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SOLID SOLUBILITY LIMITS OF Y AND Sc IN THE ELEMENTS W, Ta, Mo, Nb, AND Cr

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FOREWORD

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ABSTRACT

Alloys and diffusion couples of yttrium and scandium with the refractory elements Nb and Ta of Group V and Cr, Mo, and W of Group VI have been examined by means of the optical microscope, X-ray diffraction, and mass spectrometry. The results indicate that the solid solubility of Y and Sc in these elements is less than 1 part per million. This is in conformity with the Hume-Rothery Rule that only a very restricted range of solid solution can be expected when the atomic diameter of solvent and solute differ by more than 14 to 15 per cent.

This technical documentary report has been reviewed and is approved.

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TABLE OF CONTENTS

PAGE

INTRODUCTION 1

THERMAL AND CRYSTALLOGRAPHIC DATA 1

EXPERIMENTAL 2

RESULTS 7

I. ALLOYS WITH YTTRIUM 7

II. ALLOYS WITH SCANDIUM 12

CONCLUSIONS 15

REFERENCES 15

LIST OF ILLUSTRATIONS

1. Yttrium-Chromium Phase Diagram 16
2. Yttrium-Niobium Phase Diagram 17
3. Yttrium-Molybdenum Phase Diagram 18
4. Yttrium-Tantalum Phase Diagram 19
5. Yttrium-Tungsten Phase Diagram 20
6. Tungsten Tube High Temperature Furnace 21
7. Pointed Counter Electrode as a Mass Spectrograph Microprobe 22
8. Layout of Mass Spectrograph (Schematic) 23
9. 99.999% Cr Argon Arc Melted as Cast 24
10. 75 Cr 25Y Argon Arc Melted as Cast 24
11. 75 Cr 25Y Annealed 68 hr 1200°C 24

LIST OF ILLUSTRATIONS (cont.)

12.	Nb as Cast (Nb + Carbide Traces)	25
13.	75 Nb 25Y As Cast (Nb + Unresolved Eutectic)	25
14.	X-ray Diffraction Patterns of Nb and a 75 Nb 25Y Alloy (BCC Nb + HCP Y) (Cr $K\alpha$ Radiation)	26
15.	99.2 Nb 0.8Y Annealed 233 hr 1350° C (Nb + Y)	25
16.	99.8 Nb 0.2Y Annealed 233 hr 1350° C (Nb + Y)	25
17.	Effect of Yttrium Additions on the Lattice Parameter of Niobium	27
18.	Lattice Parameter Curve of Nb-Hf Alloys	28
19.	Mo-Y Diffusion Couple Interface. Mo + Eutectic	29
20.	Sparked Areas Near Mo-Y Interface	29
21.	Mass Spectra from Regions Near Mo-Y Interface	29
22.	Y-Ta Diffusion Couple	30
23.	Y-W Diffusion Couple	30
24.	Sparked Areas Near Y-W Interface	30
25.	Scandium Crystals on Tungsten Support Wire	31
26.	96.5 Cr 3.5 Sc as Cast	32
27.	95 Nb 5 Sc Annealed 113 hrs at 1200° C	32
28.	Mo Cylinders Encapsulating Sc-Mo Diffusion Couple	33
29.	Section Through Sc-Mo Diffusion Couple and Encapsulating Cylinder	33
30.	Sparked Areas Near Mo-Sc Interface	34
31.	Tantalum Globules in Scandium Matrix Near Sc-Ta Diffusion Couple Interface	35
32.	Sparked Areas Near Sc-Ta Interface	35
33.	Region of Tungsten Rod at W-Sc Interface	36

INTRODUCTION

The beneficial effects of adding small amounts of rare earth metals to refractory elements and alloys are well known. To mention but a few, small additions of cerium or rare earth mixtures to 80-20 Ni-Cr alloys considerably modify the oxidation processes occurring on the alloy surfaces at elevated temperatures and lead to the formation of a uniform and tenacious oxide film which increases the ability of the alloys to withstand progressive oxidation. Traces of thorium exert a beneficial influence on the mechanical properties of refractory elements such as tungsten as the result of grain refinement and the reduction of oxygen and nitrogen contamination. It would seem from these results that the elements yttrium and scandium, although not strictly rare earths on account of their not being in the Lanthanide series, could likewise exert a beneficial influence on metals in Groups V and VI of the Periodic Table, namely Nb and Ta, and Cr, Mo and W. Accordingly, the present investigation was undertaken to determine, if possible, the terminal solid-solubilities of the elements Y and Sc in the elements W, Ta, Mo, Nb, and Cr at temperatures up to 2000°C.

THERMAL AND CRYSTALLOGRAPHIC DATA

Thermal and crystallographic data for yttrium and scandium along with those of the refractory elements of Groups V and VI are given below in Table 1.

Table 1

Crystallographic and Thermal Data of Alloying Elements

Element	Structure	Lattice Parameters Å	Pauling Atomic Radius Å C.N. = 12	Melting Point °C	Boiling Point °C
21 Sc	Hex. C.P.	a = 3.3090 c = 5.2733	1.620	1547	2400
39 Y	Hex. C.P.	a = 3.6474 c = 5.7306	1.797	1200 1539*	3027
41 Nb	Cubic B. C.	a = 3.2993 to 3.3024	1.456	2400 2585*	(3000)
73 Ta	Cubic B.C.	a = 3.3058	1.457	2977	-
24 Cr	Cubic B.C.	a = 2.8848	1.276	1850	2430
42 Mo	Cubic B.C.	a = 3.1468	1.386	2620	(4700)
74 W	Cubic B.C.	a = 3.16522	1.394	3380	(6700)

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*Own MP determination

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According to Hume-Rothery (1) there are limits set upon the range of solid solution resulting from the relative sizes of the solvent and solute atoms and their valencies. When the atomic diameters of solvent and solute differ by more than 14 to 15 per cent from that of the solvent, the size factor is unfavorable and only a very restricted range of solid solution can be expected. Moreover, a metal of lower valency is more likely to dissolve one of higher valency than vice-versa, especially when the solvent obeys the "(8 - N)-rule" and forms homopolar bonds.

From the atomic radii presented in Table 1, it can readily be seen that except for Sc in Nb or Ta (radius ratio 11.3%), the size factor is extremely unfavorable, a typical example being Y in Nb or Ta where the atomic radii differ by approximately 23.5%. As a result, it can be anticipated that the solid solubilities of Y and Sc in the refractory Groups V and VI elements will be extremely small, with the possible exception of Sc in Nb or Ta.

When the present investigation was initiated, there were no data on the above-mentioned alloy systems available in the literature, but subsequently the book "Rare Earth Alloys" by K. A. Gschneidner (D. Van Nostrand and Co., Inc., 1961) appeared which gave a number of systems taken from Classified Reports. Figs. 1-5 inclusive reproduce diagrams of the systems Y-Nb, Y-Cr, Y-Mo, Y-Ta and Y-W from Gschneidner's book. It will be seen readily that the amount of Y in solid solution is extremely small, in conformity with the Hume-Rothery size-factor rule. No diagrams are available for comparable Sc-containing alloys, but from the crystallographic data in Table 1, similar results are to be expected.

EXPERIMENTAL

Materials Employed

In view of the anticipated low solid-solubility of the rare earth elements in the refractory metals W, Ta, Mo, Nb, and Cr, it was important to employ materials of the highest purity possible in order to avoid any confusion in the identification of second phases and the determination of the solid-solubility limits. The following materials were used:

Yttrium. American Potash and Chemical Co. Purity designation 99.9%. Rare earth maximum impurities 0.1% Dy + Gd + traces Tb. 0.07% O, 0.005% N, 0.001% Mo, 0.015% C.

Scandium. American Scandium Corporation. 99.5% distilled metal.

Tungsten. Westinghouse Corporation. Zone refined rod. Impurities in parts per million, 1-2O, 1-2N, 1-2H, 10C, total metallics less than 50 ppm.

Tantalum. As for tungsten, with total metallics less than 100 ppm.

Niobium (Columbium) (a) Rondelles. Union Carbide Corp. Electron bombarded material. Purity stated to be 99.99%. (b) Metals Resins Corporation. Zone refined. Maximum total impurities 25 ppm. Maximum total O_2 content 9 ppm.

Chromium. United Mineral and Chemical Corp. Pellets. 99.999% purity. Zone refined material not available.

Molybdenum. Westinghouse Corporation. Zone refined Rod. Total impurities less than 50 ppm.

Alloying and Heat Treatment Procedures

Because of the highly oxidizable nature and elevated melting points of the alloying elements, conventional alloying procedures, such as melting under flux in a ceramic crucible, were clearly out of the question. The following alternative alloying techniques were suggested:

1. (1) Alloying by direct melting in vacuum or an inert atmosphere, such as purified helium or argon, using a Kroll-type arc furnace fitted with a non-consumable tungsten electrode and a water-cooled copper hearth.

(2) Electron-beam melting in vacuum.

(3) Levitation melting in an evacuated, or inert atmosphere high frequency furnace to avoid contact with metallic or ceramic materials.

(4) Diffusion-couple techniques using either solid consitutents and solid-state diffusion or liquid Y or Sc in contact with a solid refractory element.

(5) Alloying by the admixture of a fused rare-earth element salt, such as a chloride or fluoride, which decomposes and leaves the rare-earth metal in solution.

On account of the unfavorable densities of the materials, it was found impracticable to employ levitation melting. Ultimately, the methods used were the Kroll furnace technique in which an atmosphere of pure argon was employed and the diffusion couple method in which the liquid rare-earth metal was in contact with solid, zone-refined refractory element.

Alloys made in the Kroll type furnace were in the form of small buttons, each weighing approximately 30 grams. Prior to melting, the furnace was evacuated to a pressure of 10^{-4} Torr by means of a mechanical pump, then flushed 4 times with argon and finally filled with argon to a pressure of approximately 1/2 atmos. The gas was then gettered by melting a 25 gram titanium button in the arc, after which the arc was transferred to the sample proper. Difficulties were frequently encountered with the melting of the samples owing to their tendency to separate into two liquid phases or to a solid plus liquid rare-earth constituent. Added to this difficulty, there was a tendency for the rare earth metal to volatilize and deposit on the water-cooled metal components of the furnace and on the glass enclosure. These losses could be accounted for by weighing the sample before and after melting.

When attempting to form alloys by means of the solid-liquid diffusion couple technique, specimens were in the form of zone refined cylindrical rods, approximately 1/8 inch in diameter and 0.4 inch in length. A rod sample was then placed upright in a small hollow cylinder made of the same metal machined from bar stock, the exterior diameter of the cylinder being approximately 1/2 inch and with a wall thickness of about 1/16 inch. The samples were then surrounded with pieces of Y or Sc and the cylinders closed with a 1/8" thick cap machined from the same bar stock as the encapsulating cylinder. The cylinder and its contents were then suspended in a tungsten tube resistance furnace having a tubular element 1-1/4 inches in diameter and 9-1/2 inches in length, and with a capability of attaining temperatures up to 3000°C with either an inert atmosphere such as helium, or a vacuum of 10^{-6} - 10^{-5} Torr (2), obtained by means of mercury diffusion pump fitted with a liquid nitrogen trap. (See Fig. 6). The same furnace was used for carrying out the homogenizing and equilibrating anneals on specimens prepared in the argon arc furnace and for melting-point determinations. After heat treatment the samples could be either radiation-quenched by switching off the furnace, or quenched into a bath of molten tin by fusing the fine horizontal tungsten wire to which the suspension wire was attached. Details of heat treatment will be given with individual alloys.

X-ray Diffraction Technique

X-ray diffraction patterns of annealed filings quenched from the equilibrating temperature were taken in a Philips 114.6 mm diameter cylindrical Debye-Scherrer camera employing a high intensity demountable X-ray tube (3). Filtered Co $K\alpha$ and Cr $K\alpha$ radiations were used to identify the phases present and to determine the lattice parameters of the solvent phase. The precision obtained in lattice parameter determination by plotting observed spacings against the function $1/2\ (\cos^2\theta/\theta + \cos^2\theta/\sin\theta)$ (4,5) was about one part in 50,000.

The accuracy to which a solid-solubility limit can be determined by the X-ray technique depends on the precision with which the lattice parameter can be measured and the slope of the parameter-composition curve. Thus, if the slope is constant over the solid-solubility range, and if δc is the uncertainty in atomic per cent with which the solid solubility limit can be located, and $\underline{a}$ is the lattice parameter, it follows that:

$$\frac{\delta a}{a} = \frac{\delta a}{\delta c} \cdot \frac{\delta c}{a} = \frac{1}{50,000}$$

and consequently

$$\delta c = \frac{a}{50,000\ (da/dc)}$$

where da/dc is the slope of the parameter-composition curve.

If r is the atomic radius of the solvent, and Δr is the change in atomic per cent change in composition, the above equation may be written

$$\delta c = \frac{r}{50{,}000\ (\Delta r/100)}$$

$$= \frac{r}{500 \cdot \Delta r} \text{ per cent.}$$

For the Y-Nb system, using Table 1, r = 1.456 Å and Δr = 1.797 - 1.456 = 0.341Å. Hence the precision to which the solid-solubility limit can be fixed by means of a lattice parameter determination is given by δc = 1.456/500·0.341 = 0.085 atomic per cent. Alternatively, if there is 0.085 at. % Y in solid solution in Nb, the change in lattice parameter will just be on the limit of detectability. Similarly, the limit of detectability of Sc in Nb or Ta, where the radius ratio is 11.4% and therefore favorable, would be δc = 1.456/500·0.164 = 0.18 atomic %. The X-ray technique, under favorable circumstances, is thus capable of detecting quite small amounts of solute in solid solution.

Micrographic Examination

Whereas the X-ray diffraction technique is suitable for identifying the phases present in an alloy and of determining the amount of solute in solid solution, the microscope yields information concerning the distribution of the phases and will frequently detect the presence of small quantities of a second constituent which fails to show up in the diffraction pattern owing to an unfavorable signal to background ratio. In general, all the alloys were examined in the "as cast" or homogenized and equilibrated condition. They were mounted in lucite and then ground and polished on "Automet" machines. The following etching reagents were employed.

1. Tungsten Alloys

   30 ml lactic acid
   10 ml HNO_3
   5 ml HF

2. Molybdenum Alloys

   30 ml lactic acid
   10 ml HNO_3
   5 ml HF

3. Tantalum Alloys

   15 ml HNO_3
   30 ml HCl
   30 ml HF

4. Niobium Alloys

50 ml H_2O
14 ml H_2SO_4
5 ml HNO_3
20 ml HF

5. Chromium Alloys

Unetched

Mass Spectrographic Analysis

In view of the extremely small amount of Y and Sc in solution in the refractory elements of the Vth and VIth Groups as shown by the lack of coring in the microspecimens and the X-ray diffraction results, it was decided to employ mass spectroscopy in certain cases to analyse the solvent after heat treatment. For this purpose a vacuum spark source mass spectrograph was employed having a sensitivity of approximately 10^{10} to 10^{11} atoms, thereby enabling elemental concentrations of 1 in 10^{9} atoms to be obtained. Since the ion signal is linearly proportional to the concentration, the mass spectrograph is equally sensitive to all elements.

The spectrograph was employed in conjunction with the liquid rare earth-solid refractory element diffusion couple using a specially designed needle-shaped counter-electrode which enabled a radio-frequency spark to ionize a selected region of the sample having a diameter of 25-50 microns, removing material to a depth of 3-5 microns. It was possible to employ the counter-electrode as an analytical probe by aligning it with the aid of an optical microscope so as to spark selected regions of the refractory element in the region of the liquid-solid interface. The quantity of sample consumed by the spark was of the order of 1-10 micrograms, which allowed a concentration of 1 part per million of solute to be observed. To avoid contamination, the needle-probe was made of the same material as the solvent element.

Fig. 7 illustrates schematically a vertical section taken through a diffusion couple and its encapsulating cylinder. The section is carefully polished prior to sparking, the visible mark on the surface produced by the spark enabling the spectrum to be associated with a well-defined location of the sample. In this manner it is possible to determine the concentration of rare-earth element as a function of distance from the solid-liquid interface.

Fig. 8 illustrates schematically the geometry of the mass spectrograph. The ions are detected by means of a photographic plate located in the focal plane, the design of the instrument permitting a mass-ratio of 15 to 1 to be registered in a single exposure with a mass resolution of 1 in 500.

RESULTS

I. Alloys With Yttrium

1. Y-Cr Alloys

Prior to alloying, the high purity chromium pellets were degassed by heating to 1200°C in a pure alumina crucible in a vacuum of 10^{-5}-10^{-6} Torr for 24 hours using a high frequency induction furnace fitted with a mercury diffusion pump and liquid nitrogen trap. A photomicrograph of the degassed metal after melting in the argon arc furnace is shown in Fig. 9. The material evidently contains traces of residual oxide, or possibly carbide. The initial weight of the sample was 10.13 grams before melting and 10.04 after, the net loss in weight being 0.09 grams.

A sample containing 25 atomic per cent yttrium was prepared by melting 4 times in the argon arc furnace, the initial weight of material being 27.00 grams, the weight of the "as cast" alloy being 26.91 grams -- a net weight loss of only 0.09 grams.

A photomicrograph of the as cast alloy is shown in Fig. 10. This displays a typical dendritic structure of chromium metal with an infilling of Y-Cr eutectic, as would be expected from the phase diagram shown in Fig. 1. Debye-Scherrer diffraction patterns from unannealed filings of the as cast ingot revealed no constituents other than the primary phases Cr and Y.

The 25 atomic per cent yttrium-chromium alloy was subjected to a 68 hour homogenizing anneal in a vacuum of 10^{-6} Torr at 1200°C, which is only 40°C below the eutectic temperature. As shown by the microstructure in Fig. 11, there is a considerable aggregation of the yttrium and chromium phases. X-ray diffraction patterns of alloy filings which had been subjected to a stress recovery "flash anneal" in vacuo for 2 minutes at 1200°C using Cr $K\alpha$ radiation showed only lines belonging to chromium and yttrium.

The lattice parameter of 99.999% Cr was found to be 2.8847 (5) ± 0.0001 Å, while that of the 75-25 Cr-Y alloy was 2.8848 (0) ± 0.0001 Å. The difference in parameter clearly lies within the experimental error which is approximately 1 part in 50,000 and which, based on the atomic radii of 1.797 Å for Y and 1.276 for Cr corresponds to a maximum possible solid-solubility of around 0.005 atomic per cent Y in Cr.

The published Vickers diamond hardness number of chromium varies from 548 for electroplated material (presumably due to its hydrogen content) to 127 for as cast chromium. Our own measurements on as cast chromium yielded a Vickers hardness of 126 ± 1 (mean of three) while the 75 Cr 25 Y alloy gave a value of 103 ± 1 (mean of three). This very low value is probably due to the large amount of segregated yttrium in the microstructure.

2. Y-Nb Alloys

Initially, two master Y-Nb alloys were made from Union Carbide niobium rondelles by melting under argon in the Kroll furnace, the alloys containing 5 and 25 atomic % yttrium, respectively. A photomicrograph of the niobium in the "as cast" condition is shown in Fig. 12 and reveals traces of a second phase which is probably carbide, or carbo-nitride. This phase is absent in the Nb-Y alloys. Fig. 13 illustrates the microstructure of 75 Nb 25 Y in the as cast condition and shows that the alloy is badly segregated, the dark constituent being unresolved eutectic.

Since no phase diagram of the system was available at the outset of the investigation, an attempt was made to homogenize small slices of the alloys in a vacuum of 10^{-5} to 10^{-6} Torr for 46 hours at 2000°C. Weight checks on the heat treated alloys indicated losses corresponding almost exactly to the total amount of yttrium originally present in the samples. It was subsequently discovered, when the phase diagram shown in Fig. 2 became available that the heat treatment had been carried out at approximately 400°C below the monotectic horizontal (~2400°C) and well inside the 2-phase field consisting of solid Nb + liquid.

On account of the high volatility of the γ phase, it was decided to reduce the homogenizing temperature for the remaining slices of specimen. Accordingly, these slices were heat treated in vacuo for 68 hours at 1200°C, which, from the phase diagram, is 270°C below the eutectic horizontal (1470°C). The weight losses during these anneals were found to be negligible.

In order to ascertain whether any yttrium had gone into solution, the samples were filed and the filings given a "flash" anneal to remove cold work by heating in vacuum in a niobium container for 5 minutes at 1200°C, after which Debye-Scherrer patterns were taken with Cr Kα radiation. (Fig. 14). Only lines belonging to the terminal phases Nb and Y were observed. Lattice parameter measurements of the original Union Carbide niobium and of the niobium-yttrium alloys made with it yielded the following:

Table 2

Lattice Parameters of Nb-Y Alloys Made With Union Carbide Niobium

Nominal Composition in atomic per cent Nb	Y	Heat Treatment	Phases Present	Lattice Parameter Å
100	0	Arc melted, filed, 2 min. at 1200°C.	Nb	3.3026
95	5	Lump annealed 68 hyrs. at 1200°C, filed, 5 min. at 1200°C.	Nb + Y	3.2996
75	25	Lump annealed 68 hyrs. at 1200°C, filed, 5 min. at 1200°C.	Nb + Y	3.2993

These results are rather astonishing in that the lattice parameter of niobium is actually lowered by the presence of yttrium instead of being raised. The only reasonable explanation for this effect is a possible scavenging action by the yttrium which removes any oxygen in solid solution in the niobium, converting it to yttrium oxide. This would fall in line with the work of Seybolt (6) on the solid-solubility of oxygen in niobium, where the lattice parameter of the matrix increases linearly from an extrapolated value of 3.2994 ± 0.0004 for zero oxygen to 3.3112 Å for 0.75 wt. % O_2 (4.2 At. %) in solution.

Lattice parameter determinations made on Union Carbide niobium and the zone refined material from Metals Resins Corporation yielded identical lattice parameters, namely 3.3024 ± 0.0001 Å corresponding to approximately 0.16 wt. % O_2 (8.6 At. %) in solution despite the statement that the zone refined material contained only 9 parts per million of O_2. Attempts to degas the rondelles and zone refined rod by annealing for periods of up to 70 hours in a vacuum of 10^{-5} Torr made no difference to the lattice parameter. Presumably much lower pressures and higher temperatures and the use of thin strip (~0.001 inches thick) are required to enable the oxygen to diffuse out of the material in a reasonable period of time, for an extra-long degassing period of 233 hours at 1350°C gave the Union Carbide rondelles a lattice parameter of 3.3015 ± 0.0001 Å. There is, of course, always the remote possibility that some oxygen is picked up during the preparation of the filings and the cold-work recovery anneal in vacuo at 1200°C.

In the search for the solid-solubility limit of Y in Nb, a master alloy was made up containing 1 atomic per cent Y. Although the atomic numbers of Y and Nb are close to each other (39 and 41 respectively), the pattern of free Y could not be seen in the X-ray powder diagram although the Y phase was clearly evident in the microstructure. Using the master alloy, a series of alloys containing respectively 0.8, 0.6, 0.4 and 0.2 atomic per cent Y were prepared. Photomicrographs of the alloys containing 0.2 and 0.8 atomic per cent Y after annealing for 233 hours at 1350°C are shown in Figs. 15 and 16. The presence of the yttrium phase is still clearly evident in the photomicrographs and indicates that the solid-solubility limit of Y in Nb is less than 0.05 atomic per cent.

Lattice parameter measurements and micrographic results on the alloy series ranging from 0.2 to 1.0 atomic per cent Y are given in Table 3. As may be seen from Table 3, there is a progressive, if erratic, decrease in the lattice parameter of the Nb matrix as the yttrium content is progressively increased. These results are combined with those of Table 2 and are illustrated in Fig. 17.

Table 3

Micrographic and X-ray Data on Nb-rich Nb-Y Alloys

Atomic Per Cent Y	Heat Treatment	Phases Present	Lattice Parameter of α Nb Phase, Å
0.2	Annealed 233 hours at 1350°C. Powder annealed 10 min. at 1200°C.	α Nb + Y	3.3011
0.4	Annealed 233 hours at 1350°C. Powder annealed 10 min. at 1200°C.	α Nb + Y	3.3019
0.6	Annealed 233 hours at 1350°C. Powder annealed 10 min. at 1200°C.	α Nb + Y	3.3014
0.8	Annealed 233 hours at 1350°C. Powder annealed 10 min. at 1200°C.	α Nb + Y	3.3007
1.0	Annealed 233 hours at 1350°C. Powder annealed 10 min. at 1200°C.	α Nb + Y	3.3010

It would seem that if the reduction in lattice parameter is caused by a scavenging action, the value of 3.2993 Å obtained for the alloy containing 25 atomic per cent Y is truly representative of the parameter for oxygen-free niobium. A somewhat similar scavenging effect probably occurs in the Nb primary solid-solution range of the Nb-Hf system. According to our own (unpublished) results, there is an initial drop in the lattice parameter of Nb with the addition of Hf, a minimum parameter of 3.3000 Å being reached at approximately 1.25 atomic per cent Hf, after which the lattice parameter increases in an almost linear manner with further Hf additions. The effect is shown in Fig. 18.

Based mainly on the micrographic evidence, it would seem that the solid solubility limit of yttrium in niobium is less than 0.05 atomic per cent.

Vickers diamond pyramid hardness values obtained on as cast Nb-Y alloys were as follows:

At.% Y	0.0	0.2	0.4	0.6	0.8	1.0
VDH	128	112	111	100	98	93

3. Y-Mo Alloys

Attempts to make Y-Mo, Y-Ta and Y-W alloys in the Kroll furnace proved unsatisfactory, there being a strong tendency for the yttrium to form a protective liquid coating around the unmelted refractory element and to volatilize under the arc, the loss in heat as latent heat of volatilization preventing the refractory element from melting. Based on these results, it was decided to use a diffusion couple technique employing liquid yttrium in contact with the solid refractory element and study the interface both micrographically and by means of the mass spectrometer.

As described in the section on Alloying and Heat Treatment Procedures, a rod of zone refined molybdenum was placed in an encapsulating cylinder of the same metal and surrounded by pieces of yttrium. The capped cylinder was heated in the vertical tungsten tube furnace at 1585°C under a vacuum of 10^{-5} to 10^{-6} Torr and maintained at temperature for a period of two weeks. The specimen was then radiation cooled and sectioned vertically for micrographic examination. Good wetting of the Mo rod was observed.

Fig. 19 is a photomicrograph of the interface showing the erosion of the molybdenum surface caused by the solution of molybdenum in the liquid yttrium to form a eutectic mixture on cooling in conformity with the phase diagram shown in Fig. 3. It can also be seen that small "islands" of molybdenum have floated out into the liquid phase prior to solidification.

Three regions at distances of 500, 250 and 125 microns from the interface were sparked in the mass spectrograph, as shown by the circular areas in Fig. 20. No yttrium was to be observed in the first sparking area. A trace (1-3 ppm) was recorded on the first exposure taken 250 microns from the edge but disappeared on further sparking, indicating a surface effect. The third sampling area, 125 microns from the edge, showed 1-5 ppm of yttrium on the first exposure and 1 ppm on later exposures. It is believed that this is a surface effect resulting from sectioning and polishing.

Fig. 21 shows the type of mass spectra obtained. The distance along the plate is proportional to $(m/e)^{1/2}$. The most intense lines are those of singly ionized molybdenum at masses 92, 94, 95, 96, 97, 98 and 100. This pattern is repeated at one half, one third, etc. of the mass range. Yttrium has the single isotope at mass 89. Carbon, oxygen and hydrocarbons are also present, possibly due to residual traces of polishing and cleaning compounds.

Based on the mass spectrograph results, it would seem that the solid-solubility of yttrium in molybdenum at 1585°C is less than 1 part per million.

4. Y-Ta Alloys

A diffusion couple between a zone refined tantalum rod and liquid yttrium in a tantalum cylinder was heated in vacuum at 1585°C for a period of two weeks. Photomicrographs of the interface showed very little erosion of the tantalum sample. The lower part of Fig. 22 shows part of the zone refined tantalum rod in contact with metallic yttrium which is dark on account of the over-etching produced in bringing out the boundaries in the coarse grained tantalum phase. As shown in Fig. 4, there is no eutectic in the system. The upper portion of the photomicrograph shows part of the fine-grained tantalum encapsulating cylinder. In general, the erosion of the tantalum is very much less at 1585°C than was the case with molybdenum, presumably on account of the higher melting point of Ta.

Two series of mass spectra failed to disclose the presence of yttrium in the tantalum rod. From this it may be concluded that the yttrium content was less than 1 part per million.

5. Y-W Alloys

A diffusion couple between a zone refined tungsten rod and liquid yttrium in a tungsten encapsulating cylinder was heated in vacuum for a period of two weeks at 1585°C. A typical photomicrograph of the interface is shown in Fig. 23. No visible attack has occurred on the tungsten at the interface, the upper part of the photomicrograph showing the over-etched yttrium phase which is full of voids. No evidence was found for a Y-W eutectic in conformity with the phase diagram shown in Fig. 5.

Mass spectrography at points ranging from the interface to a location 750 microns away (see Fig. 24) yielded a yttrium content of 150 ppm dropping to zero. It would seem that the initial high value is due to the spark slightly overlapping the yttrium matrix when near to the interface, as may be seen from Fig. 24. It may be concluded that at 1585°C the solid solubility of Y in W is less than 1 ppm.

II. Alloys With Scandium

Although the melting points of yttrium and scandium are very similar (1539°C and 1547°C respectively), their boiling points are very different, that of yttrium being 3027°C and that of scandium being 2400°C. As a result, it is extremely difficult to prepare scandium alloys with the refractory elements owing to the volatility of scandium at the refractory element melting points. Consequently, except for Sc-Cr and Sc-Nb alloys, diffusion couple techniques had to be employed with liquid scandium in contact with solid refractory element. Early attempts to form diffusion couples in vacuum at 1625°C (only 78° above the MP of Sc)were unsuccessful owing to the tendency of the scandium to volatilize and attack the parts of the furnace remote from the specimen. In particular, the tantalum leaf springs supporting the tungsten tube heater-element were attacked and embrittled by intergranular corrosion and fell apart. As a result, attempts were made to operate under helium at a pressure of approximately 650 mm Hg, but with limited success.

A typical phenomenon is the deposition of fine, perfectly developed hexagonal crystals of scandium on the tungsten wire supporting the encapsulating cylinders just outside the hot zone as shown in Fig. 25, the atmosphere being helium at a pressure of 650 mm Hg. Erosion of the support wire adjacent the encapsulating cylinders caused the wire to fail during the high temperature run after only one hour and it became necessary to support the cylinders on a tantalum pedestal capped with a thin thoria disc in order to prevent adhesion.

1. Sc-Cr Alloys

After several unsuccessful attempts, an alloy was prepared using the Kroll furnace. Allowing for weight losses due to volatilization of scandium, the composition of the alloy corresponded to approximately 96.5Cr 3.5Sc. X-ray diffraction patterns and photomicrographs showed only the two phases Cr and Sc along with traces of Sc_2O_3 on the surface.

The photomicrograph of the alloy, shown in Fig. 26, is interesting in that the scandium has formed cubical cavities in the chromium matrix which lie parallel to the crystallographic axes of the chromium. The scandium located in the grain boundaries shows some structure which might possibly be identified with a eutectic, but this is uncertain. No phase diagram of the system is available.

The lattice parameter of the chromium constituent of the alloy was 2.8848 ± 0.0001 Å, which is identical with that of the pure element. As a result, it may be concluded that the amount of Sc in solution is less than about 0.1 atomic per cent.

2. Sc-Nb Alloys

Only one alloy having the composition 95Nb 5Sc was prepared in the Kroll furnace. The weight losses for this alloy were less than one per cent. Micrographic and X-ray diffraction analysis after annealing for 113 hours at 1200°C revealed two phases, αNb and Sc. Traces of inhomogeneous distribution of the Sc phase are still evident in the photomicrograph shown in Fig. 27.

Lattice parameter determinations of the Nb phase yielded 3.3004 Å as compared with 3.3024 Å for Union Carbide rondelles and Metals Resins Corporation zone refined material. As in the case of Nb-Y alloys, this reduction in parameter is, in all probability, due to a reduction in the oxygen content.

3. Sc-Mo Alloys

As stated above, a diffusion couple of liquid scandium in contact with a rod of zone refined molybdenum was heated for 1 week at 1625°C in helium at a pressure of 650 mm Hg. Fig. 28 shows the molybdenum encapsulating cylinder on its sintered powder molybdenum pedestal photographed before and after heat treatment. As may be seen, as a result of the heat treatment, both the cylinder and the pedestal have undergone considerable erosion and the cylinder has become firmly welded to the pedestal and to its cap. A section through the diffusion couple and the encapsulating cylinder is shown in Fig. 29 and illustrates the degree to which the zone refined rod has been eroded and a remarkable swelling of the container which fills the interspace in the form of a spongy mass, most of the scandium having evaporated away.

The erosive attack is considerably greater than in the case of the Y-Mo diffusion couple shown in Fig. 19. It will also be noted that the molybdenum rod, which consists of a few single crystals, is very much less attacked than the finely crystalline encapsulating cylinder. It would seem from this that attack occurs mainly as a diffusion process along the grain boundaries and dislocations in the metal which are more numerous in the machined finely polycrystalline cylinder.

Fig. 30 shows four sparking areas in the vicinity of the Mo-Sc interface. Although there is considerable erosion, it is easily possible to distinquish the sparking areas from the voids. The sparking craters in this case are about 10 microns deep. No scandium was detected in this series of samplings and it can therefore be stated that the amount in solid solution is less than 1 ppm at 1625°C.

No eutectic features were observed in the Sc-Mo diffusion couple. There is no phase diagram available for the system.

4. Sc-Ta Alloys

Considerably less erosion was obtained at 1625°C in helium with the Sc-Ta diffusion couple than was obtained with Sc-Mo. Fig. 31 taken near the interface shows globules of tantalum in a scandium matrix. Three sparking areas used for mass spectrographic analysis are seen in Fig. 32 at distances ranging from 400 to 100 microns from the interface. No scandium was detected and it can therefore be stated that the amount of Sc in solid solution at 1625°C is less than 1 ppm.

5. Sc-W Alloys

In the case of the Sc-W diffusion couple heated in helium for 1 week at 1625°C, no visible attack was observed on the tungsten encapsulating cylinder and pedestal. All the scandium evaporated out of the cylinder during the course of the heat treatment, the loss being verified by weighing. Most of the scandium deposited on the cooler ends of the tungsten heater tube and on the tantalum leaf spring supports, causing several of the leaves to embrittle and fail. A second run ended in the same way. Fig. 33 shows the cross-section of the zone-refined tungsten rod after the heat treatment. The recrystallization on the surface is primarily due to the cold working of the specimen during machining followed by the heat treatment. Mass spectrometry at the interface showed no trace of scandium, the limit of detectibility in this case being 40 ppm. Thus, it would seem that under the experimental conditions, the amount of scandium in solid solution at 1625°C is below 40 ppm, and by analogy with the other elements and the degree of attack it is probably less than 1 ppm.

CONCLUSIONS

It would seem from the experimental results that the solid solubility of yttrium and scandium in the refractory elements W, Ta, Mo, Nb and Cr is of negligible proportions, being in most cases less than 1 part per million. The results are in conformity with the Hume-Rothery rule that only a very restricted range of solid solution can be expected when the atomic diameters of solvent and solute differ by more than 14 to 15 per cent. Erosion by the rare earth metal in the diffusion couples was in the inverse order of the melting points of the refractory elements, being greatest for molybdenum and least for tungsten.

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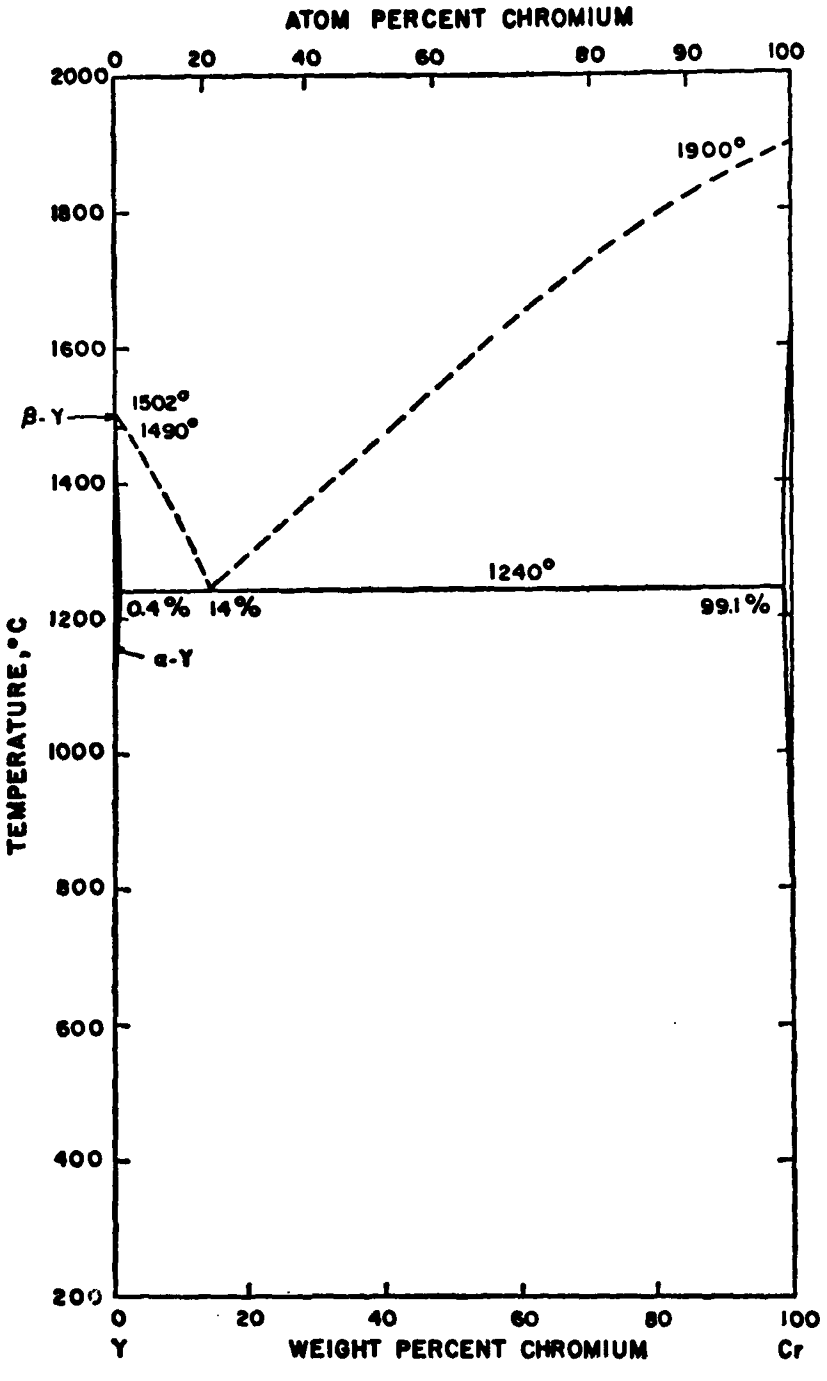


Fig. 1 Yttrium-Chromium Phase Diagram. (From "Rare Earth Alloys," K. A. Gschneidner, Jr., D. Van Nostrand Company, Inc., 1961.)

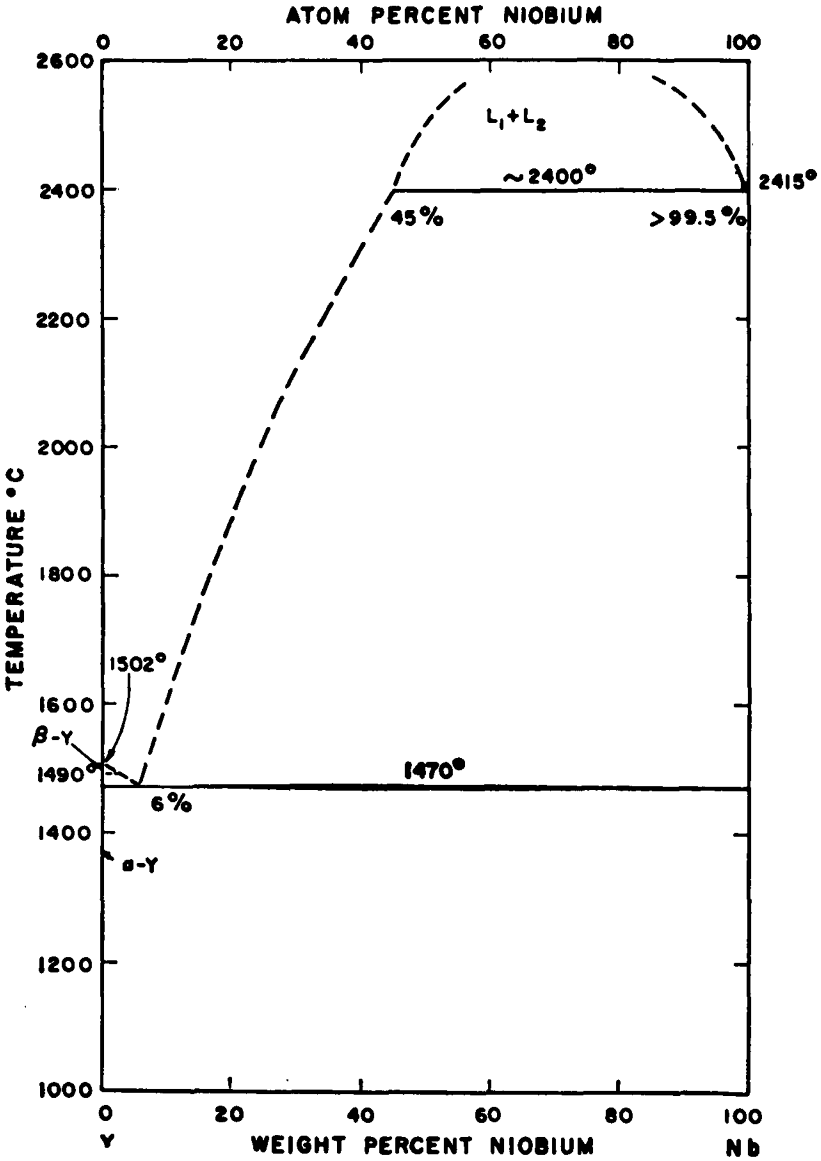


Fig. 2 Yttrium-Niobium Phase Diagram. (From "Rare Earth Alloys," K. A. Gschneidner, Jr., D. Van Nostrand Company. Inc., 1961.)

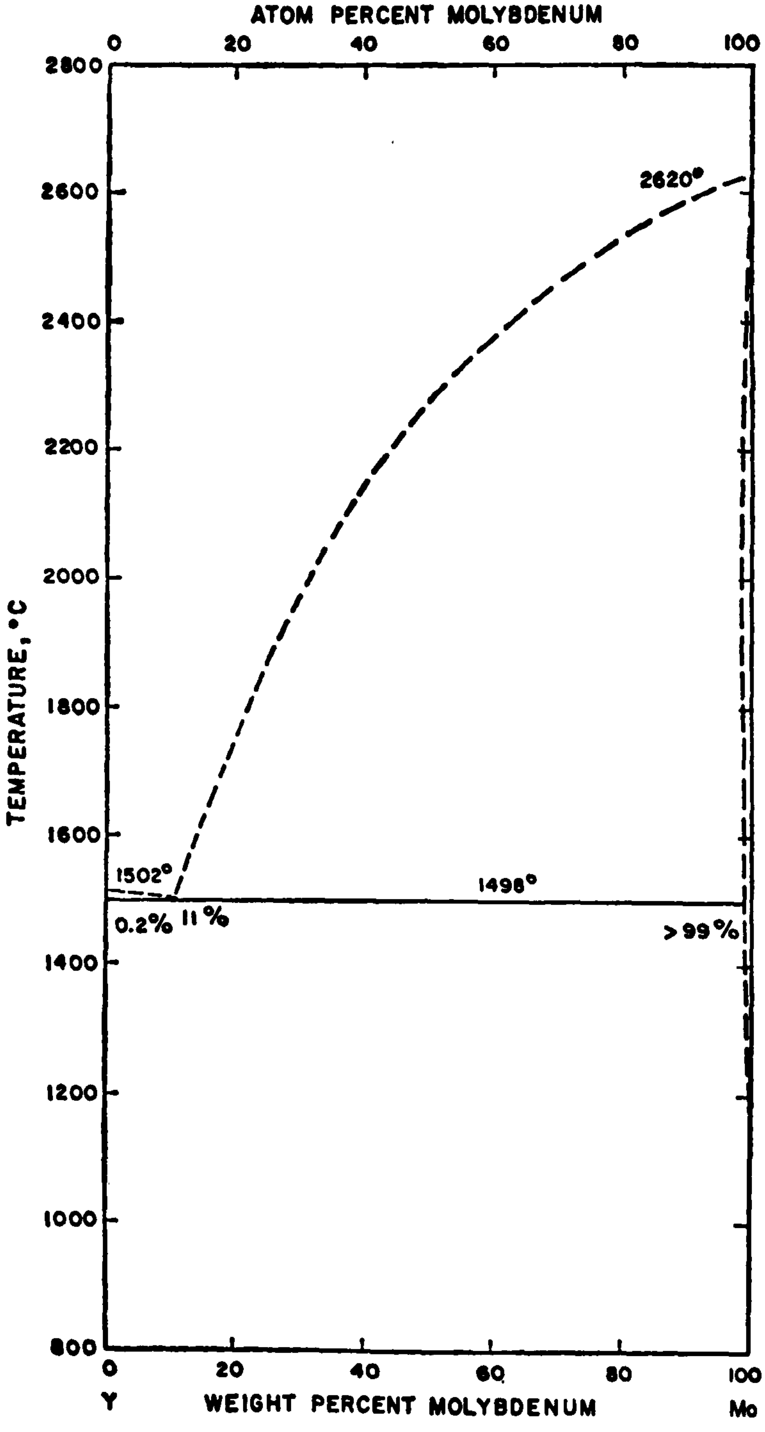


Fig. 3 Yttrium-Molybdenum Phase Diagram. (From "Rare Earth Alloys," K. A. Gschneidner, Jr., D. Van Nostrand Company, Inc., 1961.)

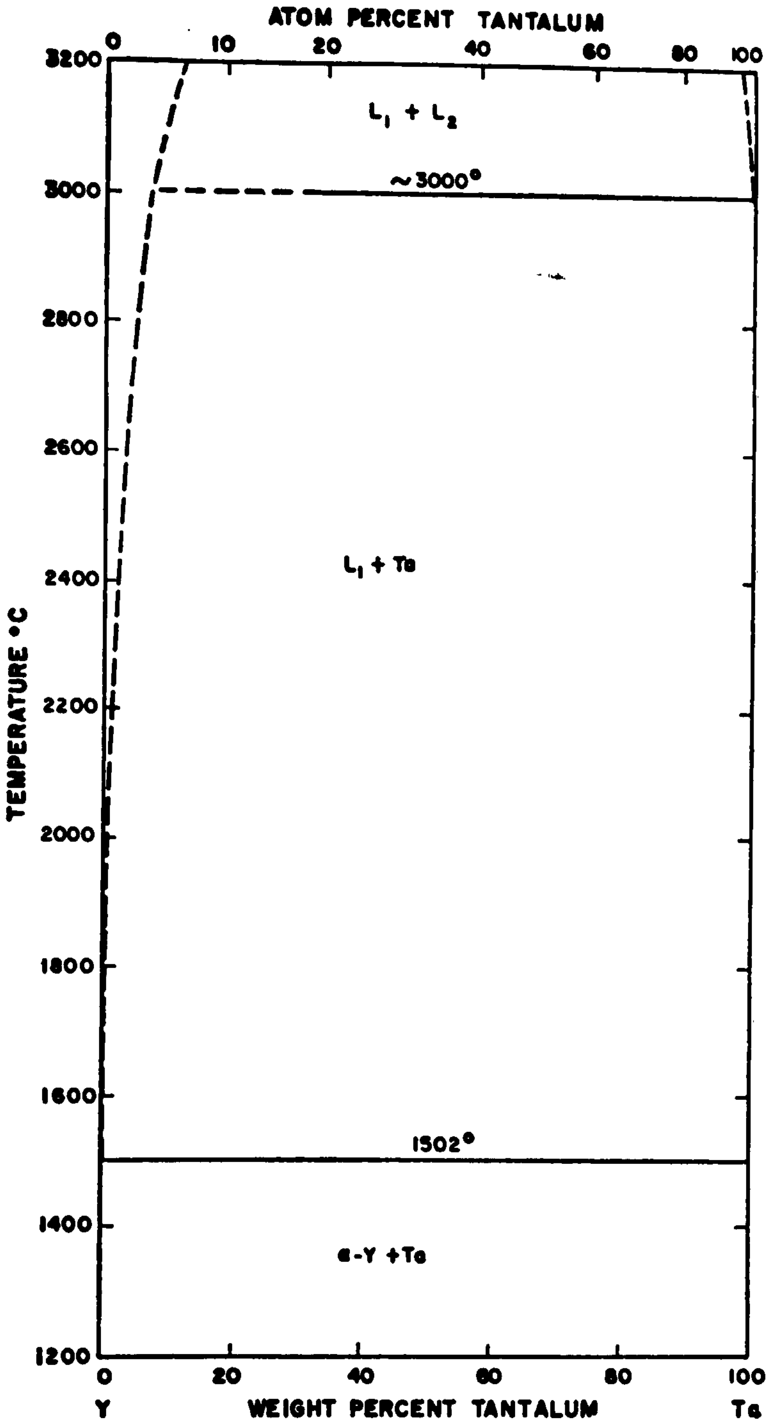


Fig. 4 Yttrium-Tantalum Phase Diagram. (From "Rare Earth Alloys," K. A. Gschneidner, Jr., D. Van Nostrand Company, Inc., 1961.)

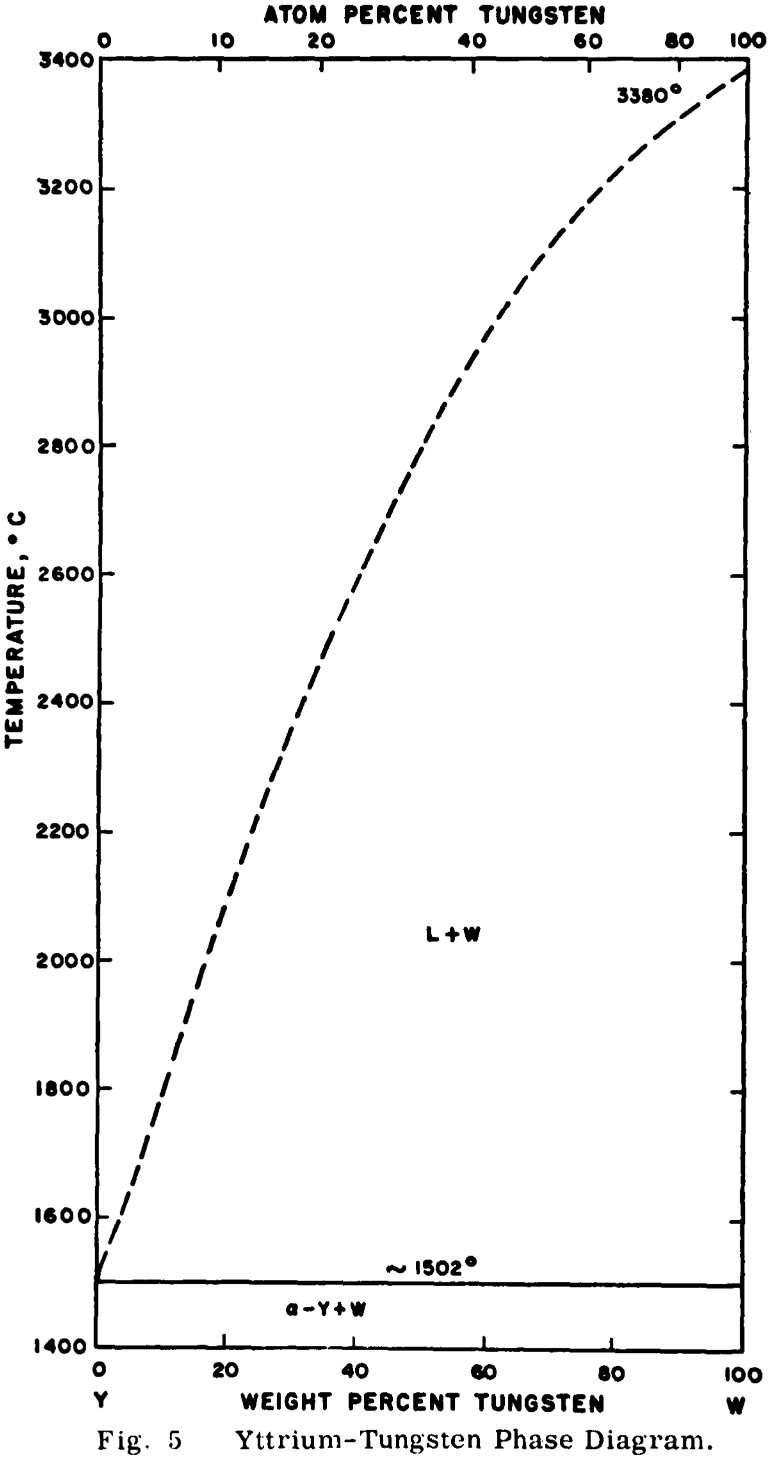


Fig. 5 Yttrium-Tungsten Phase Diagram. (From "Rare Earth Alloys," K. A. Gschneidner, Jr., D. Van Nostrand Company, Inc., 1961.)

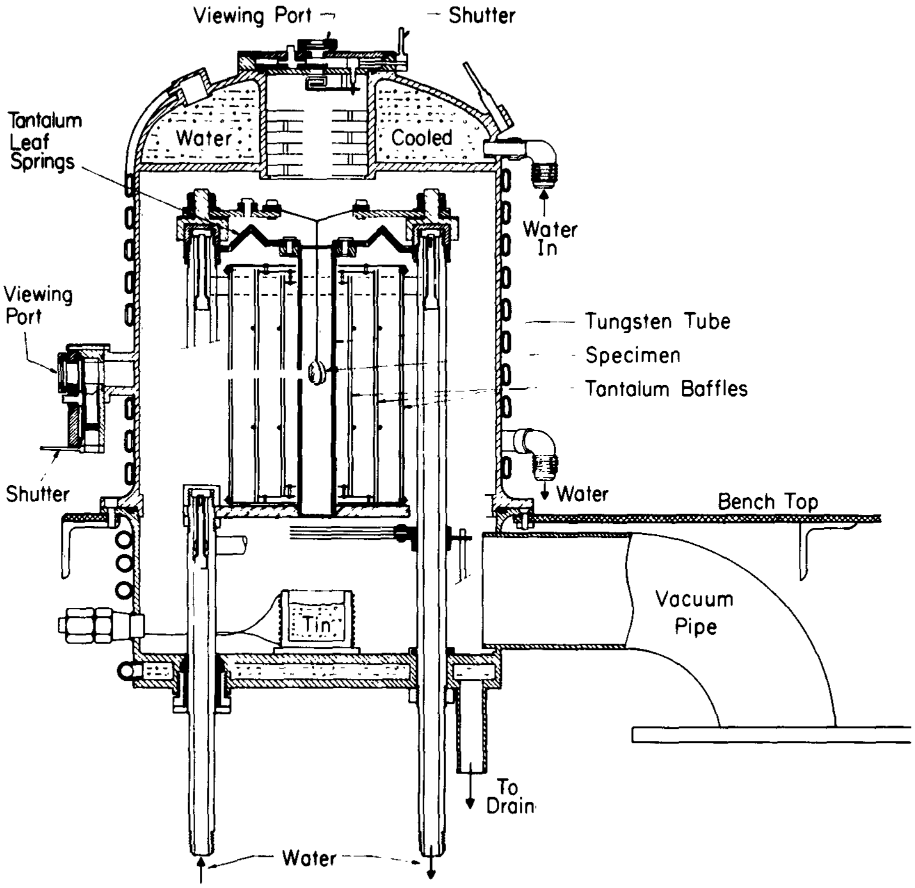


Fig. 6 – Tungsten tube high temperature furnace

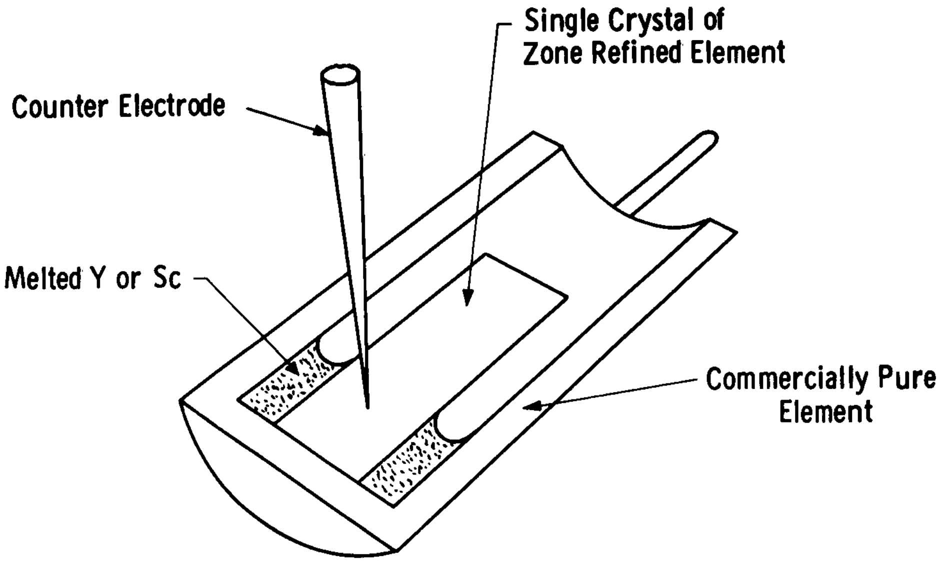


Fig. 7—Pointed counter electrode as a mass spectrograph micro probe

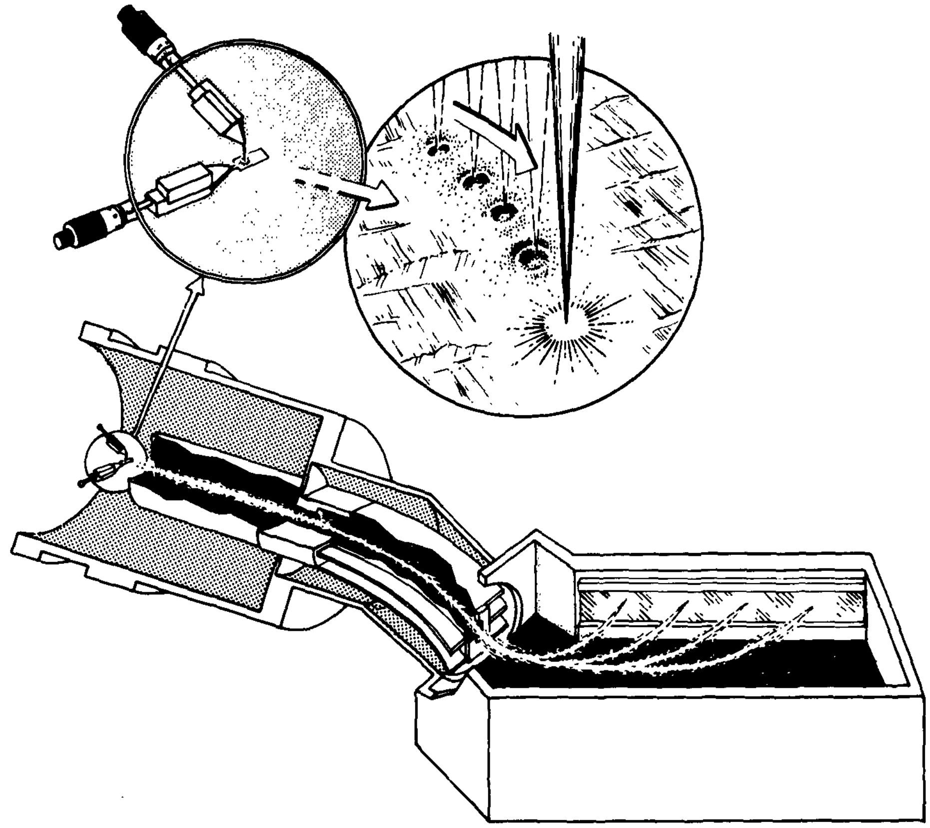
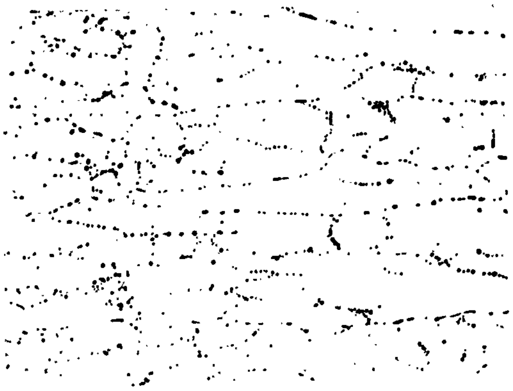


Fig. 8— Layout of mass spectrograph (schematic)

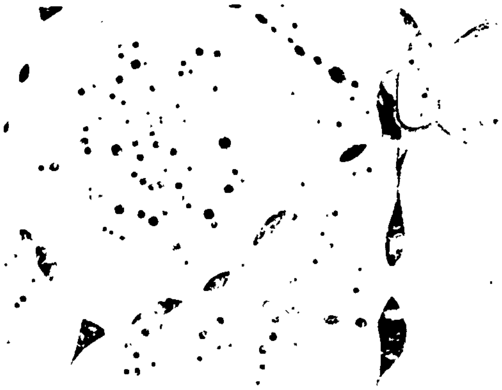


200X

Fig. 9
99.999 % Cr
Argon arc melted
As cast

200X

Fig. 10
75 Cr 25Y
Argon arc melted
As cast



200X

Fig. 11
75 Cr 25Y
Annealed 68 hr. 1200°C

Fig.12– Nb as cast
(Nb+ carbide traces)

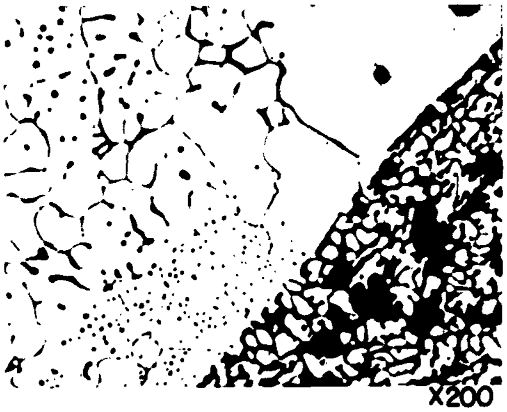


Fig.13–75Nb 25Y As cast
(Nb+ unresolved eutectic)

Fig.15–99.2 Nb 0.8Y annealed
233 hr. 1350 °C
(Nb+Y)

Fig.16–99.8 Nb 0.2Y annealed 233
hr. 1350 °C
(Nb+Y)

Fig.14–X–Ray diffraction patterns of Nb and a 75 Nb 25Y alloy (BCC Nb+ HCP Y) (Cr Kα radiation)

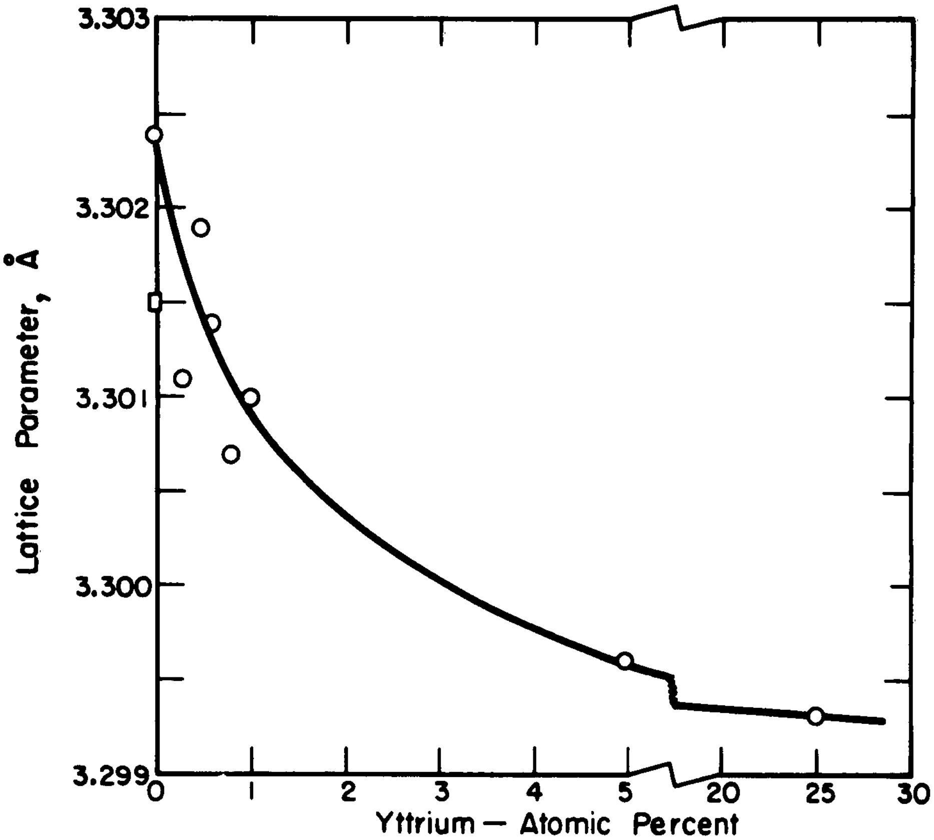


Fig.17—Effect of Yttrium additions on the lattice parameter of niobium.

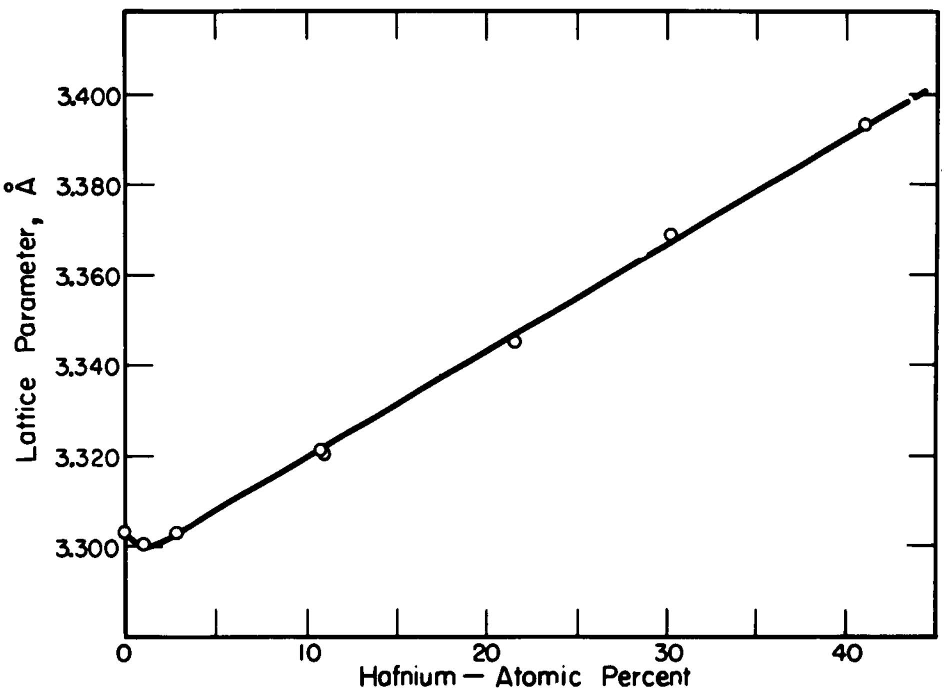


Fig. 18 - Lattice parameter curve of Nb-Hf alloys.

x200

Fig. 19

Mo-Y diffusion couple interface. Mo+ eutectic

x100

Fig. 20

Sparked areas near Mo-Y interface

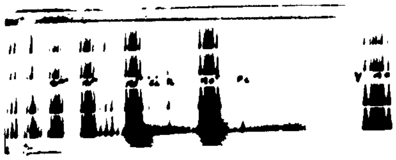


Fig. 21

Mass spectra from regions near Mo-Y interface

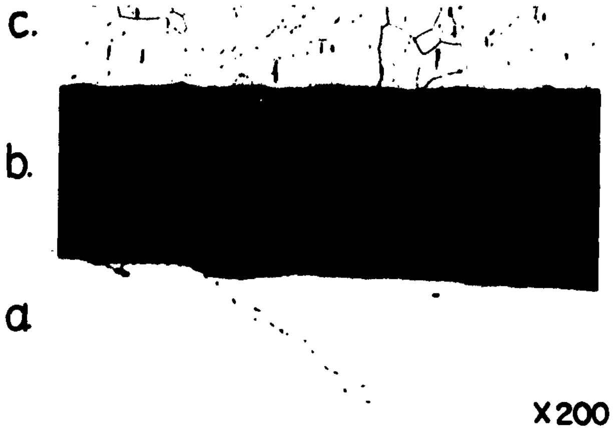


Fig. 22
Y-Ta Diffusion couple
a. Ta rod
b. Y phase
c. Ta container

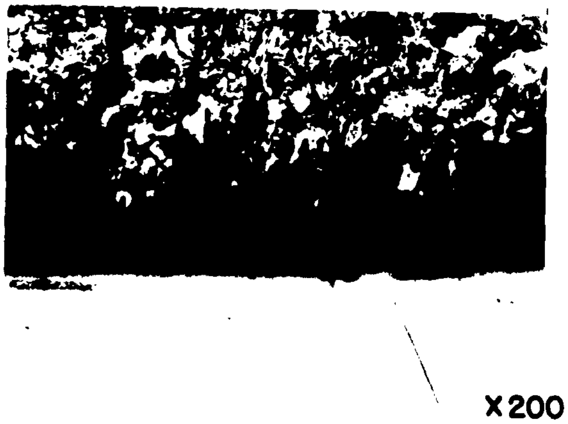


Fig. 23
Y-W Diffusion couple

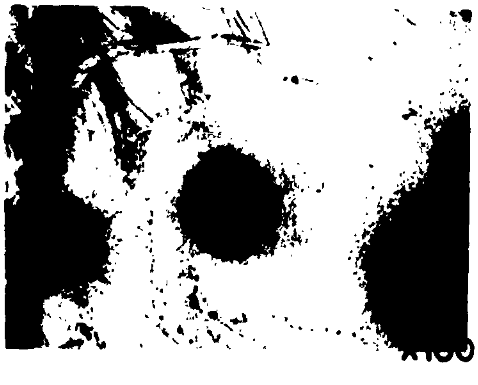


Fig. 24
Sparked areas near
Y-W interface

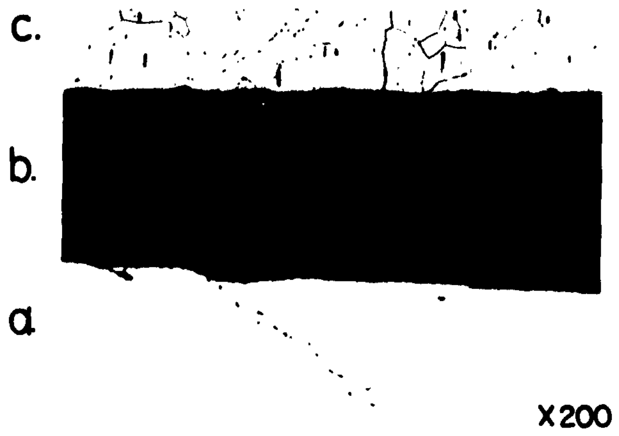


Fig. 22
Y–Ta Diffusion couple
a. Ta rod
b. Y phase
c. Ta container

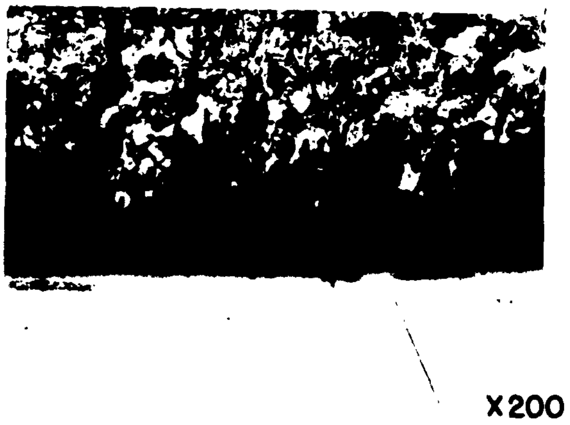


Fig. 23
Y–W Diffusion couple

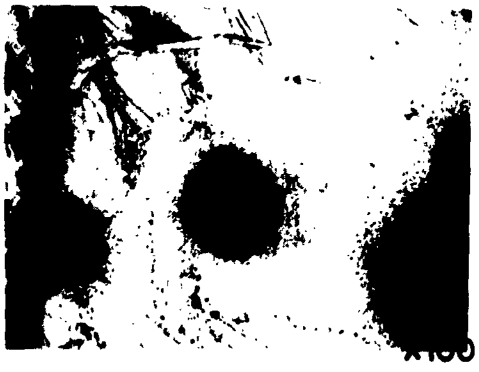


Fig. 24
Sparked areas near
Y–W interface

5X
Fig. 25— Scandium crystals on tungsten support wire

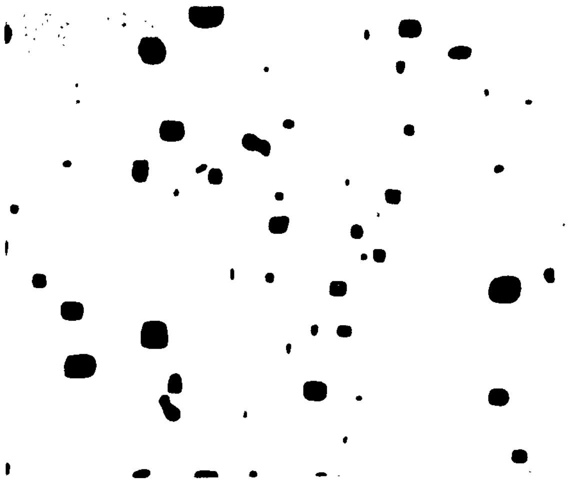


Fig. 26
96.5 Cr 3.5 Sc As cast

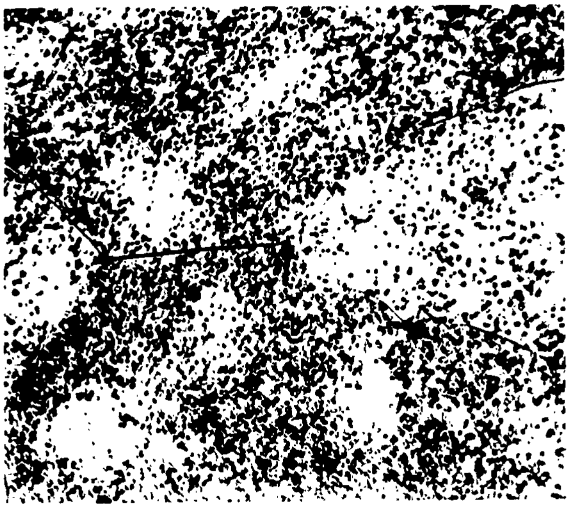


Fig. 27
95 Nb 5 Sc annealed
113 hrs. at 1200 °C

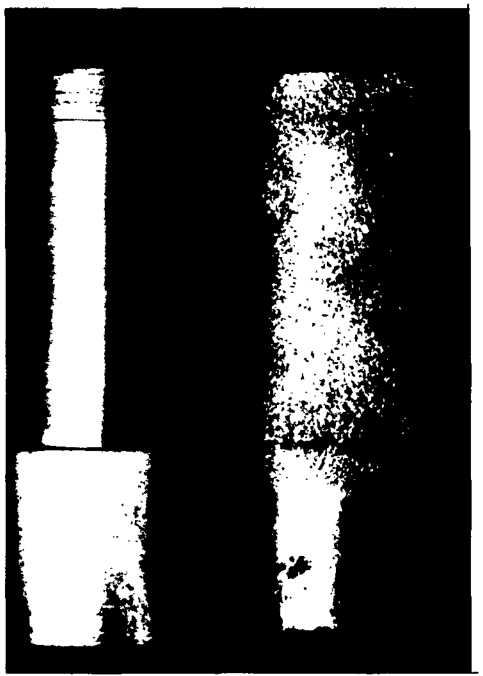


Fig.28-Mo cylinders encapsulating Sc-Mo diffusion couple

Fig.29-Section through Sc-Mo diffusion couple and encapsulating cylinder

Fig.30—Sparked areas near Mo-Sc interface

200X

Fig.31—Tantalum globules in scandium matrix near Sc-Ta diffusion couple interface

100X

Fig 32—Sparked areas near Sc-Ta interface

200X

Fig. 33– Region of tungsten rod at W–Sc interface

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Final Report, May 63, 36p. incl illus, tables, 5 refs.

Unclassified Report

Alloys and diffusion couples of yttrium and scandium with the refractory elements Nb and Ta of Group V and Cr, Mo, and W of Group VI have been examined by means of the optical microscope, X-ray diffraction, and mass spectrometry. The results indicate that the solid solubility of Y and Sc in these

(over)

1. Refractory Materials (Metals)
2. Rare Earths (Metals)
3. X-ray Diffraction Analysis
4. Mass Spectroscopy

I. AFSC Project 7351, Task 735103
II. Contract AF33(616)-8315
III. Westinghouse Electric Corp., Research Lab., Pittsburgh, Pennsylvania
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