram is somewhat different; it follows from the diagram (Fig. 81) that only one chemical compound Cr_2Nb is formed. The eutectic of the α-phase with CrNb crystallizes at 1,660° and contains ~ 31% Nb, while the eutectic Cr_2 Nb with the β-phase (~ 65% Nb) crystallizes at 1,710°. The alloys may be obtained by roasting at a temperature of 1,550° for a period of ~5 hours. This time is sufficient for total recrystallization and attainment of equilibrium state.

Niobium-zirconium /442/. According to the data in /443/ the solubility of niobium in zirconium is very close to 6% at [illegible]°, and according to the data in /444/ it is equal to 0.5% at 800°. Alloys of zirconium containing 12.9% Nb were prepared in work /445/. Alloy with 0.5% Nb was comprised basically of Widmanstatten structure and admixture of the second phase; alloy with 5.1% also had two phases, while alloy with 12.9% Nb had only one phase. Litton /446/ prepared alloys of zirconium containing 2.5 to 27.52% Nb by vacuum fusion in graphite crucibles and obtained the yield point values of alloys containing 0.6; 5.0 and 12.7% Nb, which at 649° are respectively equal to 68, 58, and 73 kg/mm^2; this according to Pfeil is explained by the fact that niobium lowers the transformation temperature of zirconium. Alloys of Zr with 12% Nb or 30% Ta possess rather good creep strength /445/.

The arc fusion of zirconium and niobium (of high purity) in a water cooled copper crucible (in argon atmosphere) in work /448/, produced an alloy of zirconium with 18 at % Nb, which deforms very easily at room temperature; and its deformation and annealing structures were studied. This alloy, which possesses a body-centered cubic lattice structure, has a structure which is very common to such a type of lattice. The annealing of the alloy at 650°, i.e., of the $\alpha \rightleftarrows \beta$-transformation region, led to an analogous structure.

In their work Rogers and Atkins /449/ conducted a systematic study of niobium-zirconium alloys. Pure zirconium, and niobium containing 0.5% Ta and 0.25% C were used for the preparation of the alloys. Alloys were obtained by the casting method. On the basis of the determined fusion temperatures, measurements of the temperature coefficient of electrical resistance, dilatometric, x-ray and metallographic studies, the state diagram of the system shown in Fig. 82 was constructed. 188

According to this diagram there is total mutual solubility of β- zirconium and niobium below the solidus line, which represents a sloping curve having a minimum near the 22% Nb content at a temperature of 1,740°. Further cooling causes the decomposition of the solid solution, with the exception of alloys which contain about 90% Nb. The lower part of the diagram, which represents alloys of zirconium-niobium, was constructed after the eutectic type of a diagram, with eutectic at 610° and 17.5% Nb. The solubility of niobium in zirconium at eutectic temperature is about 6.5%.

Tantalum-nitrogen. Tantalum nitrides in the purest form are obtained by heating the tantalum powder in the stream of nitrogen or ammonia /450, 451/. The homogenization of the obtained products is accomplished completely by heating them in vacuum at 1,100°.

It is impossible to obtain pure nitride by heating a mixture of Ta_2O_5 + 5% C.

at best the product contains 50 to 60% nitride, while the rest is TaC carbide.

Fig. 82. Diagram of the system niobium-zirconium.

(1) Temperature in °C; (11) Content in %. 157

Analogous products are obtained by nitration of tantalum powder if carbon containing admixtures are present in nitrogen.

Kinetics of the process of nitration of tantalum were studied in the work of Gulbransen /337/.

During the nitration of a metal by ammonia /452/ at 800 to 900°, and holding for a period of 5 to 18 hours, the content of nitrogen in nitride attained only at 6.12%, and only weak lines related to TaN were discovered on x-ray photographs.

When this product was heated in vacuum at 2,000° it lost a portion of nitrogen, by transforming into the nitride Ta_2N with 3.6% N. During prolonged heating in vacuum there is also an appearance of the tantalum line, which points to the further decomposition of the nitride.

Tantalum nitride may also be obtained by precipitation of the gaseous phase (mixture of $TaCl_5 + N_2 + H_2$), however here, Ta, which is reduced by hydrogen from $TaCl_5$, precipitates on the filament together with TaN. In this connection it is better to perform the nitration with a mixture of $TaCl_5 + N_2$, but at higher temperatures, on the order of 2,500 to 3,000°.

Works /453, 454/ are dedicated to the obtainment and study of the tantalum nitride composition.

A thorough x-ray study of the system was conducted by Schonberg /61/, who obtained specimens of Ta-N alloy by nitration of Ta powder with the help of nitrogen. In this system he discovered four intermetallic phases: β ($TaN_{\sim 0.05}$), γ ($TaN_{\sim 0.40}$ - $TaN_{\sim 0.45}$), δ ($TaN_{\sim 0.80}$ - $TaN_{\sim 0.90}$) and ε (TaN).

In the β-phase the positions of the tantalum atoms in the cubic lattice differ very little from the positions in the face-centered cubic lattice of pure tantalum (α phase). This superstructural phase has a lattice spacing of a = 3.369 Å, whereas pure tantalum has a spacing of 3.311 Å.

In composition the γ-phase resemble very closely the nitride of Ta_2N. It is a classical example of a nitride, formed similar to the interstitial phases, with the metal atoms arranged in a densely packed hexagonal lattice, and with the nitrogen atoms arranged in two octahedral pores, at the centers of elementary cells AAA........Nitrogen atoms are arranged at one of the centers of two triangular prisms, which are formed by the metal atoms.

The ε-phase was obtained by Schonberg by nitration of tantalum for a period of 7 days at a temperature of 1,000° (in pure nitrogen free of oxygen). It has a hexagonal elementary space lattice.

Breuer and Zapp obtained alloys of the system Ta-N rich in nitrogen by treating tantalum powder with 99.8% nitrogen for a period of 6 hours at a temperature of 1,600°. Alloys with content of nitrogen between TaN and $TaN_{0.95}$

were obtained by heating TaN in a vacuum furnace at a temperature of 1,400°, while alloys with a still lower content of nitrogen in the mixture of TaN + Ta were heated for a period of 8 hours at temperature of 1,400° in high vacuum.

Two nitride phases of Ta_2N and TaN were discovered in this work. The determination of the TaN structure gave results, which completely coincided with the Schonberg data. The shortest interatomic distances in tantalum comprised 2.90; 2.99 and 3.33 kX, and the distances Ta-N comprised 2.08 or 2.59 kX. The homogeneity region of this phase is very small because the alloy $Ta\text{-}N_{0.98}$ already contains the lowest nitride Ta_2N. The region of homogeneity possessed by this nitride ranges from $TaN_{0.41}$ to $TaN_{0.50}$ (instead of $TaN_{0.40}$ to $TaN_{0.45}$ according to Schonberg). Atoms of tantalum form the densest hexagonal packing with positions 000, 1/3, 2/3, and 1/2.

Fig. 53. Phase diagram of the system tantalum-nitrogen.

According to this data the region of solubility of nitrogen in tantalum is very small, because already at contents of nitrogen, corresponding to formula $TaN_{0.05}$, weak lines of Ta_2N phase appear on X-ray photographs. The δ-phase discovered by Schonberg was not established with sufficient certainty in the work /455/.

The highest nitride of tantalum TaN ([illegible]) is in the form of grey powder with a bluish shade. The hardness of the tantalum nitride comprises 3236 ± 57 kg/mm² /A56/. The electrical resistance according to the data of Samsonov /A57/ comprised about 1,650 ~~micro~~ohms.cm.

With respect to ~~chemical~~ properties, the nitrides of tantalum are similar to ~~non~~metallic tantalum. The same as tantalum, they react actively to the mixture of hydrofluoric and nitric acids, while hydrochloric and nitric acids have no effect on them. The highest nitride in the ~~compacted~~ close packed state is not decomposed by the mixture of $HCl + HNO_3$. The action of hot concentrated sulfuric acid for prolonged periods of time dissolves only traces of nitrides. At average temperatures TaN and Ta_2N are more resistant to the action of oxygen than is tantalum. ~~Whereas~~ ALTHOUGH tantalum and its hydrides are oxidised up to Ta_2O_5 when they are roasted for a short period of time in air (at a temperature of 570°). nitrides of tantalum roasted at the same temperature even for periods of 24 hours are oxidised only slightly.

3 Tantalum-aluminum. One of the compounds of this system - Al_3Ta - was discovered by Marignac /352/A, who obtained ~~it~~ THE COMPOUND by reducing K_2TaF_7 with aluminum. That this compound exists was ~~[illegible]~~ CONFIRMED by Brauer /A58/, who determined that it has a tetragonal crystal lattice structure with lattice spacing of a = 5.422 Å and c = 8.536 Å. 131

The study of the alloys of this system were carried out not long ago by Glazov, Mal'tsev and Chistyakov /459/ on specimens prepared from pure aluminum and tantalum, which contained 99.5% Ta, 0.2% Nb, 0.1% Al and 0.2% of other impurities. The basic alloy contained 5.15% Ta and was diluted to alloys containing from 0.1% to 2.5% Ta, which were investigated in the work. The alloys were subjected to homogenization for a period of a week at a temperature of 500° and then to subsequent step-wise annealing at 630-580-500-400-200° for a period of 40 hours at each temperature.

Fig. 84. Brinell hardness and microhardness of tantalum-aluminum alloys.

(1) Content Ta in %.

Fig. 85. Experimental diagram of the region of tantalum-aluminum system (according to Glazov, Chistyakov, Karol'kov and Mal'tsev).

(1) Content in wt. % of Ta; (11) Content in wt. % of Ta.

Investigations of these alloys were carried out by the study of the microstructure, and thermal and x-ray analyses.

Micro- and macrohardness (Fig. 84) were measured , and the diagram of the state (Fig. 85) rich in aluminum content was construted.

Additions of 0.10 to 0.20% Ta to aluminum caused strong pulverization of the grain in the solid solution (from 5 to 10 grains/cm² in aluminum and up to 150-150 grains/cm² in alloys containing from 0.10 to 0120 % Ta), which points to the modifying action of the tantalum aftercharge, 192
which is starting to be utilized in the production of aluminum alloys /460/ (see ch. 1).

The microhardness of the chemical composition of Al$_3$Ta was established to be equal to 440-450 kg/mm² (according to data /459/ - this is a lower value).

In work /354/ alloys of Ta-Al were prepared by the introduction of 98% tantalum powder into overheated aluminum up to a temperature of 1,200 - 1,350° (under BaCl$_2$ flux).

Microscopic investigation of alloy with 7% Ta showed the presence of the α solid solution of tantalum in aluminum with microhardness (under the load of 5 g) 60 kg/mm² and chemical compound of Al$_3$Ta with microhardness of 441 kg/mm². In the polarized light the Al$_3$Ta separations are colored black. Alloys of Ta-Al may be also obtained by saturating compacts made of Ta powder with melted aluminum /451/.

• Tantalum-boron. The system was studied with x-rays by Kiessling /462/, who discovered α-solid solution of boron in tantalum and four boron phases which he called β, γ, δ, and ζ-phases. The solubility of boron in the tantalum lattice is low, however, in general it is higher than in the other transition metal subgroups IVa, Va, and VIa of the periodic system. It has been established that the phase (TaB_2) is homogeneous in the region starting from 61 to 72 at % B ($TaB_{1.78}$-$TaB_{2.57}$) and is isomorphous to other metal diborides of the IVa and Va groups. This is the only phase of the system Ta-B which is stable within wide range of temperature- starting from low temperature up to the point of fusion (3,100°). TaB_2 has a hexagonal lattice with a lattice spacing of a = 3.057 Å; c = 3,292 Å; c/a = 1.078; microhardness (20g) equal to 2,537 kg/mm^2, specific electrical resistance equal to 68 mcohm .cm, and is formed from the elements with an evolution of 52 kcal/mole. Data on the properties of other borides of tantalum are given in work /463/.

TaB_2 is much more stable against the action of acids than diboride of niobium, however it is oxidized by the oxygen of the air, starting at lower temperatures it is oxidized much faster than niobium boride.

Table 30 (see page 175) gives data on the chemical stability of tantalum boride TaB_2 against the action of different acids and their mixtures /360/.

Tantalum-Oxygen /87/. As early as 1905 Pirani /464/ discovered that metallic tantalum intensely absorbs oxygen. Then Bolton /465/ obtained tantalum hydride by utilising a tantalum plate as the cathode during the electrolysis of sulfuric acid.

At a pressure of 1 at. and room temperature tantalum dissolves up to 0.42 wt. % of H, which corresponds to the ratio of H/Ta = 0.8. This solubility drops sharply with increasing temperature - at 1,000° and under a pressure of 1 at. the ratio of H/Ta = 0.03. The solubility of hydrogen in tantalum decreases also with decreasing pressure /466, 467/. Roasting of tantalum saturated in hydrogen in a vacuum at 1,000° leads to the complete elimination of hydrogen. 192

Hagg /468/ made an x-ray study of the system tantalum-hydrogen. He discovered that tantalum dissolves at 600° 12 at % H, and besides that, forms two hydrides: Ta_2H (phase) with a hexagonal close packed lattice of metallic atoms (a = 3.094 Å, c = 4.923 Å, c/a = 1.591) and TaH -phase /46-47 at % H/ with a triaxial face-centered rhombic lattice of metallic atoms having lattice spacings of: a = 4.811 Å, b = 4.78 Å, and c = 3.434 Å, a:b:c 1.40:1.392:1. This lattice can be examined as a slightly deformed body-centered lattice with lattice spacings a' = $a/\sqrt{2}$ = 3.41 Å, b' = $b/\sqrt{2}$ = 3.38 Å and c' = c = 3.434 Å.

Pitsch and Zehl /469/ assumed that tantalum has a body-centered cubic lattice structure with lattice spacing of 3.42 Å. apparently they did not notice the rhombic distortion of this lattice that was observed by Hagg. The results of Pitsch and Zahl practically coincide with the results of Borisova /470/, who also found that tantalum hydride possesses a body-centered cubic lattice with a lattice spacing of 3.40 Å. Borisova was unable to obtain hexagonal hydride. However, even from the data /450/ the Ta_2H hydride does not have a hexagonal, but a cubic lattice, and is homogeneous for a wide range of hydrogen content. In this work tantalum hydride was obtained by heating tantalum powder (99.9% pure) with a strictly predetermined quantity of hydrogen at 800°.

The work of Brauer and Herman /147/ on the investigations of the same system, and also of the system Ta-D, conducted on specimens of alloys which were obtained by hydrogenation with deuterium of tantalum sheet (which initially had all gases removed in a vacuum at a temperature of 1,000°), agree with the data of Hagg and Borisova, if we evaluate the data from the point of view of obtaining rhombic hydride.

This work /147/ gave the discovery of the α-phase solid solution of hydrogen in tantalum with the upper boundary for $RaH_{0.2}$ and an increase in the lattice spacing in this region from a = 3.296 to 3.33 kX. From $TaH_{0.2}$ to $TaH_{0.3}$ is the two-phase region (α + β), from $TaH_{0.3}$ to $TaH_{0.8}$ is the β phase region with a rhombic face-centered lattice, having lattice spacings at the upper boundary of a 4.718, b 4.768, c 3.451 kX, i.e., closely agreeing with the data of Hagg. The angle of the rhombic base is 89.[illegible], and analogous phases are formed in the system

[redacted]

tantalum-deuterium.

Gulbransen and Andrews /365/ established that the reaction of the formation of hydride starts at 340° and that the rate of absorption of hydrogen rapidly increases up to 460°. Above this temperature there is a separation of hydrogen, apparently connected with the decomposition of hydride, which is stable only at low temperatures. Above 539° there is again absorption of hydrogen with the formation of new hydride (up to 643°).

Hydrides of tantalum Ta_2H and TaH are usually obtained by the treatment of tantalum powder with a strictly predetermined amount of hydrogen at 800 to 900°. Tantalum hydride may be also obtained by reducing Ta_2O_5 with calcium hydride (see page 193).

It is noted that tantalum is a poor filter of hydrogen even at a pressure of atm /471/.

Tantalum-tungsten. According to the date in /15, 120, 367, 456/, tantalum forms with tungsten a continous series of solid solutions.

The variation of the lattice spacing of the alloys is shown in Fig. 67.

A number of mechanical and electrical properties of the alloy 92.5% Ta with 7.5% W have been studied in the work of Langmuir and Malter /368/.

The alloy of such a composition and with a density of 16.9 g/cm^3 and temperature of fusion 3,400 ± 50°K is prepared by Fansteel by sintering in vacuum of compressed powder compacts.

Comparative tests on sags of wire specimens made of Ta and W of the above specified alloy 0.381 mm in diameter and about 38 mm in length at a temperature of 2,400–2,500°K, showed that the wire made of tantalum sags under its own weight twice as much as the wire made ~~of~~ out of the alloy. Thermo-emission properties of the alloy have a complex dependence on the temperature. If the filament is heated to temperature not above 2,200° K for a period of one hour, then at lower temperatures the electronic emission of the alloy is slightly lower than that of tantalum. In time it increases at the rate, which is dependent on the temperature; thus, for a filament is heated up to 1,800°K the emission increases by 1.5 to 5% (in comparison with tantalum) after 1,200 hours. At 2,000° K the emission increases by 50% in comparison to the emission of tantalum after 600 hours. It should be noted that tantalum diffuses from the alloy to the surface of the wire when heated up to high temperatures. The work recomends that this alloy be used for grids of generator lamps; for a corresponding thermal treatment of the alloy it ipossible to obtain thermo-emission , very close to the emission of of tantalum, however with higher mechanical properties of the grid than in tantalum.

Certain properties of Ta-W alloys are shown in Fig. 86 /472/, from which it follows that the addition of 10% W to tantalum greatly strengthens the alloy and hampers its treatment at room temperature (even at 500°).

* Footnote-See page 31 for properties of TaN. See page 47 for the application of tantalum hydride in soldering of silica. 195

Deforming the alloy also greatly enhances its strength, especially when the degree of deformation is between 20 to 30%. Additions of tantalum to tungsten also greatly increase its electrical resistance , for instance, addition of 3.7% Ta increases the electrical resistance of tungsten by 30 to 40%.

Fig. 86. Mechanical and electrical properties of tantalum — molybdenum tungsten: /472/

1) is the electrical resistance; 2) is the tensile strength; 3) is the strain: 4) is the hardness.

(1) Hardness, kg/mm^2; (11) Electrical resistance, ohm . cm .10^6; (111) Yield point during tension, kg/mm^2; (1V) strain in 25mm, %; (V) Alloying element in at %.

Konstantinov and Mosharikov studied certain properties of alloys containing up ~~xxx~~ to 10 at % W and prepared by vacuum sintering of moldings, compressed from powder mixtures of tungsten (reduced by hydrogen from WO_3) and tantalum, which was obtained by sodium thermic reduction of K_2TaF_7.

The formation of the solid solution of tungsten in tantalum starts at a ~~xxx~~ temperature of 1,250° and ends at 1,500°, after which sintering takes place of the already formed solid solution with the resulting dense homogeneous alloys at 2,500-2,700°.

The shrinkage of sintered moldings at temperatures between 2,600 to 2,670° decreases with increasing content of tungsten (Fig. 87). The hardness (Fig. 88), electrical resistance, and the strength of the alloys, increase with increasing content of tungsten, while the relative strain (Fig. 89) decreases, which fact is in agreement with the data of Myers (see Fig. 86). The weldability of tantalum-tungsten alloys does not differ in any respect from the weldability of tantalum.

Fig. 87. Shrinkage of moldings made of Ta-W alloys during sintering.

(1) cross section shrinkage during sintering. %

(11) Timeof holding, hours

Fig. 88. The effect of additions of tungsten on the hardnes (Vickers) and microhardness of annealed alloys of Ta-W:
1) is the microhardness; 2) is the hardness according to Vickers.

(1) Hardness, kg/mm^2; (11) Content in At %.

Fig. 89. The effect of tungsten additions on electrical resistivity (1), yield point during tension (2) and relative strain (3) of unannealed wire 0.1mm in diameter made of Ta-W alloys.

(1) Strain,%; (11) Electrical resistivity, microhm.cm (111) Yield point strength,kg/mm^2;

(1V) Content of W in at %.

In defference to the data obtained by Mayers, it was established that the alloy Ta +7.5% W can be very well cold rolled and cold drawn. Corrosion tests performed on plates of alloys 40 × 20 × 0.1 mm, gave the results shown in table 36.

Table 36.

Corrosion resistance of alloys Ta-W
(duration of test 128 hours)

(1) Alloy composition; (11) fuming 98% HNO_3; (111) Loss in weight in g/m². hour; (1V) 55% HNO_3 at 200°; (V) 33% HCl at 200°; X(V1) 92% H_2SO_4 at 200°.

(V11) alloy ; (V111) Dissolves; (1X) plus sign denotes increase in weight

From this data it follows that the corrosion resistance of alloys Ta-W in 98% HNO_3 does not differ in any respect from the corrosion resistance of pure tantalum, while in HCl, H_2SO_4 and 55% HNO_3 the resistance somewhat decreases, nevertheless it remains comparable or even higher than the resistance of the anti-corrosion alloy Ta-Nb, whose data are given in the same table for comparison purposes.

Tantalum-germanium. The same as the system niobium-germanium, the system tantalum-germanium gave the discovery /371/ of the compound $TaGe_2$ with the $CrSi_2$ type of structure and lattice spacing of a = 4.948 Å, c = 6.737 Å.

Tantalum-iron. According to Wever /473/ in the system Ta-Fe there is a locked γ field with the maximum content of Ta equal to 4.25%. In work /474/ it is shown that the α-solid solution of tantalum in iron (6-10% Ta) forms a compound FeTa (76.42% Ta), which melts at 1,700°, and a eutectic containing about 50% Ta and having a fusion temperature of 1,400°. The compound FeTa has a hexagonal crystalline lattice structure.

A more detailed investigation of the system was performed by Genders and Harrison /475/ who used electrolytic iron (99.95% Fe) and 99.9% tantalum. The alloys were obtained by vacuum fusion in corundum crucibles by high frequency induction heating. 12

Fig. 90. Diagram of the iron-tantalum system: (I) temperature, °C; (II) Content of tantalum in %.

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Fig. 91. Section of the diagram tantalum-iron in the region of the alloys which are rich in iron.

(I) Temperature, °C; (II) Tantalum content in %. 199

The initial state diagram of the system Fe-Ta is shown in Fig. 90.

According to /475/, the compound Fe_2Ta and not FeTa exists in the system. According to the same data Fig. 91 depicts on a magnified scale the region of alloys which are rich in iron.

Nemilov and Voronov /476/ studying the tantalum-iron system by methods of thermal and microscopic analysis of the hardness and electrical resistance, did not confirm this data of the chemical composition of the compound.

They established that the solubility of tantalum in iron at 1,400° comprised 2.1 (atoms), and that the region of the solid solution contracts on lowering the temperature and at 20° approaches 0.4% at Ta.

On the fusibility curve there is a eutectic point, corresponding to 10 at % Ta at a temperature between 1,408 and 1,410°. The eutectic is formed by the solid solution of tantalum in iron and by the chemical compound FeTa or by the solid solution of iron in FeTa. The existance of the compound Fe_2Ta, discovered in work /475/, Nemilov and Voronov did not confirm.

In the region of the solid solution /0-2.1 at. Ta/ the hardness of the alloys tempered from 850° increases from 67.1 to 107 H_B, while those tempered from 1,100°, from 85 to 178 H_B, and annealed from 54 (pure iron) up to 97.0 H_B. The electrical resistivity, when the tanstalum content is increased up to 1.66 at %, increases from 9193 (pure iron) up to 13.79 mcohm.cm.

The alloy containing 48.8% at % Ta, which corresponds to the compound FeTa, is resistent against all acids, with the exception of hydrofluoric acid.

Tantalum-Oxygen. The first serious study of this system was conducted by Vasilevskiy /477/. He established that the limit of the solubility of oxygen in tantalum at 1,050° is equal to 0.9% wt. % / 9.3 at %/, and that the lattice spacing increases in a linear manner with increasing oxygen content. When the temperature is increased the solubility of oxygen in tantalum increases. The lattice structure of the metal is preserved up to 1.9 wt. O_2. However already at 1.8% O_2 [illegible] new structure [illegible] from 1.9 wt. % /9.8 at %/ O_2; this structure is observed up to 8 wt. % O_2.

This phase corresponds to formula Ta_2O and rhombic lattice structure with lattice spacing of a 5.29 A; b 4.92 A; c 3.05 A. Its x-ray density is 15.8 g/cm^3, whereas the pycnometric density is 15.5 g/cm^3. At 17 at % of O_2 the Ta_2O_5 phase is observed. The existance of the intermediate phases between Ta_2O and Ta_2O_5, according to the author is doubtful, in a particular case the "dioxide" actually represents a mixture of oxides of Ta_2O $3Ta_2O_5$.

The X-ray investigation of the system, conducted by Schönberg /51/, was carried out on specimens made by oxidizing tantalum or tantalum powder in hydrogen at 600-900° for a period of from 1 hour to 2 days, by oxidation of carbides and nitrides of tantalum under the same conditions, by the oxidation of tantalum carbide in ammonium at 1,100° from 1 to 6 hours, by the oxidation of tantalum powder by oxygen from zinc oxide at 700° and, finally, by the reduction of Ta_2O_5 by carbon black at 1,500° for a period of 2 hours.

Six phases were revealed: the α-phase, a solid solution of oxygen in tantalum; the β-phase, Ta_4O; the γ-phase, TaO; the δ-phase, TaO_2; the ε-phase, TaO_x $(2 < x < 2.5)$; and the ζ-phase,* Ta_2O_5.

The solubility limit of oxygen in tantalum is ~ 5 at.%, which corresponds to the increase in the lattice spacing from 3.311 A (pure tantalum) to 3.341 A.

The β-phase has a rhombic lattice with a homogenous region, within whose boundaries the spacings vary from a 7.194 A, b 3.266 A, and c 3.204 A to

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* Referred to TaO_5, see p. 19.

a = 7.238 A, b = 3.273 A, and c = 3.216 A. The oxide Ta_4O is analogous to the oxide $WO_{0.15-0.25}$.

The γ-phase has a lattice of the NaCl type with a spacing varying from 4.422 to 4.439 A. The elementary cell has 12 atoms of Ta and 6 atoms of O_2 with distances Ta-Ta = 3.13 A and O-O = 2.22 A. TaO is analogous to other oxides with a NaCl lattice (TiO, VO, NbO, etc.).

The δ-phase has a hexagonal lattice with a = 4.709 A, c = 3.065 A, and c/a = 0.651; the X-ray density = 10.41, and the pycnometric -9.95 g/cm^3. The distance O-O = 2.624 A, Ta - O = 2.02 A.

A Ta ion in the lattice TaO_2 can be replaced by Ti and V ions with the formation of solid solutions $(Ta, Ti)O_2$ and $(Ta, V)O_2$ on heating above 1,800° in a ThO_2 crucible. The solution of ~~the~~ oxygen in tantalum exerts a great effect on its mechanical properties. This effect was studied most thoroughly in the paper of Gebhardt and Preisendanz /478/, which ~~[illegible]~~ also ~~[illegible]~~ referred to ~~former analogous~~ similar earlier investigations. The results of their measurements are presented in Fig. 92. Figure 93 shows the variations in the magnetic susceptibility of tantalum, linearly diminishing with the solution of oxygen in tantalum (Fig. 94).

Fig. 92. Modulus of elasticity (1); Vickers hardness (2); tensile strength (3), and elongation of alloys of tantalum with oxygen (4).

a) Vickers hardness (2 kg), 30 sec, kg/mm^2

b) Rupture strength , kg/mm^2 elongation, %

c) Modulus of elasticity, kg/mm^2

d) Oxygen content, % (atomic).

Fig. 93. Magnetic susceptibility of alloys of tantalum with oxygen.

a) Specific magnetic susceptibility of Ta, mm^3/g

b) Oxygen content, % (atomic).

Fig. 94. Dependence of oxygen content in tantalum on oxygen temperature and pressure.

a) Oxygen content, mm^3/g Ta

b) Oxygen pressure, mm Hg c) Oxygen content, % (atomic).

A sharp change in hardness at 2.9-3 at.% of Ta, as well as the electrical resistance measured by the same authors in their former works, leads to the conclusion on the boundary of the solubility region of oxygen in tantalum /292 at room temperature is 2.9 at.%, which is closer to the data of Schönberg /5 at.%/ than to the data of Vasilevskiy /17.3 at.%/ at room temperature/.* Increased oxygen content in tantalum, in addition to raising the hardness (from 38 to 630 kg/mm^2) and reducing the mechanical properties (the modulus of elasticity rises from 18,100 to 19,640 kg/mm^2), also causes substantial decrease in the corrosion resistance, as follows, for example, from the graph in Fig. 95, showing the variations in the corrosion resistance to 40% HF at room temperature, depending on oxygen content in tantalum and the duration of corrosion.

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* All these data are presented for normal conditions; the oxygen content increases with rising temperature (Fig. 94).

Fig. 95. Resistance of alloys of tantalum with oxygen to corrosion by 40%-HF (at 20°):

□ ——— □ - 0.2% (atomic) O_2; x ——— x - 0.3;

△ ——— △ - 0.57; ○ ——— ○ - 0.95; ● ——— ● - 7.25%; (atomic) O_2

a) Weight decrease, %; b) Corrosion duration, hours.

K'o Ting-sui [579] investigated in detail the viscosity in solid interstitial solutions of oxygen in tantalum and establishes that the presence of oxygen (analogous to carbon) causes the appearance of an internal friction peak at a temperature of 150-170° (Fig. 96). On increasing the oxygen content in tantalum the internal friction peak shifts to the region of higher temperatures. The internal friction peaks are connected with the disturbing effect of oxygen atoms on the tantalum lattice; the peak shift on rising temperatures is explained by the fact that the oxygen atom can occupy the octahedral as well as tetrahedral interstitial position; moreover, metallic bonds form between the atoms of tantalum and that of oxygen. According to K'o Ting-sui the solubility of oxygen in tantalum at 170° is above 0.04%.

According to Ang /386/ the energy of activation during the diffusion of oxygen into tantalum amounts to 27.3 kcal/mole, ~~[illegible]~~ whereas according to Ref. /480/ to 26.7 kcal/mole; on increasing the oxygen content from 0 to 1.1% the hardness rises from 60 to 260 kg/mm^2.

Andrews/431/ indicates that for the elimination of oxygen from its solid solution in tantalum it is necessary to heat in a vacuum at 2,200-2,300°. /203

Tantalum-cobalt. A part of the phase diagram of the system has been discussed in the paper /388/. The compound Co_5Ta_2 (Co_2Ta, according to later data by Wallbaum /389/), with a melting point of 1,550°, forming a eutectic containing 31% Ta and melting at 1,275°, has been detected in the system.

Fig. 97. Effect of oxygen content in tantalum on the viscosity peak observed in a tantalum specimen containing 0.01% C:

1) starting tantalum specimen; 2) same specimen, annealed for 5 hrs in oxygen at 500°; 3) specimen once more annealed in a vacuum for 5.5 hours at 1,200°.

a) ~~[illegible]~~ Internal friction, $\frac{\Delta}{\pi}$ b) Temperature, °C

Tantalum-silicon. Hönigschmid obtained the mixture $Ta_2O_5 + SiO_2$ by aluminothermic reduction in the presence of sulfur, and, by subsequent treatment of the product with HCl and KOH, obtained the chemical compound $TaSi_2$ (a well crystallized tantalum disilicide /482/). Wallbaum /389/ prepared the same disilicide, which has (according to Wallbaum) a higher melting point than aluminum oxide, by direct synthesis: he sintered a mixture of Ta + Si powders in an aluminum oxide crucible. By analogous means the alloys of the system Ta-Si were prepared by Brewer and associates /483/, who detected, in addition to $TaSi_2$, also phases of the alloys $TaSi_{0.2}$, $TaSi_{0.4}$, and $TaSi_{0.6}$; however, they made no data available on these phases.

Campbell and associates /211/ obtained a layer of tantalum silicide on a tantalum wire by plating from the gas phase: $Ta + SiCl_4 + H_2 \rightarrow TaSi_2 + HCl$ at 1,100-1,200°.

A systematic investigation of the Ta-Si diagram was conducted by Kieffer et al. /395/ on specimens prepared by the hot pressing of mixtures of the powders of pure tantalum and a 99%- (remainder Fe) silicon by the homogenization annealing method at 1,800° for a period of 12 hours. The alloys were subjected to x-ray analysis, their melting points were determined (to 10% Ta by thermal analysis, above 10% -, pyrometric determination method because of the high melting points), the microhardness of the phases was determined, and microscopic investigation and oxidation resistance testing were conducted. The results of the x-ray analysis of these specimens were also reported in the paper of Nowotny, Schachner, Kieffer, and Benesovsky /484/. An orientational diagram of the system tantalum-silicon,

Fig. 97. Diagram of the system tantalum-silicon.

a) Si content, % (wt.) b) Temperature, °C c) Si content, % (atomic)

given in Fig. 97, has been constructed on the basis of these papers. Tantalum at 1,800° dissolves very small quantities of silicon (to 0.25 wt.% or 1.6 at.%). The formation of the solid solution occurs with insignificant growth of the lattice spacing, from 3.30 to 3.31 Å. The compound which has the highest tantalum content, $Ta_{4.5\pm0.5}Si$ (analogous to that of the $TaSi_{0.2}$ phase noted by Brewer) melts at ~2,510°. The lattice of this phase is hexagonal (type DO_{19}) with spacings: $a = 6.693$ Å, $c =$ [illegible] Å, $c/a = 0.806$, and density 12.7 g/cm³. The second chemical compound, Ta_2Si (analogous to the $TaSi_{0.4}$ phase noted by Brewer) has a narrow region of homogeneity ~~and~~ ~~[illegible]~~ melts incongruently [with ... over a wide range]. The type C16 structure (identical structure of the borides Ta_2B, Mo_2B, etc.) has lattice spacings a = 6.14_5 Å, c = 5.02_8 Å, c/a = 0.81_8. The density of Ta_2Si is ~~approximately~~ 13.5 as calculated 1205 from the lattice spacings, and >12.4 g/cm³ as determined by a ~~[illegible]~~ hot-pressed specimen. The distance between the atoms Ta-Si in Ta_2Si is less than between Ta-Ta. The third compound, the phase Ta_5Si_3 (Brewer's $TaSi_{0.6}$), to which the open maximum (~2,500°) corresponds in the Ta-Si diagram, ~~and~~ crystallizes ~~[illegible]~~ in a hexagonal-type $D8_8$ lattice with spacings a = 7.47_9 Å, c = 5.21_5 Å, c/a = 0.697, the ~~[illegible]~~ X-ray density is 13.06 g/cm³, and that determined ~~[illegible]~~ by a hot-pressed specimen is $\overset{13}{11}.6$ g/cm³. Finally, the last phase is hexagonal, $TaSi_2$, with a melting point of 2,200°, lattice spacings: a = 4.77_1 Å, c = 6.55_1 Å, c/a = 1.[illegible], ~~[illegible]~~ X-ray density 9.1_4, and pycnometric density 8.83 g/cm³. The electrical resistivity is very low, ρ [illegible] μohm-cm at 20°.

The hardness of the phases (Vickers test at P = 10 kg) is, respectively: for the $Ta_{4.5}Si$ 1,000-1,200; the Ta_2Si 1,200-1,500; the Ta_5Si_3 1,400-1,500; and the $TaSi_2$ 1,400-1,200 kg/mm².

There are four eutectics in the system: Ta-$Ta_{4.5}Si$ (~2,500°), $Ta_{4.5}Si$-Ta_2Si (~2,440°), Ta_5Si_3-$TaSi_2$ (1,980°), and $TaSi_2$-Si (~1,400°)

Resistance to oxidation increases sharply with increase silicon content to 70-90 at.% (Fig. 98). On oxidizing, the specimens are covered with a fine glass-like film consisting of SiO_2 with tantalum pentoxide dissolved in it, or the eutectic $TaSi_2$-Si protecting the specimens from further oxidation.

All alloys of the system Ta-Si are brittle and can be worked only by abrasion or by the electric-arc method. Their high heat resistance makes it basically possible to use it in a composition of special alloys together with the silicides of other metals.

According to data /390/ $TaSi_2$ does not dissolve for a period of 1 hour in HCl (concentrated and 1 : 1), HNO_3 (concentrated and 1 : 1), and NaOH solution; for a period of 3 hours in H_2SO_4 (concentrated, 1 : 1, and 1 : 10); for 5.5 hours in H_3PO_4, and for 10 hours in $KHSO_4$ + $SeOCl_2$. A large portion during 1 hour decomposes under the effect of HF and HF + H_2SO_4, and in 30 minutes is decomposed by a mixture of HF + HNO_3. It is fully decomposed by molten NaOH and Na_2CO_3, and gaseous fluorine and chlorine. Gaseous bromine and iodine effect $TaSi_2$ moderately.

Tantalum-molybdenum. The formation of a continuous series of solid solutions in this system was already established by Bolton /465/. Later Bückle /25/

produced ~~and~~ alloys of tantalum with molybdenum by sintering compacts pressed from powders and by their X-ray and metallographic analyses confirmed the conclusions of Bolton (see Fig. 67).

A more detailed investigation into the system was conducted in the paper /296 /485/ with the use of powders of 99.95% Mo and 99.98% Ta. The same paper gives a review of preceding preparatory studies of this system /472 and 486/. The alloys were made by the powder metallurgical method, the mixing of powders, the pressing of the mixtures, and the sintering of the compacts for a period of 24 hours at 1,500° in a vacuum 10^{-4} mm Hg for alloys low ~~high~~ in Ta content and at 1,850° for alloys high in Ta content. Some of the alloys were also made by

Fig. 98. Oxidation resistance of tantalum-silicon alloys in air.

a) Weight change, g/cm² b) Content, at. % ~~% (atomic)~~

Fig. 99. Effect of tantalum ~~as~~ admixtures to molybdenum on the hardness of alloys annealed at different temperatures.

a) H_V, kg/mm², load 30 kg b) Annealing temperature, °C melting in an argon atmosphere in an arc furnace compacts which had been prepressed and sintered in a vacuum (10^{-5} mm Hg) at 1,500° and held for 2 hours. X-ray and metallographic analysis confirmed the presence in the system of a continuous series of solid solutions with spacing linearly varying from 3.1408 A (molybdenum) to 2.2976 A (tantalum). The density of the alloys varies practically additively from 10.17 g/cm^3 (Mo) to 16.61 g/cm^3 (Ta).

The melting points ~~composing~~ established pyrometrically are:

melting point °C.... (figures)

Tantalum content, at. % ~~%(atomic)~~..... (figures)

Admixtures of tantalum to molybdenum in quantities of from 0.05 to 5% somewhat increase the recrystallization temperature /487/.

Figure 97 shows the dependence of the properties of alloys Ta-Mo on the composition, according to Mayers. An increase of molybdenum content to 10% /281/ considerably raises the hardness, the tensile ~~compress~~/strength, and electrical resistance of alloys ~~which~~ simultaneously diminishing elongation.

The hardness of alloys at elevated temperatures is shown, according to /402/, in Fig. 69. Alloys containing more than 10% (atomic) Mo have low workability when cold.

Alloys of the system Ta-Mo are corrosion resistant which is fortunately combined with their improved mechanical strength. The elongation of the alloys diminishes depending on the degree of strain, especially to 20%.

Cast alloys containing more than 85% Mo and 0.3-9% Ta, as well as admixtures of 0.003-0.4% Al to 0.02% C and less than 0.02% O are being patented /488/. Such alloys can be worked by pressure on heating and to a considerable degree retain their cold hardening after one hour at 1,200°.

A detailed investigation into the properties of the alloys of tantalum with molybdenum has been conducted in the study of Schumb et al. /486/. The density, hardness, thermoelectromotive force, electrical resistance, linear expansion, and the corrosion resistance of a number of alloys in the system at every 10% interval of the content of each component. The alloys were made by arc remelting of sintered specimens in an argon atmosphere. Alloys containing more than 50 at% Ta are not attacked by concentrated HCl, HNO_3, and H_2SO_4; alloys high in molybdenum content are corroded by these acids, which, according to the decreasing effect can be arranged in the series: $H_2SO_4 \rightarrow HCl \rightarrow HNO_3$. Nitric acid cause the formation of a passivating film on the alloys, protecting them from further oxidation.

Tantalum-nickel. According to reports /487 and 489/ considerable quantities up (to 30%) of tantalum can dissolve in solid nickel, forming alloys with a very high level of machinability; the Curie point drops sharply on formation of the solutions (Fig. 100). Taking into account these results as well as his own ~~[illegible]~~ ~~[illegible]~~ thermal and microscopic analysis of the alloys Ta-Ni, Terkelsen /490/ constructed a phase diagram (Fig. 100) according to which the solubility region is assumed to be more than 30%; the chemical compound Ni_3Ta with a melting point of 1,545° has been detected in the system, as well as, evidently, the compound NiTa which forms ~~[illegible]~~ peritectically. He assumed, on the basis of detecting transformation at 1,350°, that between Ni_3Ta and NiTa there is one more phase with a tantalum content higher that Ni_3Ta (50.75% Ta). An X-ray analysis of the phase Ni_3Ta was conducted by Wallbaum /491/ and revealed its transformation at 1,350°. A further investigation into the Ta-Ni diagram /492/ produced results fundamentally ~~[illegible]~~ in agreement with the data by Terkelsen. On the dissolving of tantalum in nickel the spacing of the face-centered cubic lattice of nickel increases to 3.594 A on the boundary /202 of saturation corresponding to 30% Ta. The Curie point decreases with the dissolving of Ta in Ni, and the alloy 22% Ta is paramagnetic at room temperature. There is verification of the presence of the compound Ta_3Ni and an indication of the existence of a second compound of the composition $NiTa_3$ (but not NiTa as assumed by Terkelsen), melting incongruently at 1,525°. The melting point of Ni_3Ta was established at 1,540°.

Fig. 100. Tentative diagram of the system tantalum-nickel and variations of the Curie point (according to Terkelsen).

a) Ta content, % (atomic) b) Magnetic transformation

c) Ni wt. % d) Temperature, °C e) Ta content, at. % ~~(wt.)~~

Ni_3Ta forms a eutectic with the solid solution of tantalum in nickel at 38% Ta and 1,365°, and the compound Ni_2Ta_3 at 70% Ta and 1,350°. This study did not confirm the transformation Ni_2Ta_3 (NiTa)→Ni_3Ta, assumed by Terkelsen, as well as the polymorphous transformation Ni_3Ta which was claimed by Wallbaum.

Utilizing the low solubility of the compound Ni_3Ta in hydrochloric acid, in contrast to the high solubility of nickel and its solid solutions with tantalum, Kornilov and Pylaeva /493/ precipitated the phase Ni_3Ta from the alloy with 35.15% Ta, an analogous precipitation was achieved by anodic dissolution in an alcohol-hydrochloric acid electrolyte (0.75% HCl) containing 20 g citric acid and 5 g ammonium chloride with current density 0.01 amp/cm^2. An X-ray study of the precipitated phase showed that it has a hexagonal lattice. The final version of the phase diagram of the system Ta-Ni, according to Kornilov and Pylayeva /494/, is shown in Fig. 101.

The alloy of nickel with 30% Ta (according to an assumption /155/ hardened /209 from 1,200-1,300° and retaining the structure of a solid solution) possesses, according to Terkelsen, high anticorrosion properties.

<u>Tantalum-tin.</u> In the work /407/, Ta-Sn alloys were prepared by melting tin on a layer of tantalum powder in a soldered up quartz tube at 1,200° and showed the formation of the compound Ta_3Sn by a peritectic reaction between 1,200 and 1,550°. Ta_3Sn has a β-W structure and can be converted to a superconductive state at 6°K.

Fig. 101. Diagram of the system tantalum-nickel (according to Kornilov and Pylayeva). a) Temperature, °C b) Content, wt.%

According to X-ray structural analysis, the Ta$_3$Sn lattice spacing is a = 5.276 ± 0.001 A, X-ray density 8.81 g/cm^3.

Tantalum-palladium. No intermetallic phase was detected in this system at a temperature of 1,000° /409/.

Tantalum-platinum. A single natural intermetallic δ-phase (TaPt) was detected in the system with spacings: a = 9.95 A, c = 5.16 A, c/a = 0.52 /409/. According to data /495/, the alloys of tantalum with platinum containing to 20% Ta are resistant to attack by acids, molten potassium bisulfate, aqua regia, and solutions of arsenic and phosphorus.

Tantalum-rhenium. Tantalum forms the same intermetallic phases with rhenium as niobium with rhenium /409/(see p 173): δ-phase (TaRe) with spacings: a = 9.72 A; c = 5.07 A, c/a = 0.52 and the phase of the α-Mn type with the spacing a = 9.711 A whose region of homogeneity is 37-25 at. % ~~(atomic)~~ Ta. At 1,000°, 48-36% Re dissolves in tantalum (see also p 247).

Tantalum-rhodium. The phase [illegible]$_3$, with the β-W structure, δ-phase with a = 9.754 A, c = 5.058 A, and c/a = 0.518 forms in the system, and the phase with the CE structure when there is 63% (atomic) Ta in the alloy /409/.

Tantalum-ruthenium. According to the data /409/, a tetragonal phase with the spacings: a = 3.02 A, c = 3.37 A, c/a = 1.11, was detected in the system with a ~50% (atomic) Ta content in the alloys. At 27-36% (atomic) Ta in the alloy, one more, as yet unidentified, phase was detected in the alloy. Up to 27% (atomic) Ta dissolves in ruthenium.

Tantalum-titanium. This system has been studied in detail in the paper by Maukuth et al /497/ by the methods of metallographic and X-ray analysis, measurement of electrical resistance, and pyrometric determination of the melting point.*

Alloys containing to 27.2% Ta were prepared by melting iodide titanium rods and scraps of sheet tantalum (with repeated remelting), and the alloys containing 40-95% Ta were pressed of a mixtures of Ta and Ti powders and sintered in a vacuum with subsequent remelting in an arc furnace in an argon atmosphere at a pressure of 100 mm Hg.

The diagram of the system Ta-Ti constructed according to the results of

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* – A review and a discussion of former works on the system Ta-Ti are given in the monograph of V. A. Yeremenko /[illegible]/.

investigations is shown in Fig. 102, and Fig. 103 shows a large scale portion of the diagram in a region high in titanium content. The solubility of tantalum in α-titanium increases with dropping temperature and at 550° is about 12.5%; β-titanium and tantalum form a continuous series of solid solutions. On increasing tantalum content in α-titanium, the temperature range of crystallization gradually rises with a simultaneous decrease in the $\alpha \rightleftarrows \beta$-transformation point to 600° at 70% Ta. The lattice spacings of α-titanium in the limits of the region of homogeneity of the solid solution α-Ti-Ta varies insignificantly: from a = 2.9503 Å; c = 4.6834 Å; c/a = 1.587 for Ti to a = 2.9502 Å; c = 4.6873 Å; c/a = 1.589 when the content of Ta is 5.3 wt.%.

A later study of the structure of the Ta-Ti diagram conducted by Summers-Smith /499/ verified the results of preceedings studies, except for the large curvature of the lines limiting the α+β-field (the broken line in Fig. 103). /211

Alloys containing to 9.1% Ta are readily machined (in air) by rolling at 750° into a strip 1.5 mm thick; alloys containing 17.9-27.2% Ta at 850°; 60% Ta at 980°; and the alloy with 80% Ta rolled at this temperature cracks.

Fig. 104. Mechanical properties of the alloys tantalum-titanium.

a) ultimate strength σ_b, kg/mm^2 b) Ta content, % c) elongation δ,%

The paper /500/ investigated the effect of rate of cooling and the composition of alloys on the temperature of the martensitic transformation by means of plotting cooling curves. It turned out that the temperature of the martensitic transformation was independent of the cooling rates, but decreases with increase tantalum content in the alloy.

The mechanical properties of the alloys containing up to 20% Ta and prepared by the powder metallurgical method with subsequent rolling at 900° and quenching in air were described by Cross /501/ and results are shown in Fig. 104, from which it follows that the ultimate strength as well as the elongation of the alloys increase but insignificantly on increasing the tantalum content. As a result of this, tantalum is ~~practically not~~ seldom used for alloying titanium /502/.

Tantalum-thorium. According to data /428/ an addition of tantalum to thorium decreases the temperatures of its transformation from a cubic face-centered into a cubic body? base-centered modification from 1,450 to 1,575° which is due to the solubility of tantalum, very insignificant it is true, in a base-centered thorium lattice, as well as the transfer into thorium of impurities usually found in tantalum (carbide Ta_2C).

Tantalum-carbon /507/. Tantalum carbide with 6.2% (TaC) was obtained for the first time as early as 1876 by Joli.[9] At the beginning of the 20th century interest was shown to titanium carbide with respect to tests in using it for filaments of electric bulbs. However, a systematic study of this carbide began nearly 50 years after the Joli experiments.

Burgers and Basart established that tantalum forms two carbides: TaC and Ta_2C (α and β).

The α-modification of Ta_2C has a hexagonal compact lattice of metallic atoms with the spacings: a = 3.091 ± 0.001 A, c = 4.793 ± 0.007 A, c/a = 1.59. /212

It did not prove possible to establish the crystal structure of β-Ta_2C; evidently it is very similar to the structure of the α-modification, since the radiograph of β-Ta_2C differs from that of α-Ta_2C only in that it has none of some of the lines of the latter and part of the remaining lines has been weakened (various lines to different degrees). The allotropy Ta_2C, evidently, is analogous to the allotropy W_2C.

The monocarbide TaC with a lattice of the NaCl type is capable of dissolving tantalum up to the composition described by the empirical formula $Ta_{1.2}C$. Here, the lattice spacing of the monocarbide decreases from 4.445 to 4.39 A.

Menne /447/ manufactured a tantalum monocarbide precisely agreeing with the formula TaC by means of crystallization from a molten aluminum heated to 2,000°.

A similar investigation of the conditions of obtaining tantalum carbide by heating the mixture of tantalum powder (96.34% Ta) and carbon soot in a graphite-tube furnace in a hydrogen stream, was conducted by Vol'kov and Shokhlov /430/. The best procedure for producing carbide proved to be heating for a period of 2.5 hours at 1,600°.

The most thorough investigation into the phase diagram of the alloys in the system Ta-C was conducted by Ellinger /145/, and the investigation into the lattice spacings, heat of formation, and other physical properties, by Smirnova and Ormont /504 and 505/. Ellinger studied the system by the methods of thermal, metallographic, and radiographic analyses of alloys prepared by the sintering of compacted mixtures of tantalum with carbon or tantalum carbides with tantalum in a high-frequency vacuum furnace. The phase diagram constructed by him is given in Fig. 103. Carbon, according to these data, is practically insoluble in tantalum. The phase Ta_2C, giving a eutectic with tantalum, forms at 3,400° as a result of the peritectic reaction between TaC and the liquid phase with 2.5% C content. The second eutectic forms between the phase TaC, which melts congruently, and carbon when there is ~10% of it. At 3,400° TaC is capable of dissolving up to 1.2% Ta.

K'e Ting-sui /479/, by the torsional oscillation method, detected internal friction peaks when a carbon atoms intrude into the tantalum lattice at temperatures of 150 to 350°C (Fig. 106). The presence of these peaks is explained by the excitating effect of a carbon atoms on the tantalum lattice. With rising carbon content the internal friction rises at this temperature; the solubility of carbon in tantalum can be calculated from here; at a peak temperature of 150° it is equal to ~0.02%.

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Fig. 105. Diagram of tantalum-carbon (according to Ellinger).

a) Temperature, °C b) C content, % (wt.)

Fig. 106. Internal friction variations as a function of temperature in tantalum specimens containing 0.01% C and annealed in a vacuum at different temperatures: o - starting tantalum specimen; x - specimen annealed for 5 hours in a vacuum at 600°; Δ - idem for 13 hours at 900°; ◻ - idem for 5.5 hours at 1,200°.

a) Internal friction $\frac{1}{Q}$ b) Temperature, °C

Smirnova and Ormont, who investigated the structure and boundaries of homogeneity of tantalum carbides /504/, came to the following conclusions. The boundaries of homogeneity of the phase Ta_2C correspond to the formulas $TaC_{0.38 \pm 0.02}$ to $TaC_{0.50 \pm 0.02}$, i.e., as pointed out by Smirnova and Ormont, a 3.1% C content, the data by Ellinger notwithstanding, corresponds to the lower and not to the upper limit of homogeneity of the β-phase. The lattice spacings of the latter vary from $a = 3.101_3$ Å and $c = 4.936$ Å at the lower boundary to $a = 3.104_4$ Å and $c = 4.943$ Å at the upper boundary of the phase. 121A

The carbide TaC (γ-phase) is homogeneous within the limits of from TaC 0.58 ± 0.02 to $TaC_{1.00}$. In practice, Smirnova and Ormont reached the composition $TaC_{0.91}$ in their experiments; the lattice spacing in this case varies from $a = 4.420_6$ to $a = 4.456_4$ Å. The heat, free energy, and the entropy of the formation of the γ-phase vary in the following manner in the limits of its homogeneity /505/:

Composition	ΔH^0 kal/mole	S kal/mole	ΔF^0 kal/mole
$TaC_{0.}$[illegible]	-35.500	+9.72	-35.300
$TaC_{1.00}$	-36.000	+10.14	-35.700

With increased carbon content in the γ-phase, the reaction heat of the formation of TaC_x increases; here with the addition of every succeeding 0.1% C the heat of reaction increases referred to 0.1 g-atom of carbon (i.e., the relationship $\Delta H = f(C)$ is nonlinear).

The paper /506/ investigated the microhardness and the electrical resistivity of the tantalum carbides, Ta_2C and TaC, in the regions of their homogeneity, and it was shown that the electrical resistance decreases with increased content of the bound carbon comprising for the limit content of carbon in Ta_2C and TaC, respectively, 80 and 30 μ ohm·cm, while the microhardness rises, comprising for Ta_2C 947, and for TaC 1,490 kg/mm^2.*

Tantalum-uranium. This system has been investigated in the paper /507/. The metal powders were mixed and pressed into compacts, which were remelted in an arc furnace with a copper water-cooled anode and a tantalum cathode at 3,000-4,000°.

Cast and heat-treated alloys were investigated by the methods of x-ray and metallographic analyses. The phase diagram of the system is shown in Fig. 167.

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* - For properties of the tantalum carbide TaC see also page 90.

The solubility of uranium in tantalum and tantalum in uranium is very limited (less than 2% at 1,175°). The line of solidus in the system indicates the peritectic transformation at 1,125°; the nature of the peritectic reaction is as yet unclear.

Tantalum-phosphorus. The first indications of the interaction of tantalum with phosphorus at 500° are given in the paper /433/. The investigations by /215
Zumbusch and Biltz /434 and 435/ showed the isomorphous state of the phosphides of tantalum and niobium.

Fig. 107. Diagram of the system tantalum-uranium.

a) Temperature, °C b) Ta content, % (atomic).

According to /436/ two phases have been detected in the system: α-TaP, isomorphous α-NbP (see p 184) of thecomposition $TaP_{0.95}$ (it did not prove possible to separate this phase in the pure state); and θ-TaP, a isomorpous θ-NbP, homogeneous at Ta : P = 1 : 1. The phase α-TaP has a tetragonal face-centered lattice (z = 4) with the spacings a = 3.320 A; c = 5.69 A; c/a = 1.71, and X-ray density 11.04 g/cm³. The phase θ-TaP is arranged by the space group $I_{4}2$ (z = 5); the lattice spacings: a = 3.330 A, c = 11.39 A, c/2a = 1.71;

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X-ray density 11.15, and that determined pycnometrically, 10.03 g/cm³.

Tantalum-chromium. The system has been studied in the paper /492/ by optical pyrometry methods of determining the temperature of the beginning of melting and crystallization. Alloys containing to 50% Ta were remelted in aluminum oxide boats and that with a large tantalum content in thorium oxide boats. X-ray analysis of the alloys was also conducted; the results are presented by the orientational diagram, shown in Fig. 108. 176

The solubility of tantalum in chromium (which is difficult to measure by X-ray means due to the extremely insignificant expansion of the chromium lattice on dissolving) amounts, according to metallographic analysis, ~[illegible]% at 1,[illegible]00° and ~11-12% at the eutectic temperature (~1,700°). The eutectic contains [illegible] Ta. At 62% Ta the region of homogeneity of the compound Cr_3Ta_2 begins; its crystal according to microscopic study reveal a correct hexagonal form, which is verified by X-ray analysis giving the hexagonal compact structure. The compound Cr_3Ta_2 is formed ~~gamma~~ peritectically at 1,980°.

Fig. 108. Diagram of tantalum-chromium.

a) Temperature, °C b) Content, % (wt.)

A later investigation /439/ showed the presence of one more phase in the system: Cr_2Ta, which exists in low- and high-temperature modifications. The low-temperature modification Cr_2Ta has a face-centered cubic lattice with the spacing a = 6.947 kX-unit and interatomic distances in the cell: Ta-C = 2.80 kX-unit, Ta-Ta = 3.008 kX-unit, Cr-Cr = 2.456 kX-unit. In the temperature range 1,575-1,590° there occurs the transformation to the high-temperature modification with a hexagonal lattice of the $MgZn_2$ type with spacings: a = 4.915 A, c = 8.046 kX-unit, c/a = 1.637. According to the authors, the phase Ta_3Cr_2 is actually identical to the phase Ta_2Cr.

Reference /438/ investigated the oxidation resistance of the alloys at /217/ 1,250° and showed (Fig. 80) that the highest oxidation resistance is given by alloys in the region of the chemical compound to which Kubashevskiy attributes the formula Cr_3Ta_2.

According to Kroll /508/, a sintered alloy of chromium with 5% Ta has a hardness of 120 kg/mm² and is difficult to machine.

Tantalum-Zirconium. Anderson /445/ prepared alloys Zr with 1.2-50.5% Ta by melting a porous zirconium with shavings of tantalum sheet in a graphite crucible. It was noted that the addition of tantalum causes an increase in the carbon content from 0.14 to 0.44%. Alloys with 1.2 and 5.5% Ta proved to be single-phased, whereas with 9.7 and 14.1% Ta two-phased. At 20.5% Ta this phase occupies the entire area of the cross section (the compound "$Zr_{7.5}$ Ta"), whereas the alloys with 30.5% Ta consists of the eutectic and up to 10% of the phase of dendritic structure. This paper also determined the yield point of the alloys:

Ta content, at.% ...	0.6	0.8	5.2	7.7
Yield point, kg/mm² (at 20°)	37.5	60	67.4	61.7
at 645°..........	7	12.6	14.0	12.0

Evidently, additions of Ta stabilize the β-phase.

Litton /446/ prepared alloys containing up 27.5% Ta by vacuum melting in graphite crucibles and revealed a single-phase structure in the alloy with 14.1% content. According to Keeler /509/, zirconium with 2.7% (atomic) Ta has the α→β transformation range between 807 and 8[illegible]2° which indicates a drop in the temperature range of transformation of zirconium with tantalum being added to it.

Schönberg /510/ describes the method of preparing alloys by heating the mixtures of hydrides of zirconium and tantalum at a temperatures above 1,700° in a ZrO_2 crucible in a high-vacuum induction furnace. He obtained the alloys $ZrTa_{0.33}$, $ZrTa_{0.67}$, ZrTa, $Zr_{0.67}Ta$, $Zr_{0.33}Ta$, whose properties, unfortunately, he does not give.

A complete investigation of the phase diagram of the system Ta-Zr has been recently given by [illegible], [illegible], and Levstyukhin /511/. The alloys were made by arc fusion in a highly purified argon of iodided zirconium (99.6% Zr) and a tantalum strip containing 99% Ta, and 0.5% Nb as the main admixture. The cast alloys were subjected to homogenizing annealing at 1,600°, and for the purpose of investigating the phase equilibriums, to isothermal annealing at temperatures of 600-1,500° with subsequent hardening. The points of solidus were established by visual observation of the beginning of the fusion of the specimens, and the liquidus points were established by observing the achievement of a drop-like state by the alloys. Hardness tests, electrical resistance tests, X-ray phase analysis and metallographic study of the alloys were among the main methods used. The phase diagram constructed by the investigation results is shown in Fig. 109. /218

β-zirconium with tantalum form a diagram of the eutectic type; the eutectic temperature amounts to 1,[illegible] ± 15°; [illegible]% (atomic) Ta corresponds exactly to the eutectic. The maximum solubility of tantalum in β-Zr at a eutectic temperature is 16 at.% β-Zr in tantalum, 17%. At 790° and 7% Ta there occurs a eutectoidal transformation of the β-solid solution. The solubility of tantalum in α-Zr at this temperature is below 0.22 at.%.

Reference /512/ investigated the variations in the plasticity of tantalum-zirconium alloys under the effect of hydrochloric acid. At a 60° the hydrochloric acid has almost no corrosive effect on alloys of zirconium with 5-15 wt.% Ta, at 100° the strongest corrosion is observed in the case of the alloy with 5% Ta; with increasing tantalum content and corrosion resistance of the alloys rises. Here, the highest degree of brittleness is exhibited by alloys containing 5 and 15% Ta.

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Chapter VIII

Three-Component Alloys with Tantalum- and Niobium Participation

Niobium - Nitrogen - Oxygen (Bibl. 336). The nitration of niobium pentoxide or ammonium niobate by ammonia results in the formation of a phase with an approximate composition of $NbN_{0.9}O_{0.1}$, having the lattice of NaCl type and the a-period varying within the range from 4.373 to 4.390 Å. The oxidization of NbN in the presence of hydrogen at 700° yields a phase with the deformed tetragonal structure and the homogeneity range from $NbN_{0.6}O_{0.2}$ to $NbN_{0.6}O_{0.3}$, which has its correspondence in the variation of lattice periods from a = 4.370 Å, c = 4.295 Å and c/a = 0.983 to a = 4.386 Å, c = 4.325 Å and c/a = 0.986. No other ternary phases have been detected in this system.

Niobium - Vanadium - Nitrogen (Bibl. 513). The alloys with NbN-VN profile were obtained by sintering of nitride mixtures in the induction furnace for 2 hrs at 2125°. It was noted that the diffusion is impeded in this system; all the alloys of this profile turn out to be solid solutions.

Niobium - Tantalum - Tungsten; Tantalum - Molybdenum - Tungsten; Niobium - - Tantalum - Molybdenum; Niobium - Molybdenum - Tungsten (Bibl. 15). The alloys of these systems were prepared by sintering of billets molded from powders. The X-ray diffraction analysis of these billets showed the presence of continuous series of solid solutions; the lines of similar lattice constants are marked in concentration triangles in Fig. 110, while the dots show actual results of measurements.

Fig. 110. Isoparametric lines in the following systems: W - Ta - Nb, W - Ta - Mo, Mo - Ta - Nb and W - Nb - Mo.

Legend in Fig. 110: 1a - content of Ta, % (atomic); 1b - content of Nb, % (atomic); 2a -- content of Ta, % (atomic); 2b - content of Mo, % (atomic); 3a - content of Ta, % (atomic); 3b - content of Nb, % (atomic); 4a - content of Ta, % (atomic); 4b - content of Mo, % (atomic).

Niobium (Tantalum) - Iron - Hydrogen. It was established in Karnaukhov's work (Bibl. 514) that tantalum and niobium enhance the dissolvability of hydrogen in iron, due to the formation of hydrides in the melt; Karnaukhov attributes to these hydrides the content of one or more hydrogen atoms in the molecule. On the other hand, the rate of hydrogen dissolution in a steel containing niobium or tantalum is lower than in the pure iron, inasmuch as the mobility of hydrogen is also lower when a portion of hydrogen atoms forms chemical compounds with tantalum and niobium.

Niobium - Titanium - Nitrogen (Bibl. 513). The TiN - NbN profile was studied by means of the X-ray diffraction analysis on samples prepared by sintering /220 the mixtures of TiN and NbN powders for 4 hours at 2550° (with up to 50% (mol.) of NbN), or at 2575° (with a higher content of NbN). TiN and NbN produce a continuous series of solid solutions (Fig. 111).

Fig. 111. Lattice periods of alloys in the following systems: NbN - ZrN, TiN - ZrN, TiN - NbN, TiN - VN and NbN - VN.

Legend in Fig. 111: 1 - lattice period, Å; 2 - content, % (mol.)

Niobium - Tungsten - Carbon. According to the data provided in the paper (Bibl. 515), obtained by means of the X-ray diffraction analysis on samples of alloys with NbC - WC profile, which were prepared by sintering the mixtures of parent carbides in the graphite tube furnace in hydrogen stream at 2600° (with the subsequent annealing at temperatures from 2500 to 1400°), the niobium carbide is dissolvable, to a considerable extent, in the surplus of tungsten; in addition, the dissolvability increases rather abruptly with the temperature (Fig. 112), attaining 75% (mol.) at 2500°. The dissolvability of tungsten carbide in niobium carbide is insignificant, but increases also with the temperature /221 increase. Kovalskiy and Petrova (Bibl. 516) studied the microhardness of alloys with the binary NbC - WC profile, and discovered a rapid decrease in the hardness of alloys upon addition of tungsten carbide to niobium carbide (Fig. 113).

Fig. 112. Curve of dissolvability of tungsten carbide in niobium carbide.

Legend in Fig. 112: 1 - temperature, °C; 2 - concentration, % (mol.)

Fig. 113. Microhardness of WC - NbC alloys.

Legend in Fig. 113: 1 - microhardness in kg/mm^2; 2 - content, % (mol.)

Niobium - Tungsten - Chromium (Bibl. 438). The alloys of chromium with 40% of Nb and 18% of W, as well as with 27% of Nb and 36% of W, smelted in the induction furnace at 2000°, turned out to be very brittle. Their oxidization rate at 1250° is appreciable; in addition, the shape of oxidization curves (Fig. 114) shows the absence of protective properties of the oxide film. During the oxidization the weight loss of alloys is considerable (10 mgm/cm² after 1 hour of the oxidization for the alloy with 27% of Nb and 36% of W), which is caused by evaporation of WO_3 produced on the oxidization.

Fig. 114. Oxidization resistance of alloys in the niobium-chromium-tungsten system. /222

Legend in Fig. 114: 1 - pressure decrease, mm Hg/cm²; 2 - time, min.

A highly porous film of oxides is observed also on alloys with 21% of Nb, 45% of W and with 16% of Nb, 49% of W, prepared by means of the powder-metal method and melting at very high temperatures (upward of 2400°).

Niobium (Tantalum) - Silicon - Nitrogen. The interaction of tantalum disilicide ($TaSi_2$) with nitrogen yields the ternary compound with the general formula /222 $Ta_{5-x}Si_{3-y}N_2$; the nitrides, Ta_2N, as well as $TaN_{0.8-0.9}$ and TaN, are in equilibrium with this ternary compound. The preliminary constitution diagram of Ta - Si - N_2, plotted in the paper (Bibl. 517), is shown in Fig. 115. The diagram of Nb - Si - N_2 system is similar to Ta - Si - N_2 system.

Fig. 115. Schematic representation of the constitution diagram of the tantalum-silicon-nitrogen system.

Niobium - Silicon - Carbon. The Nb_5Si_3 compound in the Nb - Si system /223 reveals a wide range of homogeneity in the presence of carbon. The hexagonal ternary phase (a = 3.117 ± 0.003 Å; c = 4.969 ± 0.005 Å), isomorphous with respect to Nb_2C, was detected in the Nb-Si-C system.

Niobium - Nickel - Chromium. Kubashevskiy and Shpan'er (Bibl. 438) - studied some properties of the system with the profile of Cr_3Nb_2-Ni. Alloys of the following compositions were prepared by smelting in argon:

1. 22% of Nb and 60% of Ni; 2. 27% of Nb and 50% of Ni; 3. 38% of Nb and 30% of Ni; 4. 44% of Nb and 20% of Ni; 5. 49% of Nb and 10% of Ni. The alloys 3, 4 and 5 turned out to be extremely brittle, while alloys 1 and 2 were more malleable. Their melting points were lower by ~300° than melting points of similar alloys with tantalum participation.

The oxidation rate of Cr_3Nb_2 depends but little on additions of nickel.

Niobium - Titanium - Vanadium. In the work (Bibl. 518), Kornilov and Vlasov studied the fusibility curve of this system on samples of alloys in profiles which are parallel to vanadium-niobium side, and with a constant titanium content in each solution, viz. 10, 20, 30, 40, 55, 60, 70, 75, 80, 85, 90 and 94% (by weight). The samples were produced by sintering of compacts molded from powder mixtures. Basing on results of the thermal analysis, it was established that alloys of the above-indicated compositions constitute a continuous series of solid solutions.

Niobium - Titanium - Carbon. The alloys of NbC-TiC profile constitute, according to the X-ray diffraction data of Kovalskiy and Umanskiy (Bibl. 519), a continuous series of solid solutions; their hardness, according to the data in (Bibl. 516), increases almost additively with an increase of TiC content. The brittleness of alloys increases in parallel.

Niobium (Tantalum) - Chromium - Boron. (Bibl. 520), The continuous series of solid solutions are formed in profiles of CrB_2-NbB_2 and CrB_2-TaB_2.

Niobium (Tantalum) - Titanium - Boron. TiB_2 forms with NbB_2 and TaB_2 continuous series of solid solution. (Bibl. 520).

The profile of TiB_2 - NbB_2 was studied by Samsonov and Neshpor (Bibl. 521 and 522) by the methods of microstructural and X-ray diffraction analyses, as well as by measurements of the microhardness, electric resistance and air-oxidation resistance of samples. The maximum of hardness (~3700 kg/mm^2) is located close to the composition containing 70% (mol.) of TiB_2, while the maximum of strength in the brittle breakdown is shifted toward NbB_2 and constitutes 140 kg/mm^2. The variations of lattice periods and their ratios are insignificant; they are expressed graphically by straight lines which are nearly parallel to the axis of compositions.

The alloy with the equimolar content of TiB_2 and NbB_2 withstands best /224 the air oxidation, apparently because the structure of a vitreous oxide film, corresponding to the alloy of such a composition, has the closest conjugation of metal-oxygen polyhedrons. The increase in the weight of samples in relation to the oxidization temperature is subordinated (in the same way as for individual borides) to the exponential law. The variation in the weight of samples as a function of the duration of oxidization at 800° obeys the parabolic law. The calculated oxidization constants turned out to be equal to $K_{NbB_2} = 12.9 \cdot 10^{-9}$, $K_{TiB_2} = 2 \cdot 10^{-9}$ and $K_{50\%\ of\ NbB_2 + 50\%\ of\ TiB_2} = 0.5 \cdot 10^{-9}$ gm/cm^2 min.

It turned out, during the X-ray diffraction analysis of the homogenizing time of solid solutions of NbB_2 and TiB_2 (upon heating the mixtures of boride powders in the vacuum furnace at 1400 - 1800° for 0.5 - 32 hours), that NbB_2 lines remain in all the cases on X-ray photographs, while TiB_2 lines vanish with a sufficiently long holding time.(Fig. 116). Thus, the lattice of niobium boride (constituting the solvent) serves as the base of the solid solution.

The dissolution of titanium boride with smaller lattice periods (a = 3.028 Å; c = 3.224 Å) in niobium boride with greater lattice periods (a = 3.082; c = 3.278 Å) is accompanied by the diminution of lattice periods of the solid solutions. /225

Fig. 116. Variation of lattice period of solid NbB_2 - TiB_2 solution in relation to the time and temperature of homogenizing.

Legend in Fig. 116: 1 - lattice period, Å; 2 - time, hr.

Niobium - Tantalum - Nickel. Kornilov and Pylaeva (Bibl. 523) studied the profile of Ni_3Nb - Ni_3Ta, employing the methods of thermal, microstructural and X-ray diffraction analyses, and also measuring the electric resistance, hardness and specific weight (Fig. 117). The alloys were produced of previously prepared compounds, Ni_3Nb and Ni_3Ta, which were obtained from the pure electrolytic nickel, 99.9% tantalum and 98.7% niobium. The researchers detected the presence of a continuous series of solid solutions of the molecular type with the minimum of crystallization-outset temperature with 6% Ni_3Ta.

Fig. 117 presents also the data regarding properties of these solutions.

Fig. 117. Diagram of Ni_3Nb - Ni_3Ta system, and some properties of alloys of these compounds.

In the subsequent work (Bibl. 524), the same authors studied a part of the ternary Nb-Ta-Ni diagram, from nickel to binary compounds of Ni_3Nb and Ni_3Ta, which - as it was established - has the form of diagram with a limited dissolvability in the solid state and a continuous transition of binary eutectics of the Nb - Ni_3Ta system into binary eutectics of the Ni - Ni_3Ta system (Fig. 118).

Fig. 118. Diagram of Ni - Ni_3Nb - Ni_3Ta system /226

Legend in Fig. 118: 1 - temperature, °C; 2 - abbreviation for "liquid")

Niobium - Carbon - Nitrogen[1]. The NbC - NbN system was studied in the work (Bibl. 513), during which the researchers detected the presence of a continuous series of solid solutions; the samples were prepared by sintering the compacts (made of mixtures of niobium carbide and nitride) at 2125°, according to the data (Bibl. 551), the alloy $NbC_{0.3}N_{0.7}$ changes over into the superconductive state at 17.8°K. As it was established in the work (Bibl. 525), NbC - NbN alloys are formed in the heat-resistant "1336" alloy on cobalt base (0.20% of C; 0.50% of Si; 1% of Mn; 19.3% of Cr; 46% of Co; 3% of Fe; 13.0% of Ni; 12% of W; 1% of Nb).

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[1] Refer to "J. Research of the National Bur. of Stand.", 55 (4), 209-13 (1955) for constitution diagrams of pseudobinary systems, Nb_2O_5 - TiO_2 and Nb_2O_5 - ZrO_2. (Editors).

Niobium (Tantalum) - Carbon - Cobalt (Iron, Nickel). In the work (Bibl. 526), the alloys of above-indicated systems were produced by mixing the powders /226 of carbides with iron, cobalt and nickel in various ratios, which were subsequently molded and remelted in the vacuum induction furnace. The samples were annealed at 1250° and water-quenched, whereupon they were subjected to the examination by metallographic and roentgenographic methods. The following areas of solid solutions were detected (at 1250°) during this examination:

Carbide	In Cobalt	In Nickel	In Iron
TaC	3%	5%	0.5%
NbC	5%	3%	1%

No tendency toward the formation of -phase was detected in these systems.

The data on systems of Ta(Nb)C with Co, Ni and Fe are confirmed by the work (Bibl. 527), in which the authors indicate also approximate compositions of TaC - Ni eutectics with 35 - 40% of Ni, and of TaC - Co with 35% of Co.

Niobium - Zirconium - Nitrogen (Bibl. 519). The alloys of this system /227 were produced on the basis of the powder-metal method, by sintering the mixtures of powders at 2550°.

ZrN and NbN form a continuous series of solid solutions; the alloy with 90% of NbN melts at ~2550°.

Niobium (Tantalum) - Zirconium - Boron. NbB_2 and TaB_2 form with ZrB_2 continuous series of solid solutions (Bibl. 520). In the work (Bibl. 528), the ZrB_2 - TaB_2 system was studied by the X-ray diffraction method, measurement of the microhardness and electric resistance, as well as by examining the microstructure. All the properties of alloys of this system are characteristic for continuous series of solid solutions (Fig. 119).

Fig. 119. Properties of alloys in ZrB_2 - TaB_2 system

Legend in Fig. 119: 1 - lattice period, Å; 2 - microhardness, kg/mm^2; 3 - electric resistivity, ohm^{-1} · cm^{-1}; 4 - average size of grinding grains, µ; 5 - content of ZrB_2, % (mol.)

Niobium - Zirconium - Carbon. The alloys of NbC - ZrC profile, obtained by Kornishin and Umanskiy (Bibl. 519), constitute a continuous series of solid solutions with the hardness curve characterized by a not-too-high maximum with 90% (mol) of ZrC (Fig. 120); refer to Bibl. 516.

Fig. 120. Microhardness of NbC - ZrC alloys

Legend in Fig. 120: 1 - microhardness H, kg/mm^2; 2 - content, % (mol.)

The solid solution, (Nb, Zr)C, is produced during the interaction of zirconium carbide with metallic niobium (Bibl. 529); at the same time, the surplus zirconium (displaced by niobium: $Nb + ZrC = NbC + Zr$) fills up the pores and cements grains of the solid solution. The alloy thus obtained has a fairly high tensile /228 strength - up to 40 - [illegible] kg/mm^2. The high thermal strength of this alloy (at 1500°) makes it possible to use it in the high-temperature engineering under conditions of exposure to the action of aggressive gases.

Tantalum - Nitrogen - Oxygen. Schonberg prepared oxy-nitrides (Bibl. 530) by oxidation of TaN (ε-phase) and $TaN_{0.80-0.90}$ (δ-phase) and nitration of Ta_2O_5 by ammonia. The following ternary phases were detected during the investigation:

$TaN_{\sim 0.90}O_{0.10}$ - lattice which is similar to the lattice of ε-phase ($z = 24$) with periods: a = [illegible]; c = 5.30 Å; c/a = 0.561.

$TaN_{\sim 0.75}O_{\sim 0.25}$ ($z = 4$) - structure of the δ-phase of the Ta - N system with $a \approx 2a_g$ and $c \approx c_g$. Periods: $a = 5.988$ Å, $c = 2.879$ Å and $c/a = 0.481$.

$TaN_{\sim 0.65}O_{\sim 0.35}$ ($z = 12$) - superstructure of the superstructure type of δ-phase of the Ta - N system with $a = 2\sqrt{3}\,a_g$ and $c \approx c_g$; $a = 10.34$ Å, $c = 2.864$ Å and $c/a = 0.277$.

$TaN_{\sim 0.50}O_{\sim 0.50}$ - hexagonal lattice ($z = 96$) with periods: $a = 5.939$ Å, $c = 2.866$ Å and $c/a = 0.483$.

The color of oxy-nitrides varies from black (for $TaN_{0.90}O_{0.10}$) to reddish (for $TaN_{\sim 0.50}O_{\sim 0.50}$). The dissolvability of nitrides in tantalum oxides was not established. The schematic diagram of Ta - N - O system is shown in Fig. 121.

Fig. 121. Schematic representation of Ta - O - N diagram /229

Tantalum (Niobium) - Vanadium - Carbon; Tantalum - Niobium - Carbon; Tantalum (Niobium) - Molybdenum - Carbon. The course of variation in microhardness with the composition of alloys in profiles of VC - NbC; VC - TaC; MoC - TaC; Mo_2C - NbC and Mo_2C - TaC was examined in these systems (Bibl. 516); refer to Fig. 122.

Fig. 122. Microhardness of Alloys.

1 - Mo_2C - TaC; 2 - VC - NbC; 3 - NbC - TaC; 4 - Mo_2C - NbC; 5 - VC - TaC.

Legend in Fig. 122: 1 - microhardness P, kg/mm^2; 2 - content, % (mol.)

In systems, VC - NbC, VC - TaC and NbC - TaC, constituting continuous series of solid solutions, the researchers detected maxima of the microhardness; the highest relative maximum is observed in the TaC - VC system; it exceeds the hardness of VC by 50%, and that of TaC by 100%.

The maxima of microhardness were detected also in alloys, Mo_2C-NbC and Mo_2C-TaC, with a limited dissolvability in the solid state; these maxima were disclosed in the dissolvability regions. It should be noted that alloys of Mo_2C with 5 and 82% (mol.) of NbC are very brittle.

Tantalum - Tungsten - Carbon. Kovalskiy and Umanskiy (Bibl. 515) examined by means of the X-ray photography the alloys of TaC-WC profile, obtained by sintering the mixtures of carbides in the graphite tube furnace in hydrogen stream at 2600° with the subsequent annealing at temperatures from 2500 - 1400°. The curve of dissolvability of WC in TaC, thus obtained, is shown in Fig. 123. /230 Kovalskiy and Umanskiy failed to detect $TaWC_2$ compound, assumed in preceding works. Fig. 124 shows the curve of microhardness variation in this system (Bibl. 515).

Fig. 122. Line of dissolvability of tungsten carbide (WC) in tantalum carbide (TaC).

Legends in Fig. 122: 1 - temperature, °C; 2 - concentration, % (mol.)

Fig. 123. Microhardness of TaC-WC alloys.

Legends in Fig. 123: 1 - microhardness H, kg/mm^2; content, % (mol.)

Small additions of TaC (not exceeding 5%) to cast tungsten carbides ($WC + W_2C$) enrich the latter, pulverizing the structure and increasing the mechanical strength.

Tantalum - Silicon - Carbon (Bibl. 517). The researchers detected in this system a singular ternary phase with the composition of $Ta_{4.3}Si_3C_{0.5}$, structure of Mn_5Si_3 and lattice periods, a = 7.494 ± 0.007 Å and c = 242 ± 0.007 Å (Fig. 125).

Fig. 125. Schematic diagram of Ta-C-Si system.

Apparently, this phase has no conspicuous region of the homogeneity. The phase density, measured by the X-ray diffraction method, constitutes 12.48 gm/cm^3, while that measured by pyknometer amounts to 12.4 gm/cm^3.

Tantalum - Manganese - Oxygen. According to the data in (Bibl. 532), there exist in this system Mn_3Ta_3O compounds with the structure of η-carbides (with oxygen atoms in centers of slightly deformed octahedrons of atoms) and lattice priod of 11.15 - 11.18 Å, as well as Mn_2TaO_3 compounds with hexagonal lattice and periods of a = 5.321 Å and c = 3.578 Å (density of 6.41 gm/cm^3).

Tantalum - Titanium (Vanadium) - Nitrogen. During the examination of TaN - TiN system in the work (Bibl. 533) the Ta-Ti alloys were prepared by sintering the mixtures of fine powders in a crucible from zirconium dioxide in the vacuum induction furnace. The alloys were pulverized in the mill, /231 placed in corundum-made analysis boats inserted into the porcelain tube and subjected to nitration by ammonia for a fairly long time (60 hrs) at 900°. The X-ray diffraction study of TaN-TiN alloys in various concentrations yielded the following results:

Parent alloy	$Ta_{0.50}Ti_{0.50}$	$Ta_{0.25}Ti_{0.75}$	$Ta_{0.10}Ti_{0.90}$
Phases, originating during nitration	Ti(Ta)N + TaN	Ti(Ta)N + TaN	Ti(Ta)N + traces of TaN

Thus, the dissolvability of TaN in TiN apparently exceeds 10% (mol.). The $(Ti_{0.90}Ta_{0.10})N$ nitride has a cube lattice with the period of a = 4.247 Å, by comparison with a = 4.238 Å for the pure TiN [50% (atom.) of N]. The patent literature contains references to the high hardness of TiN-TaN alloy with 50% (mol.) content of each component (Bibl. 534).

The following phases were detected in the TaN-VN system, analyzed in the same manner:

Parent alloy	$Ta_{0.50}V_{0.50}$	$Ta_{0.25}V_{0.75}$
Phases, originating during nitration	V(Ta)N + TaN	V(Ta)N

i. e., VN phase dissolves approximately 25% (mol.) of TaN; at the same time, the period of the cubic lattice of VN varies from a = 4.169 Å ($VN_{1.00}$) to a = 4.291 Å.

Tantalum (Cr, Mn, Fe, Co, Ni) - Nitrogen. The analysis of these systems /234 was conducted by Schoenberg (Bibl. 533), and the alloys were prepared according to methodes described above, i. e. by the nitration of alloy powders by means of ammonia for 50 hrs at 900°. The results of X-ray diffraction study of TaN alloys with nitrides of Cr, Mn, Fe, Co and Ni are summarized in the Table 37.

Table 37

Phases Observed in Binary Alloys of Tantalum Nitride

with Nitrides of Cr, Mn, Fe, Co and Ni

System	Parent Alloy	Phase Produced during Nitration
Ta - Cr - N	$Ta_{0.75}Cr_{0.25}$	x + TaN
	$Ta_{0.50}Cr_{0.50}$	x + traces of an unknown phase
	$Ta_{0.25}Cr_{0.75}$	Cr(Ta)N + traces of x-phase
Ta - Mn - N	$Ta_{0.90}Mn_{0.10}$	Ta(Mn)N + traces of $TaN_{0.8}$
	$Ta_{0.75}Mn_{0.25}$	Ta_3MnN_4
	$Ta_{0.50}Mn_{0.50}$	x + Ta_3MnN_4
	$Ta_{0.25}Mn_{0.75}$	x + nitrides of Mn
Ta - Fe - N	$Ta_{0.80}Fe_{0.20}$	Ta_2FeN_3 + TaN
	$Ta_{0.67}Fe_{0.33}$	Ta_2FeN_3
	$Ta_{0.50}Fe_{0.50}$	Ta_2FeN_3 + nitrides of Fe
Ta - Co - N	$Ta_{0.80}Co_{0.20}$	Ta_2CoN_3 + TaN
	$Ta_{0.67}Co_{0.33}$	Ta_2CoN_3
	$Ta_{0.50}Co_{0.50}$	Ta_2CoN_3 + α - Co

System	Parent Alloy	Phase Produced during Nitration
Ta - Ni - N	$Ta_{0.80}Ni_{0.20}$	$Ta_2NiN_3 + TaN$
	$Ta_{0.67}Ni_{0.33}$	Ta_2NiN_3
	$Ta_{0.50}Ni_{0.50}$	$Ta_2NiN_3 + Ni$

The researchers detected in Ta - Cr - N system the ternary phase (x-phase in the Table 37), the x-ray picture of which has a complex character. The period of CrN phase varies from $a = 4.149$ Å ($CrN_{1.00}$) to $a = 4.293$ Å; the latter value of this period occurs in the point of the highest dissolvability of TaN in CrN - - approximately 25% (mol.).

Two ternary phases were detected in Ta - Mn - N system; one of them is isomorphous with respect to x-phase of Ta - Cr - N system, while the other has the composition expressed by formula of Ta_3MnN_4. The tantalum does not dissolve in in $MnN_{0.61-0.63}$ (η-phase), and manganese - in ξ-TaN. Roughly 10% of tantalum atoms can be replaced in δ-TaN by Mn atoms, which causes the elongation of a simple hexagonal lattice along the a-axis and the compression along the c-axis. The substitution of tantalum atoms for manganese causes /233 the expansion of the lattice, inasmuch as Mn atoms are smaller than Ta atoms.

The Ta_3MnN_4 phase has a hexagonal lattice with periods: $a = 3.323$, $c = 10.49$ Å and $c/a = 3.470$ ($V = 82.39$ Å^3). The ternary phases with hexagonal lattices were detected in systems of Ta - Fe (Co, Ni) - N; Table 38 presents the fundamental characteristics of these lattices.

Table 38

Periods of Lattices and Densities of Ternary Phases in Ta-Fe(Co, Ni)-N Systems

Phase	a, Å	c, Å	c/a	Density	
				Calculated	Measured
$Ta_2 FeN_{2,60}$	5.156	10.31	2.000	12.71	11.9
$Ta_2 CoN_{2.50}$	5.161	10.30	1.996	12.74	12.3
$Ta_3 NiN_{2.45}$	5.168	10.36	2.005	12.60	12.2

Tantalum - Carbon - Nitrogen. The liquidus curve of the pseudobinary TaN - TaC profile is shown in Fig. 126 (Bibl. 535). It was established by means of the X-ray diffraction and metallographic analysis, of the alloy TaC:TaN = 1:1, that the stable solid solution does not last at the indoor temperature (Fig. 127).

Fig. 126. Fusibility line of TaN - TaC system.

Fig. 127. Microsection of Alloy of the TaN - TaC system [50:50 (mol.)]

During the work (Bibl. 211), solid solutions of TaN - TaC were prepared /224 by the joint sedimentation of TaN and TaC from the gaseous phase ($TaCl_5$, N_2 and hydrocarbons).

Schoenberg (Bibl. 530) examined the alloys of this profile by means of the X-ray diffraction analysis on samples produced through the nitration by ammonia of tantalum carbide and through carbonization of tantalum nitride by dry methane at 1100°.

The dissolvability of TaC in $TaN_{0.8-0.90}$ (δ = phase of Ta - N system) constitutes approximately 5% (atom.); at the same time, lattice periods increase slightly, viz. from a = 2.925 - 2.938 Å and c = 2.876 - 2.883 Å (for δ-phase) to a = 2.938 Å and c = 3.071 Å (for the alloy with the composition of $TaN_{0.85}C_{0.15}$). The dissolvability of TaC in TaN is apparently very low; TaN practically does not dissolve in TaC.

No ternary phases were detected in Ta - C - N system. Ta_2C and Ta_2N form, according to the data from (Bibl. 530), a continuous series of solid solutions.

Tantalum - Niobium - Chromium. Kubashevskiy and Shneyder (Bibl. 438) prepared the samples of alloys representing the profile of Cr_3Ta_2 - Cr_3Nb_2. Results of the pyrometric determination of melting points are presented in the Table 39.

Table 39

Melting Points of Tantalum and Niobium Alloys with Chromium

Nb Content, %	Ta Content, %	Melting Point, °C
40	18	1700 - 1800
27.5	35	1900
22	42	1900 - 2000
16	49	2000

All these alloys turned out to be appreciably more brittle than alloys of the corresponding binary systems. The oxidization rate at 1250°, during 40 minutes, is highest with the alloy containing 16% of Nb and 49% of Ta, and lowest with the alloy containing 27.5% of Nb and 35% of Ta; however, all the alloys are less oxidation-resistant than the alloys of binary systems and intermetallides, Cr_3Ta_2 and Cr_3Nb_2.

Tantalum - Titanium - Carbon. The analysis of this system was performed in the work (Bibl. 536) on samples of alloys prepared by the powder-metal method from powders of tantalum- and titanium hydrides and carbon black. The compacts from mixtures of these powders were sintered in the vacuum furnace at the temperature of 1820° and under the pressure of $1 \cdot 10^{-3}$ mm Hg. The alloys were studied by X-ray method combined with monitoring the content of total and free carbon. The results obtained in this work served as a basis /235 for plotting the isothermic cross section of the system at 1820°, shown in Fig. 128. At this temperature, we have 5 phases in the system, viz. liquid (y, Ti-angle), β, γ, δ and graphite.

The β-phase has a face-centered cubic lattice; no dissolvability of carbon in this phase was detected.

Fig. 128. Isothermic cross section of Ti - Ta - C system at 1820°.

The δ-phase with the hexagonal close packing (a = 3.097 Å and c/a = 1.595) corresponds in its composition almost exactly to Ta_2C.

Three binary diagrams on sides of the ternary system have 6 fields of solid solutions which are transformed in the ternary system in the following manner.

The peritectoid transformation line, β-Ti - Ta - α-Ti - TiC, in the ternary system is represented by the three-phase field, α-β-δ (Fig. 129).

Fig. 129. Titanic Space Angle of Ta - Ti - C System

Legend in Fig. 129: 1 - Ta content, % (atom.); 2 - C content, % (atom.)   1236

Two other lines, TiC - L - C and Ta - L - C, are eutectic.

The remaining three lines, TiC - β - Ti - L peritectic, TaC - Ta_2C - L peritectic and Ta_2C - L - Ta eutectic. The ternary eutectic melts at 1350°.

Kovalskiy and Umanskiy established by means of the X-ray diffraction analysis (Bibl. 519) the presence of a continuous series of solid solutions on TaC - Tic profile. The microhardness line of TaC - Tic alloys (Fig. 130) has the maximum with 20% (mol.) content of TaC (Bibl. 516).

Fig. 130. Microhardness of Alloys: /236

1 - TiC-TaC; 2 - ZrC-TaC

Legend in Fig. 130: a - temperature, °C; b - content, % (mol.)

Tantalum - Carbon - Oxygen. Schoenberg (Bibl. 530) examined by means of the X-ray diffraction analysis method the alloys of this system, prepared by oxidization of tantalum carbide in the presence of hydrogen at 700° and reduction of Ta_2O_5 by carbon black at 1800° in the vacuum furnace. One ternary and two binary phases were observed during this process. One of these binary phases has a cubic face-centered lattice with the period of a = 10.41 Å. The ternary phase has a deformed tetragonal lattice of NaCl type with periods: a = 4.303, c = 4.097 Å and c/a = 0.952. The approximate formula of this phase is $Ta_2(C, O)$; however, the ratio of C/O was not determined.

Tantalum - Uranium - Carbon. According to data in (Bibl. 507), at least two ternary phases exist in Ta - U - C system; one contains 67.3% (atom.) of Ta, 6.7% (atom.) of U and 26.0% (atom.) of C ($\sim UTa_{10}C_4$), and has a very low symmetry of the crystallic lattice, while another has a cubic face-centered lattice with the period of a = 4.41 Å. The latter phase is endowed with a high melting point (> 2500°). The formation of this phase causes the decarbonization of uranium, in which there remains less than 0.002% of C (by weight) upon the formation and elimination of this phase on the tantalum electrode of the electric arc furnace.

Tantalum - Zirconium - Carbon. Kovalskiy and U anskiy demonstrated by means of the X-ray diffraction analysis (Bibl. 519) the presence of a continuous series of solid solutions in Ta - Zr - C system on TaC - Zr - C profile. According to the data in (Bibl. 516), the microhardness line of alloys in TaC - ZrC system has a low maximum with the content of 20% (mol.) of TaC in alloys (Fig. 130).

Tantalum - Chromium - Tungsten. The alloys with 35% of Ta and 35% of W, and those with 52% of Ta and 18% of W oxidize fully in 60 min at 1250°, changing into a loose powder composed of the mixture of oxides (Bibl. 438).

Tantalum - Chromium - Silicon. In the work (Bibl. 537), $TaSi_2$-$CrSi_2$ alloys were prepared by hot molding of mixtures composed of silicide powders at 1300 - 1500° with the subsequent homogenizing annealing in hydrogen at 1300° for 2 hours.

The profile under examination reveals a discontinuity of the dissolvability, extending from 11 to 60% (mol.) of $TaSi_2$ at 1300°. The addition of $TaSi_2$ to $CrSi_2$ decreases slightly, at the beginning, the air-oxidation resistance of alloys which increases and then (beginning with 50% of $TaSi_2$) decreases once again,(Fig. 131). The oxidization resistance of alloys exceeds, within the range of 60 - 30% of $TaSi_2$ (by weight), the resistance of individual components.

Fig. 131. Oxidization Resistance of $CrSi_2$ - $TaSi_2$ Alloys

Legend in Fig. 131: 1 - change of weight, gm/cm^3; 2 - content of $TiSi_2$, $TaSi_2$ and Mo_3Si, % (by weight).

Tantalum - Chromium - Nickel. The system was studied by Kubashevskiy and Shnayder (Bibl. 432) on alloys of profiles which are parallel to sides of Ni - Cr (with the content of 10.20 and 50% of Ta (by weight)) and Ni - Ta with the content of 10.20 and 40% of Cr), by means of microstructural, X-ray diffraction- and differential thermic analyses, as well as by determination of hardness. One of profiles, thus obtained, (10% of Ta), is shown in Fig. 132; it indicates the presence of ternary eutectic at 1165°.

Fig. 132. Profile Diagram of Ta - Ni - Cr System (with 10% of Ta)

Legend in Fig. 132: 1 - temperature, °C; 2 - content of Cr, % (by weight)

The alloys for the X-ray diffraction analysis were heated for 2 hours at 900° with the subsequent hardening. During the dissolution in chromium (a= 2.878 Å), 1% of Ta and 1% of Ni, the lattice period increases only up to 2.879 Å, which points to a very narrow range of tantalum- and nickel dissolvability in chromium. On the other hand, the dissolvability of tantalum in nickel (nickel angle of diagram) attains 20% and is accompanied by the increase of nickel lattice period from 3.516 to 4.560 Å.

The study of the oxidization rate of alloys indicates that the oxidization resistance is inherent in alloys containing 10 - 40% of Ta, 50 - 80% of Ni and 10 - 25% of Cr, whose melting points amount to 1250 - 1380° and Brisell hardness - 150 - 300 kg/mm^2 (Fig. 133). When the tantalum content increases to 45 - 56%, and the nickel content varies accordingly to 25 - 50%, while that of chromium changes to 5 - 30%, the solidus temperature of alloys increases to 1350 - 1600° and the hardness exceeds 400 kg/mm^2; however, these alloys are less resistant to oxidization; in Fig. 133 the oxidization resistance is marked by digits at points, which denote the decrement of ambient-air pressure in mm Hg during the oxidization of alloy samples in the closed space. The alloys containing more than 35% of Cr have a high oxidization resistance and hardness; however they do not submit to the working and are therefore not suitable for the practical use. The additions of 2% of Na, or 1% of Ca, Be, Si, Th and Ce, reduce abruptly the oxidizability of alloys of this system; this was verified on the ternary alloy with 42% of Ta, 40% of Ni and 18% of Cr.

The mechanical properties of alloys belonging to Ta - Cr - Ni system were examined in detail by Bueckle (Bibl. 539).

Fig. 133. Melting Point and Hardness of Alloys in Ta - Ni - Cr System.
x - brittle; ● - hardness $H_B > 500$; △ - the same, 400 - 500; ◎ - the same, 300 - 400; ▨ - the same, 200 - 300; • - the same < 200; ☐ - not examined; --- solidus temperature

3¼ - 1849

Chapter IX.

Tetra and Multicomponent Systems with Participation of Tantalum and Niobium

(CHETVERNYE i MNOGOKOMPONENTNYE SISTEMY s UCHASTIYEM TANTALA i NIOBIYA)

Chapter IX from the book entitled" Tantalum and Niobium " (Tantal i Niobiy). pp.241-248

Niobium- Vanadium- Carbon-Nitrogen. According to [513] the NbC-VN system has complete mutual solubility (fig.134), in spite of the fact that the formation of these solid solutions is connected with difficulties even at 2375°. A section of NbN-VC also represents a continuous series of solid solutions forming during the heating of mixture components at 2250°.

Fig.134. Periods of VN-NbC and NbN-NbC alloy lattices (TiC, VN)

Niobium-(Tantalum)-Vanadium- Zirconium-Carbon. On the isothermal sections of TaC-VC-ZrC and NbC-VC-ZrC systems were revealed roentgenographically diphase fields (fig. 135) with maximum content 64% of TaC and 51% NbC [540] . Alloys of these systems are prepared by vacuum sintering of briquettes, pressed from mixtures of proper carbides with subsequent homogenizing tempering for a period of 12 hours at 2000°.

Niobium-Nickel-Chromium-Aluminum. Kornilov and Pryakhina [541] plotted a schematic diagram for the Ni-Cr-Al-Nb system shown in form of a tetrahedral Ni-Cr-Ni_3Al-Ni_3Nb on Fig.136. 249)

242) Fig.135. Isothermal section of a (Ta,Nb,Ti) C-ZrC-VC system at 2000° 525

Fig.136. Spatial angle of the Ni_3Al-Ni_3Nb-Cr-Ni system

The nickel peak of the tetrahedral is adjoined by a considerable zone of the fourth solid solution gamma, surrounded by heterophase regions being formed at a surplus of one or another component. And so, at a niobium surplus above its specific solubility (which in turn appears a function of the chromium and aluminum content) is separated a Ni_3Nb base phase or a phase of solid solutions based on this compound (zone gamma + delta). Analogous phase regions appears during a surplus of chromium-base chromium (alpha-solid chromium-base solution) or an Ni_3Al-base chromium solution (or chromium base solid solutions).

In this report were investigated the physical properties of a number of tetra alloys of the above indicated system according to dimensions: I - 10% Cr and 6% Al with a content of from 0 to 12.5% Nb; II - 15% Cr, 6% Al and from 0 to 12.5% Nb, III - 20% Cr, 6% Al and from 0 to 12.5% NB; IV - 30% Cr, 3 or 6% Al and from 2.5 to 7.5% Nb.

Alloys of the I and II characteristics are homogeneous up to the 7.5% Nb. of the III group - up to 5% Nb. All alloys of the IV group are heterogeneous. The heat resistance of the alloys at 800°, stresses of 22.4 kg/mm² and 446 hours of test duration has been evaluated by the time up to the point of destruction upon bending. The most refractory alloys were the ones the compositions of which (by the Nb content) correspond to the transient zone from solid solutions to alloys with heterogeneous structure. Thus, maximum heat resistance (spalling resistance) (at stresses of 24 kg/mm² and more than 400 hours up to the point of destruction) goes with the structure of finely dispersed formations of excess phases having a background of saturated and supersaturated solid solutions. The heat resistance of tetra Nb-Ni-Cr-Al alloys exceeds by much the maximum heat resistance of alloys of corresponding binary and ternary systems.

Niobium-Titanium-Carbon-Nitrogen. Judging by X-ray data [515] the NbC-TiN cut represents a continuous seria of solid solutions. Experiments were made with samples prepared by four hour heating of TiN + NbC mixtures at 2550° (at 2240° homogenisation was incomplete at that time) in a graphite-tubular furnace. The NbN-TiC system also reveals a continuous series of solid solutions (fig.134) but their formation is incomplete even at 2425° and is concluded only at 2550°

Niobium(tantalum)- Titanium- Nickel (Cobalt)- Carbon. In the systems Ni-Ti-Ta-C, CO-Ti-Ta-C and Ni-Ti-Nb-C systems were established solid η_2-carbides: $Ni_2(Ti,Ta)_4C$, $CO_2(Ti,Ta)_4C$ and $Ni_2(Ti,Nb)_4C$. [542] made a detailed evaluation of their crystallo-chemical properties.

644 Niobium-Zirconium-Carbon-Nitrogen. [513] Has not Succeeded in obtaining solid ZrN-NbC solutions even at a 2 hour heating period at 2400°. (Generally speaking here should be expected the formation of solid solutions). The reason of this appears to be, apparently, the insufficient soaking (exposure) time) (a rise in temperature to above 2450-2500° at the existing operational conditions it was impossible, for example, for the alloy with 50% (mol) of NbC and 50% (mol) of ZrN to melt at 2600°).

Tantalum-Zirconium-Nitrogen-Oxygen. Sheyaberg [510] prepared a number of tetra alloys of the Zr-Ta-N-O system by using powderous alloys of the Ta-Zr-system, expressed by conditional formulas $ZrTa_{0.67}$, ZrTa, $Zr_{0.67}Ta$, $Zr_{0.33}Ta$ which submitted to nitration with dry ammonia at 700 - 1100° up to the formation of solid nitride phases; in an analogous way were obtained binary oxide phases by the oxidation of samples in and oxygen stream in presence of hydrogen at ~ 700°. An x-ray analysis revealed a tetra phase of ZrTaNO of grayish color with a blackish metallic shine. The periods of the hexagonal lattice alpha = 3.645 Å, c = 3.882 Å, c/alpha = 1.065; rated density (at x = 1) 11.84, pycnometric - 10.6 g/cm³.

Tantalum -(Ti-Zr, Ti-Cr, V -Cr, V - Co, V - Ni, Cr Co, Mn-Cr, Co-Ni, Fe-Co)-Nitrogen. Sheyaberg [511] investigated ternary and tetra alloys of nitrides, and the composition of the phases revealed in this case is listed in table 40.

Table 40. Composition of phases in ternary and tetra nitride systems

System	Initial alloy	Phases forming during nitriding

Elements and values as in original

245 Phase y in the Ta-V-Cr-N system has a tetragonal lattice with periods alpha = 4.244, c = 4.120 Å, c/alpha = 0.971; since this alloy contained small amounts of oxygen, Sheynberg assumes, that the y phase is a hydroxynitride phase.

The $(Ta_{0.9}Ti_{0.1})_3MnN_4$ phase revealed in this investigation has a hexagonal lattice with periods alpha = 5.027 Å, c = 10.57 Å, c/alpha = 3.492, and the $Ta_2(Fe_{0.33}Co_{0.33}Ni_{0.33})N_{2.5}C$ phase also has a hexagonal lattice with periods alpha = 5.162 Å, c = 10.33 Å, c/alpha = 2.001; rated density 12.67 and the experimentally measured - 12.1 g/cm^3.

Tantalum-(niobium)-Tungsten-Titanium-Cobalt-Carbon [543,544]. Alloys of indicated components produceable by cermet (powder metallurgy) methods from carbides of WC, TiC and TaC with an admixture of cobalt, have high hardness, wear resistance and are used for the processing of metals by cutting. The hardness and ultimate strength (ultimate tensile strength) of certain alloys of this type are listed in table 41.

Table 41. Hardness and ultimate strength of Cermet solid alloys

Content, %	Hardness R_A, kg/mm^2	Ultimate strength kg/mm^2

Elements and values as in original

Metallographic investigation of WC-TiC-TaC-Co alloys, containing 2-45% TiC, 2-15% aC and 5-18% Co, indicated the presence of a cementing phase with cobalt base (gamma-phase) and two carbide phases forming the shell of the solid alloy: alpha-phase (WC) and of the solid TiC-TaC-WC solution (beta-phase). At much higher temperatures there appear solutions of the TiC-TaC series. Pseudoternary isothermal sections of the WC-TiC-TaC system (at 1450 and 2200°) are shown in fig.137 a and b.

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Fig.137. Phase diagrams of the WC-TiC-TaC system.
a - at 1450°; b - at 2200°; mol. weight.

247 **Niobium- iron- manganese- nickel- chromium.** According to Kornilov [545] the addition of 30% Fe, 20% Cr, 40% Ni, 10% Mn and from 0 to 15% Nb (at its maximum solubility in the alloy 4-5%) imparts to the alloy a maximum heat resistance at 800° at a niobium content rangingbetween 4 - 5%; in case of adding more than 5% Nb the separation togethet with the gamma-solid ~~gamma~~ solution of the excess phase reduce the heat resistance.

Niobium-Titanium-Iron-Silicon-Aluminum. Samarin, Grigorash and Yelyutin [546] announces the obtainment of an iron-niobium- ferroniobium compound, directly from a loparite concentrate, containing 8.41% Nb_2O_5, 37.31% TiO_2, 1.88% SiO_2, 1.47% Fe_2O_3, 6.01% CaO, 0.12% P, 1.08% Al_2O_3, 0.17% S, 32.24% rare earths and traces of MnO.

The melting of the ferroniobium is carried out in a steel smelting furnace with consideration of the obligatory reaction:

$$3Nb_2O_5 + 10Al = 6Nb + 5Al_2O_3;$$
$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3;$$
$$3Fe_3O_4 + 8Al = 9Fe + Al_2O_3.$$

[illegible]

The alloy obtained in this manner containes 19.63 - 22.14% Nb, 1.42 - 6.00_ Ti, and 0.07 - 1.26% Al, 3.14 - 50% Si, the rest is iron.

There is no information regarding the properties of these complex alloys. Nothing is reported in this respect.

Other niobium and tantalum alloys

Alloys with Rhenium and Platinoids [547]. Alloys of Rhenium with niobium, tantalum and platinoids possess high acid resistance, hardness, as well as sufficient thermal expansion coefficient, close to the coefficient of many industrial types of glass. Because of this such alloys can be used in the role of electrode material, melted-in into vacuum vessels (electronic tubes, rectifiers) and also in composition of electric contacts. For tips of automobile handle springs are recommended especially hard and acid resistant alloys of the composition: 0.1 - 30% Nb or Ta, 0.3 - 6% B, 0.1 -50% Pt, remaining Rhenium) special recommendation has been gained by the alloy containing 75% Re, 15% Ru, 7.5% Nb, 2.5% B). The alloy possesses higher hardness without increased brittleness (see also pp.173, 202).

Alloys with arsenic. When a tantalum and niobium powder is mixed with arsenic and heated in a sealed tube at 600° it yielded products of the composition $NbAs_{0.8}$ and $TaAs_{1.4}$ respectively, the homogeneity of which has not been proven [433].

Alloys with silver and gold. According to Moissan [548] tantalum does not fuse with silver and gold. In many cases it becomes necessary to coat the tantalum with 248) gold, which is realized, according to [549], by deposition of the gold from a cyanogen bath containing NaCN and $AuCl_3$, at 70° and current density of 0.01 amp/cm^2 within a time period of 8 minutes. After the coating the cathode is washed with water and heated to 1100° for a more firmer adhesion of the gold layer (thickness ~ 1 mm applied on a tantalum wire 3 mm in diameter). In this case was observed a good adhesion of the gold and tantalum, which allows to assume, that gold is dissolving even in tantalum.

Alloys with mercury. Bolton [465] on the basis of his own experiments to obtain

Ta and Nb amalgam, including the electrolytic deposition of mercury on a niobium cathode, arrived at a conclusion that these metals do not at all react with Hg.

Alloys with sulfur. Tantalum with sulfur form a TaS_2 sulfide (26.12% S), the derivation and properties of which are described in greater detail by [558].

Niobium with sulfur form a number of sulfides [551].

Alloys with selenium. Bolton points toward the existence of tantalum [465] and niobium [552] selenides of unknown composition.

A RESUME OF IMPORTANT PROPERTIES AND AREAS OF UTILIZATION OF ALLOYS CONTAINING NIOBIUM AND TANTALUM /249

System	Composition of the Alloy	Fundamental Characteristics	Fields of Application
Nb - N	NbN	Transition to the super conducting state in 15 degrees K	Detectors, picture tubes, bolometers
Nb - Al	A small admixture to aluminum and its alloys	Formation of the chemically stable and high melting $NbAl_3$ compound	Modifying aluminum and aluminum based alloys
Nb - B	NbB_2	High hardness, infusibility, chemical stability	In the composition of heat-resisting alloys and refractories
Nb - H	NbH	Friability, isolating hydrogen during tempering	Reprocessing niobium waste. Soldering flux
Nb - V	5 - 50% Nb	Steam corrosion resistance	Steam pipes
Nb - Fe	50 - 60% Nb	----	For the introduction of Nb into the composition of heat-resistant and corrosion-resistant steels
Nb - Si	$NbSi_2$	High resistance against oxidation in the air	In the composition of heat-resistant cermet alloys
Nb - Mo	A small admixture to molybdenum	Increases the temperature of molybdenum recrystallization	Modifying molybdenum
Nb - Ni	Alpha-solid solution of Nb in Ni <5% Nb	Resistance against the corrosion of HCl	The chemical industry

Continuation

System	Composition of the Alloy	Fundamental Characteristics	Fields of Application
	Alpha + Ni_3Nb up to 13% Nb	Resistance against the corrosion of HNO_3	The Chemical industry
Nb - Ta	0 - 100% Ta	High corrosion resistance, the properties of getters	The chemical industry
		Alloys replace Tantalum perfectly	Radio engineering
Nb - Ti	10 - 60% Nb	Corrosion resistance	The chemical industry /250
	7.5% Nb	High mechanical stability, good machinability	Construction material
Nb - C	NbC	High hardness, Infusibility, heat resistance	Admixtures to other carbides in ceramet solid alloys, used in heat-resisting alloys
Nb - C	$\gg$ 40% Nb	High resistance against oxidation	In heat-resisting alloys
Nb - Zr	12% Nb	Creep resistance	In heat-resisting alloys
Ta - N	TaN Ta_2N	High resistance against acid corrosion, hardness and infusibiligy	In heat-resisting alloys
Ta - Al	Small admixtures to Al and its alloys	Formation of the chemically stable and high melting $TaAl_3$ compound	Modifying aluminum and its alloys
Ta - B	Ta B_2	High hardness, Infusibility, resistance against oxidation	In heat-resisting alloys

Continuation

System	Composition of the Alloy	Fundamental Characteristics	Fields of Application
Ta - H	TaH Ta_2H	Friability, isolating hydrogen during tempering	Reprocessing tantalum waste and its alloys Flux in soldering semiconductors
Ta - W	up to 7.5% W	High electrical resistance and thermal emission	Radio engineering
Ta - Si	$Ta\ Si_2$ and alloys with $\geqslant$70% Si	Resistance against oxidation	In heat-resisting alloys
Ta - Mo	up to 10% Mo	High mechanical stability and electrical resistance	In electrical engineering
	up to 50% Mo	Resistance against the corrosion of HCl, HNO_3 and H_2SO_4	In the chemical industry
Ta - C	TaC	High hardness, infusibility	In the composition of ceramet solid alloys, refractories /251
Ta - Cr	$\sim Cr_3Ta$	Resistance against oxidation	In the composition of heat-resisting alloys
Nb(Ta) - C - Ni(Fe, Co)	—	Cementing alloys (binding carbide grains in solid alloys	In the composition of ceramet solid alloys
Nb - Zr - C	50% (mol.) NbC	High heat-resistance and heat stabiligy	In the composition of heat resisting alloys
Ta - W - C	—	High hardness and infusibility	In the composition of ceramet solid alloys
Ta - Nb - C	27.5% Nb; 35% Ta	Resistance against oxidation	In heat-resisting alloys

Continuation

System	Composition of the alloy	Fundamental Characteristics	Fields of Application
Ta - Ti - C	-- ----	High hardness, infusibility	In the composition of ceramet solid alloys
Ta - Cr - Si	6C - 80% (by weight); $TaSi_2$	Resistance against oxidation	In heat-resisting alloys
Ta - Cr - Ni	10 - 40% Ta	Resistance against oxidation and good mechanical stability	In the chemical industry in heat-resisting alloys
Nb - Ni - Cr-Al	10 - 15% C; 6% Al; up to 7.5% Nb	High heat resistance	Heat-resisting alloys
Nb(Ta) - W - Ti - C - CO	4 - 40% TiC; 6.9% Co; up to 6% Nb(Ta)C	High hardness, stability, and wear resistance	Ceramet solid alloys
Nb(Ta) - Re - B - Pt	0.1 - 30% Nb or 0.3 - 6% B; 01 - 50% Pt, the rest Re	High resistance against corrosion, wear resistance, hardness	Electrodes for sealing in glass in vacuum technics, pen points in fountain pens, electric contacts

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