FTD-MT-66-16

FOREIGN TECHNOLOGY DIVISION

PHASE COMPOSITION, STRUCTURE, AND PROPERTIES OF ALLOY STEELS AND ALLOYS
(SELECTED ARTICLES)

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EDITED MACHINE TRANSLATION

PHASE COMPOSITION, STRUCTURE, AND PROPERTIES OF ALLOY STEELS AND ALLOYS. (SELECTED ARTICLES).

English pages: 57

SOURCE: Fazovyy̆ Sostav, Struktura i Svoy̆stva
Legirovannykh Staley̆ i Splavov.
Izdatel'stvo "Mashinostroyeniy̆e"
(Russian), Moskva, 1965, pp 5-19,
28-38, 39-47, and 202-210.

TT65004-438

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WP-AFB, OHIO.

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

CERTAIN QUESTIONS OF ANALYSIS OF ISOLATED PHASES AND PHASE COMPOSITION OF ALLOYS

N. F. Lashko

Investigation of distribution of alloying elements between phases in different alloys is produced at present with the greatest completeness by means of isolation of phases and their subsequent analysis by chemical, X-ray, and other methods. Among the methods of isolation of phases from alloys (chemical, mechanical, magnetic and others), the most successful in many cases turned out to be electrolytical, involving selective dissolution (separation) of separate phases. Since sufficiently complete theory of anode processes does not exist, separation of phases in alloys with help of electrolytical methods was produced chiefly on the basis of acquired experience. Survey of methods of electrolytic isolation of phases from nonferrous alloys is given in article [1].

Intense development of theory of corrosion processes in metals and alloys permits outlining, at least in first approximation, ways of selection of most optimum conditions for isolating both separate and groups of heterophase alloys. It is shown that during change of basic parameters of anode processes — current density and potential — every phase of alloy passes through a number active and passive states,

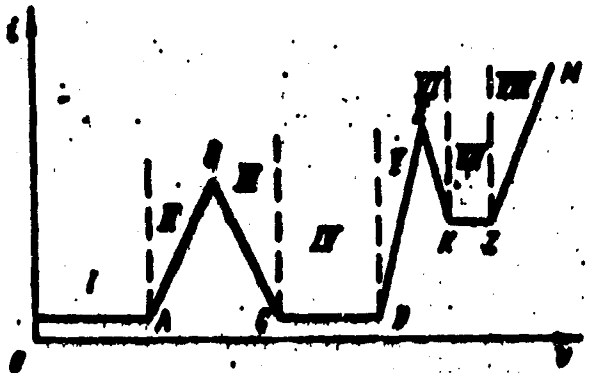

Fig. 1. Diagram of anode polarization of metals and alloys.

presented schematically in Fig. 1 [2, 3]. With increase of potential from 0 to A phase is located in inactive, and in range of values AB, in active state. In range of values of potential BC phase is partially passivated, and in range CD is completely in passive state. State of phase in range DE is usually characterized as overpassivation; it seems to us that it is more correct to call it underpassivation. Then the state, characterized by potential, in range EK corresponds to partial, and in range KL to full overpassivation. In range of values of potential LM there occurs repeated underpassivation. If the assumption about independence of states of separate phases, determined by potential and current density, is justified at least in first approximation, the problem of electrochemical separation of phases will lead to selection of electrolytes and conditions of electrolysis, ensuring creation of assigned active, inactive, passive, or underpassivation state in every phase. Research in this direction is in the initial stage. Some successes are obtained during investigation of anode processes in stainless steels, which were used for selective etching or isolation of carbides, solid solutions (α and γ), and σ-phases of steels, and also during phase-shift analysis of nickel alloys.

We clarified some additional information on behavior of phases in process of their isolation and dissolution. Apparently, it is desirable to conduct dissolution of phases in region of active state and not in region of underpassivation. This was shown, for instance, during isolation of cementite from manganese steels [4]. Anode processes in region of under passivation are complicated by processes of change of valence of some dissolved elements flowing in it (ions of highest valence are formed) and also oxygen evolution.

Oxygen evolution during anode reactions in region of underpassivation can be accompanied by formation of hydrogen peroxide, which was revealed during anode polarization of certain metals [5]. These processes are possibly the cause of chemical unstableness of certain dispersed anode deposits isolated from steels and alloys. It is necessary to indicate also that not all phases necessarily pass through all eight above-indicated states. It awaits to study the influence of various methods of transfer of seperate phases into assigned state. State of phases during electrolysis in the first place depends on character of anions [6] and to a smaller degree on cations of electrolyte, on pH solution, and such physical factors as temperature of medium.

Successful isolation of phases subsequently will be developed undoubtedly when conducting electrolysis in conditions of constant assigned anode potential, since namely every value of potential and current density uniquely connected with it corresponds to definite rate of dissolution of separate phases of alloy. Determination of chemical state and structure of separate phases of heterogeneous alloy cannot always appear successful during application of only electrolytic methods of selective dissolution and isolation of phases. In supplement to it can be used methods of chemical selective dissolution of phases of anode deposit in various solvents.

For instance, quantitative determination of state of phases of nickel alloy EI437 with raised carbon content turned out to be very difficult in connection with the fact that in electrolytes, in which phase $Ni_3(Al, Ti)$ is quantitatively isolated, chromium carbides are partially dissolved. K. P. Sorokina succeeded, combining methods of electrolytic isolation and selective chemical dissolution of phases of anode deposit, to quantitatively determine all phases present in alloys of type EI437 with raised carbon content [7].

Passive state of phases during flow of anode processes and during chemical separation of phases of anode deposit is most frequently connected with formation of oxidized protective film. Activation of anode dissolution during electrolysis of stainless steels and alloys in electrolytes containing chlorine-ion is usually explained by destroying action of the latter on oxidized film. But there exists many facts showing that film theory of passivity cannot explain many phenomena of passivation; facts are known when preliminary formation of oxidized film on iron prevents its passivation, for instance, in alkaline medium [5].

N. M. Popova proposed methods of passivation of chromium carbides and other phases rich with chromium in an acid medium with oxidants, proceeding from assumptions on formation of a protective film of oxides Cr_2O_3 [8], that did not always turn out to be effective during chemical separation of phases in anode deposits. Different behavior of two carbides, rich with chromium, based on $Cr_{23}C_6$ and based on metastable carbide Cr_2C, isolated from iron-nickel alloy (containing 58% Ni, 18% Cr, 8.9% W, 1-4% V) is revealed during their treatment in hot hydrochloric acid and in a mixture of it with hydrogen peroxide [9]. Treatment, performed by L. V. Zaslavskaya, of anode deposit consisting of mixture of carbides $Me_{23}C_6$ and Me_2C in hot solution of hydrochloric acid led to dissolution of only carbide $Me_{23}C_6$, and treatment in a mixture of hot hydrochloric acid with hydrogen peroxide led to dissolution of carbide Me_2C (carbide $Me_{23}C_6$ was not dissolved). From the viewpoint of film theory of passivation there remained inexplicable weaker passivation of carbide Cr_7C_3 as compared with carbide $Cr_{23}C_6$ [10]. Attempts to prove formation of amorphous or crystalline film of oxides on chromium carbides after their treatment in acid solutions containing oxidants turned out to be unsuccessful. Thus, for example, during electron diffraction investigation of carbides isolated from steel EI961, we revealed a structure corresponding only to carbide $Me_{23}C_6$. Reflections from oxidized films on carbides were not obtained. We consider that different action of solutions containing oxidants is connected with crystal structure of carbides. It is not accidental that in these solutions carbide phases of type TiC and Mo_2C (or Cr_2C) are dissolved relatively easy, regardless of their composition, and carbides of type Cr_7C_3 and $C_{23}C_6$ are difficultly or hardly dissolved. In crystal structure of first carbides, atoms of carbon occupy such places that at their removal the crystal lattice becomes unstable and is destroyed (in carbides of type Cr_2C atoms of carbon form continuous layers, in carbides of type TiC – continuous linear chains), while in the last carbides, atoms of carbon are isolated from one another. It is possible that during treatment of carbides by oxidants, atoms of carbon are easily oxidized to CO and are evaporated, thereby promoting destruction of carbides. It is natural that this process can occur only during influence on carbides with structure of type TiC and Cr_2C.

Electrolytic methods of isolation of phases have their own threshold of sensitivity, as optical methods of metallography have defined resolving power. There are no sufficient data for indicating quantitative threshold of sensitivity of electrolytic methods of isolation of phases. It is possible to indicate only comparative merits of data of methods and also methods of optical metallography and X-ray structural methods. Isolation of phases by each given electrolytic method is possible with linear dimensions of phases, limited by $l_1 \leq x \leq l_2$. Phases more dispersed than those characterized by magnitude l_1 and larger than those characterized by magnitude l_2 are not isolated. It is known that alloy EI437 and austenitic steel EI696 are strengthened by very dispersed particles of phase $Ni_3(Al, Ti)$ and phase $\beta = Ni_3Ti$ respectively, in process of short-time aging, which can be indicated by change of characteristics of strength and plasticity, but during application of existing electrolytic methods, dispersed particles of strengthening phases are not isolated, but are dissolved. It is known also that large particles of primary phase $Ni_3(Al, Ti)$ in nickel alloys, and large particles of δ-ferrite in two-phase $(\gamma + \delta)$ steels also are not isolated in known electrolytes. It is known also that particles of phase $Ni_3(Al, Ti)$ in alloy EI437, not visible with 1000 magnification in optical microscope, are isolated in known electrolytes containing ions SO_{4}^{2-} or PO_4^{3-}. Threshold of sensitivity of electrolytic method in this case is the same as X-ray structural method of powders, but higher than resolving power of optical microscope at existing methods of etching.

We will give the second example from the area of phase-shift analysis of alloy steels containing dispersed particles of carbides MeC, Me_2C, and others, formed during tempering in 400-500° range. These carbides are responsible for so-called "secondary hardness." Such dispersed carbides are not revealed by X-ray structural method of powders and in optical microscope, but are well isolated in different electrolytes. It is possible to also determine chemical composition of such dispersed carbides [11]. Consequently, threshold of sensitivity of electrolytic methods of isolation of phases is approximately the same or even higher than methods of optical metallography or X-ray structural method of powders. Electrolytic separation of phases is more precise and directly establishes interface of single-phase and two-phase regions of alloys. Thus, for instance, with help of method of determination of hardness, electrical resistance, and optical metallography of a number of two-component titanium alloys, we approximately established limiting contents of alloying elements (Cr, Cu, Si, Mo, V) of α-phase during annealing by various conditions [12]. The region of homogeneity of α-phase of these alloys was established directly and more precise by methods of electrolytic isolation of second phase (dissolution of α-phase). X-ray structural investigation of isolated phases permitted establishing their crystal structure besides and also stability or metastability [13].

It is not always possible to produce quantitative determination of phases with sufficient accuracy, especially in the presence of highly-dispersed phases when "suitable yield" can appear less than 100%. Determination of phases can be carried out with great reliability with combination of methods of electrolytic separation of chemical and X-ray diffraction analysis (isolated phases and in monolith samples).

As it is known, X-ray structural method of determination of relative quantity of phases in alloy is based on assumption of direct ratio of intensity I of diffractional lines and reflecting volume of phase V.

$$I = CF^2pN^2LPAV,$$

where C — constant, F — structural factor, including atomic factor, p — recurrence factor, N — number of unit cells in unit of volume, L — Lorentz factor, P — polarizability factor, A — absorption factor. Usually during determination by this method, quantity of phases, being two polymorphous modifications in two-phase alloy, is not considered difference of atomic factors in connection with their unequal chemical composition. Such approximation to a known degree is permissible during determination of residual austenite in steel, where composition of γ-phase is close to that of α-phase (ferrite), but is impermissible during determination of β-phase in α + β titanium alloys, in which α and β phases can strongly differ with respect to chemical composition.

Preliminary determination of chemical composition of isolated β-phase, and also calculated determination of α-phase will permit more precisely calculating atomic factor in formula, connecting intensity of diffraction lines and reflecting volumes of α and β-phases, and also more exactly establishing relative volumes of α and β-phases in alloy.

Possible chemical side reactions, occuring during electrolysis (connected with phenomenon of disproportionation, with interaction of ions of metals passing into electrolyte with ions of the latter, etc.), leading to formation of solid particles, obstruct anode deposit. Suppression of side reactions, as it is known, is attained in particular by application of corresponding complexers.

During isolation of phases of such chemically active alloys as alloys based on magnesium and titanium, protection of anode deposit from decomposition in electrolyte particularly as a result of hydrolysis, has special value. Among other measures applied for preventing processes of decomposition of anode deposits, proposal of G. I. Morozova to apply surface-active hydrophobic substances, adsorbing phases selective on isolated particles, and protecting them from influence of ions of electrolyte, deserves attention.

Into composition of some electrolytes enter compounds containing sulfur, which possesses ability to destroy passivating film forming on stainless steels. It is necessary to consider that during isolation of carbides from certain steels (especially from steels containing titanium and nickel) or from nickel alloys in electrolytes containing hyposulphite, insoluble sulfide can be formed in anode deposits. V. F. Mal'tsev and L. P. Luk'yanenko showed that it is more rational to replace hyposulphite by thiourea [14].

Application of analogous electrolytes for isolating phases from titanium alloys, alloyed with tin, also can lead to amorphous solid particles, forming as a result of chemical side reactions, getting into anode deposit. This was revealed, for instance, during isolation of intermetallic phase of type Ti_2Cu from titanium alloy containing 5.4% Al, 3.3% Cu, and 2.3% Sn (Table 1).

Table 1. Chemical Analysis of Anode Deposits, Isolated in Various Electrolytes from Titanium Alloy Containing 5.4% Al, 3.3% Cu, and 2.3% Sn

No. in sequence	Composition of electrolyte	Content of elements in anode deposits, %				Sum of elements, %	Atomic ratio $\frac{\text{Ti + Al}}{\text{Cu}}$
		Ti	Al	Cu	Sn		
1	3 g KSCN, 10 g citric acid, 50 g glycerine, 1 liter methanol	4.53	0.13	2.53	0.93	8.13	—
2	5 g citrate lithium, 3 ml H_2SO_4, 1 liter methanol	4.39	0.12	2.88	None	7.39	2.1
3	3 g succinic acid, 3 ml H_2SO_4(1.84), 1 liter methanol	4.25	0.11	2.60	None	6.96	2.2
4	3 g dianthipyridolmethane, 3 ml H_2SO_4(1.84), 1 liter methanol	4.45	0.12	2.85	None	7.43	2.2
5	10 g malonic acid, 3 ml H_2SO_4(1.84), 1 liter methanol	4.25	0.10	2.83	None	7.24	2.03

Anode deposits, isolated containing potassium thiocyanate, are contaminated by amorphous solid particles containing tin, forming as a result of chemical side reactions. Due to large chemical affinity of tin with sulfur, it is possible to assume that amorphous deposit is tin sulfide. In [15] amorphous solid particles were not revealed and intermetallic phase was ascribed composition $(Ti, Al, Sn)_3Cu$ instead of $(Ti, Al)_2Cu$.

Exact determination of chemical composition of isolated phases in many cases is impeded in connection with chemical activity of dispersed anode deposits, and also their ability to adsorb gases and moisture. In principle it is possible to establish weignt of pure anode deposits (applying special methods of removal of gases and moisture), but it is very complicated. Therefore, content of elements in isolated phases and in phases passed into electrolyte during anode dissolution is most often carried to weight of electrolytically removed layer. Determination of chemical composition of isolated and soluble phases, described in this collection, was carried out by this method. Chemical composition of phases soluble in electrolyte are usually determined by difference of average content of elements in investigated homogeneous alloy and their content in isolated phases. Special analysis of composition of soluble phases of homogeneous alloy in electrolyte has no advantages as compared to calculation by difference. Chemical analysis of electrolyte is entirely necessary in the case when alloys with heterogeneous composition are subjected to investigation, in particular during investigation of alloys with layered distribution of alloying elements.

Determination of chemical composition of carbide phases presents considerable difficulties, since there are no reliable methods of separation of bound carbon and free carbon found in solid solution. It is considered that all carbon from steel or alloys passes into anode deposit during electrolysis.

During electrolytic or chemical separation of phases due to disturbance of bond between them and contact with electrolyte, change of dimensions, structure, and even chemical composition of isolated phases is possible.

Change of dimensions of phases occurs during isolation in unbalanced alloys as a result of removal of permanent deformations and stresses appearing in alloys for various reasons. While investigating particles of martensite remaining on anode after electrolysis of hardened carbon steel in electrolyte by X-ray method, N. M. Popova and Arbuzov [16] revealed a considerably smaller line broadening than in monolith, which was correctly ascribed to removal of elastic stresses. Arbuzov affirmed that during this separate martensite needles or plates were isolated questionably.

Formation of phases of separations during disintegration of solid solution in unbalanced conditions leads to permanent deformations and stresses due to various specific volumes of appearing phase and matrix, and also difference of properties during heating and cooling (coefficients of linear expansion, etc.). Various methods of appraisal of elastic stresses were offered, which affect forming phases [17, 18]. Change of dimensions of phases, formed in process of aging of alloys after their isolation is revealed most simply by variation of parameters of elementary crystal cell. This is revealed in particular during isolation of phase $Ni_3(Al, Ti)$ with face-centered structure from nickel alloys [19, 20]. Depending upon degree of coherent bonding between phase $Ni_3(Al, Ti)$ and solid solution, and their chemical composition in process of isolation, there occurs decrease or increase of parameters of unit cell. Therefore, in those cases when knowledge of state of strain between phases in alloy is required, preliminary X-ray structural investigation of monolith is necessary.

There are known unbalanced phases not existing independently, but existing only in coherent bond with another phase. They include ω-phases with hexagonal structure, revealed always together with β-phase with body-centered structure in titanium and zirconium alloys (β- and sometimes in $\beta + \alpha$-alloys). ω-phase is not isolated from shown alloys, apparently in connection with the fact that there occurs break of coherent bond and transformation of ω to β-phase.

It is necessary to consider also the possibility of change of chemical composition of phase in those cases when during electrolysis elements from electrolyte diffuse into isolated phase.

There is not excluded, for instance, possibility of diffusion of ions of hydrogen during isolation of certain phases from alloys in water electrolytes. The ability of β-phase in ($\alpha + \beta$)-titanium alloys to absorb hydrogen during etching in solutions containing hydrogen is known. Parameter of unit cell of β-phase is changed noticeably. This was revealed by us during X-ray investigation of β-titanium alloy [VT15] (BT15) (Table 2). The noticeable effect of etching of ($\alpha + \beta$)-titanium alloys containing molybdenum is shown in article [21]. The very sharp difference of parameters of β-phase, revealed by us, isolated from alloy VT14 after hardening from various temperatures, as compared to their value in monoliths [22] is impossible to explain while not considering possible diffusion of hydrogen during etching of monolithic samples.

Isolation of phases from ($\alpha + \beta$)-titanium or zirconium alloys should be, therefore, produced in conditions which remove formation of hydrogen.

Table 2. Parameters of Unit Cell of β-phase of Alloy VT15 (After Hardening from 800° in Air and Subsequent Aging at 450° for 25 hr) Before and After Etching of Samples

State of samples	Parameters in A	
	after hardening	after hardening and aging
Before etching	3.23_6	3.20
After etching	3.24_9	3.23_3

In connection with investigation of multicomponent heterophase alloys containing phases with great region of homogeneity, there repeatedly appeared difficulties with distribution of elements in crystal structure of separate phases and also with mutual substitution of elements in region of homogeneity.

Theory of spherical and polyhedral packings of crystal structure in a number of cases permits determining formula composition of phases. Thus, for example, N. V. Belov [23] showed that crystal structure of carbides of type $Cr_{23}C_6$ can be tightly filled with different polyhedrons; polyhedrons in which there are disposed metal atoms, and they are broken into two groups with ratio of 21:2, distinguished by form and volume. Differentiated phase-shift analysis shows that elements replacing chromium in these carbides can be divided into two groups: 1) Fe, Ni, Co, Mn; 2) Mo and W. Limit of ratio of sum of elements of second group to sum of first does not exceed 2:21. It is known that there are carbides based on Fe_{21}, Mo_2C_6 in which iron can be replaced by elements of first group, and molybdenum by tungsten. Question on distribution of atoms of vanadium in these carbides remains vague. But theory of polyhedral packings of crystal structures does not explain why atoms of transition metals of fourth group Ti and Zr, and also such metals of fifth group as Nb and Ta, which was exactly established during differentiation analysis of carbides isolated from steels, carbides $Me_{23}C_6$ [24]. In steels alloyed in a number of other and with these elements, besides carbides $Me_{23}C_6$, carbides MeC (Me = Ti, Zr, Nb, Ta, V) are formed.

In the structure of binary carbides $Me^1_n\ Me^2_mC$* (n and m can have values 2 and 4, 4 and 2, 3 and 3, 6 and 6 respectively) there are two groupings of atoms that are bonded and not bonded with carbon; the first includes – Fe, Co, Ni, Si, the second – Mo, W, Cr, V, Nb, Ta. Metals of fourth group Ti and Zr, present in steels or alloys, do not enter binary carbide and form independent carbides MeC. In alloys with large concentrations of Nb or Ta, carbon bonds chiefly in carbides MeC on the basis of NbC or Nb_2C and TaC or Ta_2C. During this, carbide-forming ability of elements bound with structure of unit shell of atoms has basic value.

Recently there appeared discussion of relative distribution of atoms of different elements and their mutual substitution in ordered phase with a great region of homogeneity based on Ni_3Al, being the basic strengthening phase in heat-resisting nickel-chromium alloys.

Three viewpoints are presented concerning this equation. According to out investigations, formula composition of phase $Me^1_3Me^2$ of type Cu_3Au on the basis of Ni_3Al is determined by atomic radii with elements, their chemical affinity, bonding with position in periodic system, and existence in stable and metastable state of the following phases with face-centered structure: Ni_3V, Ni_3Si, Ni_3Fe, Ni_3Nb, Ti_3Ta, Ni_3Ti.

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*The original document gives $Me^1_nMe^2_nC$, apparently a misprint for $Me^1_nMe^2_mC$.

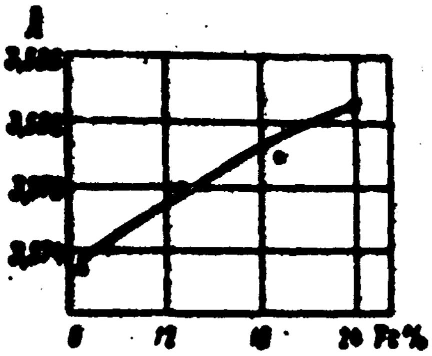

Fig. 2. Change of parameter of unit cell of phase $Ni_3(Al, Ti)$, isolated from alloy of type ZhC6 with variable iron content.

In accordance with this atoms of nickel in phase Ni_3Al can be replaced by elements Fe, Co, Cr, Mn, and atoms of aluminum by elements Si, Fe, V, Ti, Nb, Ta, Mo, W. It was shown, for example, that parameter of unit cell of phase Ni_3Al base, isolated from alloys, is increased continuously with increase of iron content in alloys with an indentical content of remaining elements (Fig. 2). This is correct with respect to alloys with various content of chromium.

According to Guard and Westbrook [25] elements replacing atoms of nickel and aluminun are divided into three groups: 1) Co, Cu, replacing atoms of nickel; 2) Si, Ti, Mn, V, replacing atoms of aluminum; 3) Fe, Cr, Mo, replacing atoms of nickel and aluminum simultaneously.

To these conclusions of authors came analyzing variation of parameters of unit cell of phase $Me^1_3Me^2$ with various content of alloying elements. It is characteristic that parameter of pure phase Ni_3Al turned out to be equal to 3.57 A according to [25].

In the article by Arbuzov and Zelenkov [26] on the basis of investigation of parameters of phase Ni_3Al alloyed with chromium, titanium, molybdenum, and tungsten, the following distribution of elements is accepted in phase $\alpha^1(\gamma^1)$:$(Ni, Al)_3(Al, Me)$, where Me—Cr, Ti, Mo, W. Parameter of unit cell of phase Ni_3Al turned out to be 3.56 A.

During distribution of elements in phase Ni_3Al authors implicitly proceeded from assumption that this phase is strictly stoichiometric composition, whereas it has a region of homogeneity of aluminum within limits of 22-26.5 atomic %. Consequently, phase Ni_3Al can contain surplus or deficiency of atoms Me^1 and Me^2 with empty places in nodes of crystal lattice. Taking into account this circumstance, explicitness of conclusions in [25, 26] loses its force, and argumentations in favor of our assumptions are strengthened. Question on formula composition of phase $Me^1_3Me^2$ is raised by solvable means of chemical and X-ray analysis and is not hopeless as follows from conclusions of articles [25, 26]. Practice of phase-shift analysis of nickel alloys shows in favor of the first method of distribution of elements in phase Ni_3Al.

Finding overall regularities of unbalanced phase transitions during disintegration of solid solutions in various alloys receives great interest. At present the following hypothesis is the most widespread: in alloys there occurs accumulation of alloying elements in metastable phase (or in zones of type Preston-Guignet), forming in first stages of disintegration, in the process of isothermal heating as a result of diffusion processes. During achievement of concentration of alloying elements in metastable phase, there occurs rearrangement of crystal structure with formation of a more stable (with respect to composition and structure) phase. Such hypothesis of the phase transitions was expressed by Yu. A. Bagaryatskiy and others with respect to many alloys (aluminum, nickel, etc.). It can be called hypothesis of continuous phase transitions, since overall content of bound alloying elements should be continuously increased during isothermal heating after hardening to solid solution.

Such phase transitions undoubtedly occur as a pure case among varied processes of possible metastable transformations.

In many steels and alloys there is observed another perhaps more wide-spread type of phase transition during isothermal disintegration

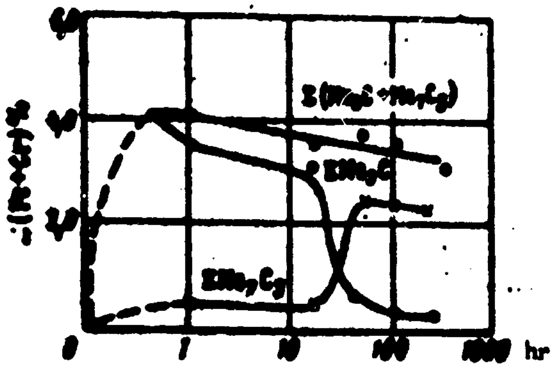

Fig. 3. Change of iron and chromium content in carbides Me_3C and Me_7C_3, isolated from medium-carbon steel (0.35% Cr and 2.34% Cr) after hardening from 1050° in oil and tempering at 600° of different duration.

of solid solution: at first metastable phase will be formed, in process of its formation and growth a considerable quantity of alloying element is bonded to it, but then as a result of change of composition of solid solution the relative equilibrium of phase with it is disturbed. Metastable phase is partially or complete dissolved, alloying elements bonded to it pass into solid solution, which facilitates formation (especially but not necessarily in places of dissolution) of a stabler phase. Such type of phase transitions can be called discontinuous. It is revealed in many pearlitic, martensite, and austenitic steels, in which there occurs replacement of carbide phases or carbide phase is replaced by metallic compound during isothermal disintegration of solid solution.

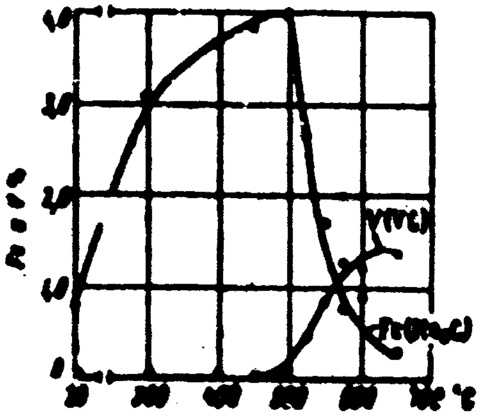

Fig. 4. Change of content of iron and vanadium in carbides Me_3C and VC, isolated from medium-carbon vanadium steel (0.39% Cr and 1.42% V) after hardening from 1200° in oil and tempering at 300-650° for 1 hr.

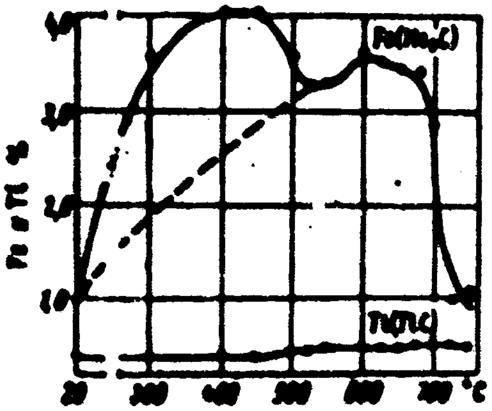

Fig. 5. Change of content of iron and Titanium in carbides Me_3C and TiC, isolated from steel (0.39% C, 0.35% Ti, 1.98% Mn), after hardening from 1250° in oil and hardening at 300-800° for 1 hour.

Figures 3-5 show typical cases of similar phase transitions for steels. Composition of separate carbides was determined by differentiated phase-shift analysis.

Figure 3 pertains to steel containing 0.35% C and 2.34% Cr, hardened in oil from 1050° and subjected to tempering at 600°. In initial stage of tempering cementite $(Fe, Cr)_3C$ is formed mainly, in which practically all the carbon is bonded combined with a small quantity of carbide $(Cr, Fe)_7C_3$ in 20 hours. Development of stabler carbide starts 20 hours after decrease of quantity of cementite, which in view of different structure of both carbides and their incompatibility, can occur only by means of dissolution in solid solution. Concentration of chromium in remaining cementite is decreased.

Figure 4 shows case of transition from cementite to vanadium carbide during tempering of steel containing 0.38% C and 1.42% V after hardening and tempering at different temperatures for 1 hour; Fig. 5 shows case of transition of part of metastable cementite into titanium carbide after tempering in steel containing 0.39% C, 0.38% Ti and 1.98% Mn (N. F. Lashko, A. F. Platonova, N. M. Popova). It is known that vanadium and titanium are practically insoluble in cementite and in carbides VC and TiC → iron.

Dispersed secondary particles of alloyed carbides are formed only after dissolution of considerable part of cementite (at 500°C) during transition of $Fe_3C \rightarrow VC$ or the most metastable part of cementite — during transition of $Fe_3C \rightarrow TiC$.

In first approximation supersaturated solid solution is considered uniform. Proceeding from such assumptions processes of formation of nuclei of new phase are explained basically by fluctuating phenomena. Nuclei of new phase, having region of homogeneity with respect to composition, in complicated solid solution in the beginning should have, as a rule, the least possible concentration of alloying elements; their concentration should gradually be increased in the process of aging to alloy close to equilibrium state. Such processes were actually revealed. For instance, during isothermal tempering of many steels containing chromium, the following sequence of formation of carbide phases (from metastable to stable) is revealed: $(Fe, Cr)_3C \rightarrow (Cr, Fe)_7C_3 \rightarrow (Cr, Fe)_{23}C_6$. Concentration of chromium in carbides is gradually increased. It is possible to augment similar examples.

But is the given diagram of disintegration of solid solution, accompanied by formation of new phase, the only possible one?

There are revealed cases of metastable disintegration of solid solution of austenite in alloy steels when nuclei of carbides, forming in first stage of isothermal aging, are enriched by alloying elements, but then during approach to equilibrium state the quantity of these carbides gradually decreases. Such disintegration of solid solution is naturally impossible to explain proceeding only from assumptions on homogeneity of solid solution and on participation of fluctuating phenomena in the formation of nuclei of carbides.

In a number of martensite and austenite steels containing more than 10% Cr, and also molybdenum, tungsten, and vanadium, we revealed the earlier mentioned phase on metastable chromium carbide base Cr_2C with crystal structure of type Mo_2C (W_2C, V_2C and others). With this carbide, in particular, are bound certain properties of martensite heat-resisting steels containing 12% Cr (hardening, "secondary hardness," and others) [27]. Temperature range of existence of this metastable carbide in steel is expanded with increase of quantity of carbon and elements (Mo, W, V), forming carbides of this type. Carbide $Me_{23}C_6$ is stable at higher temperatures, less than alloy.

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PHASE-SHIFT ANALYSIS OF ALLOYS OF TYPE EI437B WITH VARIABLE CARBON CONTENT

N. I. Blok, N. F. Lashko and K. P. Sorokina

High characteristic of heat resistance of nickel alloys containing aluminum and titanium are connected with formation of dispersed strengthening phase in them on Ni_3Al or $Ni_3(Al, Ti)$ base. Alloying with boron also has essential value for increase of heat resistance of these alloys. Alloying with carbon at first did not give any value, although it is inevitably introduced into alloys with charge materials (from 0.03 to 0.06%).

Some researchers considered that introduction of carbon to alloy of type EI437 causes lowering of stress-rupture strength since it binds part of titanium into carbides, and thereby decreases quantity of basic strengthening intermetallic phase [1]. English researchers gave great value to carbide phases of type $Me_{23}C_6$ and Me_7C_3, forming along grain boundaries in alloys of nimonic 80 type [2, 3].

Role of carbon in nickel alloys can be varied. It is also a strong refining element during melting, promoting purification of alloys from oxygen and oxides. The probability of entry of carbon into strengthening α'-phase with formation of compound $Ni_3(Al, Ti)C_x$ is not excluded.* Binding energy of α'-phase and its other features should be changed during this.

It is known that around the carbide phase, especially along boundaries of grains, there occurs redistribution of alloy components, causing noticeable change of structure. In connection with diffusion of elements forming carbide (Ti, Cr, W, Mo) to nuclei of carbide phase, their concentration around carbides is decreased. In these sections solubility of aluminum and titanium is increased, which leads to partial dissolution of α'-phase and formation of solid solution enriched with these elements. Formation of border of solid solution around carbides, especially along boundaries of grains where carbides of type $Me_{23}C_6$, Me_7C_3 can be disposed in the form of broken or continuous rigid network, has an essential effect on mechanical properties of alloys. Rigid network of carbides causes lowering of resilience, but increases resistivity to plastic deformation. Border of solid solution partially weakens the alloy, but can have favorable effect on properties of alloys, promoting relaxation of stresses along grain boundaries and decrease peaks of overstrains, which should prevent premature failure of alloys.

Formation of carbide phases also has a modifying action on alloys, which has large value for certain characteristics of alloy, in particular for such important characteristic as fatigue limit.

Recently there appeared a number of heat-resisting alloys on

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*There is a rather large group of chemical compounds being carbon-intermetallic compounds. Compunds with general formula $Me^1_3Me^2C_x$, where Me^1 = Fe, Co, Ni, are the most known. There is the same compound Ni_3AlC_x.

nickel base with raised carbon content. It is quite difficult to find optimum carbon content in nickel alloys in connection with the above noted varied affect on properties of alloys. Effect of carbon on phase composition and structure is also little studied.

Investigation of phase composition of nickel alloys containing intermetallic compounds and carbides is complicated by difficulties of determination of exact chemical composition of α'-phase, since content of alloy components in it is according to difference of results of analysis of two anode deposits, isolated in electrolytes with different composition. Preliminary data on phase composition of certain nickel alloys with carbon have shown that determination of content of elements in α'-phase with help of such method gives satisfactory results only for alloys containing not more than 0.2% carbon.

This work contains methods of quantitative determination of chemical composition of α'-phase, isolated from alloys of type EI437B, which contain carbon within limits of 0.04-0.65%.

EI437B alloys have following phase composition: α'-phase, titanium carbide, titanium carbonitride, titanium nitride, and carbides of type $Cr_{23}C_6$ and Cr_7C_3. In low-carbon alloy of type EI437 with low content of aluminum there are: α'-phase, $Me_{23}C_6$, and TiN.

Since aluminum decreases solubility of carbon, with increase of its content in alloy the probability of formation of carbide Me_7C_3 is increased. Besides, a primary phase carbonitride Ti(C, N) or almost pure titanium nitride with parameter equal to 4.25-4.26 A is released.

It was shown in [3] that carbide Me_7C_3 in low-carbon alloys of of nimonic 80 type is a metastable phase at low temperatures, transient during aging in carbide $Me_{23}C_6$.

Three alloys of type EI437B were taken for investigation.* Their chemical composition is given in Table 1.

Table 1. Chemical Composition of Investigated Alloys

No. of alloy	Content of elements, %				
	C	Cr	Ti	Al	Ni
1	0,067	20,02	2,64	0,68	Remaining
2	0,28	19,40	2,66	0,68	•
3	0,05	19,25	2,90	0,64	•

Heat treatment of alloys was conducted according to the following conditions:

1. Hardening from 1250° (holding 4 hours) in air;

2. Hardening from 1080° (holding 8 hours) in air;

3. Hardening from 1080° (holding 8 hours) in air, aging at 700°, 16 hours, cooling in air.

4. Hardening from 1080° (holding 8 hours) in air, aging at 750° – 16 hours, cooling in air;

5. Hardening from 1080° (holding 8 hours) in air, aging at 800° – 16 hours, cooling in air.

During heat treatment by first conditions, α'-phase is completely dissolved, and by second is almost completely dissolved; primary carbide and nitride phases remain undissolved. In aging process α'-phase and chromium carbides are separated from solid solution.

Investigation was conducted on cylindrical samples with 12 mm diameter and 50 mm length. For electrolytic separation of phases electrolytes of following composition were applied:

Alloys for investigation were assigned by D. Ye. Livshits.

1. 10 g $(NH_4)_2SO_4$; 10 g citric acid, 1200 ml H_2O [6].
2. 3% $FeSO_4 \cdot 7H_2O$; 3.5% NaCl; 5% H_2SO_4 [5].
3. 50 ml HCl, 100 ml glycerine, 1050 ml CH_3OH [6].

Conditions of electrolysis in all cases were the following: current density 0.05 amp/cm^2, duration of electrolysis 1 hour.

α'-phase, carbide and nitride phases are isolated in first two electrolytes; in third electrolyte only carbide and nitride phases. Chemical analysis of anode deposits is given in Table 2.

Table 2. Content of Elements in Anode Deposits Separated from Alloy EI437B, in Various Electrolytes*

No. of alloy	C %	Heat Treatment	Electrolyte 1: [illegible] + citric acid in 1 liter H_2O				Electrolyte 2 [illegible] $FeSO_4$+NaCl+ +H_2SO_4				Electrolyte 3: HCl+CH_3OH			Phase composition of anode deposits
			Contents of elements in deposit, in %											
			Ni	Ti	Cr	Al	Ni	Ti	Cr	Al	Ni	Ti	Cr	
1	[illegible]	Hardening from 1250° (4 hr) in air	—	[illegible]	[illegible]	Traces	—	—	—	—	Traces	0.11	Traces	TiN
2	0.23		[illegible]	[illegible]	[illegible]	None	—	—	—	—	[illegible]	[illegible]	0.20	$Me_{23}C_6$, Ti(C, N)
3	0.65		[illegible]	[illegible]	[illegible]	None	—	—	—	—	[illegible]	[illegible]	[illegible]	$Me_{23}C_6$, TiN, TiC
1	[illegible]	Hardening from 1000° (8 hr) in air	[illegible]	[illegible]	[illegible]	Traces	[illegible]	0.11	[illegible]	—	[illegible]	[illegible]	[illegible]	TiN
2	0.23		[illegible]	[illegible]	[illegible]	Traces	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	$Me_{23}C_6$, Ti(C, N)
3	0.65		[illegible]	[illegible]	[illegible]	Traces	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	$Me_{23}C_6$, TiC, Ti(C, N)
1	0.007	Hardening from 1000° (8 hr) in air and aging 700° – 16 hr	[illegible]	[illegible]	0.47	0.16	4.31	[illegible]	0.51	[illegible]	[illegible]	0.14	[illegible]	α', TiN, $Me_{23}C_6$
2	0.23		[illegible]	[illegible]	[illegible]	0.24	4.12	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.70	α', $Me_{23}C_6$, Ti(C, N)
3	0.65		3.11	[illegible]	[illegible]	0.15	[illegible]	[illegible]	[illegible]	[illegible]	0.27	[illegible]	6.25	α', $Me_{23}C_6$, TiC, TiN
1	[illegible]	Hardening from 1000° (8 hr) in air and aging 700° – 16 hr	[illegible]	1.17	[illegible]	0.25	5.41	1.17	[illegible]	—	[illegible]	0.14	[illegible]	α', TiN, $Me_{23}C_6$
2	0.23		[illegible]	[illegible]	[illegible]	0.17	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	α', $Me_{23}C_6$, Ti(C, N)
3	0.65		[illegible]	[illegible]	[illegible]	0.11	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	α', $Me_{23}C_6$, TiC, TiN
1	[illegible]	Hardening from 1000° (8 hr) in air and aging 800° – 16 hr	[illegible]	[illegible]	[illegible]	0.18	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.14	0.27	α', $Me_{23}C_6$, TiN
2	0.23		[illegible]	[illegible]	[illegible]	0.21	4.11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	α', $Me_{23}C_6$, Ti(C, N)
3	0.65		[illegible]	[illegible]	[illegible]	0.07	[illegible]	0.71	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	α', $Me_{23}C_6$, TiC, TiN

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*G. G. Georgiyeva and A. N. Kopotova participated in experimental work.

**Central Scientific Research Institute of Ferrous Metallurgy [TsNIIChM] ([illegible])

In anode deposits separated from low-carbon hardened alloy, in electrolytes 1 and 3 is revealed an approximately identical content of titanium and chromium; whereas in deposits isolated in electrolyte from hardened and aged alloy the quantity of alloy components turned out to be greater than in carbide electrolyte.

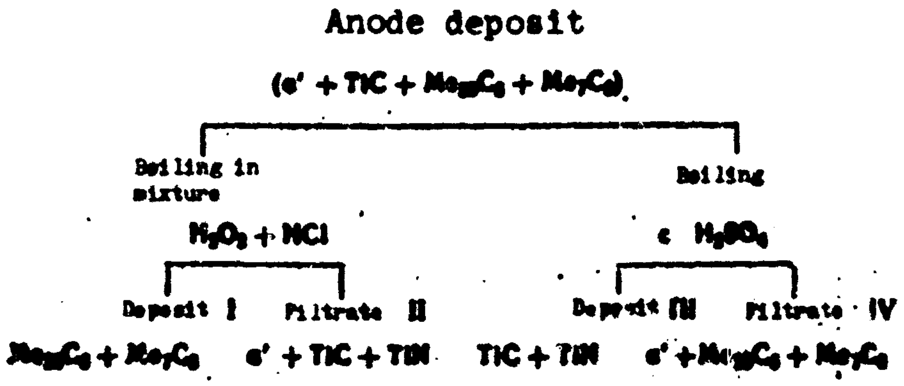
In anode deposits isolated in electrolyte 3 from hardened alloys with raised carbon content [2, 3], in which there is no α'-phase, ther is a considerably larger chromium content than those isolated in electrolyte 1. The presence of α'-phase in these alloys after hardening and aging naturally causes increase of quantity of titanium in anode deposits separated in electrolyte 1 as compared to deposits separated in electrolyte 3. The chromium content is approximately equal in deposits isolated from alloy 2 in various electrolytes, but is considerably larger in deposits isolated from alloy 3 in carbide electrolyte. This indicates rather strong dissolution of chromium carbides in it during their isolation from alloys with raised carbon content.

It is characteristic that anode deposits isolated in electrolyte (electrolyte of TsNIIChM) contain considerably more chromium than deposits isolated in electrolyte 1. This is probably explained by presence of ions of chlorine in electrolyte 2, which promote more complete separation of carbide phase at anode.

Thus, conclusion can be made that in alloys with raised carbon content it is impossible to determine composition of α'-phase by difference of results obtained during isolation of phases in two electrolytes.

For determination of chemical composition of α'-phase in alloys with raised carbon content we used the earlier established aspect of α'-phase, titanium carbides and nitrides to be dissolved in acid solutions containing hydrogen peroxide and ability of chromium carbides to be passivated in these conditions. Besides it was indicated that α'-phase and chromium carbides are dissolved while boiling in diluted solutions with sulfuric acid; whereas titanium carbide is not dissolved.

Therefore, for determination of chemical composition of α'-phase we conducted chemical separation of phases in anode deposits isolated in electrolyte 1 according to the following diagram:



Anode deposits separated in electrolytes 1 and 2 were heated for 1.5 hours in a mixture consisting of 50 ml H_2O_2; 25 ml HCl, and 100 ml H_2O with continuous addition of excess hydrogen peroxide, during which chromium carbides of type Me_7C_3 and $Me_{23}C_6$ were passivated and remained in insoluble residue, and α'-phase and titanium carbide TiC and Ti(C, N) passed into solution [4].

Anode deposits obtained from the same samples were heated with 20% sulfuric acid for 1.5 hours; carbide and nitride of titanium remained in insoluble residue, and chromium carbides and α'-phase were dissolved. Thus, composition of α'-phase could be calculated by two ways.

Chemical composition of carbides was determined in an anode deposit separated in electrolyte 3.

Differentiated analysis of anode deposits is given in Table 3. In the last columns of table is shown composition of α'-phase, calculated by difference of data of differentiated analysis and by

Table 3. Differentiated Analysis of Anode Deposits Isolated from Alloy EI437B with Variable Content of Carbon, Hardened and Aged by Different Conditions

No. of alloy	C %	Heat treatment	Content of elements in alloys												Content of element in α'-phase, %						Content of elements in α'-phase, calculated by difference with double electrolytic dissolution, %		
			deposit I/H_2O_2 ($Me_7C_3+Me_{23}C_6$)			filtrate II/H_2O_2 ($\alpha'+TiC$)			deposit III/H_2SO_4 TiC			filtrate IV/H_2SO_4 $\alpha'+Me_7C_3+$ $+Me_{23}C_6$			α'-II—III			α'-IV—I					
			Ni	Ti	Cr	Ni	Ti	Cr	Ni	Ti	Cr	Ni	Ti	Cr	Ni	Ti	Cr	Ni	Ti	Cr	Ni	Ti	Cr
1	0,087	Hardening and aging at 700° – 16 hr	Traces	Traces	Traces	4,61	1,00	0,46	Traces	0,14	Traces	4,70	0,85	0,53	4,67	0,84	0,46	4,66	0,85	0,53	4,70	0,87	0,37
2	0,23		0,04	0,02	1,52	4,34	0,97	0,39	•	0,24	0,05	4,32	0,78	2,00	4,31	0,73	0,34	4,32	0,76	0,48	4,37	0,77	0,11
3	0,65		0,10	0,10	2,41	2,83	0,90	0,26	0,01	0,55	0,31	3,11	0,48	2,40	2,82	0,36	Нет	3,01	0,38	Нет	2,84	0,35	—3,74
1	0,087	Hardening and aging at 750° – 16 hr	Traces	Traces	0,06	5,91	1,15	0,36	Traces	0,15	Traces	5,91	1,00	0,41	5,91	1,00	0,36	5,91	1,00	0,35	5,77	1,03	0,33
2	0,23		0,10	0,02	1,42	4,92	1,11	0,31	0,01	0,29	0,13	5,04	0,61	1,57	4,91	0,82	0,18	4,94	0,79	0,15	4,95	0,74	0,16
3	0,65		0,08	0,06	1,94	3,02	1,00	0,21	0,087	0,47	0,24	3,15	0,47	1,09	2,99	0,53	Нет	3,07	0,41	Нет	2,77	0,45	—3,67
1	0,087	Hardening and aging at 800° – 16 hr	Traces	Traces	0,07	6,04	1,02	0,22	Traces	0,14	Traces	5,85	0,91	0,26	6,04	0,88	0,22	5,85	0,91	0,19	6,00	0,98	0,15
2	0,23		0,03	Traces	1,19	4,89	1,02	0,26	0,09	0,28	0,21	4,96	0,77	1,34	4,80	0,74	0,05	4,93	0,77	0,15	4,79	0,69	—0,07
3	0,65		0,04	0,09	0,80	1,99	0,74	0,05	Traces	0,55	0,05	2,00	0,32	0,70	1,99	0,19	Нет	1,96	0,23	Нет	1,71	0,19	—4,39

difference of data obtained during double electrolytic separation of phases in electrolytes 1 and 3. From obtained data it is possible to note that with a small content of carbon in alloy differentiated analysis is not necessary, inasmuch as results calculated by different methods coincide well. In addition to that, operations of differentiated analysis are very time-consuming. For determination of composition of α'-phase in alloys containing more than 0.2% C it is necessary to apply differentiated analysis of anode deposit separated in electrolyte 1.

Content of titanium in anode deposits, corresponding to carbides or nitrides of titanium separated in electrolyte 3, and also in insoluble residue of anode deposit separated in electrolyte 1, is approximately equal or is within limits of errors of analysis (Tables 2 and 3).

Content of chromium in α'-phase during double electrolytic dissolution can be determined by means of calculation only in alloys with small carbon content (up to 0.2%).

By results of differentiated analysis the conclusion can be made that chromium content in α'-phase is decreased with increase of content of carbon in alloy and also with increase of temperature of aging. This is especially noticeable after aging of alloy 3, containing 0.65% C, when chromium is absent in α'-phase.

Data, given in Tables 2 and 3, give clear presentation of role of carbon in change of phase composition and chemical composition of seperate phases in investigated alloys.

In low-carbon alloy the carbon is bound basically in dispersed chromium carbides, forming in process of aging. Besides up to 0.27% Cr is bound. Part of titanium (up to ~0.12%) is bound in primary titanium nitrides.

Chromium carbides should participate in hardening of alloy along with dispersed particles of α'-phase, causing slowing down of plastic deformation.

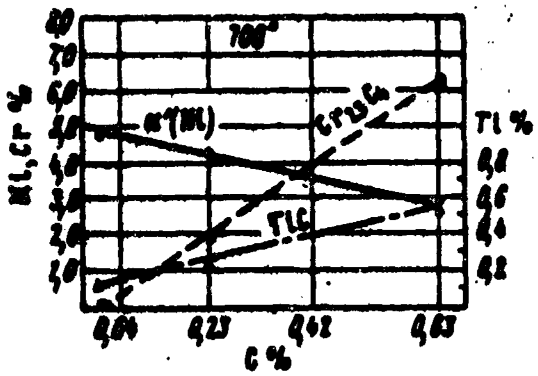
In alloy containing 0.23% C, hardened from 1080°, about 80% carbon is bound in primary titanium carbides and carbides of chromium. These carbides, in view of their rough dispersity, participate little in hardening of alloy. During subsequent aging excess carbon is consumed on formation of dispersed carbides of chromium. Content of titanium carbides is not changed. 0.30% Ti and 1.5-1.7% Cr are bonded into carbides.

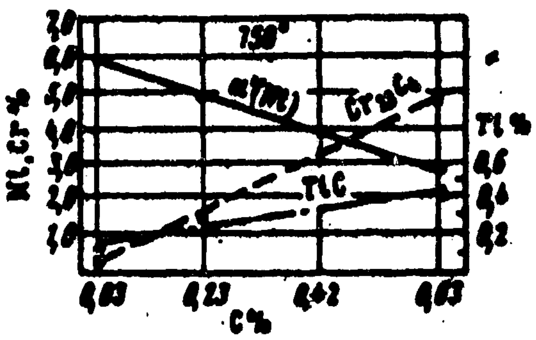
Quantity of α'-phase in alloys 2 and 3 is less than in alloy 1, which is explained by two reasons: a) smaller content of titanium not bonded into carbides, and b) increase of solubility of titanium and aluminum in solid solution of nickel, in connection with decrease of chromium content in it. Hardening of alloy is decreased in spite of some compensating action of forming dispersed chromium carbides.

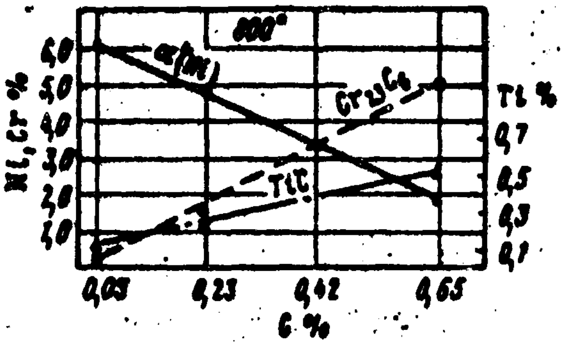
In hardened alloy containing 0.65% C, also about 80% carbon is bonded into primary carbides of titanium and chromium. Moreover, 0.60% Ti and 5% Cr is bonded into carbides, which causes sharper decrease of quantity of strengthening α'-phase.

Change of quantity of phases forming in alloys: α', TiC, $Me_{23}C_6$, depending upon carbon content, can be seen from the figure, on which is shown content of basic elements forming these phases: Ni (α'-phase), Ti (titanium carbide), Cr (carbide of chromium).

Characteristics of heat resistance of investigated alloys are determined mainly by quantity, composition, dispersity, and distribution of strengthening α'-phase, and also by composition and thin structure of solid solution.







Change of content of basic alloy components — Ni(α'-phase), Ti(TiN, TiC) and Cr(Cr_7C_3, $Cr_{23}C_6$) in anode deposits depending upon carbon content in alloys of type EI437 after hardening in air from 1080° and aging for 16 hours at: 700°, 750°, and 800°

Table 4 shows results of tests at 700° and $\sigma = 42$ kg/mm^2 of samples from alloys of type EI437B with different content of carbon, having been subjected to hardening in air from 1080° and aging at 700° for 16 hours.

Decrease of strength of alloys with increase of their carbon content is connected with decrease of content of α'-phase. Characteristics of plasticity in process of stress-rupture test are increased with increase of carbon content in alloys; besides alloys are weakened.

Table 4. Results of Stress-Rupture Tests of Alloys of Type EI437B with Different Content of Carbon

Content, %		Time to failure, hr	δ %	ψ %
carbon	α'-phase			
0,067	9,44	66,0 63,0 82,0	2,8 3,2 4,0	3,6 3,9 5,9
0,23	5,66	36,5 18,5 20,0	4,8 2,8 4,2	5,1 9,6 12,0
0,65	3,40	6,0 8,0 11,5	7,4 5,2 7,4	10,2 10,8 8,8

Conclusions

As a result of conducted investigation we established the following:

1. In water electrolytes with sulfate of iron and ammonium from alloys of type EI437, α'-phase and titanium carbive TiC are quantitatively isolated, and chromium carbides in alloys with raised content of carbon are partially dissolved in these conditions.

2. For determination of chemical composition of α'-phase in alloys with low carbon content (<0.2%), it is possible to apply double electrolytic dissolution of phases.

3. For determination of chemical composition of α'-phase in alloys with raised carbon content (>0.2%), it is necessary to conduct differentiated analysis of anode deposits separated in water electrolytes, while treating deposits in a mixture of hydrogen peroxide and hydrochloric acid, and in 20% sulfuric acid. In the solution with hydrogen peroxide carbides of chromium and α'-phase remain in insoluble deposit, and chromium carbides are dissolved. Chemical composition of α'-phase is calculated by difference.

4. With carbon content 0.23% and more rupture strength of alloys decreases and characteristics of plasticity are somewhat increased. This is basically caused by decrease of quantity of strengthening α'-phase as a result of binding of titanium and chromium into carbides TiC and $Me_{23}C_6$ and a increase of solubility of titanium and aluminum in solid solution.

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SURFACE OXIDATION AND PHASE CHANGE IN HEAT-RESISTING NICKEL ALLOYS IN LOADED STATE

N. I. Blok, N. F. Lashko, G. I. Morozova,
and E. M. Radetskaya

It is known that with increase of temperature the rate of structural transformations connected with diffusion processes is increased. Influence of deformation and type of load on rate of diffusion processes cannot be considered definitely clarified. Most researchers consider that diffusion processes in plastically and elastically-deformed metals and alloys flow faster than during heating without deformation. However, recently there appeared works indicating that loaded state of alloy can not always noticeably affect the diffusion rate [1, 2, 3].

Heating of heat-resisting alloys in air is accompanied by formation of oxides and depletion of surface layers by alloy components. As a result the structure and chemical composition of surface layers are changed, which leads to lowering of mechanical properties of alloys. Investigation of processes of depletion by alloy components when heating in various conditions is necessary for determination of life of structure operating at high temperatures. Clarification of role of variable load during heating of alloys in air is of obvious interest.

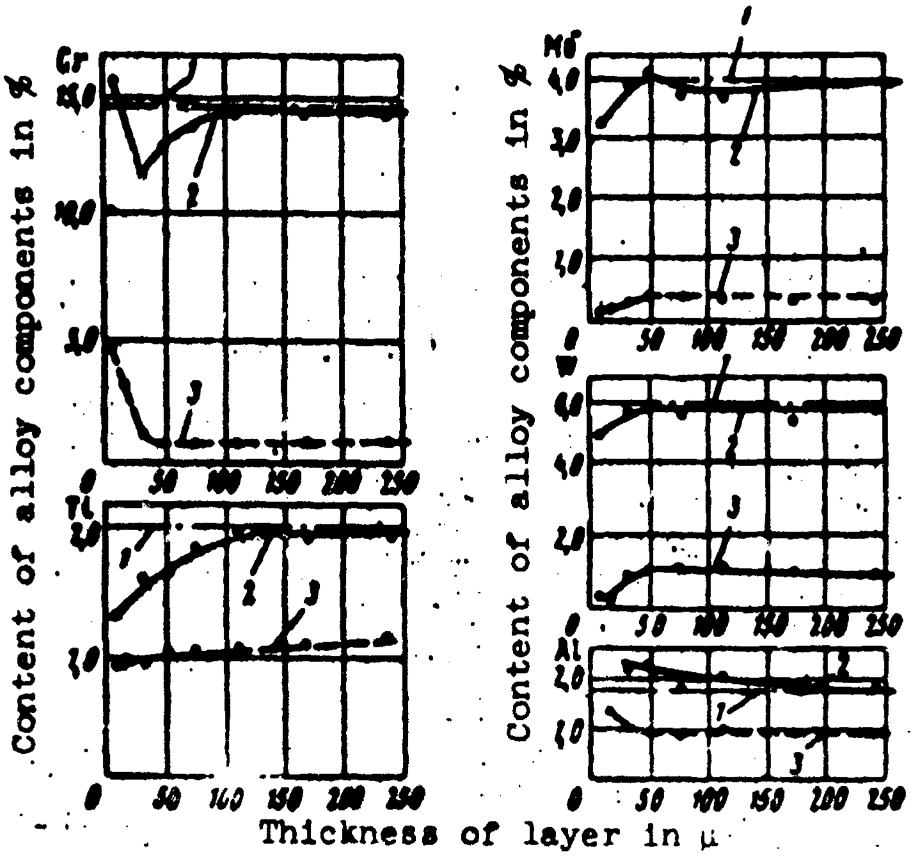


Fig. 1. Distribution of alloy components in surface layers of alloy EI617 in process of endurance test 800° for 1018 hr. 1 – average content of alloy components in alloy, 2 – total content of alloy components in anode deposit and electrolyte, 3 – content of alloy components in anode deposit.

This work traced effect of loaded state on structural changes connected with diffusion processes in surface and internal layers of heat-resisting nickel alloys EI437B, EI617, and EI929.

Samples of alloy EI617 were tested for endurance at 800° for 1018 hr with maximum stress equal to 18 kg/mm^2. Simultaneously in the working part of furnace we heated a sample without loading ("blank sample"). After test we produced layered phase-shift analysis of samples [4].

By anode dissolution in electrolyte containing 10 g ammonium sulphate and 10 g citric acid in 1 liter water we removed 8 layers with overall thickness up to 240 μ both from sample "blank sample" and from sample tested for endurance. Anode deposits and corresponding batches of electrolyte, corresponding to solid solution by composition, were subjected to chemical analysis.

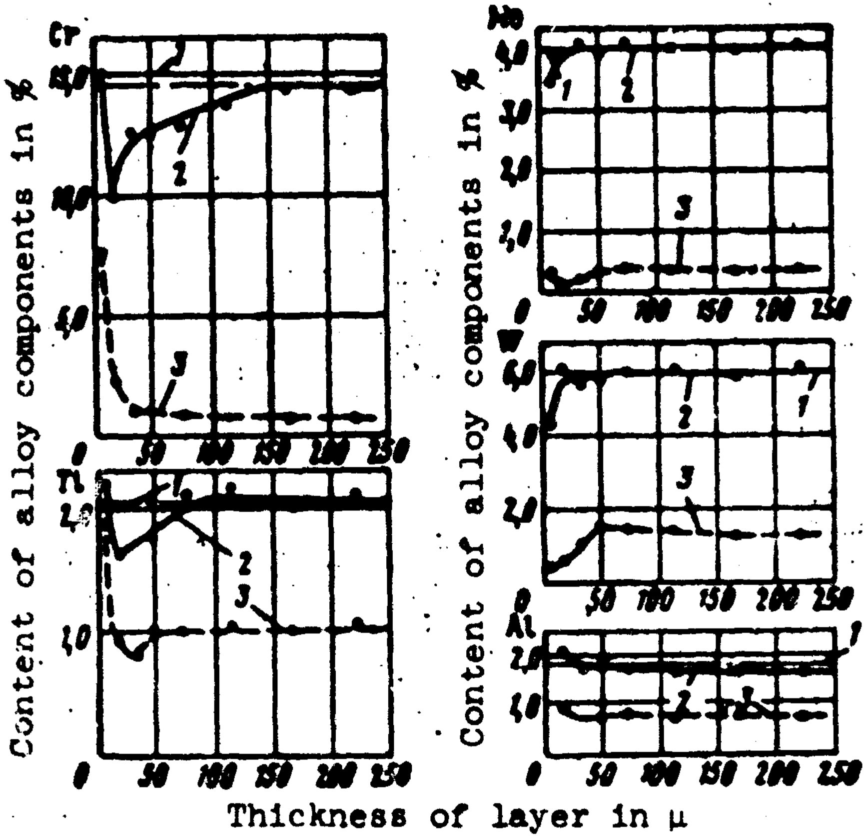


Fig. 2. Distribution of alloy components in surface layers of alloy EI617 after heating without load at 800° for 1018 hr. 1 – average content of alloy components in alloy; 2 – total content of alloy components in anode deposit and electrolyte; 3 – content of alloy components in anode deposit.

Results of layered chemical analysis of anode deposits are presented in Figs. 1 and 2. First surface layer of 5-7 μ thickness consists mainly of oxides of type Me_2O_3 with trigonal crystal structure. This layer is a solid solution of isomorphic oxides Cr_2O_3, Al_2O_3, $NiTiO_3$ on Cr_2O_3 base. In the sample tested for endurance there are somewhat less oxides than in sample "blank sample." This is possibly connected with mechanical losses during variable deformation. In the thin surface layer the overall content of titanium, molybdenum, and tungsten in anode deposit and electrolyte is less than in internal layers of alloy, which is caused by volatility of oxides of molybdenum and tungsten.

Strengthening intermetallic α'-phase was not revealed in surface layer.

In investigated samples oxides are present in a layer of up to 40 μ thickness. Content of strengthening α'-phase is less than normal in it. Solid solution is strongly depleted by alloy components, especially chromium and titanium. Layers with thickness from 40 to 120 μ are also depleted by alloy components, but to a smaller degree than the preceding. It is characteristic that in these layers only solid solution is depleted by chromium, whereas intermetallic phase is not changed qualitatively and quantitatively.

Overall thickness of surface layer is approximately identical and composes 120-150 μ with noticeable change of chemical and phase composition in sample tested for endurance and in sample "blank sample."

The influence of loaded state at high temperatures on phase changes of internal layers of heat-resisting nickel alloy EI437B, EI617, EI929 was studied.

Samples of shown alloys were stress-rupture tested and fatigue tested at temperatures corresponding to hardening and softening during aging. Fatigue tests were conducted during repeated-alternating bend on P-391 machine with 200 cps frequency. Unloaded samples "blank samples" were stacked in working space of heating furnaces simultaneously with tested sample. Phase composition of alloys was determined by means of electrolytic separation of phases and subsequent X-ray structural and chemical analysis of isolated deposits.

For separation of phases we applied electrolytes 1 and 3 (see p. 26). In electrolyte 1 strengthening intermetallic phase, carbide, and boride phases are isolated; in electrolyte 3 only carbide and boride phases. Surface oxidized layers of alloys were preliminarily removed by anode dissolution in electrolyte 3. Internal layers of alloys corresponded to average chemical and phase composition.

Samples of alloy EI437B, heat treated according to specifications, were fatigue tested and stress-rupture tested at a temperature of softening (800°).

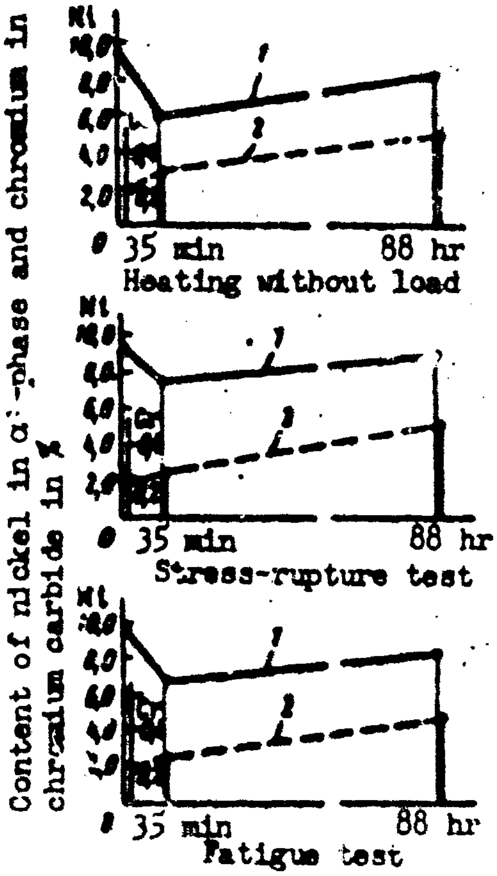


Fig. 3. Change of content of α'-phase and chromium carbides in alloy EI437B in process of stress-rupture test and fatigue test at 800°. 1 — content of nickel in α'-phase; 2 — content of chromium in chromium carbides.

Time of holding was 35 minutes and 88 hours. By X-ray diffraction analysis of anode deposits the following phases were revealed: intermetallic α'-phase $Ni_3(Al, Ti)$ containing an insignificant quantity of chromium; chromium carbides of type Cr_7C_3 and $Cr_{33}C_6$; titanium carbonitride Ti(C, N). Phases $Ni_3(Al\ Ti)$; Cr_7C_3; Ti(C, N) were revealed in alloy in initial state.

In various heat-resisting alloys the intermetallic phase differs mainly by ratio of content of titanium to aluminum. In investigated alloy EI437B the ratio of Ti to Al with respect to weight is 3.25; in α'-phase of initial alloy and alloy aged at 800° this ratio is practically the same.

Loaded state also does not noticeably affect the composition of α'-phase, but causes change of its quantity. The change of quantity of α'-phase and chromium carbides can be indicated approximately by change of content of nickel and aluminum in them respectively (Fig. 3).

Aging of samples of alloy EI437B at 800° occurs under conditions when so-called phenomenon of "recovery during aging" appears. This phenomenon is studied most in detail on aluminum alloys; it was revealed earlier in alloy EI437 [5].

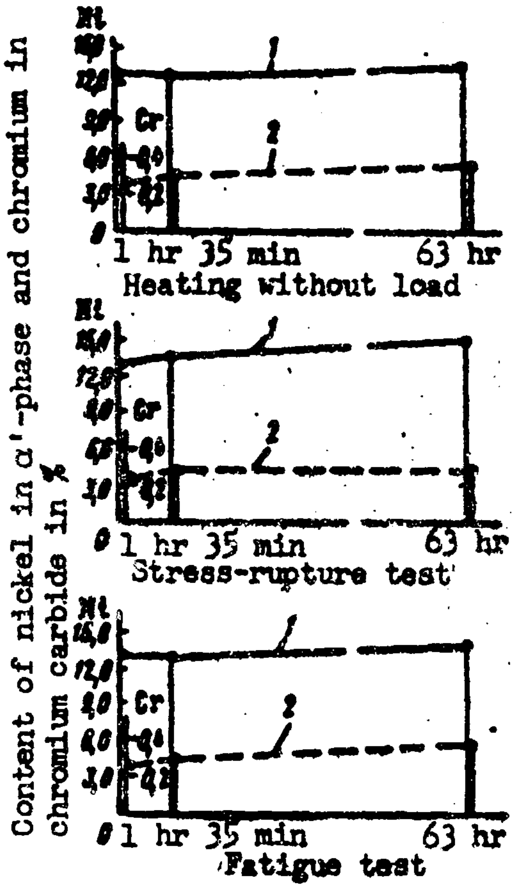
Phenomenon of recovery is usually explained by the fact that products of disintegration of solid solution, forming during low-temperature aging, are partially or completely destroyed at higher temperature.

During low-temperature aging (up to 600°) of alloy EI437B so-called k-state is revealed, characterized in particular by unusually large electrical resistance [6]. Phenomenon of recovery in process of aging at 800° in first interval of time (35 minutes) is accompanied apparently by destruction of k-state and dissolution of unstable particles of α'-phase. Increase of duration of aging to 88 hours promotes separation of α'-phase. Analogous processes connected with phenomenon of "recovery" ta place in alloy EI437B, test at 800° under load, but flow with somewhat different speed. As can be seen from Fig. 3, process of recovery during aging occurs during stress-rupture test with lower rate than during fatigue test or during heating without load. Thus, loaded state can accelerate when heating alloy EI437B, but can somewhat delay processes connected with phenomenon of recovery during aging.

Aging of alloy EI437B at 800° both in conditions of load and without does not affect content of primary carbonitride phase Ti(C, N). With increase of duration of aging the content of chromium carbides is continuously increased. This process occurs with lower rate during fatigue test.

By X-ray diffraction analysis in alloy EI437B, taken in initial state, we revealed trigonal chromium carbide Cr_7C_3. In alloy aged at

800° for 88 hours both under load and without it we revealed cubic chromium carbide $Cr_{23}C_6$ along with trigonal carbide Cr_7C_3. Phase transformations in samples, weakening without load, flow more intensely than in samples of alloy subjected to fatigue and stress-rupture tests.



Heating without load

Stress-rupture test

Fatigue test

Fig. 4. Change of content of α'-phase and chromium carbides in alloy EI617 in process of fatigue and stress-rupture tests at 800°. 1 – content of nickel in α'-phase, 2 – content of chromium in chromium carbide.

Samples of alloy EI617, heat treated according to specifications, were fatigue and stress-rupture tested at 800° for 1 hour 35 minutes and 63 hours, at 900° for 1 hour 20 minutes and 42 hours 38 minutes. According to X-ray structural analysis, in alloy EI617 the following phases were revealed: α'-phase on Ni_3Al base, titanium carbide TiC, binary carbide $Ni_3(Mo, W, Cr)_3C$, cubic chromium carbide $(Cr, W, Mo, V)_{23}C_6$.

Since alloy EI617 differs from alloy EI437B by large content of alloy components, aging processes are developed less intensely in it. In alloy EI617 the ratio of weight of titanium to aluminum is close to one (~1.20). In intermetallic phase of this alloy the ratio of Ti to Al is approximately the same; it is not changed during heating under load and without load. Intermetallic phase in given alloy contains, besides aluminum and titanium, some quantity of chromium, tungsten, molybdenum, and vanadium.

Content of titanium carbide TiC and binary carbide $Ni_3(Mo, W, Cr)_3C$ in practice does not change in process of tests with

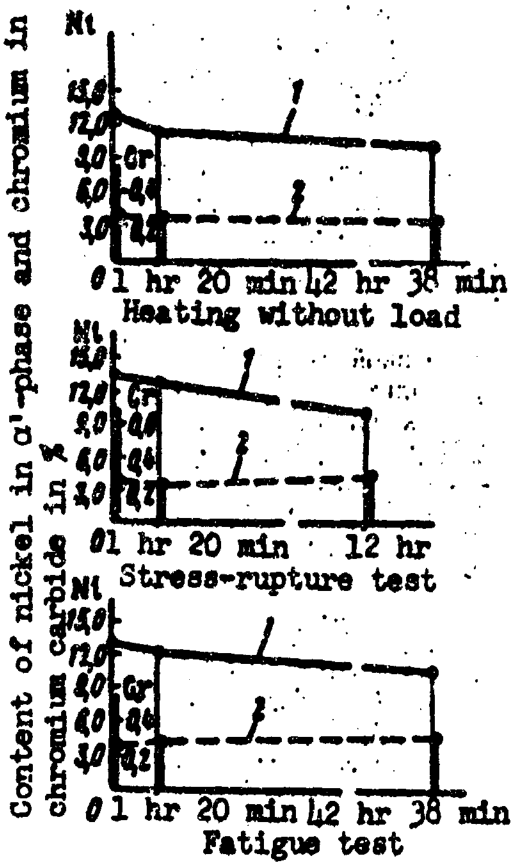


Fig. 5. Change of content of α'-phase and chromium carbides in alloy EI617 in process of fatigue and stress-rupture tests at 900°, 1 – content of nickel in α'-phase, 2 – content of chromium in carbide phases.

these same conditions. Change of content of carbide phase in process of aging at 800 and 900° leads basically to change of quantity of cubic carbide $Me_{23}C_6$. As can be seen from Figs. 4 and 5, chromium content (basic element entering composition of phase $Me_{23}C_6$) is increased somewhat with increase of duration of aging. Loaded state of alloy EI617 scarcely affects behavior of cubic chromium carbide.

Heating of alloy EI617 at 800° leads to some increase of content of α'-phase, more intense in samples that are stress-rupture tested. Aging of alloy at 900° is accompanied by dissolution of α'-phase and the alloy is softened. Intensity of softening of alloy is the greatest when stress-rupture testing samples.

Samples of alloy EI929, heat treated according to specifications, were subjected to alternating load in process of fatigue test, and also complex loading, including static tension and alternating bend. Tests were conducted at 900° for 82-87 hours. Given alloy differs from alloys EI437B and EI617 by more complicated alloying and a higher content of strengthening α'-phase (more than 30% α'phase is present in alloy). By X-ray diffraction analysis of carbide deposits we revealed phase TiC, binding ~0.04% titanium, binary carbide $Me^1_nMe^2_mC$, containing 0.11-0.16% nickel, and cubic carbide $Me_{23}C_6$. Besides, a small quantity of boride

$(Mo, W, Cr)_3B_2$ was revealed in the alloy. As can be seen from results of phase-shift analysis (Table 1), content of carbide and boride phases does not change in practice in process of aging at 900°.

Table 1. Influence of Character of Load at 900° on Phase Composition of Alloy EI929

Method of loading of sample	Magnitude of load and duration of test	Content of elements in anode deposits separated in electrolyte 1 in %*				Content of elements in carbide phase in %*					Phase composition of anode deposits
		Ni	Cr	Al	Ti	Ni	Cr	Ti	Mo	W	
Without load	—	27,0	1,04	2,73	1,31	0,16	0,10	0,04	0,22	0,14	α' and carbides
Without load (sample – blank sample)	$\sigma=0$ kg/mm²; $\tau=82$ hr 35 min	26,9	1,06	2,29	1,40	0,14	0,12	0,04	0,33	0,13	α' and carbies
Alternating load (Endurance)	$\sigma=30$ kg/mm²; $\tau=87$ hr 50 min	27,3	1,05	2,33	1,35	0,11	0,11	0,04	0,21	0,13	α' and carbides
Complex load	$\sigma_{max}=19,5$ kg/mm² $\sigma_{st}=15$ kg/mm² $\tau=82$ hr 35 min	27,7	1,12	2,14	1,44	0,13	0,12	0,05	0,20	0,10	α' and carbides

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*Remaining elements in anode deposits were not determined.

In process of aging of alloy at 900° for 82 hours 35 minutes, content of α'-phase also does not change. Fatigue test of samples of given alloy with maximum bending stress equal to 30 kg/mm² at 900° did not cause change of quantity of α'-phase, but according to X-ray diffraction analysis it led to its coagulation. Simultaneous action of repeated-alternating, and static loads also does not affect quantity of α'-phase in alloy.

Conclusions

1. Alternating load of samples of alloy EI617 during fatigue test (800° - 1018 hours) does not noticeably affect intensity of process of oxidation and also depletion of surface layers by alloy components as compared to action of only heating.

2. In alloy EI437B, heat treated according to specifications, fatigue and stress-rupture tested at temperature of softening 800°; and also in alloy heated at 800° without load, there occurs process of recovery, causing partial dissolution of α'-phase in initial stage of aging. Processes of recovery during aging flow less intensely in process of stress-rupture test of alloy than during fatigue test and during its heating without load.

3. In alloy EI617 the influence of loaded state on phase changes shows in smaller degree than in low-alloy EI437B.

Aging of alloy EI617 at 900° is accompanied by softening, occurring intensely both during fatigue test and heat without load.

In high-alloy EI929 action of loads at 900° hardly affects phase composition.

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PHASE COMPOSITION OF SURFACE LAYERS OF HEAT-RESISTING ALLOYS AFTER HEATING IN DIFFERENT MEDIA*

M. N. Kozlova, N. F. Lashko, and N. M. Rudneva

Structure and composition of surface layer has great effect on efficiency of parts from heat-resisting alloys at high temperatures. The most noticeable change of structure and properties of surface layer is observed during interaction of alloys with oxidizing medium, and also a result of work hardening, created during machining.

Oxidation of alloys causes depletion of surface layer by alloy components, which leads to its softening and change of heat-resisting properties. Surface work hardening also causes lowering of characteristics of heat resistance, since plastic deformation accelerates diffusion processes.

In connection with this it is necessary on one hand to protect heat-resisting alloys from oxidation, on the other – to produce removal of work hardening in surface layer.

For prevention of oxidation it is expedient to carry out heating during heat treatment and during hot deformation, in particular

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*N. A. Shumilina, Senior Technician V. K. Manokhina, and K. V. Smirnova participated in experimental part of work.

stamping in a medium of inert gases. In medium of inert gases it is expedient to produce annealing of parts for removal of residual stresses appearing as a result of work hardening. Experiments of treatment of heat-resisting alloys in medium of argon and helium showed that they protect surface of alloys from oxidation, but effectiveness of protection depends on purity of applied media. Technical neutral media, containing some oxygen, can cause partial oxidation of surface layer. Thus, for example, during annealing of alloy ZhS6-K at 1000° in argon, there is observed decrease of hardness in layer with ~20 μ thickness, in connection with oxidation of alloy and depletion of surface by alloy components.

Application of these gaseous environments is limited in connection with their scarity and high cost. Therefore, it was proposed to apply technical or purified nitrogen during annealing, and also ammonia or halide salt of ammonium, disintegration products of which are nitrogen and hydrogen at high temperatures.

Surface of alloys heated in these media is actually obtained pure and oxidation is relatively insignificant. Media containing nitrogen were recommended for application during heat treatment, annealing, and brazing of stainless steels and heat-resisting nickel and titanium alloys [1]. It was assumed that disintegration products of halide of ammonium during interaction with oxide on surface of alloy reduces them. However, possibility of interaction of alloy with nitrogen was not taken into account in recommendations. For clarification of this question we conducted layered phase-shift analysis of certain heat-resisting nickel alloys after their treatment in different gaseous environments containing nitrogen.

We investigated phase and overall chemical composition of surface layers of alloy EI437B after its annealing for removal of work hardening, created by machining, in medium of nitrogen, ammonia, and air.

For investigation we took 40 × 50 mm plates cut from discs, annealed at 850° in various nitrogen-containing media, and aged at 700° in air. For separation of phases we applied water (5 ml H_2SO_4 (1.84), 10 g citric acid, 1000 ml of water) and in certain cases alcohol electrolyte (50 ml HCl, 1000 ml methanol). Electrolysis was conducted at current density 0.06 amp/cm^2, in first case – at room temperature, in second – with cooling of electrolyte to -5, -7°.

In water electrolyte solid solution is dissolved anodely, and strengthening α'-phase on $Ni_3(Al, Ti)$ base, nitride, carbide, and boride phases are separated in the form of deposit. In alcohol electrolyte solid solution and α'-phase are dissolved anodely and nitride, carbide, and boride phases are separated in the form of deposit. Application of alcohol electrolyte has special value during establishment of nature of phases by X-ray structural method, since solid solution and α'-phase are dissolved which permits determining small quantities of other phases, particularly carbide, nitride, and boride, with greater accuracy.

When annealing in all investigated media (Table 1) there is observed oxidation of surface layers in connection with the fact that final operation of annealing is conducted in air furnaces, and also possibly in connection with the fact that gaseous media are not always sufficiently pure. Oxides of type Me_2O_3 are formed on surface of alloy mainly Cr_2O_3. Thickness of oxidized layer at all conditions of annealing is approximately identical and composes 0.020-0.030 mm.

Table 1. Distribution of Alloy Components Between Phases in Surface Layers of Alloy EI437B, Annealed in Different Conditions

Depth of layer, mm	Conditions of annealing	Contents of elements in anode deposits* %				Content of elements in electrolyte* %				Depth of layer, mm	Phase composition of anode deposits
		Ni	Cr	Ti	N	Ni	Cr	Ti	N		
0,005	Annealing at 750° - 8 hr in air furnaces	8,82	2,08	2,04	—	60,00	19,55	1,33	—	0,005	$\alpha' + Me_2O_3 + \alpha^*$ (depleted solid solution)
0,016		7,02	1,61	1,31	—	64,50	19,83	1,15	—	0,013	
0,030		7,62	0,04	1,30	—	65,65	20,50	1,33	—	0,028	$\alpha' + Me_2O_3$
0,059		7,59	0,51	1,29	—	65,63	19,93	1,22	—	0,077	α'
0,008	Annealing at 850° - 2 hr in nitrogen + aging at 700° - 8 hr, cooling in air	12,3	3,70	1,59	—	56,0	15,30	0,79	—	0,006	$\alpha' + Me_2O_3$
0,020		8,30	1,11	1,69	1,63	65,5	18,10	1,07	0,63	0,029	$\alpha' + Me_2O_3$
0,041		8,78	0,69	1,69	0,90	65,0	21,20	1,09	0,59	0.065	α'
0,078		9.00	0,78	1,59	0,51	64,6	21,10	1,15	—	0,127	α'
0,006	Annealing at 850° - 2 hr in nitrogen + aging at 700° - 8 hr, cooling in air	8,50	2,00	1,73	0,75	65,1	17,60	0,76	0,34	0,006	$\alpha' + Me_2O_3$
0,017		9,10	1,09	1,62	0,13	63,5	17,90	0,90	0,13	0,022	$\alpha' + Me_2O_3$
0,038		9,80	0,78	1,69	0,11	64,9	20,30	0,98	0,09	0,052	α'
0,081		9,30	0,70	1,62	0,09	65,0	20,50	0,96	0,09	0,102	α'
0,006	Annealing at 850° - 2 hr in argon + aging at 700° - 8 hr, cooling in air	8,80	1,30	0,98	—	—	18,70	0,73	—	0,007	$\alpha' + Me_2O_3$
0,017		9,92	0,92	1,03	—	—	19,20	0,83	—	0,016	α'
0,049		9,34	0,61	1,14	—	—	19,70	0,83	—	0,051	α'
0,083		9,12	0,58	1,22	—	—	19,60	0,76	—	0,085	α'

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*To weight of alloy.

Formation of oxides in case of annealing in air furnaces can be explained by diffusion of oxygen in depth of metal. Interdiffusion of atoms of chromium to surface, which is characteristic during heating of alloy to higher temperatures, does not occur in given case (content of alloy components in each separate layer is approximately equal to their average content in alloy). Apparently the same mechanism of formation of oxides acts during annealing of alloy in nitrogen an ammonia. Formation of chromium oxides occurs due to their depletion of solid solution. Presence of particles of depleted solid solution (parameter of crystal lattice is considerably less than that of solid solution of alloy in normal state) in anode deposits isolated from samples annealed in air furnaces, indicates some disturbance of structure of the upper layers. When annealing in medium of nitrogen and ammonia, diffusion of nitrogen occurs in alloy. The most intense saturation by nitrogen occurs during annealing in medium of ammonia. During X-ray structural investigation of anode deposits isolated in alcohol and water electrolytes from samples annealed in medium of nitrogen and ammonia, nitride phases were not revealed. Possibly nitrogen is partially dissolved in oxides, partially in α'-phase. Considerable part of nitrogen passes into solid solution.

We investigated phase composition or surface layer of alloy ZhS6-K after its annealing in vapors of ammonium chloride. Annealing was produced at 970° for two hours. Samples were loaded into container with ammonium chloride (0.5-1 g NH_4Cl in 1 liter of volume of container) in mixture with sand.

Table 2 contains basic results of investigation of phase and chemical composition of surface layer of alloy.

Table 2. Content of Alloy Components in Anode Deposits Separated from Alloy ZhS6-K After Its Annealing in Vapors of Ammonium Chloride

Depth of layer, mm	Conditions of treatment of blades	Content of elements in anode deposit							Content of nitrogen in electrolyte, %	Depth of layer, mm	Phase composition of anode deposits
		Ni	Co	Al	Ti	Cr	Mo	N			
0,009	Annealing at NH_4Cl	0,37	Traces	0,20	1,[illegible]	0,[illegible]	Traces	1,20	0,[illegible]	0,013	Al_2O_3, TiN, TiC
0,027	The same	[illegible],7	1,16	3,25	2,[illegible]	1,15	1,17	0,[illegible]	0,[illegible]	0,[illegible]	α'
0,054	The same	41,9	1,46	3,[illegible]	2,42	1,[illegible]	1,[illegible]	0,[illegible]	0,16	0,[illegible]	α'
0,[illegible]	The same	43,[illegible]	1,[illegible]	3,04	2,[illegible]	1,[illegible]	1,[illegible]	0,20	0,12	0,1[illegible]	α'
0,[illegible]	Machining	—	—	—	—	—	—	None	None	—	α'
0,007	The same	—	—	—	—	—	—	None	None	—	α'

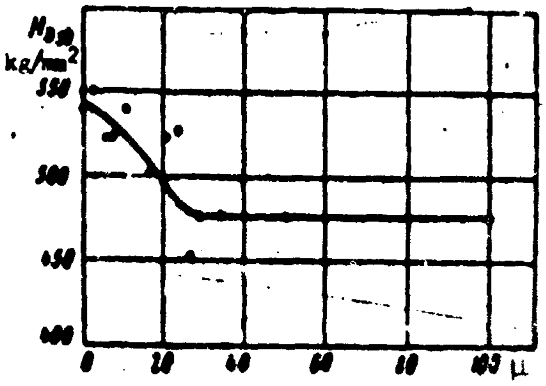

Fig. 1. Change of microhardness through depth of surface layer of alloy ZhS6-K, having past annealing in medium of ammonium chloride.

When annealing in vapors of ammonium chloride there occur noticeable changes of phase composition in surface layer. The sharpest of these changes occur in layer with depth up to ~10 μ. Here oxides are formed and α'-phase is destroyed completely. The alloy is enriched by nitrogen, which enters composition of solid solution and forms nitride phases. In anode deposits isolated from layer at a depth up to 10 μ, titanium nitride TiN and oxides on Al_2O_3 base are revealed by X-ray diffraction analysis. At a depth of ~25 μ the composition of alloy is practically the same as in initial state.

During the study of phase composition of a similar sample after machining (without annealing in vapors of ammonium chloride), nitrogen was not revealed in surface layers.

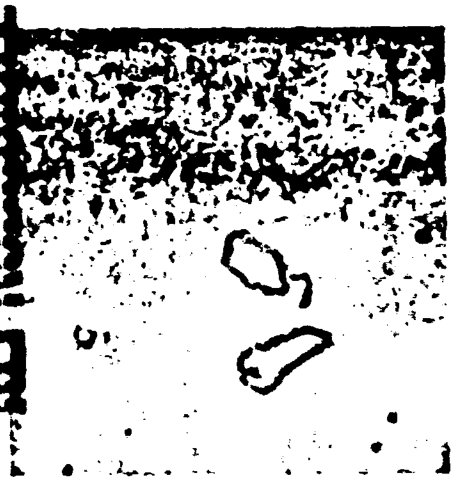

Fig. 2. Microstructure of alloy ZhS6-K, having past annealing in medium of ammonium chloride.

Microhardness of surface layer of blade annealed in vapors of ammonium (Fig. 1) turned out to be 75 kg/mm² higher than microhardness of core, which is probably connected with presence of nitrides, oxides, and solid solution entriched by nitrogen.

During investigation of microstructure (Fig. 2), it was noticed that layer with modified structure spreads to a depth of ~20 μ.

Heat resistance of alloy ZhS6-K (according to T. V. Levchenko) after annealing in vapors of ammonium chloride and also alloy EI437B (according to T. A. Gordeyeva) after annealing in medium of ammonia, is considerably lowered.

Experiments of application of nitrogen as a neutral medium during heat treatment of alloy ZhS6-K and also during heating under stamping and subsequent heat treatment of alloy EI617* showed that surface layers of alloys are saturated by nitrogen during this.

Heating of alloy under stamping was produced at 1190° in nitrogen in 4 stages (according to number of passes during stamping) with overall duration of 3.5 hours. After each heating the alloy was cooled to 800°. After stamping, parts and samples were subjected to heat treatment also in nitrogen according to the following conditions: heating at 1190° ± 10 for 2 hours, cooling to 800° in nitrogen, and then from 800° to room temperature in air; second heating at 1050° for 4 hours with cooling to 800° in nitrogen, aging at 800° for 16 hours in air.

Table 3. Content of Elements in Anode Deposits Separated in Alcohol Electrolyte from Alloy EI617 After Heating Under Stamping and Heat Treatment in Nitrogen

Depth of layer, mm	Content of elements in anode deposits, %					Content of nitrogen in electrolyte, %	Depth of layer, mm	Phase composition of anode deposits
	[illegible]	Cr	Ti	Mo	W			
[illegible]	[illegible]	0,47	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Al_2O_3, TiN, Cr_2O_3
[illegible]	[illegible]	[illegible]	[illegible]	0,11	[illegible]	[illegible]	[illegible]	Al_2O_3, TiN, Cr_2O_3
[illegible]	[illegible]	[illegible]	[illegible]	0,11	[illegible]	[illegible]	[illegible]	TiN, Al_2O_3, Cr_2O_3
[illegible]	0,14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	TiN, Al_2O_3, Cr_2O_3 solid solution
[illegible]	[illegible]	[illegible]	0,15	0,11	[illegible]	[illegible]	—	—

Results of phase-shift analysis of surface layers of alloy EI617 are given in Tables 3 and 4.

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*Investigation was conducted jointly with A. P. Vlasov.

Table 4. Content of Elements in Anode Deposits Separated in Water Electrolyte from Alloy EI617 After Heating Under Stamping and Heat Treatment in Nitrogen

Depth of layer, mm	Content of elements in anode deposits, %						Content of nitrogen in electrolyte, %	Depth of layer, mm	Phase composition of anode deposits
	Ni	Al	Ti	Cr	Mo	N			
0,005	1,66	0,35	2,09	1,28	0,27	2,15	0.60	0,005	Al_2O_3, Cr_2O_3+ +solid solution
0,016	2,70	0,68	1,55	0,69	0,25	1,12	0,28	0,018	Al_2O_3, Cr_2O_3+ +solid solution
0,040	6,24	0,76	1,48	0,95	0,27	0,55	0,25	0,040	Solid solution + +α′
0,105	9,14	—	1,23	1,07	0,32	0,32	0.14	0,096	α′+solid solution
0,160	13,47	—	1,22	0,82	0,38	0,05	0,17	0,150	α′
0,241	14,55	0,93	1,32	0,93	0,40	0,02	0,13	0,200	α′
0,320	14,50	0,90	1,32	0,99	0,41	0,02	0,04	—	—

Heating of alloy in purified nitrogen, as phase-shift analysis shows l ads to formation of nitrides, to saturation of solid solution by nitrogen, and to partial oxidation.

Layer of modified chemical and phase composition is revealed at a depth of up to 0.1 mm. Nitrogen diffuses to approximately the same depth. Nonuniform enrichment by nitrogen of different samples subjected to heating in medium containing nitrogen is characteristic. Content of nitrogen in solid solution (electrolyte) for separate samples oscillates within limits of 0.2-0.6%. Large part of nitrogen is in bound form – in titanium nitrides and possibly in oxides being hydroxynitrides. It is known that formation of hydroxynitrides was observed in various alloys, from example, in niobium alloys [2]. The possibility of formation of hydroxynitrides of type $Me_2(O, N)_3$ on Me_2O_3 oxide base, revealed in alloy EI617, is not excluded.

Alloy ZhS6-K was heated at 1220° for 4 hours and was cooled to 800° in medium of purified technical nitrogen. Further cooling was produced in air.

Table 5. Phase Composition of Anode Deposits Isolated from Surface Layers of Alloy ZhS6-K, Heat Treated in Purified Technical Nitrogen

Depth of layer, mm	Phase composition of anode deposits
0,013	α', TiN, Al_2O_3
0,04	α', Ti (C. N), Al_2O_3
0,07	α', TiC, Al_2O_3
0,12	α', TiC, Me_3B_2
0,20	α', TiC, Me_3B_2

Results of phase-shift analysis of anode deposits isolated from surface layers of alloy ZhS6-K are given in Table 5.

Table 6 contains content of nitrogen in isolated phases and in electrolyte throughout depth of surface layer.

Table 6. Content of Nitrogen in Electrolyte and in Anode Deposits Separated from Surface Layers of Alloy ZhS6-K

Depth of layer, mm	Content of nitrogen, %	
	in anode deposits	in electrolyte
0,014	0,84	0,56
0,04	0,60	0,29
0,09	0,12	0,14
0,11	0,02	0,08
0,20	0,01	0,01

Phase composition and structure of surface layer of alloy ZhS6-K after heat treatment in nitrogen are essentially changed at a depth approximately up to 0.1 mm. In layer with ~0.05 mm thickness dispersed nitrides and carbonitrides of titanium are formed. Separations of intermetallic phase $Ni_3(Al, Ti)$ in this layer are more than dispersed in core of alloy. In layer with depth up to ~0.1 mm dispersed aluminum oxides are also revealed. Regarding nitrogen, it enters composition of isolated phases and solid solution. Raised content of nitrogen is observed to a depth of ~0.2 mm.

Table 7. Stability of Alloy ZhS6-K, Heat Treated in Pure Technical Nitrogen, During Stress-Rupture Test at 975° and $\sigma = 20$ kg/mm^2

Time to failure, hr	δ %	ψ %	Allowance on radius, mm
50	1,2	2,3	Without allowance
49	3,8	4,0	0,1
47	3,5	3,5	0,3
60	2,7	3,3	0,5
48	2,7	3,2	0,7

Layer with up to ~0.1 mm from surface has lowered characteristics of plasticity. This appears particularly in lowering of elongation per unit length and transverse compression of samples destroyed during stress-rupture test at 975° and $\sigma = 20$ kg/mm^2. After removal of surface layer with depth ≥0.1 mm, influence of nitration and partial oxidation does not show on properties of alloy in practice (Table 7).

Conclusions

1. Annealing and heat treatment of heat-resisting alloys, conducted in media containing nitrogen, especially in ammonia and ammonium chloride, causes enrichment of surface layer by nitrogen, which leads to lowering of mechanical characteristics of alloy. Application of heat treatment in these media is possible under condition of removal of layer entriched by nitrogen.

Literature

1. A. Ya. Ishchenko and V. I. Kolchinskiy. "Metal science and heat treatment of metals," 1960, No. 11.

2. G. Brauer. Less-Common Metals, 1960, Vol. 2, p. 131.