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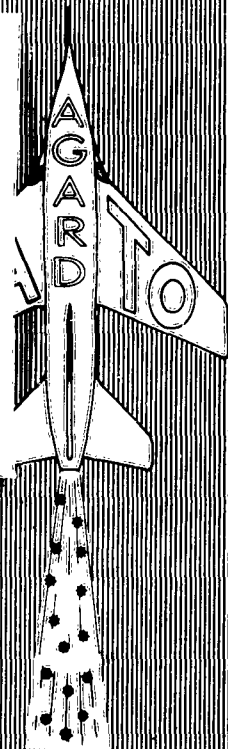


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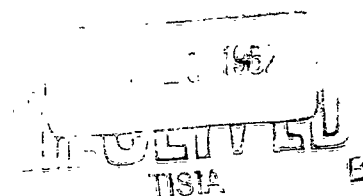
AGARDograph

NIOBIUM, MOLYBDENUM, TANTALUM AND TUNGSTEN

A SUMMARY OF THEIR PROPERTIES
WITH RECOMMENDATIONS
FOR RESEARCH AND DEVELOPMENT

by
R. SYRE

1961



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NORTH ATLANTIC TREATY ORGANIZATION
ADVISORY GROUP FOR AERONAUTICAL RESEARCH AND DEVELOPMENT

64, rue de Valenciennes, Paris VII

NORTH ATLANTIC TREATY ORGANIZATION
ADVISORY GROUP FOR AERONAUTICAL RESEARCH AND DEVELOPMENT
(ORGANISATION DU TRAITE DE L'ATLANTIQUE NORD)

NIOBIUM, MOLYBDENUM, TANTALUM AND TUNGSTEN
A SUMMARY OF THEIR PROPERTIES WITH
RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

by

R. Syre

Note: This work is the result of a study initiated by the Structures and Materials Panel of AGARD and its content was first published in part as Research Memorandum 30.

SUMMARY

This four-part report deals with the metals niobium, molybdenum, tantalum and tungsten. The first part describes (a) physical properties, (b) mechanical characteristics at various temperatures (unalloyed metal and main alloys) and (c) oxidation behaviour. Reference is also made to the problems of protective coatings, joining and fabrication.

Following on the examination of the present state of knowledge, the second part of the report makes recommendations for research and development and stresses the need for basic research, for production development and for research to develop new alloys.

Since basic research appears to be essential for progress in regard to refractory metals and their alloys, the third part of the report makes a detailed study of the state of knowledge of each of the metals in regard to phase diagrams, impurities (determination and effects), diffusion couples, behaviour at high temperature under exposure to different gases, and protective coatings.

The fourth section contains a bibliography of the studies of four metals and their alloys.

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SOMMAIRE

Pour les quatre métaux: niobium, molybdène, tantale, tungstène, la première partie du document mentionne les propriétés physiques, les caractéristiques mécaniques aux différentes températures pour le métal non allié et les principaux alliages, le comportement vis-à-vis de l'oxydation et les problèmes de revêtements protecteurs, et enfin les problèmes relatifs au soudage et à la fabrication.

Dé l'examen de la situation actuelle pour ces quatre métaux la deuxième partie propose des recommandations pour les recherches et développements, insistant plus particulièrement sur les sujets de recherches de base, de développement de la production et de la recherche de nouveaux alliages.

Les recherches de base apparaissant comme l'élément essentiel pour les progrès futurs des alliages réfractaires, l'état des connaissances actuelles est développé dans une troisième partie en examinant successivement: les diagrammes de phase, les impuretés (effets et analyses), les couples de diffusion, le comportement à haute température dans différents milieux gazeux, les revêtements protecteurs.

Enfin, une quatrième partie comporte une sélection de références concernant l'ensemble des connaissances sur les métaux réfractaires et leurs alliages.

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INTRODUCTION

Because of the increasing demand in aeronautical engineering for materials to operate at elevated temperatures, metals with a high melting point, such as niobium, molybdenum, tantalum and tungsten, and their alloys, are of special interest. Because of their generally recognised importance and the major efforts (both in research and development) which are still needed to make them available as production materials, the Structures and Materials Panel of AGARD has chosen the subject of Refractory Metals as first priority for international cooperative research and development.

This document has been prepared with the aim of assisting the formulation and development of common programs and consists of four parts, as follows:

Part I General summary of the state of the art of refractory metals and their alloys.

Part II Recommendations for research and development, covering the following 6 main items:-

1. *Alloy Development*. Methods for the production of new refractory alloys
2. *Coatings*. Examination of the application of suitable coatings
3. *Production Development*. Methods of improving the production of high-quality mill products
4. *Joining*
5. *Basic Research*. The main items are:-
 - 5.1 Phase diagrams
 - 5.2 Diffusion couples
 - 5.3 Impurity effects
 - 5.4 New fabrication techniques
 - 5.5 Oxidation studies
6. *Design Data*. Main properties and characteristics required by designers.

After a detailed examination of the above recommendations, the Panel decided that their first cooperative program should cover the following five points:-

Production Development. A program based on the requirements and capacity available in each country has been prepared.

Phase Diagrams. A list of the phase diagrams which need study has been drawn up.

Diffusion Couples. A list of the diffusion couples recommended for consideration has been prepared.

Impurity Effects. A program for the exchange of samples between analytical laboratories in each country to determine the most suitable methods of analysis for impurities has been undertaken by a number of NATO countries.

Oxidation Studies. A detailed program for cooperative research on deterioration due to gases is being prepared, in collaboration with experts from each country.

Part III Basic research, giving, for each metal, the present state of knowledge from all the papers published (up to 1st February 1960), on the following subjects:-

- Phase diagrams
- Impurities (effects and analysis)
- Diffusion
- Behaviour in gaseous environment at elevated temperature
- Coatings.

Part IV Applied research and development, with literature references and a short summary of the most important papers (up to 1st February 1960), on the following subjects:-

- General information
- Mineral resources
- Production and purification processes
- Sintering, melting, fabrication
- Physical properties
- Mechanical properties (unalloyed metal)
- Mechanical properties (alloys)
- Joining
- Miscellaneous.

It is felt that the references given in Parts III and IV are essential for the basic knowledge of all research or technical workers participating in the different stages of current or future programs.

R. SYRE
25th July 1960

INTRODUCTION

Du fait des besoins toujours plus pressants de l'Aéronautique en matériaux résistant aux températures élevées, les métaux possédant une température de fusion élevée, tels que Nb, Mo, Ta, W, et évidemment leurs alliages, représentent une position tout à fait particulière. Du fait de leur importance universellement reconnue, et de leur haute priorité, du fait également des efforts considérables (dans la recherche comme dans le développement) qui sont encore nécessaires pour les mettre au point, le Panel des Matériaux & Structures a choisi ce sujet des Métaux Réfractaires comme objectif n° 1 pour 'international cooperative research and development'.

Le présent document a été établi dans le but d'aider à l'établissement et au développement des programmes communs. A cet effet, il comporte:

I Une première partie exposant l'état actuel des connaissances des métaux réfractaires et de leurs alliages.

II Une deuxième partie présentant les recommandations dans les domaines de la recherche et du développement, divisée en 6 points principaux:

1. *Développement des alliages*, indiquant les voies dans lesquelles on peut s'orienter pour l'obtention de nouveaux alliages réfractaires;
2. *Couches protectrices*, examinant comment assurer la réalisation de couches convenables;
3. *Mise au point des procédés de production*. Des perfectionnements sont nécessaires aux procédés de production de produits laminés de haute qualité, et il est recommandé d'établir un programme pour l'étude de pièces forgées et de tôles en métaux réfractaires;
4. *Soudage*, qui est également un problème essentiel dans l'utilisation de ces métaux;
5. *Etudes fondamentales* dont les points principaux sont:
 - 5.1 Diagrammes d'équilibre
 - 5.2 Etudes sur la diffusion
 - 5.3 Influence des impuretés et analyse
 - 5.4 Nouvelles méthodes de transformation
 - 5.5 Etudes de l'oxydation
6. *Caractéristiques*, définissant les différentes caractéristiques nécessaires à déterminer pour l'usage des constructeurs.

Après un examen détaillé de ces différentes recommandations, le Panel a décidé de faire porter les premiers efforts de Programmes Coopératifs sur 5 points:

Mise au point des procédés de production: un programme de travaux basé sur les besoins exprimés et sur les possibilités de chaque pays a été établi.

Diagrammes d'équilibre: une liste des diagrammes d'équilibre qu'il est souhaitable de voir étudier a été préparée.

Diffusion: une liste des 'diffusion couples' qu'il est recommandé d'étudier a été établie.

Influence des impuretés: un programme comprenant l'échange d'échantillons entre les laboratoires d'analyse des différents pays dans le but de savoir les procédés d'analyse les plus aptes à la détermination des impuretés a été entrepris par un certain nombre des pays OTAN.

Etudes de l'oxydation: un programme détaillé pour une étude coopérative des détériorations dues aux gaz est en préparation avec l'aide des principaux experts des différents pays.

III Une troisième partie relative aux études fondamentales indiquant, pour chacun des métaux, l'état des connaissances d'après toutes les publications faites jusqu'au 1er février 1960, sur les sujets suivants:

- diagrammes d'équilibre
- impuretés (influence - analyse)
- diffusion
- réaction en milieu gazeux à haute température
- couches protectrices.

IV Une quatrième partie relative aux applications et développements, indiquant toutes les références connues au 1er février 1960 (avec un court résumé pour les plus importantes), correspondant à:

- généralités
- ressources minérales
- procédés de production et purification
- frittage - fusion - transformation
- propriétés physiques
- caractéristiques mécaniques (métal non allié)
- caractéristiques mécaniques (alliages)
- soudage
- divers

Nous avons pensé en effet que les références données dans les parties III et IV sont essentielles à connaître pour tous les chercheurs et techniciens amenés à participer aux différentes phases des programmes déjà entrepris ou futurs.

R. SYRE
25 juillet 1960

PART I

THE STATE OF THE ART

NIOBium

1. PHYSICAL PROPERTIES

(a) Density	8.66 g/cm ³ , 0.31 lb/in ³
(b) Melting Point	2468°C, 4475°F
(c) Specific Heat	0.064 cal/g°C at 0°C, increasing linearly to 0.157 at 600°C
(d) Thermal Conductivity	0.125 cal/cm sec °C at 0°C, increasing linearly to 0.157 at 600°C
(e) Mean Coefficient of Thermal Expansion	7.0 × 10 ⁻⁶ /°C at 93°C, increasing linearly to 7.9-8.1 × 10 ⁻⁶ at 1090°C
(f) Crystal Structure	Body-centered cubic
(g) Thermal Neutron Cross Section	1.1 barns per atom
(h) Emissivity	0.37 at a mean wavelength of 6500 Å

2. MECHANICAL PROPERTIES

2.1 Unalloyed Niobium

2.1.1 Static Tensile Strength (in kg/mm²)

	Room Temperature	800°C	970°C	1050°C	1200°C
Ultimate stress (annealed)	28 to 42	29	18	11.5	7
0.2% offset yield stress (annealed)	17.5 to 35	9	8	6.5	-
Elongation (annealed) (%)	20 to 30	25	38	43	45

The recrystallized annealed metal possesses the highest ductility.

The level of strength depends on interstitial elements, processing variables and the amount of cold work.

NIOBIUM

2.1.2 Influence of Impurities (Oxygen - Nitrogen)

(a) Effect on the metal properties at 20°C (annealed metal)*:

Oxygen (per cent)	Limit of Proportionality (kg/mm ²)	Ultimate Tensile Stress (kg/mm ²)	Elongation (per cent)
0.03	21	29	29
0.16	42	56	17
0.20	49	63	17
0.28	56	70	20
0.32	69	95	20
0.37	74	95	10
0.41	76	91	9

(b) Effect on the metal properties at high temperatures (annealed metal)

Ultimate strength (kg/mm²)

Temperature (°C)	Oxygen (per cent)						
	0.02	0.04	0.06	0.08	0.10	0.12	0.14
300	30	45	62				
500	28	32	35	38	40	43	48

(c) Hardness at 20°C (annealed metal)†

O ₂ (%)	0.02	0.03	0.05	0.1	0.2	0.3	0.6	0.75
HV	60	87	100	160	200	240	300	350

O ₂ + N ₂ (%)	0.07	0.5	1
HV	100	250	300

The recrystallization temperature depends on the amount of cold-working, as follows:-

Amount of Cold-working (%)	Recrystallization Temperature (°C)
20	1260 - 1370
50	1090 - 1200
85	1000 - 1150

* Tottle (Reference 98)

† Seybolt (Reference 1)

2.1.3 Creep

Temperature		Stress Rupture Strength of Recrystallized Nb (in kg/mm ²) for lives of:-		
°F	°C	0.1 hr	1 hr	100 hr
1600	870	-	-	6
1800	980	13 - 21	12 - 18	12
2000	1090	8 - 14	10	9
2200	1200	9	-	3
2300	1260	7	-	-

Creep Strength

A stress of 12 kg/mm² gives, at 1800°F (980°C), a creep elongation of 1% in one hour and 2% in four hours (on Nb cold-worked).

2.2 Alloys

2.2.1 Designations

A certain number of alloys are already at an advanced stage of development in the United States; a general list is given below.

No.	Composition (%)							Ultimate Tensile Strength (kg/mm ²) (as extruded)					Stress-Rupture Strength (kg/mm ²) for 10 hr. life			Temperature recrys- talli- zation (50 % in 1hr °C
	Mo	W	Ta	Ti	Zr	V	C	Room	1090°C	1200°C	1320°C	1430°C	1090°C	1200°C	1260°C	
General Electric	F 48	5	15		1	x	70*	46	29	21				17		1375
	F 50	5	15	5	1	x	84	35	25	14				11		
Fanstell	S 80				0.75	x	33+						17			
	S 82			32.5	0.75	x	39	21	15	8			16			
	S 83	5	33		1	x	77****	32	25							
Du Pont	D 31	10		10			70*	25	18	14	8			6	3	1320
	D 41	6	20	10			91***		33					8		
Union Carbide	Cb 7		28	7			102		29					13		
	Cb 16		20	10		3		36	18					8		
	Cb 65			7	0.8	x		16	11							
	Cb 74	10		5			63**		26	21				13		1320
Westinghouse	Nc155	5				5	67	28								
	Nc181	5			1	5	x	39								
x Present in small amounts * Elongation 22 % as extruded																
+ Annealed ** " 27 % "																
*** " 8 % "																
**** " 15 % "																

NIOBIUM

2.2.2 Creep Strength

Further data on alloy Du Pont D 31 are given below:

Temperature °F °C		Stress (kg/mm ²)	Time (hr) to Produce	
			1% Def.	2% Def.
2300	1260	7	0.084	0.167
2300	1260	4	0.2	0.5
2600	1425	7	0.025	0.04
2600	1425	4	0.125	0.25

It should be noted that although the primary fabrication of the unalloyed niobium is easy and is cold-worked generally, very high temperatures (1200 to 1700°C) and special techniques must be used for the alloys.

2.3 Modulus of Elasticity : 10,500 to 11,200 kg/mm²

Effect of temperature at least to 820°C and effect of alloying is small.

2.4 Transition Temperature

2.4.1 For the unalloyed annealed metal of average purity (for instance, C:0.01%, O₂: 0.01%, N₂:0.02%, Fe:0.08%, Ta:0.2%), the ductile-to-brittle transition temperature is less than -196°C. It is increased by coarse grain and the amount of interstitial elements.

2.4.2 The conditions under which alloys are fabricated play a very important part. As an example, the values of the transition temperatures for alloy D 31 are given below (based on a tensile test):-

Cold-worked : -180°C to -130°C

Recrystallized (400 ppm interstitials) : 0 to + 65°C

Recrystallized (1200 ppm interstitials) : + 200 to + 230°C

2.4.3 It should also be noted that, according to the amount of interstitial elements (and especially oxygen), a strain-aging effect at + 150, + 180°C is observed on unalloyed niobium.

3. OXIDATION

Oxidation Rate of Nb at Various Temperatures* in Air

Temperature °F °C		Oxygen Penetration (mils)	Interface Recession (mils)	Total (mils)
1000	540	4	-	4
1200	650	4	-	4
1400	760	12	-	12
1600	870	31	46	77
1800	980	39	47	86
2000	1090	> 98	49	> 147
2200	1200	>450 (10 hr. only)		

In contrast to the behaviour of molybdenum, the oxide of niobium (Nb_2O_5) is relatively stable. However, the diffusion of oxygen leads to scaling and progressive attack and embrittlement. Protective coatings will probably be required at temperatures above 980°C, but failure of the coating would not be expected to lead to catastrophic failure.

Some alloying elements that tend to reduce the oxidation rate are Ti, Cr, Mo, Zr, V, Ta[†], producing alloys with an improvement in scaling resistance by a factor of 25 or more, and in resistance to internal oxidation by a factor greater than this. Such improvement, however, is probably still inadequate for the service requirements, and such alloys may be weak or unfabricable.

A general idea can be given in the following table:

	Weight Increase (mg/cm ²) after 100 hours in pure oxygen		
	800°C	1000°C	1200°C
Pure Nb	3,600	6,000	24,000
Single phase Nb alloys	20-50	70-100	200
Two phase Nb alloys	8	12	16
Type 304 Stainless Steel	9	10	800
Haynes Stellite HS 31	0.5	10	30
Tungsten	600	6,000	60,000

For comparative purposes, the following table shows the behaviour of some of the high strength alloys:

* 16 hours on samples 0.375 inch diameter x ½ in long

† See, for example, the work of Klopp, Sims and Jaffee (Battelle Memorial Institute)

NIOBIUM

<i>Alloy</i>	<i>Cb16</i>	<i>D41</i>	<i>Cb7</i>	<i>D 31</i>	<i>F 50</i>	<i>Cb65</i>	<i>F48</i>	<i>82</i>	<i>Unalloyed</i>
Oxygen Contamination (depth in mils) after 10 hr at 1200°C in air	7	12	17	28*	32	56	75	145	450

4. COATINGS

It appears that pure niobium can be successfully protected by coating up to 1150°C. The coating of oxidation-resistant alloys would conceivably extend the service limit and time. The upper temperature limit would still be about 1300°C for existing coatings, but research effort may extend this limit to 1370°C or more. Porcelain enamels seem to offer considerable promise. Work in progress on zinc coatings also offers considerable promise (up to 1150°C).

5. WELDING

Niobium can be welded by vacuum or inert atmosphere techniques. As the metal undergoes no phase transformation, such welds can be as ductile as the base metal.

Work is in progress on alloys to determine the purity level required to lower the transition temperature to the point where they can be welded and remain ductile at room or low temperatures.

6. FABRICATION

Niobium is much more ductile than molybdenum or tungsten, and can be much more readily fabricated by bending, drawing, etc. There will, however, be further problems in the fabrication of alloys.

* 7 mils at 1100°F (593°C)

M O L Y B D E N U M

The following data refer to pure molybdenum and the alloy with 0.5% titanium, both being commercially available. Alloys containing titanium, zirconium and carbon have improved properties, principally higher recrystallization temperatures, but are at an earlier stage of commercial development.

1. PHYSICAL PROPERTIES

(a) Density	10.22 g/cm ³ ; 0.369 lb/in ³
(b) Melting Point	2622 ± 10°C, 4750°F
(c) Specific Heat	0.059 cal/g°C at 0°C; 0.075 cal/g°C at 475°C
(d) Thermal Conductivity	0.32 cal/sec cm°C at 0°C 0.26 cal/sec cm°C at 1473°C (2685°F)
(e) Coefficient of Thermal Expansion	5.1 × 10 ⁻⁶ per °C at 27°C (80°F) 5.5 × 10 ⁻⁶ per °C at 1000°C (1830°F) 6.2 × 10 ⁻⁶ per °C at 1500°C (2730°F)
(f) Crystal Structure	Body-centered cubic
(g) Thermal Neutron Cross Section	2.5 barns per atom
(h) Emissivity (total)	0.08 at 500°C 0.13 at 1000°C 0.24 at 2000°C

2. COMPARISON BETWEEN METAL MADE BY POWDER METALLURGY AND CAST METAL

The current process for producing molybdenum by powder metallurgy consists in compressing the cold powder under pressure of 12 to 25 kg/mm² into the form of long bars, and then sintering the bars (with or without previous sintering at 1000°C) at 2000-2340°C in hydrogen or in vacuo. Sintering in vacuo usually necessitates the addition of deoxidants to the powder. Heating is done either by passing a current through the bar, or by radiation or induction. Objections to this form of feed process are that weight is limited (30 to 40 kg) and bars are not convenient.

The Westinghouse process uses a sintering at low temperature (1500-1700°C) in a hydrogen atmosphere saturated with water vapour, which results in a reversible reaction of oxidation and reduction leading to a product having a density approaching the theoretical density. The sintering can therefore be performed in a radiation furnace with a molybdenum resistor, which makes it possible to manufacture the metal in any required form. Also, the grain is very small. The powder is previously compressed under hydrostatic pressure at 10-20 kg/mm². Batches of 200 kg are normally produced.

M O L Y B D E N U M

The following data refer to pure molybdenum and the alloy with 0.5% titanium, both being commercially available. Alloys containing titanium, zirconium and carbon have improved properties, principally higher recrystallization temperatures, but are at an earlier stage of commercial development.

1. PHYSICAL PROPERTIES

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(c) Specific Heat	0.059 cal/g°C at 0°C; 0.075 cal/g°C at 475°C
(d) Thermal Conductivity	0.32 cal/sec cm°C at 0°C 0.26 cal/sec cm°C at 1473°C (2685°F)
(e) Coefficient of Thermal Expansion	5.1 × 10 ⁻⁶ per °C at 27°C (80°F) 5.5 × 10 ⁻⁶ per °C at 1000°C (1830°F) 6.2 × 10 ⁻⁶ per °C at 1500°C (2730°F)
(f) Crystal Structure	Body-centered cubic
(g) Thermal Neutron Cross Section	2.5 barns per atom
(h) Emissivity (total)	0.08 at 500°C 0.13 at 1000°C 0.24 at 2000°C

2. COMPARISON BETWEEN METAL MADE BY POWDER METALLURGY AND CAST METAL

The current process for producing molybdenum by powder metallurgy consists in compressing the cold powder under pressure of 12 to 25 kg/mm² into the form of long bars, and then sintering the bars (with or without previous sintering at 1000°C) at 2000-2340°C in hydrogen or in vacuo. Sintering in vacuo usually necessitates the addition of deoxidants to the powder. Heating is done either by passing a current through the bar, or by radiation or induction. Objections to this form of feed process are that weight is limited (30 to 40 kg) and bars are not convenient.

The Westinghouse process uses a sintering at low temperature (1500-1700°C) in a hydrogen atmosphere saturated with water vapour, which results in a reversible reaction of oxidation and reduction leading to a product having a density approaching the theoretical density. The sintering can therefore be performed in a radiation furnace with a molybdenum resistor, which makes it possible to manufacture the metal in any required form. Also, the grain is very small. The powder is previously compressed under hydrostatic pressure at 10-20 kg/mm². Batches of 200 kg are normally produced.

MOLYBDENUM

Generally speaking, the properties of molybdenum and its alloys made either by powder metallurgy or by consumable arc melting are similar, provided that the structure and impurity percentages are similar. The following differences occur:-

A purer product is obtained by consumable arc melting in vacuo, greater ductility being developed.

The products obtained from powder metallurgy (fine grain) are more easily workable (initial breakdown) than cast ingots (coarse grain). As far as the latter are concerned, it is necessary to perform an extrusion first.

Cast alloys appear to be more homogeneous than powder alloys.

The addition of easily oxidisable alloy elements, e.g. titanium or zirconium in arc melting, leads to the formation of a ternary alloy Mo-X-XO, the XO being an insoluble dispersion, contributing to strength at elevated temperature. The same result can be obtained in powder alloys by the direct addition of the contemplated oxide.

A larger ingot can be obtained by casting than by powder metallurgy.

The fabrication of powder is less expensive, because the losses in fabrication are less. From 100 kg of molybdenum powder, it is possible to obtain 65 to 75 kg of sheet by powder metallurgy, or 35 kg of sheet by casting. Scrap reclamation is therefore an important problem.

Production by casting is steadily increasing in the United States:-

In 1957 : 500 tons of semi-manufactured products (80% by powder, 20% by casting)

In 1958 : 750 tons of semi-manufactured products (50% by powder, 50% by casting)

3. MECHANICAL PROPERTIES

3.1 Static Tensile

3.1.1 *Unalloyed (as-rolled)*: Tensile strength, 70-80 kg/mm²; yield strength, 53-60 kg/mm² (0.1% offset). Elongation: 6-18%.

3.1.2 *Mo-0.5% Ti*: Tensile strength, 80-90 kg/mm²; yield strength, 66-70 kg/mm² (0.1% offset); elongation, 13%.

3.2 Modulus of Elasticity

Temperature °C °F		Modulus (kg/mm ²)	
		Arc Cast	Powder
27	80	30,200	31,600
590	1100	-	29,400
635	1175	28,700	-
870	1600	27,900	-

3.3 Transition Temperature

The impact transition temperature for $\frac{5}{8}$ in. diameter bars is usually in the range of 260-480°C for both pure molybdenum and for the Mo-0.5% Ti alloy. The tensile transition temperature for smooth specimens would be in the range of -50 to about +100°F (-46 to +38°C). The type of stress system has a large effect on the transition temperature; a sharp notch can raise the transition temperature 300°C above that of a smooth specimen.

The transition temperature depends largely on the quantities of interstitials.

The typical characteristics just given are for molybdenum cast in vacuo, extruded and rolled, having the following impurity percentages:- oxygen : 0.005%, carbon : 0.02%, nitrogen : 0.005%.

Examples of the influence of these impurities on the transition temperature (under constant test conditions) are*:-

Oxygen (%)	Transition T (°C)	Nitrogen (%)	Transition T (°C)	Carbon (%)	Transition T (°C)
0.0001	- 60	0.0008	- 40	0.003	- 40
0.0002	+ 200	0.0014	- 60	0.006	- 30
0.0006	+ 200	0.0037	+ 40	0.008	- 10
		0.0330	+ 140	0.010	0
				0.020	+ 40
				0.024	+ 50
(High purity molybdenum: - 80°C)					

Other factors that play an important part in the ductility of molybdenum are:- the orientation of the structure, the lack of recrystallization, the grain size, annealing temperatures, and the conditions under which annealing was carried out, i.e. the history of the operation and the atmosphere. The effects of these factors are such as to prevent a sample of the metal being described completely by its chemical composition.

* Olds (Ref. 748)

MOLYBDENUM

3.4 Elevated-Temperature Tensile Strength (under Helium)

Temperature °F °C	Pure Molybdenum		Mo-0.5% Ti Alloy	
	Tensile Strength (kg/mm ²)	Elongation (%)	Tensile Strength (kg/mm ²)	Elongation (%)
1600 870	36	24	61	17
1800 980	32	30	46	25
2000 1090	28	40	42*	15
2200 1200	--	--	35*	--
2400 1315	--	--	24	21
2500 1370	11	53	14	53
2750 1510	7	53	10	53
3000 1650	5	59	7	56

3.5 Stress-Rupture Strength under Helium (kg/mm²)

	1800°F (980°C)			2000°F (1090°C)			2900°F 3630°F 4530°F (1600°C) (2000°C) (2500°C)		
	0.1hr	1hr	100hr	0.1hr	1hr	100hr	1hr	1hr	1hr
Unalloyed	28	23	15	25*	18	9	6	1	0.5
Mo + 0.5 Ti	54*	49	37	52*	43	24	-	-	-
Mo + 0.5 Ti + 0.07Zr	-	70*	49	-	60*	36	-	-	-

3.6 Creep Strength

Creep and Stress-Rupture Properties of 0.5% Titanium Alloy
Coated with Chromalloy W-2 Coating (in Air)

Temp. °F °C	Stress kg/mm ²	Time (sec) to obtain creep strain of					Time (sec) to Rupture	Total Elongation (%)
		1.0%	2.0%	3.0%	4.0%	5.0%		
2400 1315	20	180	280	296	-	-	300	7
2600 1425	7	37	82	122	266	-	272	8
2600 1425	5	860	1800	2900	3810	4900	5400†	5.8
2800 1540	5.5	57	180	336	505	663	1405	14
2800 1540	4	1474	2520	-	-	-	3300†	2.5
3000 1650	3.2	56	113	170	214	246	290	12
3000 1650	2.8	252	472	700	835	1060	1380	13
3000 1650	2.5	238	720	-**	-**	-**	2883	16

* Estimated

** Extensometer slipped off specimen

† Test stopped at this time and elongation

3.7 Other Alloys

Composition (%)				Ultimate Tensile Strength (kg/mm ²) (as extruded)			Stress-Rupture Strength (kg/mm ²) for 100 hr. Life	
Ti	Zr	C	W	1200°C	1300°C	1500°C	1200°C	1300°C
0.5	0.06	0.04 (1)		49	36	18	25	-
1.25	0.15	0.15 (2)		43	32	-	24	18
-	0.05	0.02		-	15	-	-	-
-	0.5	0.05		-	30	-	20	-
	0.1	0.05	25	-	40-49	-	-	10
(1) alloy TZM				(2) alloy TZC				

* Estimate.

4. OXIDATION AND COATINGS

Unprotected molybdenum begins to oxidize at 250°C and oxidizes very rapidly at temperatures above 850°C in air under atmospheric pressure. The oxide has a melting point of 795°C but is already volatile at 700°C, exposing metal for progressive attack.

The rate of oxidation in still air is in the range 1400-2000 mg/cm² hr. It increases with increase in the velocity of the air. The oxidation rate in air decreases with the pressure, in particular with the partial pressure of oxygen. From the values obtained, the oxidation rate at 1138°C at an altitude of 175,000 ft is 1/100 of that obtained at normal pressure. The oxidation rate is also decreased in reducing gases such as combustion gases. A life of 100 hours is obtainable at 1427°C. Gulbransen (Trans. Electrochemical Society, Vol.91, 1947, p.594) has shown the influence of oxygen pressure on the oxidation rate.

A number of systems that protect molybdenum against oxidation have been developed. All the systems are subject to limitations. As a result no one protective system has become predominant over the others and intelligent application requires knowledge of the advantages and limitations of the various systems to enable the most suitable system for the particular application to be selected. For instance, the use of a particular coating process may depend on whether the process is to be used on mill products or on finished parts.

Complete surveys of the protection of molybdenum are:-

- Harwood - The Metal Molybdenum (ASM, p.420)
- Bartlett - Defense Metals Information Center TR 109
- Buckle - La Recherche Aéronautique, November 1957, p.35

MOLYBDENUM

R. Jaffee - Protection against oxidation, Materials Advisory Board Report on Mo
(to be published)

R. Jaffee - Fabrication of Molybdenum (ASM, 1959, p.119)

MacLoud - Metal Progress, August 1958.

Metallic coatings for molybdenum are almost invariably nickel or nickel base alloys of the order of 0.002 to 0.003 in thick. The advantage of coatings of this type is that if local breakdown occurs, e.g. by oxygen penetration at local defects or by diffusion of the base metal, the oxidation product is nickel molybdate, a relatively refractory compound, whereas molybdenum trioxide is volatile and iron molybdate is relatively fusible. Unfortunately nickel molybdate spalls during cooling and for this reason the nickel type alloys are not outstanding in their resistance to thermal cycling.

Chromium is usually present in metallic coatings in order to improve oxidation resistance. In multilayer electroplated coatings, chromium is next to the molybdenum so as to retard diffusion of nickel and to improve adhesion. The high ductility of nickel and nickel-chromium coatings fits them for applications where formability and resistance to impact are required. Such coatings will withstand a few hundred hours in air at 1090°C.

Roll clad nickel has good impact resistance and ductility in bending but Inconel is better at 980°C. Such coatings are in part self-healing but start to melt at about 1300°C. How to obtain efficient protection at edges is a big problem in parts that are not plated after fabrication.

Sprayed coatings based on aluminium are somewhat less ductile than the nickel or nickel chromium coatings, but have improved resistance to thermal cycling and erosion. Chief among these are the spray coatings of aluminium with refractory powders such as aluminium silicon chromium. Although these coatings are relatively brittle at room temperature they have sufficient ductility when hot to enable some distortion of the part to occur without rupturing the coating. A coating of this type may be used at higher temperatures than are feasible with nickel base coatings. Such a coating has some self-healing tendencies but, in common with other sprayed coatings, it can be applied only to relatively simple shapes without recesses or areas difficult of access.

Vapour-deposited, flame-sprayed, or paint and sinter coatings that have molybdenum disilicide as the outermost layer are relatively brittle, even at elevated temperatures. The maximum temperature at which they will afford protection is very high, which limits their use on alloys with high recrystallization temperatures. Silicide coatings have the advantage of being self-healing, as a silica forms at discontinuities.

Ceramic type coatings also have been investigated. These are usually combined with metal, otherwise they would offer little protection. Typical mixtures are glass and Cr-Ni-B, or chromium powder plus frit. Such coatings are thick and very brittle at room temperature but some plasticity in the glassy phase permits limited deformation at high temperature.

Importance of Thermal Shock

The resistance to thermal shock is proportional to

$$\frac{TR}{aEdc}$$

where T is the thermal conductivity, R is the ultimate tensile strength, a is the coefficient of thermal expansion, E is Young's modulus, d is the density, and c is the specific heat.

The low coefficient of expansion (5×10^{-6} at 1000°C) of molybdenum confers on it a high resistance to thermal shock, but the difference between the expansion coefficients of the metal and the refractory coatings available is a primary cause of failure of coatings. Thermal shock tests (cycles of heating and cooling) vary considerably from one laboratory to another and there is need to standardise the test. Examples of tests now being used are as follows:-

- (a) Heat in furnace at 980°C , attaining temperature in 30 seconds, soak for 15 seconds and cool in air for 45 seconds.
- (b) Heat in jet at 1450°C for 15 seconds, quench in liquid nitrogen (30 cycles of heating and cooling are used).
- (c) Heat in jet at 1090 or 1370°C for 12 seconds, cool in air jet for 18 seconds.
- (d) Heat at the appropriate rate (surface heat transfer coefficient up to 0.03 cal/cm^2) in a temperature-controlled air fluidised bed and cool in a similar bed at room temperature (maximum heat transfer coefficient 0.02 cal/cm^2).

5. WELDING

Welds in molybdenum have been made by a variety of processes. At present shielded arc welding is the most highly developed process and has been the most widely used. Early work on the fusion welding of metal prepared by powder metallurgy methods showed that cracking and weld porosity were the major defects encountered. The use of carbon de-oxidized arc-cast material with appropriate shielding has largely eliminated these, but low ductility of welds at room temperature is still a major deterrent to the use of molybdenum for many applications. In shielded arc welding the molten molybdenum should be well shielded from the atmosphere with argon or helium containing less than 0.005% oxygen. Leading and trailing shields are desirable if the welding is done in the open.

Percussive and ultrasonic welding methods result in welds without recrystallized areas, thereby reducing brittleness, but improvement in the ductility of the unwelded material is necessary if brittleness is to be eliminated.

When titanium and carbon are added to molybdenum they tend to behave as de-oxidants and welds in alloys containing titanium and carbon may be somewhat more ductile than those in pure metal.

MOLYBDENUM

6. FABRICATION

6.1 Formability

Molybdenum can be formed by the standard methods such as deep drawing, spinning, roll forming, blanking and stretch forming. Because the transition from ductile to brittle behaviour in tension occurs near room temperature, it is desirable to use some heat in the forming of molybdenum parts, except for bending operations on very thin sheet. A temperature of 200-430°C is usually satisfactory for bending, drawing or spinning of sheet up to 1/16 - 3/32 in. thickness. For heavy plate and rod it may be necessary to heat the material to 980-1200°C before forming. The high thermal conductivity of molybdenum makes it difficult to maintain this elevated temperature during forming and it may be necessary to use heated dies, or to apply heat to the material (or even to do both) during the operation.

Operations such as shearing and punching should be carried out at temperatures in line with those given for forming.

6.2 Machinability

Machining practices in general are similar for the powder metallurgy and the arc-cast materials, with opinion divided as to the relative merits of high speed steel or carbide tools. Molybdenum is not a hard material, but the powder and chips produced are abrasive. The low coefficient of expansion of molybdenum makes it necessary to keep the tool cool in drilling to prevent seizing of the tool and possible cracking of the molybdenum.

Molybdenum can be machined by any of the standard methods such as milling, turning, drilling, boring, grinding, shaping, etc. In many shops it is common practice to machine without a coolant or to use carbon tetrachloride or trichlorethylene. Sulphurized oil may be used where the residue is not objectionable. It is also possible to contour-etch molybdenum, but with some difficulty.

TANTALUM

1. PHYSICAL PROPERTIES

(a) Density	16.6 g/cm ³
(b) Melting Point	2996°C, 5425°F
(c) Specific Heat	0.033 cal/g °C at 0°C 0.037 cal/g °C at 1090°C 0.050 cal/g °C at 2700°C
(d) Thermal Conductivity	0.13 cal/sec cm°C at 20°C
(e) Coefficient of Thermal Expansion	6.5 × 10 ⁻⁶ per °C at 20°C
(f) Crystal Structure	Body-centered cubic
(g) Thermal Neutron Cross Section	21.3 barns per atom
(h) Emissivity (total)	The emissivity increases from a value of about 0.18 for polished metal to a maximum of about 0.8, with oxidation, decreasing again as the thickness and nature of oxide change.

2. MECHANICAL PROPERTIES

2.1 Tensile Properties

For unalloyed annealed tantalum, at room temperature:-

Ultimate tensile strength	= 50 kg/mm ²
Yield strength	= 40 kg/mm ²
Elongation	= 25%

Strength is strongly temperature-dependent at lower temperatures and brittle behaviour is encountered at -155°C (-250°F) where strength is 105 kg/mm² for commercial purity.

Discontinuities in the strength vs. temperature curves are encountered at about 260°C (500°F), suggestive of strain aging.

Tensile strength at 1093°C (2000°F) (in inert atmosphere) is still about 13 kg/mm², yield strength about 7 kg/mm², and at 1200°C (2200°F) the ultimate strength is about 10.5 kg/mm².

TANTALUM

2.2 Variation of Properties with Temperature

Test Temperature	°F -320 -100 + 72 390 500 600							1000	1500	2000	2200
	°C -195 - 73 + 20 200 260 320							540	820	1090	1200
0.2% Yield Strength (kg/mm ²)	105	50	40	25	28	28		18	8	6	5
Ultimate Tensile Strength (kg/mm ²)	105	52	47	40	49	52		42	15	13	10.5
Elongation (%)	4	23	25	12	15	20		16	25	43	47.5
Atmosphere	Air							Inert			

Alloy development has been very limited and useful data are not available. Additions of tungsten or hafnium and, to a less extent, additions of titanium, molybdenum or vanadium, raise the tensile strength, with some loss in ductility.

2.3 Modulus of Elasticity

18,900 kg/mm² at room temperature, and 5950-7350 kg/mm² at 3000°F (1650°C).

2.4 Stress Rupture and Creep Strengths

Cold-rolled tantalum sheet tested in helium withstood 6 kg/mm² at 1200°C (2200°F). At higher temperatures, the following values were obtained:-

Test Temp.		Stress (kg/mm ²)	Time in sec. to Produce			Rupture Life (sec.)
°F	°C		1% Def.	2% Def.	5% Def.	
3000	1650	3.5	15	25	65	150
4000	2200	1	10	30	100	-
5000	2760	0.5	15	30	90	250

2.5 Alloys

Composition (%)				Ultimate Tensile Strength (kg/mm ²) (as extruded)		
W	Nb	Hf	V	1200°C	1400°C	1600°C
10				29-40	14	9
		5		35		
	30		5	29		
5		10		35	15	

3. OXIDATION

Tantalum is slightly, but not significantly, more oxidation-resistant than niobium.

Oxidation Rate of Tantalum at Various Temperatures*

Temperature °F °C		Oxygen Penetration (mils)	Interface Recession (mils)	Total (mils)
1000	540	4	-	4
1200	650	4	-	4
1400	760	12	-	12
1600	870	31	23	54
1800	980	59	33	92
2000	1090	98	46	144
An alloy with 33% Ti and 18% Co showed a low rate of oxidation after 20 hours at 1093°C (2000°F)				

4. COATINGS

Tantalum has been used largely for its corrosion resistance at moderate temperatures, or within electron tubes in vacuum. Very little work has been reported on coating development.

5. WELDING AND FABRICATION

The discussions in the section on niobium apply also to tantalum.

* 16 hr. test on samples 0.375 in. diameter × ½ in. long

TUNGSTEN

The property data available on this metal are sparse. They usually refer to bar or wire specimens, and thus do not indicate transverse properties. There are no known elevated-temperature data on alloys of tungsten.

1. PHYSICAL PROPERTIES

(a) Density	19.3 g/cm ³ , 0.697 lb/in ³								
(b) Melting Point	3410°C, 6170°F								
(c) Specific Heat	0.032 cal/g°C at 20°C (68°F) 0.036 cal/g°C at 1000°C (1830°F)								
(d) Thermal Conductivity	0.310 cal/cm sec°C at 20°C 0.260 cal/cm sec°C at 1327°C (2420°F) 0.245 cal/cm sec°C at 1727°C (3140°F)								
(e) Coefficient of Thermal Expansion	4.44 × 10 ⁻⁶ per °C at 27°C 5.19 × 10 ⁻⁶ per °C at 1027°C (1875°F) 7.26 × 10 ⁻⁶ per °C at 2027°C (3675°F)								
(f) Crystal Structure	Body-centered cubic								
(g) Thermal-Neutron Cross Section (barns per atom)	Usually reported as 19.2 but ranges from 19 to 22. The absorptions of individual isotopes are:-								
	<table> <tr> <td>W₁₈₀</td><td>less than 20</td></tr> <tr> <td>W₁₈₃</td><td>11</td></tr> <tr> <td>W₁₈₄</td><td>2</td></tr> <tr> <td>W₁₈₆</td><td>36</td></tr> </table>	W ₁₈₀	less than 20	W ₁₈₃	11	W ₁₈₄	2	W ₁₈₆	36
W ₁₈₀	less than 20								
W ₁₈₃	11								
W ₁₈₄	2								
W ₁₈₆	36								
(h) Emissivity (total)	727°C (1340°F) : 0.105 1227°C (2060°F) : 0.192 1727°C (3140°F) : 0.259 2227°C (4030°F) : 0.301 2727°C (4940°F) : 0.334 3227°C (5840°F) : 0.351								

2. COMPARISON BETWEEN POWDER METALLURGY AND ARC MELTING

Attempts to use the Westinghouse process (see the section on molybdenum) have failed. However, the first stage (hydrostatic pressure) is useful, and by this means samples of 50 kg have been produced.

Arc melting in vacuo has the advantage of purifying the metal and of permitting the re-use of waste, but it is difficult because of the power consumption. The ingots produced are coarse grained and not easily workable. (Extrusion has to be done at 2300°C). There have been hardly any production quantities produced and it is not possible yet to give comparative characteristics for products made by the two processes.

Electromet, who seem to have the most advanced techniques, are able to melt ingots of 50 mm diameter (length : 1 meter) and more recently have made ingots of 75 mm diameter. Arc melted ingots of 100 mm diameter have been recently produced by General Electric. Electron beam melting, tried by Temescal, has run into great difficulties.

Slip casting appears to be a process very suitable to tungsten and Electromet are able to produce batches of 75 kg having normal characteristics.

3. MECHANICAL PROPERTIES

Properties vary considerably with the degree of cold-working, the thermal history, the impurities added, accidentally or intentionally, and the grain size developed by the processing. For the most part, tungsten may be considered to be a brittle material at ambient or room temperature. A small degree of ductility can be developed by severe warm-cold working but, upon annealing, room temperature brittleness is again encountered.

3.1 Tensile Strength

Sintered ingot	13 kg/mm ²
Swaged rod	35-150 kg/mm ²
0.250 in (6.3 mm) diameter	50 kg/mm ²
0.100 in (2.5 mm) "	105 kg/mm ²
0.050 in (1.25 mm) "	140 kg/mm ²
Drawn Wire	140-420 kg/mm ²
0.025 in (0.65 mm) "	150 kg/mm ²
0.010 in (0.25 mm) "	175 kg/mm ²
0.005 in (0.12 mm) "	210 kg/mm ²
0.0005 in (0.01 mm) "	420 kg/mm ²
Annealed wire	105 kg/mm ²

TUNGSTEN

Rolled sheet

0.040 in (1.0 mm) thick	84 kg/mm ²
0.020 in (0.5 mm) thick	140 kg/mm ²
0.010 in (0.25 mm) thick	210 kg/mm ²

3.2 Yield Strength (Room Temperature)

Annealed (recrystallized) tungsten has a brittle fracture when tested in tension. The yield strength is therefore equal to the ultimate tensile strength in such instances. Well-worked tungsten has a small degree of ductility (up to 4% elongation in tension) so that the yield strength is $90 \pm 5\%$ of the ultimate, depending upon the percentage offset used to establish this value. Yield strength data are very limited.

3.3 Ductility (Room Temperature)

Tungsten is brittle at room temperature, especially when recrystallized. Ductility in bending of small diameter wire or thin sheet is good. Very few data on bend ductility or reduction in area are available.

3.4 Elevated-Temperature Strength

Data in the range of interest (above 2200°F) (1200°C) are limited. However, the ultimate tensile strength of wrought wire is of the order of 49 kg/mm² at 1200°C (2200°F), 28 kg/mm² at 1600°C (2910°F), and 20 kg/mm² at 1800°C (3270°F). The strength of ¼ in. diameter wrought bar specimens ranges from 18 kg/mm² at 1600°C (2910°F), 10 kg/mm² at 1800°C (3270°F), to 3 kg/mm² at 2760°C (4500°F).

The stress-rupture strength (kg/mm²) under helium on rods produced by powder metallurgy and having ultimate tensile strength at room temperature of 100 kg/mm² and elongation of 0-1 % is given by the following table:

Test Temperature		Life	
°C	°F	1 hr	10 hr
2250	4100	3.1	2
2500	4530	1.8	1.1
2700	4900	1.4	1.0
2800	5100	1.2	0.8

3.5 Modulus of Elasticity

35,000 kg/mm² at room temperature.

3.6 Brittle to Ductile Transition Temperature

The brittle temperature zone for tungsten lies above ambient or room temperature, but below 150°C (302°F). A transition region exists between 150°C and 450°C (842°F) where either brittle or ductile behaviour may be encountered, depending on the sample history and the testing procedure. Above 450°C, ductile behaviour is developed and a large drop in yield stress is encountered with a corresponding increase in ductility.

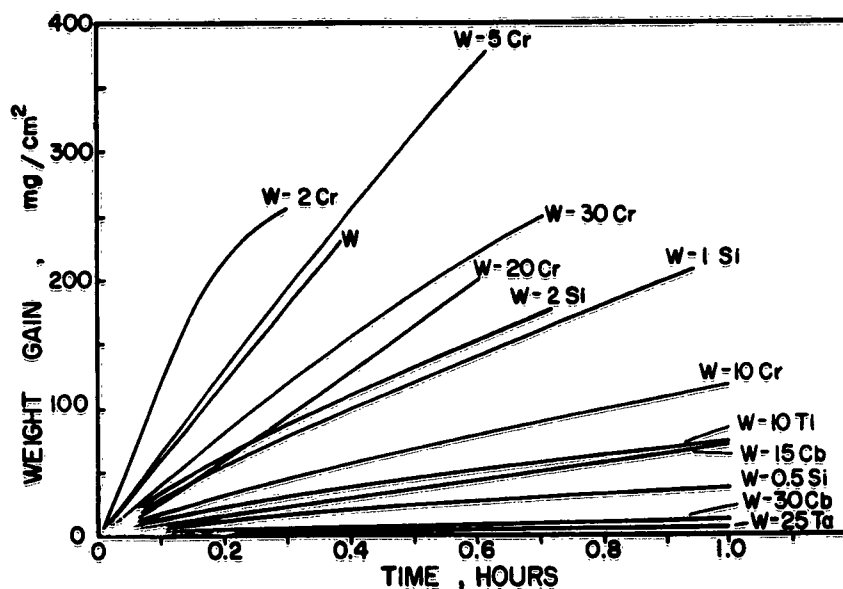
3.7 Alloys

Composition (%)					Ultimate Tensile Strength (kg/mm ²) (as extruded)		
Nb	Zr	C	ThO ₂	TaC	1400°C	1600°C	1900°C
0.9		0.02				32	14
	0.1	0.005				34	11
			2		29	22	
				0.4	47-55		

4. OXIDATION

Tungsten begins to oxidize rapidly above 600°C (1110°F) with a rate about equal to that of niobium and tantalum, up to 2100°F (1150°C), above which it has not been determined. Work on protective coatings for tungsten has begun only recently.

The study of coatings of *rhodium* (or other metals of the platinum group) with underlayers of Cr + Si, seems very promising.



Oxidation Rates of Tungsten and Some Binary Alloys in Dry Oxygen at 1200 C°

TUNGSTEN

The diagram and the following list show that certain additions can reduce the speed of oxidation, but it is probable that protective coatings will still be necessary at the working temperatures that are envisaged.

Thickness loss on one face (mils) in dry air

Test Temperature (°C)	1090		1260		Observations
Test Time	1 hr	8 hr	1 hr	8 hr	
Unalloyed Mo	33	261	40	238	No contamination, finer grain size in cast material. Brittleness by contamination
" W	5	27	6	15	
" Nb	4	31	13	75	
W + 20% Nb or W + 30% Ta	1.5	3.4	4.2	14.6	
Nb + 17.5% Ti	0.7	3.8	3.7	17.0	

5. JOINING

Tungsten cannot be joined by riveting with tungsten rivets. However, in some instances, molybdenum rivets can be used successfully. Tungsten can be arc-welded with suitable atmosphere protection, and can also be brazed. In most commercial fabricated parts, brazing is the preferable method of joining. Silver solder, copper, or nickel can be used for brazing in either controlled atmosphere furnaces by induction heating or in resistance welding equipment. Spot welded joints are commonly made using a layer of nickel between the tungsten parts. Although tungsten can be arc-welded, difficulties are often encountered due to excessive brittleness of coarse grained weld deposits and heat affected zones at room temperature.

6. FABRICATION

Tungsten can be produced in the form of hot rolled sheet, although it must, of course, be heated for rolling in an inert atmosphere. It can be machined but, because of its high hardness, only hard metal tools can be used for turning, milling, and drilling. Both tungsten rod and sheet can be formed if heated to a proper temperature range. In no circumstances should attempts be made to form tungsten at room temperature. Tungsten sheets can be formed at temperatures of 800 to 1000°C (1500 to 1800°F), and rod can be bent only at a good, red heat. Thin sheet can be formed at somewhat lower temperatures than the thicker sheet materials. In general, tungsten can be formed by simple bending, stamping, and spinning. However, the processes must be approached with a great degree of caution, and large deformation cannot be accomplished in one operation. Deep drawing of tungsten is virtually unknown in the industry in its present state of development.

PART II

RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

The following remarks apply, in general, to all the refractory metals under consideration.

1. ALLOY DEVELOPMENT

Certain molybdenum and niobium alloys are either presently available or will be in the near future. These, however, have serious limitations. The development of alloys of tungsten and of tantalum is in a very early stage. Research and development with the objective of producing new alloys of all four metals are therefore needed. Although it is unlikely that a single alloy able to satisfy all the requirements will be evolved, research objectives should include the following:

- (a) Improvement of strength at high temperature, including particularly an increase in the temperature of recrystallization
- (b) Improvement in resistance to oxidation
- (c) Improvement in formability, including the lowering of the ductile-brittle transition temperature
- (d) Improvement in weldability
- (e) Improvement in primary workability (ingot breakdown, rolling, forging, etc.)
- (f) Improvement in special properties such as melting point, coefficient of expansion, etc.

Particular emphasis must be given to point (a). It is recognised that the limiting temperature of usefulness of a metal is of the order of $0.4T_f$ where T_f is the melting point in $^{\circ}\text{K}$. This temperature corresponds roughly to the temperature of recrystallization. Alloys of the metal might be usable at a temperature of $0.8T_f$. Metals having a high melting point (Nb, Mo, Ta, W and Re) possess therefore an obvious advantage over other metals. Unfortunately molybdenum and tungsten and the alloys of niobium, molybdenum, tantalum and tungsten of current commercial purity, cannot be used at their recrystallization temperatures because recrystallization is accompanied by almost total embrittlement, due mainly to the segregation of interstitial solute atoms at grain boundaries. In order to raise the usable temperature from $0.4T_f$ to $0.8T_f$, the following features need to be studied:

- (a) The possible hardening mechanisms

- (b) How the effectiveness of those mechanisms is affected by increase in temperature
- (c) How temperature effects may be delayed.

The basic strengthening mechanism is essentially the pinning of dislocations. There are four primary pinning mechanisms, viz.

- (a) Pinning by further dislocations
- (b) Pinning by dissolved atoms or solid solution strengthening
- (c) Locking by order-disorder structure
- (d) Locking by a second phase.

A. Pinning by further dislocations

Straining creates further dislocations which form obstacles, which result in considerable improvement in room temperature mechanical properties. Examples are improvement of niobium and tantalum by cold working, of molybdenum and tungsten by hot-cold working followed by cold working, and of alloys of molybdenum, niobium, tantalum and tungsten by hot-cold working. These improvements are not, however, maintained with increase of operating temperature and in addition the temperature of recrystallization tends to decrease as the degree of cold working increases. There is though a possibility that close control of the conditions of cold working and of stress-relieving heat treatments might result in high density of dislocations by the formation of sub-structures. Improvements of this kind have already been obtained in molybdenum and the alloys of molybdenum with 0.5% titanium. It is unlikely though that a usable temperature in excess of $0.6T_f$ will be attained by this means.

B. Pinning by dissolved atoms, or solid solution strengthening

Dislocations are pinned by a group of dissolved atoms in their immediate neighbourhood. This mechanism effectively pins dislocations at room temperature but owing to reduction in the density of the atom cloud of the dissolved element and the tendency of the cloud to move with the dislocations instead of anchoring them its effect decreases with increase in temperature. The effects of increase in temperature on these two mechanisms can be combated by increasing the content of the dissolved element and by using a dissolved element of higher melting point or lower coefficient of diffusion. In refractory metal alloys this method of strengthening has been used to a large extent, being a result of the high mutual solubility of the high melting point metals such as niobium, tantalum, molybdenum and tungsten and the appreciable solid solubility of other high melting point metals such as titanium and zirconium.

Taking the four metals in turn the position is:

Niobium

Proposed alloys are almost all strengthened by solid solution with molybdenum, titanium, tungsten and tantalum*. Numerous other additions have been investigated to some extent.

* See table under niobium section in Part I

Tantalum

Laboratory investigations have consisted in examination of the effects of niobium, tungsten, molybdenum, titanium, hafnium, chromium and zirconium.

Molybdenum

Studies of molybdenum alloys have so far yielded rather disappointing results. They cover additions of tungsten, tantalum, vanadium, niobium, titanium and chromium. Alloys based on an addition of 25% tungsten are being developed. Rhenium also has been tried as an alloying element. Rhenium additions however may result in the formation of a brittle sigma phase (Mo_2Re_3). The actions of zirconium (solubility 7.5 atoms %) and manganese (solubility 15 atoms %) deserve special consideration.

Tungsten

Solid solutions are obtained with vanadium, niobium, tantalum and molybdenum. Studies in hand deal more particularly with alloys having a tungsten-molybdenum base or a tungsten-tantalum base or combinations of tungsten-tantalum-molybdenum and niobium. The effects of elements with a more limited solid solubility such as rhenium, titanium, zirconium and hafnium have received preliminary investigation.

It is evident that a thorough study of the behaviour of other metals, alone or combined, in addition to those mentioned above, is needed. The factors that should be taken into consideration are:

Degree of solid solubility

Difference in atomic diameter

Valency

Coefficient of diffusion

Melting point.

The need for information on phase diagrams and coefficients of diffusion is evidently urgent.

C. Locking by order-disorder structure (short range order)

This mechanism also is effective at room temperature but disappears when the temperature is raised, owing to reduction in the degree of short-range order and to increased diffusion and self-diffusion rates which cause the zones of disorder, due to dislocations, to rearrange themselves. Knowledge of the coefficients of diffusion is important when using this process.

There is no precise example of this behaviour in refractory alloys.

D. Locking by a second phase

The effectiveness of this mechanism depends on a fine dispersion of the second phase. A classic example is the aluminium-copper alloys in which solution of the element (copper) is first obtained by heat treatment followed by quenching. Precipitation of the CuAl_2 phase subsequently occurs. A more recently discovered example is that of titanium alloys in which a dispersed precipitate (Ti_2Cu) is obtained by eutectoid reaction following solution in the beta phase.

There are no typical examples in the alloys of the refractory metals. The behaviour of iron, nickel and cobalt in niobium, and of iron, nickel, aluminium, silicon and cobalt in molybdenum has been considered but the lack of complete phase diagrams prevents much speculation on the possibilities of the process. It must be borne in mind though that such dispersed precipitated phases are, by their very nature, thermodynamically unstable when the temperature rises and either grow, which decreases their dispersion and reduces their efficiency as obstacles, or dissolve and are lost as obstacles. The potentialities of the process may be increased:

1. By the precipitation of compounds that have a high melting point and that would, owing to reduction in diffusion rate, retard coalescence.
2. By obtaining secondary hardening by a second more stable phase which precipitates when the first dissolves or coalesces (this method has already been applied to certain steels and 'superalloys').
3. By finding a second stable and insoluble phase.

It is the third possibility which is being investigated to the greatest extent. The first example was sintered aluminium powder (SAP). This phenomenon gave a clue to the behaviour of alloys when carbon was added as a deoxidant during the alloy work on molybdenum, when the molybdenum-0.5% titanium alloy was developed. In fact it was clearly demonstrated later that when one adds to a refractory metal M (containing always a certain proportion of oxide or of oxygen) a metal X that readily forms an oxide, the result was not an alloy MX, but the oxide XO, hence the ternary alloy $\text{M}=\text{XO}-\text{X}$, where the insoluble oxide phase is formed in situ and therefore finely dispersed. In the refractory alloys titanium and zirconium are the most widely used additives but there is need to determine whether other metals having very stable oxides formed at high temperatures can be used to still better advantage. Carbides, nitrides, borides, etc. may be considered in addition to oxides.

On these bases, alloys already in existence or in a late stage of development are:-

$\text{Mo} + 0.5\% \text{ Ti}, \text{Mo} + \text{Zr} (0.08\%) + \text{Ti} (0.2\%) + \text{C} (0.05\%)$

$\text{Mo} + 0.5\% \text{ Ti} + 0.07\% \text{ Zr} + (\text{C})$

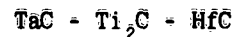
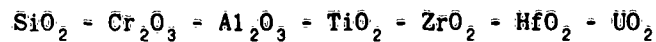
$\text{Nb} + 0.75\% \text{ Zr}$ (Fansteel's No. 80)

Similarly, alloys of $\text{Ta} + 1\% \text{ Zr} + \text{C}$ or $\text{Ta} + 1\% \text{ Ti} + \text{C}$ are being considered.

There is evidently a wide and potentially very fruitful field waiting to be explored.

The ways in which the advantages of a dispersed insoluble second phase may be explored are:

- (a) By direct addition of the metallic element before melting or sintering; promising elements being silicon, cobalt, titanium, zirconium and hafnium. (Boron seems to be unlikely to be useful in this connection). Particular attention should be given to the action of rare earths and yttrium, not only because they form volatile compounds at the expense of interstitial elements, with improvement of the fabricability but because of the possibility that stable dispersed compounds may be formed.
- (b) By additions of oxides (or nitrides, carbides or borides) during sintering, or melting, e.g.



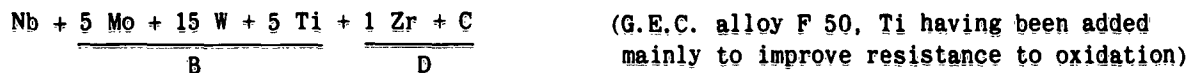
The addition to a metal of its own oxide, nitride or carbide should be included. Work of this type is being done with tantalum.

- (c) By controlled internal oxidation at sintering temperature.

Combinations of the various processes

As a general rule it would be profitable to combine two or more of the foregoing processes A to D. Process A will probably always be an essential in the production of refractory alloys.

The most profitable combination would seem to be A + B + D. Examples of these are:





2. COATINGS

Since it is unlikely that for most applications alloys can be developed with adequate resistance to oxidation, protective coatings must be devised. To be successful, a coating must be tailored to a specific alloy, to the conditions to be met in the particular service in mind, and must be appropriate for the fabrication practice employed (possibly applicable on an assembled unit). The development of realistic simulated service tests (including thermal-shock or thermal-cycling) would be of value. Coatings possessing high emissivity will be required especially for tungsten. The use of plasma-torch spraying could be of great assistance.

3. PRODUCTION DEVELOPMENT

The refractory metals are not now available in the desired alloys and in the required sizes of mill products. There has not been sufficient production of alloys even for the determination of properties to indicate the relative value for specific applications. For example, for tungsten there are no data except for the pure metal, and in the form of rod or wire. Furthermore, a very high quality product will be needed for aircraft applications. This will require a period of process development, especially with regard to wide, thin sheet alloy forms. Because of the great expense of producing these metals in the required mill forms, even in limited quantity, radically different methods from the conventional should be explored.

4. JOINING

It is obviously desirable to be able to assemble structures by welding. With proper procedures, the refractory metals can be welded, but the mechanical properties of the resulting joint are often unfavourable, especially in the case of Mo and W (pure Nb or Ta can be successfully fusion welded). This is because, with these two metals, usable ductility has only been associated with a structure having elongated grains resulting from previous deformation. The trend toward application of composite structures, such as honeycomb, may make mandatory the welding of thin sheet.

Research should be directed mainly in the following directions:-

Development of alloys leading to better behaviour in standard processes (inert gas shielding, with consumable or non-consumable electrode)

Development or improvement of new techniques

Electron-beam welding

Ultrasonic welding

Percussive or pressure welding

Fusion welding with the addition of processes to break down the coarse grain (ultrasonic or forge-welding)

Solid state bonding, preventing the formation of coarse grain.

5. BASIC RESEARCH

A variety of topics are now listed which obviously need further attention if the technology of refractory metals is to make progress.

5.1 Phase Diagrams

Many advances could be made by the availability of equilibrium diagrams. In most cases, the complete system is not required; the solid solubility limit, liquidus and solidus surfaces and identification of the first compound being usually sufficient.

It is recommended that, in selecting systems for study, the following considerations be borne in mind:-

- I. That the systems selected be related to the purposes for which the material might be used, such as in studies of alloying, coating, joining, influence of gaseous environment, exploration of properties and metal behaviour.
- II. That, since the effects of gases in these metals are so important, a high priority be given to metal-gas systems which the final report shows have not yet been adequately covered (tungsten).
- III. That the systems should not be restricted to binary systems, but careful consideration and suitable priority should be given to systems with more components.

The phase diagrams whose study is considered desirable, on the refractory metal side at least, but which does not seem to have been undertaken, are as follows:

Niobium

Nb-Co	Nb-Si
Nb-Zn	
Nb-B	Nb-Be
Nb-platinum group metals (Ir-Os-Pd-Pt-Rh)	
Nb-Ce	Nb-La Nb-Y

Tantalum

Ta-Co	Ta-Cr	Ta-Fe	Ta-Ni	Ta-Cu	Ta-Mn
Ta-Be	Ta-Al				
Ta-Hf					
Ta-Pt	Ta-Rh	Ta-Pd			
Ta-Ce	Ta-La	Ta-Y			

Tungsten

W-Fe	W-Cu	W-Mn
W-Ti		
W-Th		
W-Pd		
W-O	W-N	W-H
W-Ce	W-La	W-Y

Molybdenum

Mo-V		
Mo-Th		
Mo-B		
Mo-Ce	Mo-La	Mo-Y

5.2 Diffusion Couples

5.2.1 Studies of the diffusion couples in refractory metals are of the highest importance in connection with:-

- (a) Successful production of alloys by powder metallurgy
- (b) Homogenization of sintered or cast refractory alloys
- (c) Strengthening by solid solution or dispersion.

The following are suggested for study:-

- (i) In every refractory metal, rates of diffusion of the high melting point metals :
W-Ta-Re-Mo-Nb.
- (ii) In niobium : Ti-Zr-V-Fe-Hf
- (iii) In tantalum : Ti-Hf-Zr-V
- (iv) In tungsten : Ti-Zr-Hf-Cr-V
- (v) In molybdenum : Ti-Zr-V-Co.

5.2.2 As far as sintering or melting in vacuo can be considered as a purification process, rates of diffusion of some impurities have to be studied, for example:-

Fe-Si in Niobium
Fe-Si in Tantalum
O-N-H-C-Fe-Mo in Tungsten
O-N-H-C-Fe-Mn in Molybdenum.

5.2.3 The success of metallic protective coatings mainly depends on adequate diffusion rates. In the field of the four refractory metals, it is recommended to study diffusion couples with

platinum-group metals and among these Rh (especially with tungsten),
Ni-Cr-Al-Si-B.

5.3 Impurity Effects

The presence of small amounts of certain impurities has a profound influence on the mechanical behaviour of the refractory metals. This is especially true of the interstitial elements, oxygen, nitrogen, carbon and hydrogen. More work is needed to understand this behaviour.

Examining the work which might be done under this heading, at least five important areas are recognised:-

- I. The effect of impurities on mechanical properties at a given temperature, or over a range of temperature, including such items as ductile-brittle transition, crack initiation and propagation, fabricability, etc., and the mechanisms involved relating to these phenomena. In such studies, the method of study and test should be clearly indicated, such as impact studies, microscopic investigation, specimen details, deformation rates, dislocation studies, etc.
- II. The effect of impurities on diffusion processes; for example, in coating and joining.
- III. The effect of impurities on physical properties; for example, thermal conductivity.
- IV. The effect of impurities on chemical properties; for example, in stress and intergranular corrosion.
- V. Methods for minimizing the injurious effects of these impurities.

In all these situations, interest is mainly concentrated on the interstitial elements.

A related problem concerns the determination of these elements in the important range 1 to 100 parts per million. This is a problem not yet under control, especially with regard to oxygen.

A program of cooperation between a certain number of the NATO countries has been set up to analyse samples (powder and solid) which have been exchanged between the different countries participating, and to define the best methods for analysis.

5.4 New Fabrication Techniques

Compared to most metals, the refractory metals are very intractable. Unusual methods for making products may be the most efficient approach. Typical of the new techniques are slip casting, rolling of sheet from powder, and flame spraying to form a metallic body.

5.5 Oxidation Studies

The behaviour of the refractory metals with regard to oxidation is well known up to about 1000°C. Data above this temperature are fragmentary. Compared to intermediate

temperatures, the situation at very high temperatures may be substantially different. For example, it is possible that the oxide of tungsten may decompose at a sufficiently high temperature. Basic studies may be of great value in assisting the devising of protective systems.

In studying this problem it is suggested that the following be taken into consideration.

5.5.1 Physical and mechanical condition of the samples: for example; composition, shape, size, surface-finish, heat-treatment, grain size, texture.

5.5.2 Nature and conditions of the gas: for example; oxygen, hydrogen, nitrogen, air, water vapour, metal vapour, or other elements in the gaseous state, individually or mixed; and such physical conditions as pressure, velocity, physical state (molecular - dissociated - ionized).

5.5.3 External conditions such as temperature and time: for example; gradients, whether stagnant or cyclic, etc.

5.5.4 Agreement on a standard test or tests under conditions closely approaching particular service conditions.

5.5.5 Design of equipment for this research : facilities.

5.5.6 Nature of deterioration and methods for its evaluation: for example; weight gain or loss, whether intergranular, or pitting type of attack, mechanical and physical nature of corrosion products, etc.

6. DESIGN DATA

To allow a selection of a refractory metal, at least a certain minimum amount of data will be required by a designer. Much more will be needed in preparing an actual design. For the most part, sufficient data are not existent to make even the preliminary estimate adequately.

The types of properties on which data are desired to permit a selection of alloys are given below.

Physical Properties

Density

Specific heat

Thermal expansion as a function of temperature

Thermal conductivity at room temperature and 2000°F

Melting point

Emissivity.

Mechanical Properties (testing conditions indicated)

Ambient Temperatures

Tensile ultimate strength and elongation at fracture
Tensile yield strength
Compressive yield strength
Modulus of elasticity
Notch sensitivity and transition temperature.

Elevated Temperature (data at temperatures between 1000°C and 1650°C)

Tensile strength and elongation at fracture
Stress-rupture strength for 1 and 100 hr lives. Curves showing total deformation (including thermal expansion, elastic and plastic deformation) would be valuable to supplement rupture strength.
Thermal shock resistance
Modulus of elasticity as a function of temperature.

Chemical Properties

Corrosion resistance at room temperature
Total weight change (coated and uncoated) or weight loss (uncoated after descaling) after exposure to temperatures from 1000°C to 1650°C as mg/cm² after X hours exposure. Also, if possible, thickness of layer (in mm) and internal penetration, including localized effects, resulting from X hours at temperatures.
Embrittlement after exposure to above temperatures.

Fabricability

Ease of primary fabrication
Formability
Machinability
Weldability.

Availability of Mill Products

Forms and sizes.

PART III *

BASIC RESEARCH - THE PRESENT STATE OF KNOWLEDGE FOR EACH METAL

1 NIOBIUM

1.1 Phase Diagrams

- 1a. Klopp *Diffusion rates and Solubilities of Interstitials in Refractory Metals.* DMIC Memo 50, April 1960.

1.1.1 Systems which can be Regarded as Known

- Nb-O
1. Seybolt *Solid Solubility of O_2 in Nb.* JOM, June 1954, p.774.
 2. Elliott *Columbium + Oxygen System.* ASM Preprint No. 143, 1959.

See also references in Section 1.4(a) (reaction of Nb with oxygen).

- Nb-N
3. Brauer *Nitrides of Nb.* ZAC, Vol.270, 1952, p.160.
 4. Brauer *Nitrides of Nb.* ZAC, Vol.274, 1953, p.11.
 5. Schöenberg *Some Features on the Nb-N System.* ACS, Vol.8, 1954, p.208.

See also references in Section 1.4(b) (reaction of Nb with nitrogen).

- Nb-H
6. Brauer *Hydrides of Nb.* Ref.3.
 7. Albrecht *Nb-H.* JES, April 1958, p.219.
 8. Paxton *Observations on the Nb-H System.* TAIME, August 1959, p.725.
 9. Wainwright *The Nb-H System.* Bulletin of the Institute of Metals, July 1958, p.68.
 10. Albrecht *Reactions in the Nb-H System.* JES, November 1959, p.981.
 - 10a. Komjathy *The Nb-H System.* JLCM, December 1960, p.466.

See also references in Section 1.4(c) (reaction of Nb with hydrogen).

- Nb-C
11. Brauer *Carbides of Nb.* ZAC, Vol.277, 1954, p.249.
 12. Brauer & Lesser *Karbidphasen des Niobs.* ZM, Vol.50, 1959, p.8.

* For Notes and Abbreviations used in Parts III and IV, please see the Appendix on p.129.

	13.	Norton & Mowry	<i>Solubility Relationships of the Refractory Monocarbides.</i> TAIME, Vol.185, 1949, p.133.
	13a.	Elliott	<i>The Cb-C System.</i> ASM Preprint 179, 1960.
Nb-Mo	14.	Bückle	<i>Aufbau und Mikrohärtigkeit der Zwei- und Dreistoffsysteme der Metalle Niob, Tantal, Molybdän und Wolfram.</i> ZM, Vol.37, 1946, p.53. (Solid solutions for all proportions).
Nb-Re	15.	Knapton	<i>The Niobium-Rhenium System.</i> JLCM, Vol.1, 1959, p.480.
	16.	Knapton	<i>Nb and Ta Alloys.</i> JLCM, Vol.2, 1960, p.113. (Complete diagram).
	17.	Knapton	<i>An X-ray Survey of Certain Transition-Metal Systems for Sigma-Phases.</i> JIM, Vol.87, September 1958, p.28.
	18.	Greenfield & Beck	<i>Intermediate Phases in Binary Systems of Certain Transition Elements.</i> TAIME, Vol.206, 1956, p.265 (also JOM, Vol.8).
	19.	Grant	Work performed at MIT under US Government Contract.
	20.	Savitskii	<i>Atomnaya Energiya,</i> Vol.7, 1959, p.470. (Complete diagram).
	20a.	Levesque	<i>The Cb-Re System.</i> ASM Preprint 192, 1960.
Nb-Ru	21.	Knapton	Ref.16.
	22.	Greenfield	Ref.18.
	23.	Grant	Ref.19.
Nb-Ta	24.	Bückle	Ref.14. (Solid solutions for all proportions).
	25.	Williams & Pechin	<i>The Tantalum-Columbium Alloy System.</i> TASM, Vol.50, 1958, p.1081.
Nb-Ti	26.	Hansen et alii	<i>Systems Titanium-Molybdenum and Titanium-Niobium.</i> TAIME, Vol.191, 1951, p.881. (also JOM, Vol.3).
	27.	Gonser	<i>Titanium Alloys.</i> Industrial and Engineering Chemistry, Vol.42, 1950, p.222.
Nb-V	28.	Wilhelm et alii	<i>Columbium-Vanadium Alloy System.</i> TAIME, Vol.200, 1954, p.915.
Nb-W	29.	Bückle	Ref.14. (Solid solutions for all proportions).
1.1.2 Partially Determined Systems			
Nb-Co**	30.	Köster & Mulfinger	<i>Die Systeme des Kobalts mit Bor, Arsen, Kirkon, Niob und Tantal.</i> ZM, Vol.30, 1938, p.348.
	31.	Wallbaum	<i>Ergebnisse der Röntgenographischen Strukturuntersuchung von Legierungen der Zusammensetzung AB₂ der Eisenmetalle mit Titan, Zirkon, Niob und Tantal.</i> ZK, Vol.103, 1941, p.391.

Nb-Fe**	32.	Eggers & Peter	<i>Das Zustandsdiagramm Eisen-Niob.</i> Mit. K-W Inst. Eisenforschung zu Düsseldorf, Vol.20, 1938, p.199.
	33.	Vogel & Erlang	<i>Das System Eisen-Eisenwolframid-Eisentitanich.</i> Archiv für das Eisenhüttenwesen, Vol.12, 1938, p.149.
	34.	Wallbaum	Ref.31.
	35.	Elliott	Armour Research Foundation OSR TN 247, August 1954.
	36.	Begley	<i>Development of Niobium-Base Alloys.</i> WADC Technical Report 57-344, Part I, May 1958, p.83 (ASTIA No.AD-155583).
Nb-Hf*	37.	Duwez	<i>The Allotropic Transformation of Hafnium.</i> JAP, Vol.22, 1951, p.1174.
	38.	Elliott	Ref.35.
Nb-Ni*	39.	Grube et alii	<i>Über die Gewinnung von Festen Niob-Nickel-Legierungen durch Reduktion von Niobpentoxyd bei Gegenwart von Nickel.</i> Zeitschrift für Elektrochemie, Vol.45, 1939, p.881.
	40.	Pogodin	<i>The Constitution Diagram of Ni-Nb System.</i> Comptes Rendus, Académie des Sciences, URSS, Vol.31, 1941, p.895.
	41.	Kubaschewski & Schneider	<i>Measurements on the Oxidation-Resistance of High-Melting-Point Alloys.</i> JIM, Vol.75, 1948, p.403 (414). (Solid solution of Ni in Nb).
	42.	Wallbaum	<i>Zur Legierungschemie der Übergangsmetalle.</i> Naturwissenschaften, Vol.31, 1943, p.91.
Nb-Si**	43.	Brewer & Krikorian	<i>Reactions of the Refractory Silicides with Carbon and with Nitrogen.</i> USAEC, University of California Radiation Laboratory Report 2544, 1954.
	44.	Knapton	<i>The System Niobium-Silicon and the Effect of Carbon on the Structures of Certain Silicides.</i> Nature, Vol.175, 1955, p.730.
	45.	Kieffer et alii	<i>Beitrag zum Aufbau der Systeme Vanadin-Silizium und Niob-Silizium.</i> ZM, Vol.47, 1956, p.247.
Nb-Th	47.†	Carlson et alii	<i>Thorium-Niobium and Thorium-Titanium Alloy Systems.</i> TAIME, Vol.206, 1956, p.132 (also JOM, Vol.8).
	48.	Chiotti	<i>High Temperature Crystal Structure of Thorium.</i> JES, Vol.101, 1954, p.567.
Nb-U	49.	Saller	<i>Compilation of U.S. and U.K. Uranium and Thorium Constitutional Diagrams.</i> BMI Report 1000, June 1955.

† There is no Reference 46

	50.	McIntosh & Bagley	<i>Selection of Canning Materials for Reactors Cooled by Sodium/Potassium and Carbon Dioxide.</i> JIM, Vol.84, 1956, p.260.
	51.	Pfeil et alii	<i>The Uranium-Niobium Alloy System in the Solid State.</i> JIM, Vol.87, Feb.1959, p.204.
Nb-Zr*	52.	Rogers & Atkins	<i>The Zirconium-Columbium Diagram.</i> USAEC, Report ISC-500, 1954.
	53.	Rogers & Atkins	<i>Zirconium-Columbium Diagram.</i> TAIME, Vol.203, 1955, p.1034.
	54.	Knapton	Ref.16.

1.1.3 Systems Studied in a Few Respects only

General	55.	Begley	<i>Development of Niobium-Base Alloys.</i> WADC Technical Report 57-344, Part II, Dec.1958, (ASTIA No.AD-155583), p.100 (Critical survey of 55 possible additive elements).
	56.	Sims	<i>A Columbium Primer.</i> JOM, May 1958, p.340. (General aspect of Nb-X equilibria).
	57.	McIntosh	<i>The Development of Niobium.</i> JIM, Vol.85, April 1957, p.367 (General survey).
Nb-Al*	58.	Olshausen	<i>Strukturuntersuchungen nach der Debye-Scherrer-Methode.</i> ZK, Vol.61, 1925, p.475.
	59.	Brauer	<i>Über die Kristallstruktur von $TiAl_3$, $NbAl_3$, $TaAl_3$ und $ZrAl_3$.</i> ZAC, Vol.242, 1939, p.1.
Nb-As	60.	Heinerth & Biltz	<i>Darstellung und Dichten einiger Phosphide und Arsenide.</i> ZAC, Vol.198, 1931, p.171.
Nb-B**	61.	Andersson & Kiessling	<i>Investigations on the Binary Systems of Boron with Chromium, Columbium, Nickel and Thorium, Including a Discussion of the Phase 'TiB' in the Titanium-Boron System.</i> ACS, Vol.4, 1950, p.160.
	62.	Norton	Ref.13, p.749.
	63.	Andersson & Kiessling	Ref.61.
Nb-Be**	65.	Kaufmann et alii	<i>The Metallurgy of Beryllium.</i> TASM, Vol.42, 1950, p.801.
Nb-Ce**	66.	Savitsky et alii	<i>Investigation of Alloys of Niobium with Lanthanum and Cerium.</i> JIM, Metallurgical Abstracts, Vol.27, 1959, p.175.
Nb-Cr*	67.	Elliott	Ref.35, p.18.
	68.	Begley	Ref.36.
	69.	Elyutin	USSR Academy of Sciences, Vol.3, 1956, p.68.
	70.	Kubaschewski	Ref.41, p.410.

	71.	Duwez & Martens	<i>Crystal Structure of TaCr₂ and NbCr₂</i> . TAIME, Vol.194, 1952, p.72.
	71a.	Goldschmidt	<i>The Nb-Cr System</i> . JLCM, Vol.3, No.1, 1961, p.44.
Nb-Cu*	72.	Elliott	Ref.35.
Nb-Ge	73.	Hardy & Hulm	<i>The Superconductivity of Some Transition Metal Compounds</i> . Physical Review, Vol.93, 1954, p.1004.
	74.	Carpenter	<i>Journal of the American Ceramic Society</i> , Vol.77, 1955, p.1502.
Nb-Ir**	75.	Dwight & Beck	<i>Close-Packed Ordered Structures in Binary AB₃ Alloys of Transition Elements</i> . TAIME, Vol.215, 1959, p.976. Trans. Metallurgical Society of AIME.
	76.	Geller et alii	<i>Some New Intermetallic Compounds with the 'B-Wolfram' Structure</i> . Journal of the American Chemical Society, Vol.77, 1955, p.1502.
Nb-La**	77.	Savitsky et alii	Ref.66.
Nb-Mn*	78.	Wallbaum	Ref.31.
	79.	Greenfield & Beck	<i>The Sigma Phase in Binary Alloys</i> . TAIME, Vol.200, 1954, p.253.
	80.	Elliott	Ref.35.
Nb-Os**	81.	Geller	Ref.76.
	82.	Knapton	Ref.17.
Nb-P	83.	Schönberg	Ref.5, p.226.
	84.	Biltz & Köcher	<i>Über das System Tantal/Schwefel</i> . ZAC, Vol.238, 1938, p.81.
Nb-Pd**	85.	Knapton	Ref.16.
	86.	Greenfield & Beck	Ref.18.
Nb-Pt**	87.	Geller	Ref.76.
	88.	Greenfield & Beck	Ref.18.
Nb-Rh**	89.	Greenfield & Beck	Ref.18.
	90.	Dwight	Ref.75.
Nb-S	91.	Biltz & Köcher	<i>Über das System Niob/Schwefel</i> . ZAC, Vol.237, 1938, p.369.
	92.	Schönberg	<i>The Tungsten Carbide and Nickel Arsenide Structures</i> . Acta Metallurgica, Vol.2, 1954, p.427.

Nb-Sn	93.	Geller	Ref.76.
	94.	Matthias et alii	<i>Superconductivity of Nb₃Sn</i> . Physical Review, Vol.95, 1954, p.1435.

1.1.4 Unstudied Systems

Nb-Ag* = Nb-Au = Nb-Ba = Nb-Bi = Nb-Ca = Nb-Cd* = - Nb-Hg = Nb-In = Nb-K =
 = Nb-Li = Nb-Mg = Nb-Na = Nb-Pb = - Nb-Sr = Nb-Te = Nb-Y** = Nb-Zn**.

1.2 Impurity Effects and Analysis

95a.	Mincher	<i>Effects of Structure and Purity on Cb</i> . TAIME, February 1961, p.19.
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1.2.1 Effects

Oxygen See also Section 1.4(a).

95.	Begley	Ref.36. (Effect of O and N on the contamination of welded pieces)
96.	Seybolt	Ref.1. (Influence of O on hardness).
97.	Schofield	<i>The Melting Point of Niobium</i> . JIM, Vol.85, 1957, p.372. (Influence of O on hardness).
98.	Tottle	<i>The Physical and Mechanical Properties of Niobium</i> . JIM, Vol.85, 1957, p.375.
99.	Saller	<i>Initial Investigations of Nb and Nb Alloys</i> . BMI Report 1003, 23/5/58.
100.	Klopp	<i>High O Oxidation and Contamination of Nb</i> . BMI Report 1170 or TASM, Vol.51, 1959, p.282.
101.	Vaughan & Rose	<i>The Tensile Properties of Niobium</i> . UKAEA Report IGR-TN/C-583, Nov.1958.
101a.	Begley	<i>Effects of Oxygen and Nitrogen on Workability of Cb</i> . ASTM Special Technical Publication No.272, 1960, p.56.
101b.	Leadbetter	<i>Effects of Oxygen on the Properties of Zone- Refined Nb</i> . JLCM, Vol.3, No.1, 1961, p.19.

Nitrogen	102.	Brauer	Refs. 3 and 4.
	103.	Ang & Wert	<i>Some Properties of Columbium Containing Nitrogen</i> . TAIME, Vol.197, 1953, p.1032.
	104.	Saller	Ref.99, p.7 and pp.10-17.
	105.	Klopp	Ref.100.
	106.	Begley	Ref.36.

Hydrogen	107.	O'Driscoll & Miller	<i>Purification of Niobium by Sintering</i> . JIM, Vol.85, 1957, p.379.
	108.	Brauer	Ref.4.
	108a.	Wilcox	<i>Effects of Hydrogen on Dislocation Locking in Nb</i> . JLCM, Vol.2, No.2, 1960, p.297.

Carbon	109.	Saller	Ref.99.
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1.2.2 Analysis

General Review	110.	Mallett	<i>Determination of O - N - H - C in Mo - W - Nb - Ta.</i> DMIC Memo 49, 31 March 1960.
	111.	Niebuhr	<i>Praxis der Gasbestimmung in hochschmelzenden Metallen (Gas Determination in Refractory Metals).</i> Proceedings of Third Plansee Seminar, Metallwerk Mansee, Reutte, Tyrol, June 1958, p.313.
	112.	Fassel	<i>Spectrographic Determination of O₂ N - H in Metals.</i> Atomic Energy Conference, United Nations, Geneva, Sept.1958, No.917.
	113.	Fagel	<i>Determination of O - N - H in Refractory Metals.</i> Analytical Chemistry, Vol.31, 1959, p.1115.
Oxygen	114.	Harris	Westinghouse Research Report 6-94602-9-R13, August 1957.
	115.	Harris	<i>Technology of Cb.</i> Report of the Electrochemical Society Meeting, 12 May 1957, Washington, p.57.
	116.	Begley	Ref.36, pp.94-97.
	117.	Société Kulhmann	Levallois, France, unpublished.
	118.	Codell	<i>Determination of O₂ in Metals.</i> ASTM Special Technical Publication No.222, 1958.
	119.	Hansen	<i>Determination of O₂ in Nb.</i> Analytical Chemistry, Vol.29, 1957, p.1868.
	120.	Durand	<i>Dosage de O₂.</i> Société Française de Métallurgie, October 1959.
Nitrogen	121.	Harris	Westinghouse Research Report 6-94602-9-R10, June 1957.
	122.	Harris	Ref.115.
	123.	Begley	Ref.36, p.94.
	124.	Société Kulhmann	Levallois, France, unpublished.
	125.	Gonard	<i>The Determination of N in Nb.</i> Westinghouse WAPD-CTA 203-UC4, 24 April 1956.
Tantalum	126.	Begley	Ref.36, p.94.
	127.	Theodore	Westinghouse Materials Eng. Rep. 5704-4015-A, April 1957.
Fe-Zr-Si-Ti etc.	128.	Begley	Ref.36, p.94.
	129.	Reed	<i>Technology of Cb.</i> Electrochemical Society Meeting, 12 May 1957, Washington, p.54.
	130.	Société Kulhmann	Ref.124.
	131.	Palilla et alii	<i>Analytical Chemistry of Niobium and Tantalum.</i> Analytical Chemistry, Vol.25, 1953, p.926.

1.3 Diffusion

The knowledge of the characteristics of the diffusion couples Nb-X is limited, in the case of niobium, to elements O, N, H, C. No information concerning metallic elements seems to have been provided yet.

This question is therefore closely connected with that considered in Section 1.4 (behaviour in a gaseous medium). One should especially quote:

Nb	132.	Resnick	<i>The Self-Diffusion of Cb.</i> TAIME, April 1960, p.307.
Nitrogen and Oxygen	133.	Ang	<i>Activation Energies and Diffusion Coefficient of O and N in Nb.</i> Acta Metallurgica, Vol.1, 1953, p.123.
	134.	Klopp	Ref.100.
	135.	Sims	<i>Studies of the Oxidation and Contamination Resistance of Binary Nb Alloys. (Ti - Cr - Zr - V - Mo - Ta - W) at 800-1,000° in Air.</i> BMI Report 1169 or Trans.ASM, Vol.51, 1959, p.256.
	136.	Klopp	<i>Oxidation and Contamination Reactions of Niobium and Niobium Alloys.</i> Battelle Memorial Institute Report 1317, February 1959. [Diffusion of O and N in Nb (p.16) and in binary alloys (p.34)].
	137.	du Pont de Nemours	<i>Diffusion of O and N in Alloys of Nb 10Ti 10Mo (p.10-12).</i> Technical Memo Nb 10Ti 10Mo and U.S. Patent 2, 822, 268, 1958.
	138.	Michael	<i>Oxidation of Nb-Base Alloys.</i> AIME Conference, Buffalo, May 1958.
	139.	Kling	<i>Development of Oxidation Resistant Alloys.</i> Technology of Cb. Wiley, New York, 1958, p.87.
	139a.	Klopp	Ref.1a.
Metals	140.	Beach	<i>Electroplated Metals on Nb.</i> Technology of Cb. Wiley, New York, 1958, p.81.
	141.	Beach	<i>Electroplated Metals.</i> BMI No.1004, May 1955.
General	142.	Wert	<i>Measurements of the Diffusion of Interstitial Atoms in BCC Lattices.</i> JAP, Vol.21, 1950, p.1196.
	143.	Wagner	<i>The Formation of Composite Scales.</i> JES, Vol.103, p.571, November 1956.
	144.	Kubaschewski	<i>Oxidation of Metals and Alloys.</i> Butterworths, London, 1953.
	145.	Marx	<i>The Internal Friction of Nb.</i> Acta Metallurgica, Vol.1, 1953, p.193.
	145a.	Powers	<i>Some Internal Friction Studies in Nb.</i> TAIME, Vol.209, 1957, p.1285.

1.4 Behaviour in a Gaseous Environment at Elevated Temperature

(a) Oxygen		Metal	T (°C)	Pressure	Remarks
146. Gulbransen & Andrew	<i>Reactions of Zirconium, Titanium, Columbium and Tantalum with the Gases, Oxygen, Nitrogen, and Hydrogen at Elevated Temperatures. JES, Vol. 96, December 1949, p. 364.</i>	Nb	100-370	0.1 atm	parabolic laws
147. Gulbransen	<i>Kinetics of the Reactions of Niobium and Tantalum with Oxygen, Nitrogen, and Hydrogen. TAIME, Vol. 188, 1950, p. 586, (in Journal of Metals).</i>	Nb	200-375	0.1 atm	parabolic laws
148. Begley	<i>Ref. 36, p. 39-59.</i>	Nb	350-700	0.1 atm	transition
149. Aylmore et alii	<i>Oxidation of Niobium in the Temperature Range 350°-750°C. JES, Vol. 107, June 1960, p. 495.</i>	Nb	350-700	1-0.1 atm dry or wet	from parabolic to linear at 400°
150. Gulbransen & Andrew	<i>Oxidation of Niobium Between 375°C and 700°C. JES, Vol. 105, Jan. 1958, p. 4.</i>	Nb	375-700		
151. Kolski	<i>Columbium-Oxygen Reactions from 450 to 1200°C. AIME Conference, Chicago, 2 November 1959.</i>	Nb	450-1200	1 atm dry	
151a. Jaffee	<i>High Temperature Oxidation of Cb. TASM, Vol. 51, 1959, p. 282.</i>				
151b. Zmeskal & Brey	<i>Oxidation of Zirconium-Niobium Alloys in Oxygen at 525-1090°C. ASM Preprint 53, No. 207, 1960.</i>	Alloys Nb + Zr	525-1090	100 mm	
151c. Cathcart & Young	<i>Influence of Reactor Radiation on the Oxidation of Niobium. Corrosion, Vol. 17, No. 2, 1961, p. 77.</i>	Nb	400	760	Under irradiation
151d. Kofstad & Kjöllesdal	<i>Oxidation of Niobium (Columbium) in the Temperature Range 500° to 1200°C. TAIME, Vol. 221, April 1961, p. 285.</i>	Nb	500-1200	0.1-760	

			Metal	T (°C)	Pressure	Remarks
152.	Klopp et alii	<i>Effect of Alloying on the Kinetics of Oxidation of Niobium.</i> Peaceful Uses of Atomic Energy, Conference, Geneva, September 1958, No. 712, Vol. 6, p. 293.	Nb	400-1200	1 atm	
153.	Klopp	Ref. 100.				
154.	Klopp	Ref. 136.	Nb	400-1400	1 atm	
155.	Bridges & Fassell	<i>High Pressure Oxidation of Niobium.</i> JES, Vol. 103, 1956, p. 326.	Nb	400-800	0.2 at 40	
156.	Goldschmidt	<i>X-Ray Investigation on Nb₂O₅.</i> JIM, March 59, p. 235.	Nb	400-1,050	1 atm dry or wet	influence of sample size
157.	Argent & Phelps	<i>The Oxidation of Niobium.</i> JIM, Vol. 88, March 1960, p. 301.	Nb	400-1,050	1 atm dry or wet	influence of sample size
(b) Nitrogen						
158.	Gulbransen	Ref. 146.	Nb	100-370	0.1 atm	
159.	Gulbransen	Ref. 147.	Nb	200-375	0.1 atm	
160.	Klopp	Ref. 100.	Nb	600-1400	1 atm	
161.	Klopp	Ref. 136.	Nb	800-1000	1 atm	
162.	Albrecht	<i>Reaction of Nitrogen with Niobium.</i> BMI Report 1360, July 1959.	Nb	675-1600	1 atm	parabolic laws
(c) Hydrogen						
163.	Gulbransen	Ref. 146.	Nb	100-370		
164.	Gulbransen	Ref. 147.	Nb	200-375		
165.	Brauer	Ref. 4.				
166.	Albrecht	Ref. 7.				
167.	Wilcox & Huggins	<i>Effect of Hydrogen on Dislocation Locking in Niobium.</i> JLCM, Vol. 2, April-August 1960, p. 292.				
(d) Air						
168.	Argent	Ref. 157.	Nb	400-1050	dry or wet	
169.	Inouye	<i>Scaling of Cb in Air.</i> Oakridge National Laboratory Report 1565, September 1955.	Nb	400-1200	dry or wet	parabolic at 400°, linear above
170.	Klopp	Ref. 100.	Nb	600-1400	dry	

			Metal	T (°C)	Pressure	Remarks
171.	Klopp	Ref.136.	Nb alloys	600-1200 600-1000	dry or wet dry or wet	binary or ternary alloys with Cr- Ti-Zr-Mo-Ta-W-V- Be-B-Co-Fe-Mn- Ni-Si
172.	Klopp	Ref.152.	Nb alloys alloys	400-1200 1000-1200 600-1000	dry or damp dry or damp dry	humidity: 35 - 76 and 100% binary with V- Mo-Cr-Ti-Zr-W ternary with Mo-Cr-Ti-W
173.	Sims	Ref.135.	alloys	600-1000	dry	binary with Ti- Cr-Zr-V-Mo-Ta-W
174.	Paprocki	<i>Investigation of Some Niobium-Base Alloys.</i> BMI, Report 1143, October 1956.	alloys	980	dry	binary with Zr- Al-Mo-Fe-Cr-Ni- V-W-Ta
175.	Michael	Ref.138.	alloys	1000	dry	binary and ternary with W-Cr-Al-Si-Co-Ta
176.	Bridges	Ref.155, p.10-12.	alloys	1000-1300	dry	alloys Nb 10Ti 10Mo
177.	Kling	Ref.139.	alloys	1000	dry	binary with Ti- V-Mo
178.	Clauss	<i>Effect of Binary Alloy Additions on the Oxidation Resistance of Cb.</i> Technology of Cb, Wiley, New York, 1958, p.92.	alloys	1000-1200	dry	binary with Al- Si-Ti-V-Cr-Fe- Co-Ni-Cu-Ge-Se- Zr-Mo-Ta-W-Re- Ir
179.	Barrett	<i>Oxidation of Cb-Cr Alloys at Elevated θ.</i> Technology of Cb. Wiley, New York, 1958, p.96.	alloys	800-1200	dry	alloys Cb-Cr (1 to 17%)
180.	Inouye	<i>Scaling of Nb in Air.</i> AIME Conference, Buffalo, 19 March 1956.				
181.	Cathcart	<i>The Microtopography of Oxide Films in Nb.</i> JES, Vol.105, 1958, p.442.				

181a. Klopp *Oxidation Behaviour of Cb.* DMIC 123, January 1960.

(e) Water vapour

182. Begley Ref.55, p.77-94 (Nb unalloyed, temperatures 200-1100°C, p = 50 mm).

(f) Miscellaneous

183. Sibert *Study of the Equilibrium of C and O in Nb with CO above 1600°C.*
Third Reactive Metals Conference, Buffalo, May 1958.

183a. Maykuth *The Fabrication of Cb Alloys for Use in Pressurized Water Reactors.*
AIME Symposium on Columbium, Lake George, June 1960.

183b. Klopp *The Hot Water Corrosion of Cb.* AIME Symposium on Columbium, Lake
George, June 1960.

183c. Maykuth *Development of Corrosion Resistant Cb Alloys.* BMI Report 1437,
May 1960.

1.5 Protective Coatings

Publications on this subject still present many gaps.

184. Beach *Procedures for Electroplating Coatings on Refractory Metals.* DMIC
Memo 35, 9 Oct.1959.

185. Beach Ref.140.

186. Beach Ref.141.

187. Faust *Plating on Unusual Metals.* Plating, Sept. 1956, p.1134.

188. Spretnak *Protection of Nb Against Oxidation at Elevated Temperature.* Status
Report 467, U.S. Dept. of Navy, p.16.

189. Saubestre *Electroplating on Certain Transition Metals.* JES, April 1959, p.305.

190. Naval *Zn Process Prevents Cb Oxide.* Missiles and Rockets, 4 Jan.1960,
Research p.22,
Labora-
tory
Washing-
ton

191. Hirakis *Research for Coatings for Nb.* Report Horizons No.4, April 1957.

192. Kates 7th Quarterly Progress Report, Sylvania Corning Nuclear Corporation,
255, 15 February 1958.

193. Paprocki *Cladding of Nb with Fe-Cr-Al Alloy.* BMI Report 1207, 16 July 1957.

194. Bückle *Coating with Refractory Oxides or Cladding with Platinum Group Metals.*
Metallforschung, Vol.1, 1946, p.81.

195. Klopp *Oxidation Behaviour and Protective Coatings for Nb and Nb Alloys.*
DMIC 123, 15 Jan.1960.

- 196. Sandoz *Coating Cb for Higher Temperatures.* JOM, April 60, p.340, (Zn).
- 196a. Wainer *Protection of Cb from Oxidation.* U.S. Patent 2.833,282, April 1959.
- 196b. Klopp *Zinc Coatings for Protection of Cb.* DMIC Memo 88, March 1961.
- 196c. Klopp *Review of Recent Development on Coatings.* DMIC Memo 102, April 1961.
- 196d. Wlodek *Coatings for Cb.* JES, Vol.108, No.2, 1961, p.177.

The University of Illinois is conducting, under a WADC contract, a research program on protective ceramic coatings : various types of coating : paint type, flame sprayed type, china-enamel type; this last type seems to offer the most interesting prospects.

Union Carbide Corporation has developed satisfactory coatings which stand up to over 1000 hours at a temperature of 1,150°C, or over 700 hours at a temperature of 1,250°C. Behaviour is satisfactory after 20 successive quenchings by water at 1,150°C and creep characteristics under normal atmospheric pressure for 100 hours at 1,150°C are identical to behaviour in vacuo.

Investigations are directed towards reaching temperatures of 1,350-1,650°C.

2. TANTALUM

2.1 Phase Diagrams

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| 197a. | Klopp | Ref.1a. |
| 197b. | Vaughan | <i>Determination of Interstitial Solubilities in Ta.</i> BMI 1472, October 1960. |

2.1.1 Systems which can be Regarded as Known

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|-------------|------|---------------------|---|
| Ta-O | 197. | Gebhardt | The Solubility of Oxygen in Ta and its Effect on the Properties. ZM, Vol.48, 1957, p.430. |
| | 198. | Gebhardt | Solution and Oxidation in Ta-O. ZM, Vol.48, 1957, p.503. |
| | 199. | Gebhardt & Seghezzi | Vorgänge bei der Wärmebehandlung von sauerstoffhaltigen und oxydiertem Tantal. ZM, Vol.48, 1957, p.559. |
| | 200. | Gebhardt | Solubility of O in Ta and the Related Changes in Properties. ZM, Vol.46, 1955, p.560. |
| | 201. | Wasilewsky | The Solubility of Oxygen in, and the Oxides of, Tantalum. Journal of the American Chemical Society, Vol.75, 1953, p.1001. |
| | 202. | Schönberg | Ref.5, p.240. |
| | 203. | Andrews | Reaction of Gases with Incandescent Tantalum. Journal of the American Chemical Society, Vol.54, 1932, p.1845. |

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| 204. | Myers | <i>Some Properties of Tantalum.</i> Metallurgia, Vol.41, 1950, p.301. |
| 205. | Gebhardt et alii | <i>Nevere Untersuchungen im System Tantal-Stickstoff.</i> Proceedings, Third Plansee Seminar, Metallwerk Plansee, Reutte, Tyrol, 1958, p.291. (New investigations). |

See also Section 2.4.1.

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|------|------|---------------------|---|
| Ta-N | 206. | Brauer | Ref.11, p. 129. |
| | 207. | Schönberg | Ref.5, p. 199. |
| | 208. | Horne & Ziegler | <i>Superconductivity and Structure of Hydrides and Nitrides of Tantalum and Columbium.</i> Journal of the American Chemical Society, Vol.69, 1947, p.2762. |
| | 209. | Gebhardt et alii | <i>Untersuchungen im System Tantal-Stickstoff.</i> ZM, Vol.49, 1958, p.577. |
| | 210. | Ke | <i>Precipitation from Solid Solution of N in Ta.</i> Physical Review, Vol.74, 1948, p.914. |
| | 211. | Gebhardt & Seghezzi | <i>Nevere Erkenntnisse im System Tantal-Sauerstoff.</i> Proceedings, Third Plansee Seminar, Metallwerk Plansee, Reutte, Tyrol, 1958, p.280. (New investigations). |

See also Section 2.4.2.

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|------|------|---------------|--|
| Ta-H | 212. | Kelley | <i>The Specific Heat of Tantalum at Low Temperatures and the Effect of Small Amounts of Dissolved Hydrogen.</i> Journal of Chemical Physics, Vol.8, 1940, p.316. |
| | 213. | Waite et alii | <i>Structures and Phase Relationships in the Tantalum-Hydrogen System between -145° and 70°C.</i> Journal of Chemical Physics, Vol.24, 1956, p.634. |
| | 214. | Brauer | Ref.4. |
| | 215. | Hägg | <i>Röntgenuntersuchungen über die Hydride von Titan, Zirkonium, Vanadin und Tantal.</i> Zeitschrift für Physikalische Chemie, Vol.B 11, 1931, p.433. |

See also Section 2.4.3.

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|------|------|-----------------|--|
| Ta-B | 216. | Brewer et alii | <i>A Study of the Refractory Borides.</i> Journal of the American Ceramic Society, Vol.34, 1951, p.173. |
| | 217. | Kiessling | <i>The Borides of Tantalum.</i> Acta Chemica Scandinavia, Vol.3, 1949, p.603. |
| | 218. | Norton | Ref. 13, p. 749. |
| | 219. | Kieffer et alii | <i>Über ein neues Verfahren zur Herstellung von Metallboriden der Übergangsmetalle, insbesondere von Titan - und Zirkonborid.</i> ZAC, Vol.268, 1952, p.191. |

	220.	Post et alii	<i>Transition Metal Diborides. Acta Metallurgica</i> , Vol.2, 1954, p.20.
	221.	Nowotny	Ref.64.
Ta-Mo	222.	Bückle	Ref.14. (Solubility in all proportions).
	223.	Geach & Summers-Smith	<i>The Alloys of Molybdenum and Tantalum. JIM</i> , Vol.80, 1951, p.143.
	224.	Radtke et alii	<i>The Alloys of Molybdenum and Tantalum. JIM</i> , Vol.80, 1951, p.528. (Discussion on Ref.223).
	225.	Myers	<i>Some Properties of Tantalum-Rich Alloys with Wolfram and Molybdenum. Metallurgia</i> , Vol.42, 1950, p.3.
	226.	Elliott	Ref.35, p.25.
Ta-Nb	227.	Bückle	Ref.14. (Solubility in all proportions).
	228.	Williams	Ref.25.
Ta-W	229.	Bückle	Ref.14. (Solubility in all proportions).
	230.	Schramm et alii	<i>The Alloy Systems Uranium-Tungsten, Uranium- Tantalum, and Tungsten-Tantalum. TAIME</i> , Vol.188, 1950, p.195 (In Journal of Metals).
	231.	Elliott	Ref.38, p 25.
	232.	Myers	Ref.225.

2.1.2 Partially Defined Systems (especially for low Ta percentages)

Ta-C**	233.	Ellinger	<i>The Tantalum-Carbon System. TASM</i> , Vol.31, 1943, p.89.
	234.	McMullin & Norton	<i>The Ternary System Ti-Ta-C. TAIME</i> , Vol.197, 1953, p.1205.
	235.	Geach & Jones	<i>Interactions in Mixtures of Hard Materials at Very High Temperatures. Proceedings, Second Plansee Seminar, Metallwerk Plansee, Reutte/ Tyrol, 1955, p.80 (and Pergamon Press 1960).</i>
	236.	Myers	<i>The Sintering of Electrolytic Ta Powder.</i> <i>Metallurgia</i> , Vol.38, 1948, p.307.
	237.	Norton & Mowry	Ref.13.
Ta-Co**	238.	Myers	Ref.236.
	239.	Koster & Mulfinger	Ref.30.
	240.	Elliott	Ref.35, p.22.
	241.	Greenfield & Beck	Ref.79.
	242.	Wallbaum	Ref.31.
Ta-Cr**	243	Kubaschewski	Ref.41, pp.410 & 418.
	244.	Duwez	Ref.71.
	245.	Elliott	Ref.35, p.23.

Ta-Fe**	246.	Genders	<i>Tantalum-Iron Alloys and Tantalum Steels.</i> Journal of the Iron and Steel Institute, Vol. 134, 1936, p.173.
	247.	Wallbaum	Ref.31.
	248	Myers	Ref.236.
Ta-Ir	249.	Wulff	Work Performed at MIT under US Government Contract. Report NMI-g.205, Feb.1959.
	250.	Knapton	Ref.16.
Ta-Ni**	251.	Therkelsen	<i>Properties of the Alloys of Nickel with Tantalum.</i> Metals and Alloys, Vol.4, 1933, p.105.
	252.	Kubaschewski	Ref.41, p.417.
Ta-Os	253.	Nevitt & Downey	<i>Sigma Phases Containing Osmium and Iridium.</i> TAIME, Vol.209, 1957, p.1072 (in Journal of Metals, Vol.9, 1957).
	254.	Kaufmann	Work Performed at Nuclear Metals under US Government Contracts.
	255.	Knapton	Ref.16.
Ta-Re	256.	Greenfield	Ref.79.
	257.	Wulff	Ref.249.
	257a.	Brophy et alii	<i>The Tantalum-Rhenium Systems.</i> TAIME, Vol.218, October 1960, p.910.
Ta-Ru	258.	Greenfield	Ref.79.
	259.	Kaufmann	Ref.65.
	260.	USAF Contract	(Complete diagram).
Ta-Si*	261	Geach	Ref.235.
	262.	Brewer et alii	<i>High Melting Silicides.</i> USAEC Report AECU-607, 1949.
	263.	Kieffer et alii	<i>Beitrag zum System Tantal-Silizium.</i> ZM, Vol.44, 1953, p.242.
	264.	Wallbaum	<i>Disilizide des Niobs, Tantal, Vanadiums und Rheniums.</i> ZM, Vol.33, 1941, p.378.
	265.	Knapton	Ref.44.
Ta-Ti*	266.	Maykuth et alii	<i>Titanium-Tungsten and Titanium-Tantalum Systems.</i> TAIME, Vol.197, 1953, p.231.
	267.	Summers-Smith	<i>The Constitution of Tantalum-Titanium Alloys.</i> JIM, Vol.81, 1952, p.73.
	268.	Duwez	<i>The Martensite Transformation Temperature in Titanium Binary Alloys.</i> TASM, Vol.45, 1953, p.934.
Ta-U	269.	Schramm	Ref.230.

Ta-Zr*	270.	Shelton	<i>Zirconium Alloys for High Temperature Service.</i> USAEC-AF-TR-5932, 1949.
	271.	Anderson et alii	<i>A Preliminary Survey of Zirconium Alloys.</i> US Bureau of Mines, Report 4658, 1950.
	272.	Domagala	Armour Research Foundation, B 068, August 1955.
	273.	Elliott	Ref.35.
	274.	Wulff	Ref.249.

2.1.3 Systems Studied in Certain Respects Only

Ta-Al**	275.	Brauer	Ref.59.
	276.	Brauer	<i>Kristallstruktur intermetallischer Verbindungen des Aluminiums mit Titan, Zirkon, Thorium, Niob und Tantal.</i> Naturwissenschaften, Vol.26, 1938, p.710.
Ta-Be**	277.	Kaufman	Ref.65.
Ta-Cu**	278.	Elliott	Ref.35, p.23.
	279.	Dowson	<i>Some Alloys of Copper [with Tantalum and with Vanadium].</i> Metallurgical Abstracts, Vol.4, 1937, p.606.
Ta-Hf**	280.	Elliott	Ref.35.
Ta-Mn**	281.	Wallbaum	Ref.31.
	282.	Elliott	Ref.35, p.25.
	283.	Greenfield	Ref.79.
	284.	Schönberg	<i>Metallic Ternary Phases in the Mn-Ta-O System.</i> Acta Metallurgica, Vol.3, 1955, p.14.
Ta-P	285.	Schönberg	Ref.5, p.226.
	286.	Zumbusch & Biltz	<i>Ein Vergleich der Phosphide von Vanadium, Niob und Tantal.</i> ZAC, Vol.249, 1942, p.20.
Ta-Pt**	287.	Greenfield	Ref.18.
	288.	Knapton	Ref.16.
Ta-Rh**	289.	Greenfield	Ref.18.
	290.	USAF Contract	(Complete diagram).
Ta-S	291.	Biltz	Ref.84.
Ta-Sn	292.	Matthias	Ref.94.
	293.	Geller	Ref.76.
Ta-Th	294.	Saller	Ref.49.
Ta-V*	295.	Rostoker & Yamamoto	<i>A Survey of Vanadium Binary Systems.</i> TASM, Vol.46, 1954, p.1136.
	296.	Elliott	Ref.35, p.25.

2.1.4 Ta-Ternary Alloys with Two of the Following: W-Nb-V-Mo-Cr-Re-Os

297. Rostoker *A Study of Ternary Phase Diagrams of W and Ta.* WADC TR 59-492, March 1960.

2.1.5 Unstudied Systems

Ta-Ag* - Ta-As - Ta-Au - Ta-Ba - Ta-Bi - Ta-Ca - Ta-Cd* - Ta-Ce** - Ta-Hg - Ta-In - Ta-K - Ta-La - Ta-La** - Ta-Li - Ta-Mg* - Ta-Na - Ta-Pb - Ta-Pd** - Ta-Sb - Ta-Sr - Ta-Te - Ta-V** - Ta-Zn*.

2.2 Impurity Effects and Analysis

2.2.1 Effects

Oxygen	298.	Gebhardt	Ref.197.
	299.	Gebhardt	Ref.198.
	300.	Gebhardt	Ref.200.
	301.	Yancey	<i>Metallurgical Characteristics of Ta.</i> Proceedings of the Conference on Reactive Metals, Buffalo, 1956. AIME, Institute of Metals Division, IMD Special Report No.5, 1956, p.102.
	302.	Klopp	<i>Investigation of the Properties of Tantalum and its Alloys.</i> WADC TR 58-525, Nov.1958, pp.4-6 and 14-25.
	303.	Andrews	Ref.203.
	304.	Parkins	<i>Hardness Effects of Dissolved Gases in Ta.</i> Los Alamos Rep. LA 2316, 15 May 1958.
	305.	Dravnieks	<i>Oxidation of Metals in Oxygen at High Temperature.</i> Journal of the American Chemical Society, Vol.72, 1950, p.3761.
Nitrogen	306.	Gebhardt et alii	Ref.209.
	307.	Parkins	Ref.304.
	308.	Wright	<i>Absorption of Gases by Ta.</i> Nature, Vol.142, 1938, p.794.
	309.	Klopp	Ref.302.
Air	310.	Wright	Ref.308.
	311.	Klopp	Ref.302.
	312.	Parkins	Ref.307.
Hydrogen	313.	Andrews	Ref.203.
	314.	Parkins	Ref.307.
	315.	Wright	Ref.308.
	316.	Sieverts	<i>The Electrical Resistivity of Ta Saturated with H.</i> Zeitschrift für Physikalische Chemie, Vol.A 174, 1935, p.365.
	317.	Clauss-Forestier	<i>Fragilité du Tantale en Présence d'Hydrogène.</i> Comptes Rendus, Académie des Sciences, No.23-246-3241, June 1958.

Miscellaneous	318.	Andrews	Ref.203 (water vapour at 900-1,200°C)
	319.	Myers	Ref.236 (C - Fe - Ni).

2.2.2 Analysis

General	320.	Mallett	Ref.110.
Review	321.	Fassel	Ref.112
	322.	Niebuhr	Ref.111.
Fe-Ti-Cu-Nb-Mo-K	323.	Hastings & McClarity	<i>Determination of Small Amounts of Niobium in Pure Tantalum and its Oxide.</i> Analytical Chemistry, Vol.26, 1954, p.683.
Miscellaneous, concerning Nb	324.	Klinger et alii	<i>Beitrag zur Analyse des Tantalmetalls.</i> Metall und Erz, Vol.38, 1941, p.124.
Miscellaneous	325.	Palilla	Ref.131.
	326.	Schoeller	<i>Analytical Chemistry of Ta and Nb.</i> Chapman and Hall, London, 1937, pp.121-133.
	328.†	Roisten	<i>High Purity Tantalum.</i> TAIME, June 1959, p.472.
Oxygen	329.	Codell	Ref.118.

2.3 Diffusion

As in the case of niobium, the knowledge of the characteristics of the diffusion couples Ta-X is limited to gaseous elements.

Besides, the problem is closely connected to that studied in Section 2.4.

Nitrogen and oxygen	330.	Ang	Ref.133.
	331.	Dravnieks	Ref.305.
	332.	Ke	<i>Internal Friction in the Solid Solution of O in Ta.</i> Physical Review, Vol.74, 1948, p.9.
	333.	Ke	<i>Stress Relaxation by Internal Diffusion in Ta.</i> Physical Review, Vol.74, 1948, p.16.
	334.	Ke	Ref.210.
	335.	Gebhardt	<i>The Diffusion of Oxygen in Ta.</i> ZM, Vol.48, 1957, p.624.
	336.	Powers	<i>Internal Friction of Solid Solution of O in Ta.</i> Acta Metallurgica, Vol.3, 1955, p.135.
	337.	Michael	<i>Oxidation of Ta Base Alloys.</i> AIME Conference, Buffalo, May 1958.
	338.	Bakish	<i>Metallographic Manifestations of the Air Oxidation of Tantalum at 750°C.</i> JES, Vol.105, 1958, p.71.
	339.	Klopp	<i>Investigation of the Properties of Tantalum and its Alloys.</i> BMI Quarterly Report, Jan.1959, Contract AF 33-616-5668.

† There is no Reference No. 327

	339a.	Klopp	Ref.1a.
Carbon	340.	Ke	<i>Internal Friction in the Solid Solution of C in Ta.</i> Physical Review, Vol.74, 1948.
	341.	Powers	<i>C-Ta Internal Friction.</i> JAP, Vol.28, 1957, p.255.
Iron	342.	Vasilev	Universite Lenina, Vol.65, 1955, p.47.
Miscellaneous	343.	Klopp	Ref.302, pp.37-42.
	344.	Ke	Ref.333.
	345.	Marx	<i>The Internal Friction of Ta.</i> Acta Metallurgica, Vol.1, 1953, p.193.
	346.	Wert	Ref.142.
	347.	Kubaschewski	Ref.144.
	348.	Powers	<i>Internal Friction of Solid Solution in Ta.</i> Acta Metallurgica, Vol.4, 1956, p.233.
	348a.	Doyle	<i>Internal Friction in Solid Solutions of Ta.</i> Acta Metallurgica, Vol.4, 1956, p.233.

2.4 Behaviour in a Gaseous Environment at Elevated Temperature

2.4.1 Oxygen

			Metal	T (°C)	Pressure	Remarks
349.	Gulbransen	Ref.146.	Ta	100-370	0.1 atm	parabolic laws
350.	Vermilyea	<i>The Oxidation of Ta at 50-300°C.</i> Acta Metallurgica, Vol.6, 1958, p.166.	Ta	50-300	1 atm	linear laws
351.	Gulbransen & Andrew	<i>Reactions of Columbium and Tantalum with O₂, N₂ and H₂.</i> JOM, Vol.188, March 1950, p.586.	Ta	250-450	0.1 atm	parabolic laws
352.	Dravnieks	Ref.305.	Ta	500	0.5 mm	linear laws
353.	Peterson et al.	<i>High Pressure Oxidation of Metals: Tantalum in Oxygen.</i> TAIME, Vol.200, 1954, p.1038.	Ta	500-1000	0.2-40 atm	linear laws
354.	Gebhardt	Ref.198.	Ta	800-1500	1 micron	linear laws
355.	Albrecht	<i>Investigation of the Properties of Tantalum and Its Alloys.</i> Battelle Memorial Institute, BMI Quarterly Report, Jan.1959, Contract AF 33-616-5668.	Ta	600-1400	0.2-1 atm	linear laws

			Metal	T (°C)	Pressure	Remarks
356.	Baur et alii	High Pressure Oxidation of Metals. Oxidation of Metals under Conditions of Linear Temperature Increase. JES, Vol.102, 1955, p.490.	Ta	500-900	1 to 7 atm	
357.	Bakish	Some Observations on the Effect of the Inter- action of Tantalum with Oxygen, Nitrogen, and Hydrogen. JES, Vol.105, 1958, p.574.	Ta	750	-	
358.	Andrews	Ref.203.				
358a.	Cowgill & Stringer	The Effect of Oxygen Pressure on the High Temperature Oxidation of Tantalum. JLCM, Vol.2, No.2, 1960, p.233.	Ta	600-900	1-760	
358b.	Cathcart et alii	Oxidation Properties of Tantalum between 400° and 530°C. JES, Vol.107, No. 8, Aug.1960, p.668.	Ta	400-530	760	
358c.	Pawel et alii	Microtopography of Oxide Films Formed on Tantalum. JES, Vol.107, No.12, December 1960, p.956.	Ta	300-700	760	
2.4.2 Nitrogen						
359.	Gulbransen	Ref.351.	Ta	250-350	0.1 atm	
360.	Gulbransen	Ref.146.	Ta	500-850	0.1 atm	parabolic laws
361.	Bakish	Ref.357.	Ta	750	-	
362.	Albrecht	Ref.355.	Ta	1500	1 atm	parabolic laws
2.4.3 Hydrogen						
363.	Andrews	Ref.203.				
364.	Wagner	Ref.143.				
365.	Kubas- chewski	Ref.144.				
366.	Gulbransen	Ref.146.				
367.	Bakish	Ref.357.	Ta	350-800	0.1 atm	linear
368.	Clauss	Revue de Métallurgie Scientifique, November 1959 (Fragilisation de Ta par H ²) p.614; also Proceedings, Third Plansee Seminar, Metallwerk Plansee, Reutte/Tyrol, 1958, p.277.	Ta	20°	-	-

			Metal	T (°C)	Pressure	Remarks
2.4.4	Air					
369.	Waber et alii	<i>A Spectrophotometric Study of the Oxidation of Tantalum.</i> JES, Vol. 99, 1952, p. 121.	Ta	200-300 320-350	dry dry	logarithmic law parabolic law
370.	Bakish	Ref. 357.	Ta	750	dry	linear law
371.	Michael	Ref. 337.	Ta alloys	870-1100 1100	dry dry	linear law binary alloys with Mo-W-V-Zr- Ti-Fe-Co-Ni-Cr and ternary
372.	Klopp	Ref. 339.	Ta alloys	500-1000 1200	dry	binary alloys Zr-Hf-V-Nb-Mo-W
373.	Kubas- chewski	Ref. 41.	Ta alloys	1250 1250	dry dry	alloys Ta-Ni, Ta-Cr and Ta-Ni-Cr
374.	Myers	Ref. 225.	alloys	-	-	alloys Ta-Mo and Ta-W
374a.	Albrecht	<i>Reactions of Pure Ta with Air, Oxygen, Nitrogen.</i> TAIME, February 1961, p. 110.	Ta	400-1500	dry or wet	
374b.	Klopp	<i>Effect of Alloying in Ta.</i> ASM Preprint 221, 1960.	alloys	1000-1400		binary & ternary with Ti-Zr-Hf- V-Cb-W-Mo-Re

2.4.5 Miscellaneous

375. Andrews Ref. 203 (Ta, 800-1200°C, water vapour hydrocarbons).
 376. Wright Ref. 308.

2.5 Protective Coatings

Publications in this subject are almost non-existent

377. van Gilder *Electrodeposition of Gold on Ta.* U.S. Patent 2492 204, Dec. 1949.
 378. Beach Ref. 184.
 379. Faust Ref. 187.
 380. Saubestre Ref. 189.
 380a. Klopp Ref. 196c.

The research work carried out by the University of Illinois and mentioned in relation to Nb is similarly conducted for Ta.

Flame sprayed Al_2O_3 coatings have also been contemplated.

3. TUNGSTEN

3.1 Phase Diagrams

	381a.	Klopp	Ref. 1a.
3.1.1 Systems which can be Regarded as Known			
W-Mo	381.	Bückle	Ref. 14. (Solid solubility in all proportions).
	382.	Jeffries	<i>Tungsten-Molybdenum Equilibrium Diagram and System of Crystallization.</i> TAIME, Vol. 56, 1917, p. 600.
	383.	Geiss & van Liempt	<i>Zur Kenntnis des binären Systems Wolfram-Molybdän.</i> ZAC, Vol. 128, 1923, p. 355.
	384.	Richards	<i>The System of Tungsten-Molybdenum.</i> TAIME, Vol. 56, 1917, p. 618. [Discussion of the papers of Z. Jeffries (p. 600) and F. A. Fahrenwald (p. 612)].
	385.	Kaya & Kussmann	<i>Ferromagnetismus und Phasengestaltung im Zweistoffsystem Nickel-Magnan.</i> Zeitschrift für Physik, Vol. 72, 1931, p. 293.
W-Nb	386.	Bückle	Ref. 14. (Solid solubility in all proportions).
W-Ta	387.	Bückle	Ref. 14. (Solid solubility in all proportions).
	388.	Schramm	Ref. 230.
	389.	Elliott	Ref. 35, p. 23.
	390.	Myers	Ref. 225.
3.1.2 Partially Defined Systems			
W-Al**	391.	Clark	<i>The Aluminium-Tungsten Equilibrium Diagram.</i> JIM, Vol. 66, 1940, p. 271.
	392.	Adam & Rich	<i>The Crystal Structure of WAl_{12}, $MoAl_{12}$ and $(Mn, Cr)Al_{12}$.</i> Acta Crystallographica, Vol. 7, 1954, p. 813.
W-B	393.	Kiessling	<i>The Crystal Structures of Molybdenum and Tungsten Borides.</i> ACS, Vol. 1, 1947, p. 893.
	394.	Brewer	Ref. 216.
	395.	Kieffer	Ref. 219.
	396.	Glaser	<i>Contribution to the Metal-Carbon-Boron Systems.</i> TAIME, Vol. 194, 1952, p. 391.
W-Be	397.	Kaufmann	Ref. 65.
	398.	Misch	<i>Kristallstrukturelle Untersuchungen von einigen Berylliumlegierungen.</i> Metallwirtschaft Wissenschaft Technik, Vol. 15, 1936, p. 163.
	399.	-	Work Performed at WADC under US Government Contract.
W-C*	400.	Schwartzkopf	<i>Refractory Hard Metals.</i> MacMillan, 1953, p. 153.
	401.	Nowotny et alii	<i>Das Dreistoffsystem Titan-Wolfram-Kohlenstoff.</i> ZM, Vol. 45, 1954, p. 97.

	402.	Pfau & Rix	<i>Über die Kristallform des Wolframkarbides WC und die Verteilung der Kohlenstoffatome in seinem Gitter.</i> ZM, Vol.45, 1954, p.116.
	403.	Brewer	Ref.216.
	404.	Nowotny & Kieffer	<i>Röntgenographische Untersuchung von Karbid-systemen.</i> ZM, Vol.38, 1947, p.257 (published as <i>Metallforschung</i> , Vol.2, No.6, 1947, p.257).
W-Co**	405.	Kreitz	<i>Kobalt-Wolframlegierungen.</i> Metall und Erz, Vol.19, 1922, p.137.
	406.	Köster & Tonn	<i>Die Zweistoffsysteme Kobalt-Wolfram und Kobalt-Molybdän.</i> ZM, Vol.24, 1932, p.296.
	407.	Greenfield	Ref.18.
	408.	Sykes	<i>The Cobalt-Tungsten System.</i> Transactions, ASST, Vol.21, 1933, p.385.
W-Cr**	409.	Trzebiatowski et alii	<i>X-Ray Analysis of Chromium-Molybdenum and Chromium-Tungsten Alloys.</i> Analytical Chemistry, Vol.19, 1947, p.93.
	410.	Greenaway	<i>The Constitutional Diagram of the Chromium-Tungsten System.</i> JIM, Vol.80, 1951, p.589.
	411.	Kubaschewski & Schneider	<i>Über die Systeme des Chroms mit Wolfram und Molybdän.</i> Zeitschrift für Elektrochemie, Vol.48, 1942, p.671.
	412.	McQuillan	<i>Discussion on Constitution of Transition-Metal Alloys.</i> JIM, Vol.80, 1951, p.697.
	413.	Greenaway	<i>Discussion on Constitution of Transition-Metal Alloys.</i> JIM, Vol.80, 1951, p.698.
W-Fe**	414.	Gregg	<i>The Alloys of Iron and Tungsten.</i> McGraw-Hill, 1934.
	415.	Sykes	<i>Notes on the Solidus Temperatures in the Systems Iron-Tungsten and Iron-Molybdenum.</i> TASM, Vol.24, 1936, p.541.
	416.	Sykes & van Horn	<i>The Intermediate Phases of the Iron-Tungsten System.</i> TAIME, Vol.105, 1933, p.198.
	417.	Elliott	Ref.35.
	418.	Goldschmidt	<i>The Structure of Carbides in Alloy Steels. Part II - Carbide Formation in High-Speed Steels.</i> Journal of the Iron and Steel Institute, Vol.170, 1952, p.189.
	419.	Goldschmidt	<i>A Further High Temperature σ-Phase and a Note on the σ-ξ Relations.</i> Research, Vol.4, 1951, p.343.
	420.	Greenfield	Ref.18.
	421.	Smith	<i>Precipitation Hardening in the Fe-W System.</i> JAP, Vol.12, 1941, p.817.
	422.	Sykes	<i>Composition Limits of the Alpha-Gamma Loop in the Iron-Tungsten System.</i> TAIME, Vol.95, 1931, p.307.
	423.	Sykes	<i>The Iron-Tungsten System.</i> TAIME, Vol.73, 1926, p.968.

W-H**	424.	Smith	<i>Hydrogen in Metals.</i> University of Chicago Press, 1948.
	425.	Dillon	<i>Presence of Hydride in W.</i> Proceedings of the Physical Society, Vol.41, 1929, p.546.
	426.	Smithells	<i>High Temperature Phenomena of Tungsten Filaments.</i> Transactions of the Faraday Society, Vol.17, 1921, p.485.
W-Hf	427.	van Liempt	<i>Hafnium Oxide in Tungsten Filaments.</i> Nature, Vol.115, 1925, p.194.
	428.	Elliott	Ref.35.
	429.	Grant	Work performed at MIT under US Government Contract.
W-Ir	430.	Raub	<i>100 - Jahringen Jubilauhs.</i> Firma Heraeus, Hanau, 1951, p.124. Also ZM, Vol.48, 1957, p.53.
	431.	Knapton	Ref.17.
	432.	Taylor	Work performed at Westinghouse Jet Propulsion Laboratory under US Government Contract.
W-N**	433.	Smithells & Rooksby	<i>Reactions of Incandescent Tungsten with Nitrogen and with Water Vapour.</i> Journal of the Chemical Society, 1927, p.1882.
	434.	Davis	<i>The Activated Adsorption of Nitrogen on a Finely Divided Tungsten Powder.</i> Journal of the American Chemical Society, Vol.68, 1946, p.1395.
	435.	Dushman	<i>Scientific Foundations of Vacuum Technology.</i> Wiley, New York, 1949, p.599.
	436.	Schönberg	Ref.5, p.204.
	437.	Kiessling & Peterson	<i>The Nitrides and Oxide-Nitrides of Tungsten.</i> Acta Metallurgica, Vol.2, 1954, p.675.
	438.	Kiessling & Liu	<i>Thermal Stability of the Chromium, Iron and Tungsten Borides in Streaming Ammonia and the Existence of a New Tungsten Nitride.</i> TAIME, Vol.191, 1951, p.639.
W-Ni*	439.	Bückle	<i>Etude à l'Aide de la Micrographie et de la Microdureté des Alliages Tungstène-Chrome-Nickel, Riches en W-Cr.</i> La Recherche Aéronautique, No.24, 1951, p.49.
	440.	Hazlett & Parker	<i>Effect of Some Solid Solution Alloying Elements on the Creep Parameters of Nickel.</i> TASM, Vol.46, 1954, p.701.
	441.	Epremian & Harker	<i>The Crystal Structure of Ni₄W.</i> TAIME, Vol.185, 1949, p.267.
	442.	Ellinger & Sykes	<i>The Nickel-Tungsten System.</i> TASM, Vol.28, 1940, p.619.
	443.	Vogel	<i>Über Wolfram-Nickellegierungen.</i> ZAC, Vol.116, 1921, p.231.

W-O**	444.	Glemser & Sauer	Über Wolframoxyde. ZAC, Vol.252, 1943, p.144.
	445.	Hägg & Schönberg	β -Tungsten as a Tungsten Oxide. Acta Crystallographica, Vol.7, 1954, p.351.
	446.	Magnéli	Structure of β -Tungsten Oxide. Nature, Vol.165, 1950, p.356.
	447.	Magnéli	X-Ray Studies on the System Molybdenum Trioxide-Tungsten Trioxide. ACS, Vol.3, 1949, p.88.
	448.	Andersson	On the Crystal Structure of Tungsten Trioxide. ACS, Vol.7, 1953, p.154.
	449.	Matthias & Wood	Low Temperature Polymorphic Transformation in WO_3 . Physical Review, Vol.84, 1951, p.1255.
	450.	Kehl et alii	The Structure of Tetragonal Tungsten Trioxide. Journal of Applied Physics, Vol.23, 1952, p.212.
	451.	Charlton & Davis	Allotropes of Tungsten. Nature, Vol.175, 1955, p.131.
	452.	Rosen et alii	The Thermal Expansion and Phase Transitions of WO_3 . Acta Crystallographica, Vol.9, 1956, p.475.
W-0s	453.	Raub	Ref.430.
W-Pt	454.	Jafee & Nielson	Platinum-Tungsten Alloys. TAIME, Vol.180, 1949, p.603.
	455.	Hultgren & Jaffee	A Preliminary X-Ray Study of Binary Alloys of Platinum with Cobalt, Molybdenum and Tungsten. JAP, Vol.12, 1941, p.501.
	456.	Greenfield	Ref.18.
W-Re	457.	Greenfield	Ref.18.
	458.	Knapton	Sigma Phases in Rhenium Alloys. Bulletin of the Institute of Metals, Vol.3, 1955, p.21.
	459.	Becker & Moers	Über die Schmelzpunkte im System Wolfram-Rhenium. Metallwirtschaft und Technik, Vol.9, 1930, p.1063.
	460.	Dickinson & Richardson	The Constitution of Rhenium-Tungsten Alloys. TASM, Vol.51, 1959, p.758.
W-Ru	461.	Raub	Ref.430.
	462.	Greenfield	Ref.18.
	463.	Kaufmann	Work performed at Nuclear Metals under US Government Contract.
W-Si	464.	Kieffer et alii	Beitrag zum System Wolfram-Silizium und Über die Zunderbeständigkeit einiger silizide. ZM, Vol.43, 1952, p.284.
	465.	Blanchard & Cueilieron	Etude du Diagramme de Fusion Tungstène-Silicium. Comptes Rendus, Académie des Sciences, Vol.244, 1957, p.1782.
	466.	Aronsson	The Crystal Structure of $Ni_3P(Fe_3P\text{-Type})$. ACS, Vol.9, 1955, p.137.

	467.	Knapton	Ref.44.
	468.	Brewer et alii	<i>High-Melting Silicides.</i> Journal of the American Ceramic Society, Vol.33, No.10, 1950, p.291.
	469.	Schwarzkopf	Ref.400.
W-Ti**	470.	Maykuth	Ref.266.
	471.	Eastwood	<i>The Ti-Mn, Ti-W, Ti-Ta Phase Diagrams.</i> BMI, AFTR 6516, Part I, 1951.
	472.	Nowotny	Ref.401.
	473.	Duwez	Ref.268.
W-Zr**	474.	Domagala et alii	<i>Systems Zirconium-Molybdenum and Zirconium-</i> <i>Wolfram.</i> TAI ME, Vol.197, 1953, p.73.
	475.	Geach & Slattery	<i>Systems Zirconium-Molybdenum and Zirconium-</i> <i>Wolfram.</i> TAI ME, Vol.197, 1953, p.747.
	476.	Shelton	Ref.270.
	477.	Elliott	Ref.35, p.23.

3.1.3 Systems Studied in Certain Respects Only

W-Ag*	478.	Bernoulli	<i>Ueber Wolfram und einige seiner Verbindungen.</i> Annalen der Physik und Chemie, Vol.III, 1860, p.573.
W-As	479.	Heinerth & Biltz	Ref.60.
W-Bi	480.	Sargent	<i>The Production of Alloys of Tungsten and of</i> <i>Molybdenum in the Electric Furnace.</i> Journal of the American Chemical Society, Vol.22, 1900, p.783.
W-Ca	481.	Kremer	<i>Notiz über Wolfram und seinen Legierungen.</i> Abhandlungen aus dem Institut für Metallhütten- wesen Technische Hochschule, Aachen, Vol.1, 1916, No.2, p.7.
W-Cu**	482.	Kremer	Ref.481.
W-Ga	483.	Jaffee	<i>Gallium in Nuclear Reactors: Considerations</i> <i>for Use as a Primary Coolant.</i> BMI, T-17, 1949.
W-Ge	484.	Wallbaum	<i>Über Intermetallische Germanium verbindungen.</i> Naturwissenschaften, Vol.32, 1944, p.76.
	485.	Hardy	Ref.73.
W-Hg	486.	Irvin & Russell	<i>The Solubilities of Copper, Manganese, and some</i> <i>Sparingly Soluble Metals in Mercury.</i> Journal of the Chemical Society, Part 1, 1932, p.891.

	487.	Tammann & Hinnüber	<i>Über die Löslichkeit von Metallen im Quecksilber und die Potentiale sehr verdünnter Amalgame.</i> ZAC, Vol.160, 1927, p.260.
W-Mg	488.	Busk	<i>Lattice Parameters of Magnesium Alloys.</i> TAIME, Vol.188, 1950, p.1460.
	489.	Sauerwald	<i>Zur Systematik der Verwandtschaft den hochschmelzenden und hexagonalen Metalle mit Magnesium und über hochwarmste Legierungen auf Mg-Th-Zr-Basis.</i> ZAC, Vol.258, 1949, p.296.
W-Mn**	490.	Kremer	Ref.481.
	491.	Zwicker	<i>Über die Gamma-Phase des Mangans. (1) Der Einfluss von Zusätzen auf die bei Raumtemperatur auftretende Struktur der aus dem Gamma-Gebiet abgeschreckten Legierungen.</i> ZM, Vol.42, 1951, p.251.
W-P	492.	Faller & Biltz	<i>Über Phosphide von Wolfram, Molybdän und Chrom.</i> ZAC, Vol.248, 1941, p.209.
	493.	Schönberg	Ref.5, p.226.
	494.	Hartmann & Orban	<i>Elektrolyse in Phosphatschmelzen II über ein neues Wolframphosphid W_4P.</i> ZAC, Vol.226, 1936, p.257.
	495.	Heinerth & Biltz	Ref.60.
W-Pb	496.	Kremer	Ref.481.
W-Pd**	497.	Raub	Ref.430.
	498.	Greenfield	Ref.18.
W-Rh**	499.	Raub	Ref.430.
	500.	Greenfield	Ref.18.
W-S	501.	Glemser et alii	<i>Über Wolframsulfide und Wolframselenide.</i> ZAC, Vol.257, 1948, p.241.
	502.	Ehrlich	<i>Untersuchungen an Wolframsulfiden.</i> ZAC, Vol.257, 1948, p.247.
W-Se	503.	Glemser	Ref.501.
W-Te	504.	Knop & Haraldsen	<i>A Note on the System Wolfram-Tellurium.</i> Canadian Journal of Chemistry, Vol.34, 1956, p.1142.
W-Th**	505.	Geiss & van Liempt	<i>Zum Verhalten des Thotoxyds in Wolframglühdrähten.</i> ZAC, Vol.168, 1927, p.110.
	506.	Saller	Ref.49.

W-U	507.	Schramm	Ref.230.
	508.	Summers-Smith	<i>The System Uranium-Tungsten.</i> JIM, Vol.83, 1954, p.383.
W-V	509.	Rostoker	Ref.295.
	510.	Kieffer et alii	<i>Tungsten Alloys of High Melting Point.</i> JLCM, Vol.1, Feb.1959, p.19.
	511.	Armour Research Foundation	Continuous Solid Solution (unpublished).
W-Zn	512.	Köster & Schmid	<i>Über die Legierungsfähigkeit von Zink mit Wolfram und Molybdän.</i> ZM, Vol.46, 1955, p.462.
	513.	Heumann	<i>Beitrag zur Kenntnis des Systems Zink=Chrom.</i> ZM, Vol.39, 1948, p.45.

3.1.4 Unstudied Systems

W-Au = W-Ba = W-Cd = W-Ce** = W-Gd = W-In = W-K = W-La** = W-Li = W-Na = W-Sb = W-Sn = W-Se* = W-Y** = W-Zn

3.1.5 Ternary Systems

The following ternary systems are being studied at the present time:

= W-Ta-Re by Wulff - MIT - under contract with the US Government.

= W-Ta-Zr under the responsibility of the WADC.

W with two of the following: Ta - Nb - V - Mo - Cr - Re - Os

514.	Rostoker	Ref.297.
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3.2 Impurity Effects and Analysis

3.2.1 Effects

ThO ₂	515.	Jeffries & Tarasov	<i>Tungsten and Thoria.</i> Proceedings of the Institute of Metals Divn. 1927 [Vol.1]. American Institute of Mining and Metallurgical Engineers, p.395.
	516.	Smithells	<i>Reduction of Thorium Oxide by Metallic Tungsten.</i> Transactions of the Chemical Society, Vol.121, 1922, Part 2, p.2236.
	517.	Burgers & van Liempt	<i>Zum Verhalten des Thoroxys in Wolframglüdröhren.</i> Zeitschrift für anorganische und allgemeine Chemie, Vol.193, 1930, p.144.
	518.	Hüniger	<i>Krystallbildung in Wolframsinterstäben.</i> Chemisches Zentralblatt, Vol.101, 1930, p.2992.
Fe-Ca	519.	Smithells & Rooksby	<i>Unusual Microstructure in Iron and Tungsten.</i> Nature, Vol.120, 1927, p.227.

C	520.	Zapffe & Landgraf	<i>Fractographic Examination of Tungsten.</i> TASM, Vol.41, 1949, p.396.
Al₂O₃ - SiO₂ - Na₂O - K₂O - ThO₂			
	521.	British Patents	121.596, 186.497, 188.706, 155.851.
Miscellaneous	522.	Jaffee	<i>Effects of Impurities on the Properties of Tungsten.</i> Ref.1169.
	523.	Swalin & Geisler	<i>The Recrystallization Process in Tungsten as Influenced by Impurities.</i> JIM, Vol.86, Nov.1957, p.129. (Fe + Co).
	524.	Davis	<i>Embrittlement of Tungsten Wires by Contaminants.</i> Nature, Vol.181, April 1958, p.1198.

3.2.2 Analysis

General Review	525.	Mallett	Ref.110.
	526.	Fassel	Ref.112.
	527.	Niebuhr	Ref.111.
	528.	Haymes	<i>Impurities Analysis in W.</i> Ref.1169.
Chemical Methods	529.	Smithells	<i>Tungsten</i> , Chapman and Hall, London, 1952, p.305, (ThO ₂ - Mo - Na - K - Si - Al - B - L - Ti - Fe - Ca).
	530.	Smithells	Ref.529.
Spectrographic Methods	531.	Gentry	<i>The Spectrochemical Analysis of Tungsten.</i> Metallurgia, Vol.46, July 1952, pp.47-51.
	532.	Dyck	<i>Spectrographic Analysis of W Metal Powder.</i> Analytical Chemistry, March 59, p.390 (Metallic Elements).
	533.	Rohrer	<i>Spectrographic Determination of Ni in Tungsten Powder.</i> Analytical Chemistry, July 55, p.1200.
	534.	Veleker	<i>Determination of Al, Fe, K and Si in Tungsten Oxide.</i> Analytical Chemistry, March 59, p.387.
Oxygen	535.	Codell	Ref.118.

3.3 Diffusion

Oxygen	536a.	Klopp	Ref.1a.
	536.	Michael	Ref.337.
	537.	Tungsten Institute (in progress)	(alloys W-Ni, W-Co, W-Cr).
Mo	538.	van Liempt	<i>Die Diffusion von Molybdän in Wolfram.</i> Recueil des Travaux Chimiques des Pays-Bas, Vol.51, 1932, p.114.
Cu	539.	MacLennan & Smithells	<i>A New Alloy Specially Suitable for use in Radium Beam Therapy.</i> Journal of Scientific Instruments, Vol.12, 1935, p.159.

540. Smithells *A New Alloy of High Density. Nature, Vol.139, 1937, p.490.*
541. Price *Sintered Alloys. Part I - Copper-Nickel-Tungsten Alloys Sintered with a Liquid Phase Present. JIM, Vol.62, 1938, p.239.*
et alii

The MAB Panel on tungsten recommends the study of the diffusion coefficients of
Cr - Rh - In - Pd - Pt - Si - Al.

3.4 Behaviour in Gaseous Environment at Elevated Temperature

(a) Oxygen			Metal	T (°C)	Pressure	Remarks
542.	Gulbransen	Ref.1169. (See also <i>Oxidation of W and W-based Alloys. WADC TR-59-575, Feb.1960. (Fundamental study of the oxidation of W).</i>	W	500-1600°	0.001 atm 0.1 atm	
543.	Gulbransen & Wysong	<i>Thin Oxide Films on Tungsten. TAIME, Vol.175, 1948, p.611.</i>	W	25-550	0.1 atm	parabolic law
544.	Nachtigall	<i>Properties of Molybdenum at Low and Medium Temperature. ZM, Vol.42, 1952, p.23.</i>	W	500-800	-	parabolic, then linear law
545.	Scheil	<i>Über das Zundern von Metallen und Legierungen. ZM, Vol.29, 1937, p.209.</i>	W	500-900	-	
546.	Speiser	Ref.1169.	W	500-1400	< 1 atm	
547.	Millner	<i>Volatility of the Oxides of Tungsten and Molybdenum in the Presence of Water Vapour. Nature, Vol.163, 1949, p.601.</i>	W	500-1000	oxygen dry or wet	
548.	Webb et alii	<i>Oxidation of Tungsten. JES, Vol.103, 1956, p.107.</i>	W	700-1000	oxygen dry	parabolic, then linear
549.	Baur et alii	<i>High Pressure Oxidation of Metals - Tungsten in Oxygen. JES, Vol.103, 1956, p.266.</i>	W	700 600-850	oxygen wet 1.5 to 35 atm	linear law
550.	Hickman	<i>Oxide Films Formed on Metals and Binary Alloys. An Electron Diffraction Study. TAIME, Vol.180, 1949, p.547.</i>	alloys	300-700	1 mm	binary with Ni-Co-Cu-Cr-Mo

			Metal	T (°C)	Pressure	Remarks
551. Perkins	Electromet (Union Carbide Metals Company, Niagara Falls) Progress Report AF 33-616-5600, October 1958.		alloys	1200	0.1 atm	binary with Si-Cr-Ti-Nb-Ta
551a. Gulbransen	<i>Kinetics of Oxidation of Pure W.</i> JES, July 1960, p.619.					
(b) Nitrogen						
552. Ehrlich G.	<i>The Interaction of Nitrogen with a Tungsten Surface.</i> Journal of Physical Chemistry, Vol. 60 (10), 1956, p.1388.					
553. Ehrlich G.	<i>State of Nitrogen Adsorbed in Tungsten.</i> Journal of Chemical Physics, Vol.23(8), 1955, p.1543.		W	1700		
(c) Air						
554. Dunn	<i>The Oxidation of Tungsten: Evidence for the Complexity of Tungsten Oxide WO₃.</i> Journal of the Chemical Society, Part I, 1929, p.1149.		W	700-1000	dry	parabolic law
555. Michael	Ref.337.		W	1100	dry	
556. Semmel	<i>The Oxidation of W and Mo.</i> High Temperature Metallurgy Conference, April 1957. Wiley, New York, 1957.		W	1000-1350	dry	
557. Kubachewski	Ref.41.		alloys	900-1250	dry	alloys W-Cr
558. Tungsten Institute (in progress)			alloys	1100	dry	binary with Ni-Co-Cr-Fe-Ta-Nb
559. Semmel	<i>The High Temperature Oxidation of W-Cb Alloys.</i> ASM Preprint 161, 1959.		alloys	100-1250	dry	alloys W-Cb

(d) Ammonia

560. Davis *The Embrittlement of Tungsten by Ammonia.* Metallurgia, Vol.54, July 1956, p.18.

(e) CO

561. Eisinger *Adsorption of Carbon Monoxide on W.* Journal of Chemical Physics, Vol.27 (5), 1957, p.1206.

Metal	T (°C)	Pressure	Remarks
W	1200	0.2%	tendency to surface brittleness
W	-	-	

3.5 Protective Coatings

Few studies have been published.

In the United States, tests are being directed towards:-

claddings (WADC) : with rare metals (Rh) (New York University)

ceramics (University of Illinois).

562. Carminarro *Process of Electroplating on W.* US Patent 2443 651, June 1948.
563. Goetzel *Preliminary Study of the Protection of W by Coatings of Rh.* Ref.1169.
564. Robbins *Plating on Tungsten.* Metallurgia, Vol.55, 1957, p.257.
565. Saubestre Ref.189.
566. Beach Ref.184.
567. Boosz *Chemical and Electrochemical Surface Treatment of Mo and W.* Metall, Vol.12, 1958, p.508.
568. Boosz *On the Formation of Oxide Films on Tungsten.* Metall, Vol.11 (6), 1956, p.511-17.
569. Stephenson *Plating of Tungsten with Titanium and Zirconium.* Abstract No.118, Electrochemical Society, New York, 1958.

4. MOLYBDENUM

4.1 Phase Diagrams

4.1.1 General

570. Northcott *Alloys of Mo. Molybdenum*, Butterworth, 1956, Ch.7, p.115.
571. Ham *An Introduction to Arc-Cast Mo and its Alloys*. ASME, Report 50-A-70, 1950.
572. Harwood (Editor) *The Metal Molybdenum*. Proceedings of a Symposium sponsored by the (U.S.) Office of Naval Research, September 1956. ASM Publication, 1958, p.555.
573. Semchysen *Development and Properties of Arc-Cast Mo Alloys*. Ref.572, p.287.
574. Pipitz *The Effect of Alloying Additions on Mo*. ZM, Vol.46-3/1955, p.187.
575. Ward *The Alloying Behaviour of Mo. A Survey of Published Work*. Armament Research Establishment, Metallurgy Report 25/54, November 1954.
576. Bignon *Molybdenum and its Compounds*. Industrie Chimique, March 1956, p.85.
577. Greenfield *Intermediate Phases in Binary Systems of Certain Transition Elements*. JOM, February 1956, p.265.
578. Bloom *An Investigation of the Systems Formed by Cr-Mo-Ni*. JOM, February 1954, p.261.
579. Greenfield *The Sigma Phase in Binary Alloys*. JOM, February 1954, p.253.
580. Raub *Metals and Alloys of the Pt Group*. JLCM, February 1959, p.3.
- 580a. Klopp Ref.1a.

4.1.2 Well-known Systems

Mo-Cr

(Complete solid solubility)

- | | | |
|------|------------------|---|
| 581. | Baen & Duwez | <i>Constitution of Iron-Chromium-Molybdenum Alloys at 1200°F.</i> TAIME, Vol.191, 1951, p.331. |
| 582. | Kubaschewski | Ref.411. |
| 583. | Putnam et alii | <i>The Ternary System Chromium-Molybdenum-Iron.</i> TASM, Vol.43, 1951, p.824. |
| 584. | Kessler & Hansen | <i>A Study of Arc-Melted Molybdenum-Rich Chromium-Molybdenum Alloys.</i> TASM, Vol.42, 1950, p.1008. |
| 585. | Bloom & Grant | <i>An Investigation of the Systems Formed by Chromium, Molybdenum, and Nickel.</i> TAIME, Vol.200, 1954, p.261. |
| 586. | Ham | <i>Arc-Cast Molybdenum-Base Alloys.</i> Climax Molybdenum Company First Annual Report, Project NR 031-331, April 1, 1950. |
| 587. | Ham | <i>An Introduction to Arc-Cast Molybdenum and its Alloys.</i> TASME, Vol.73, 1951, p.723. |
| 588. | Trzebiatowski | Ref.409. |

Mo-Nb

- | | | |
|------|--------|--|
| 589. | Bückle | Ref.14. (Solid solution in all proportions). |
|------|--------|--|

Mo-Ta

- | | | |
|------|--------|--|
| 590. | Bückle | Ref.14. (Solubility in all proportions). |
| 591. | Geach | Ref.223. |
| 592. | Schumb | Ref.224. |
| 593. | Myers | Ref.225. |
| 594. | Elliot | Ref.35, p.25. |

Mo-W

(Complete solid solubility)

- | | | |
|------|----------|----------|
| 595. | Bückle | Ref.14. |
| 596. | Jeffries | Ref.382. |
| 597. | Geiss | Ref.383. |
| 598. | Richards | Ref.384. |
| 599. | Kaya | Ref.385. |

4.1.3 Partially Defined Systems

**Mo-Al

- | | | |
|------|-----|----------|
| 600. | Ham | Ref.587. |
|------|-----|----------|

**Mo-B

- | | | |
|------|------------------|--|
| 601. | Andersson | Ref.61. |
| 602. | Brewer | Ref.216. |
| 603. | Post | Ref.220. |
| 604. | Steinitz et alii | <i>System Molybdenum-Boron and Some Properties of the Molybdenum-Borides.</i> JOM, Vol.5, May 1953, p.747. |
| 605. | Gilles & Pollock | <i>The Molybdenum-Boron System.</i> JOM, Vol.5, November 1953, p.1537. |

*Mo-Be	606.	Kaufmann	Ref. 65.
	607.	Ham	Ref. 586.
	608.	Gordon et alii	<i>Intermetallic Compounds in the System Molybdenum-Beryllium.</i> JOM, Vol. 3, August 1951, p. 637.
	609.	Semchysen	Ref. 572, p. 289.
*Mo-C	610.	Geach	Ref. 235.
	611.	Speiser et alii	<i>Influence of Carbon on the Lattice Parameter of Molybdenum.</i> JOM, Vol. 4, 1952, p. 275.
	612.	Few & Manning	<i>Solubility of Carbon and Oxygen in Molybdenum.</i> (a) JOM, Vol. 4, March 1952, p. 271. (b) JOM, Vol. 5, March 1953, p. 746.
	613.	Nowotny & Kieffer	<i>Eine Bemerkung zur Existenz des kubischen Molybdäncarbides.</i> ZAC, Vol. 267, 1952, p. 261.
	614.	Sykes et alii	<i>A Study of the Molybdenum-Carbon System.</i> TAIME, Vol. 117, 1935, p. 173.
	615.	Nowotny et alii	<i>Das Dreistoffsystem: Molybdän-Silizium- Kohlenstoff.</i> Monatshefte für Chemie, Vol. 85, 1954, p. 255.
*Mo-Co	616.	Sykes & Graff	<i>The Cobalt-Molybdenum System.</i> TASM, Vol. 23, 1935, p. 249.
	617.	Ham	Ref. 586.
	618.	Ham	Ref. 587.
	619.	Goldschmidt	<i>High Temperature Steels for Gas Turbines.</i> Research, Vol. 2, 1949, p. 343.
Mo-Fe	620.	Ham	Ref. 586.
	621.	Ham	Ref. 587.
	622.	Elliott	Ref. 35, p. 16.
	623.	Chartkoff	<i>X-Ray Notes on the Iron-Molybdenum and Iron- Tungsten Systems.</i> TAIME, Vol. 89, 1930, p. 566.
	624.	Bain	<i>The Nature of Solid Solutions.</i> Chemical and Metallurgical Engineering, Vol. 28, 1923, p. 23.
	625. 626.	Goldschmidt Arnfeldt	Ref. 619. <i>On the Constitution of the Iron-Tungsten and the Iron-Molybdenum Alloys.</i> Iron and Steel Institute, Carnegie Scholarship Memoirs, Vol. 17, 1928, p. 13.
*Mo-Hf	627.	Elliott	Ref. 35, p. 16.
	628.	Taylor	Work performed at Westinghouse Jet Propulsion Laboratory under US Government Contract.
*Mo-Mn	629.	Greenfield & Beck	Ref. 79.
	630.	Elliott	Ref. 35, p. 16.
	631.	Ham	Ref. 586.
	632.	Ham	Ref. 587.
	633.	Pipitz	Ref. 574.

	634.	Decker et alii	<i>Evidence for Order in the Manganese-Molybdenum Sigma Phase (and the Structure of the Chromium-Cobalt Sigma Phase).</i> JOM, Vol.6, December 1954, p.1406. <i>Formation of Sigma Phase in the Mn-Mo System.</i> JOM, Vol.5, 1953, p.1476.
*Mo-N ₂	635.	Norton & Marshall	<i>The Degassing of Metals. Absorption of Nitrogen and Carbon Monoxide by Molybdenum and Tungsten.</i> TAIME, Vol.156, 1944, p.369.
	636.	Schönberg	Ref.5, p.204.
	637.	Hägg	<i>Röntgenuntersuchungen über Molybdän und Wolframnitrile.</i> Zeitschrift für Physikalische Chemie, Vol.7, Part B, 1930, p.339.
*Mo-Ni	638.	Ham	Ref.586.
	639.	Ham	Ref.587.
	640.	Koster	<i>Untersuchungen im System Mo-Ni.</i> Archiv für das Eisenhüttenwesen, Vol.8, 1934, p.23.
	641.	Marián	<i>Ferromagnetic Curie Points and the Saturation of some Nickel Alloys.</i> Ann. Physique, Vol.7, 1937, p.459.
	642.	Ellinger	<i>The Nickel-Molybdenum System.</i> TASM, Vol.30, 1942, p.607.
*Mo-Os	643.	Raub	<i>Die Legierungen der Platinmetalle mit Molybdän.</i> ZM, Vol.45, January 1954, p.23.
	644.	Greenfield	Ref.18.
	645.	Knapton	Ref.17.
	646.	Baird et alii	<i>A Note on Certain Properties of Osmium and of its Alloys with Molybdenum.</i> Proceedings, Third Plansee Seminar, Metallwerk Plansee, Reutte, Tyrol, June 1958, p.371.
*Mo-Re	647.	Dickinson & Richardson	<i>The Constitution of Rhenium-Molybdenum Alloys.</i> TASM, Vol.51, 1959, p.1055.
	648.	Knapton	Associated Electrical Industries (A.E.I.) Research Report A474, August 1955.
	649.	Knapton	<i>Molybdenum-Rhenium System.</i> JIM, Vol.85, March 1957, p.161.
	650.	Knapton	<i>The Molybdenum-Rhenium System.</i> JIM, Vol.87, October 1958, p.62.
	651.	Geach	<i>The Alloys of Rhenium with Mo.</i> Proceedings. Plansee Seminar, Metallwerk Plansee, Reutte, Tyrol, 1956, p.246. (Workability - hot hardness - recrystallization).
	652.	Greenfield	Ref.18.
	653.	McHargue & Maynor	<i>Notes on a Molybdenum-Rhenium Alloy</i> JOM, Vol.5, 1953, p.1382.

*Mo-Si	654.	Ham	Ref.586.
	655.	Ham	Ref.587.
	656.	Nowotny	Ref.613.
	657.	Schachner et alii	<i>New Silicides of the M_5Si_3 Type with $D8_8$ Structure.</i> Monatshefte für Chemie, Vol.85, 1954, p.245.
	658.	Johnson	USAF Technical Report 6383, June 1951.
	659.	Kieffer	<i>Beitrag zum System Mo-Si.</i> ZM, Vol.43, 1952, p.101.
	660.	Brewer et alii	<i>High-Melting Silicides.</i> Journal of the American Ceramic Society, Vol.33, No.10, 1950, p.291.
**Mo-Ti		(Extensive solid solubility)	
	661.	Hansen	Ref.26.
	662.	Ham	Ref.586.
	663.	Rostoker	<i>Analytical Representation of Certain Phase Boundaries.</i> JOM, Vol.3, 1951, p.1203.
	664.	Duwez	<i>Effect of Rate of Cooling on the Alpha-Beta Transformation in Titanium (Zirconium, Thallium, and Iron) and Titanium-Molybdenum Alloys.</i> JOM, Vol.3, 1951, p.765.
	665.	Duwez	<i>Effect of Rate of Cooling on the Alpha-Beta Transformation in Titanium and Titanium-Molybdenum Alloys.</i> JOM, Vol.4, 1952, p.518.
Mo-U	666.	Pfeil	<i>The Constitution of Uranium-Molybdenum Alloys.</i> JIM, Vol.77, 1950, p.553.
	667.	Saller	Ref.49. <i>Transformation Kinetics of Uranium-Molybdenum Alloys.</i> BMI Report 957, October 1955. <i>The Constitution Diagram of Molybdenum-Rich Uranium.</i> BMI Report 730, March 1952.
**Mo-Zr	668.	Domagala	Ref.474.
	669.	-	US-AEC - 000-89, 14/4/52 (Armour Research Foundation).
	670.	Hägg	Ref.445.
	671.	Elliott	Ref.35, p.38.
	672.	Pipitz	Ref.574.
	673.	Ham	Ref.587.

4.1.4 Systems Studied in Certain Respects Only

Mo-Ag	674.	Dreibholz	<i>Untersuchungen Binärer und Ternärer Molybdänlegierungen.</i> Zeitschrift für Physikalische Chemie, Vol.108, 1924, p.4. (5% Mo is soluble in Ag).
Mo-Au	675.	Geach & Summers-Smith	<i>The Constitution of Gold-Molybdenum Alloys, with Particular Reference to the Solubility of Molybdenum in Gold.</i> JIM, Vol.82, 1953-54, p.471.

*Mo-Cu	676.	Linde	<i>Elektrische Eigenschaften verdünnter Mischkristallegierungen. III: Widerstand von Kupfer- und Goldlegierungen Gesetzmäßigkeiten der Widerstandserhöhungen. Annalen der Physik, Vol.15, 1932, p.219.</i>
Mo-Ga	677.	Kelman	Argonne National Laboratory, Lemont, Illinois. Report ANL-4417, July 1950.
Mo-Ge	678.	Searcy et alii	<i>Preparation of Mo₃Ge and Determination of its Structure. Journal of the American Chemical Society, Vol.74, 1952, p.566.</i>
	679.	Searcy & Peavler	<i>The Preparation and Properties of Molybdenum-Germanium Compounds. Journal of the American Chemical Society, Vol.75, 1953, p.5657.</i>
	680.	Thurmond	<i>Equilibrium Thermochemistry of Solid and Liquid Alloys of Germanium and of Silicon. I: The Solubility of Ge and Si in Elements of Groups III, IV, and V. Journal of Physical Chemistry, Vol.57, 1953, p.827.</i>
*Mo-H	681.	Sieverts & Brüning	<i>The Absorptive Power of Iron-Molybdenum Alloys for Hydrogen and Nitrogen. Archiv für das Eisenhüttenwesen, Vol.7, 1933-1934, p.641.</i>
Mo-Hg	682.	Irvin	Ref.486.
	683.	Miller	<i>Molybdenum : Production, Properties and Applications. Metal Industry, Vol.75, 1949, p.411.</i>
*Mo-Ir	684.	Raub	Ref.643.
	685.	Knapton	Ref.17.
Mo-Mg	686.	Sauerwald	<i>Zur Systematik der Verwandtschaft der Hochschmelzenden und Hexagonalen Metalle mit Magnesium und über Hochwarmfeste Legierungen auf Mg-Th-Zr-Basis. ZAC, Vol.258, 1949, p.296.</i>
	687.	Ham	Climax Molybdenum Company Reports 031-331, 1/4/50, and 034-401, April 1951.
Mo-O	688	Schönberg	Ref.5, p.630, p.617.
	689.	Rathenau & Meijering	<i>Rapid Oxidation of Metals and Alloys in the Presence of MoO₃. Metallurgia, Vol.42, 1950, p.167.</i>
	690.	Few	Ref.612(a).
	691.	Perry et alii	<i>Effect of Oxygen on Welding and Brazing Molybdenum. Welding Journal, Vol.33, Supplement, 1954, p.442-5.</i>
	692.	Few	Ref.612(b).

Mo-P	693. 694.	Schönberg Vogel & Horstmann	Ref. 5, p. 226. <i>Das Zustandsschaubild Eisen-Eisenphosphid-Molybdanphosphid-Molybdän.</i> Archiv für das Eisenhüttenwesen, Vol. 24, 1953, p. 369.
Mo-Pb	695.	Guertler	<i>Molybdän als Legierungsbestandteil.</i> ZM, Vol. 15, 1923, p. 152.
Mo-Pd	696. 697. 698. 699. 700.	Raub Greenfield Knapton Baird Haworth & Hume-Rothery	Ref. 643. Ref. 18. Ref. 17. Ref. 646. <i>The Constitution of Molybdenum-Rhodium and Molybdenum-Palladium Alloys.</i> JIM, Vol. 87, April 1959, p. 265.
Mo-Pt	701. 702. 703. 704. 705. 706.	Raub Greenfield Knapton Baird Knapton Knapton	Ref. 643. Ref. 18. Ref. 17. Ref. 646. <i>An X-Ray Survey of Certain Transition-Metal Systems for Sigma Phases.</i> JIM, Vol. 87, October 1958, p. 28. <i>A Survey of the Molybdenum-Platinum System.</i> Planseeberichte für Pulvermetallurgie, 1959, Vol. 7, No. 1, p. 2.
Mo-Rh	707. 708. 709. 710. 711. 711a.	Raub Greenfield Knapton Baird Haworth Anderson & Hume-Rothery	Ref. 643. Ref. 18. Ref. 17. Ref. 646. Ref. 700. <i>The Equilibrium Diagram of the System Molybdenum- Rhodium.</i> JLCM, Vol. 2, February 1960, p. 19.
Mo-Ru	712. 713. 714. 715. 716. 716a.	Raub Greenfield Knapton Baird Bloom Anderson & Hume-Rothery	Ref. 643. Ref. 18. Ref. 17. Ref. 646. <i>Sigma Phase in the Molybdenum-Ruthenium System.</i> TAIME, Vol. 203, February 1955, p. 420 (in JOM, Vol. 7, 1955). <i>The Equilibrium Diagram of the System Molybdenum- Ruthenium.</i> JLCM, Vol. 2, December 1960, p. 443.
Mo-S	717.	McCabe	<i>Sulphur-Pressure Measurements of Molybdenum Sesqui-Sulphide in Equilibrium with Molybdenum.</i> TAIME, Vol. 203, 1955, p. 61 (in JOM, Vol. 7, 1955).

Mo-Se	718.	Wendehorst	Gewichtsanalytische Molybdänbestimmungen.. ZAC, Vol.73, 1928, p.452.
Mo-Te	719.	Morette	Sur le Système Binaire Tellure-Molybdène. Tellurures de Molybdène Te_2MO et Te_3MO_2 . Comptes Rendus de l'Académie des Sciences, Vol.215, 1942, p.86.
**Mo-Th	720.	Pipitz	Ref.574.
**Mo-V	721.	Ham	Ref.586.
	722.	Ham	Ref.587.
	723.	Rostoker	Ref.295.
Mo-Zn	724.	Koster	Ref.512.

4.1.5 Unstudied Systems

Mo-As	Mo-Ba	Mo-Bi	Mo-Ca	Mo-Cd	Mo-Ce**	Mo-Cs	Mo-In	Mo-K	Mo-La**
Mo-Li	Mo-Na	Mo-Sb	Mo-Sn	Mo-Tl	Mo-V**				

Ternary or quaternary equilibrium diagrams

Mo-W-Re	725.	Sims & Jaffee	Properties of Refractory Alloys Containing Rhenium. TASM, Vol.52, 1960, p.929. (Paper presented at the 41st ASM Meeting, Chicago, 2 November 1959).
Mo-W-C	726.	Albert & Norton	Isothermschnitte in den Systemen Molybdän-Wolfram-Kohlenstoff und Molybdän-Titan-Kohlenstoff. Planseeberichte für Pulvermetallurgie, Vol.4, No.1, April 1956, p.2. (Isothermal sections).
Mo-Fe-C	727.	Lyman (Editor)	Metals Handbook. American Society for Metals, Cleveland, 1948.
Mo-Si-C	728.	Nowotny	Investigation on Silicide System. Monatshefte für Chemie, Vol.85, 1954, p.241.
Mo-Ni-Fe	729.	Das & Beck	Survey of Portions of the Iron-Nickel-Molybdenum and Cobalt-Iron-Molybdenum Ternary. NACA TN 2896, February 1953.
Mo-Co-Fe	730.	Das et alii	Intermediate Phases in the Mo-Fe-Co, Mo-Fe-Ni, and Mo-Ni-Co Ternary Systems. JOM, Vol.4, October 1952, p.1071.
Mo-Re-Hf	731.	Taylor	Work performed at Westinghouse Jet Propulsion Laboratory under U.S. Government Contract.
Mo-Ni-Co	732.	Das	Ref.730.

Mo-Ni-Cr	733.	Das	Ref. 730.
	734.	Bloom & Grant	<i>Chromium-Nickel Phase Diagram.</i> JOM, Vol. 6, 1954, p. 261. JOM, Vol. 3, 1951, p. 1009.
Mo-Cr-Fe	735.	Putnam	Ref. 583.
	736.	Goldschmidt	<i>Phase Diagrams of the Ternary Systems Fe-Cr-W and Fe-Cr-Mo at Low Temperatures.</i> Iron and Steel Institute Special Report, Vol. 43, 1952, pp. 249 and 345.
	737.	Baen & Duwez	<i>Constitution of Iron-Chromium-Molybdenum Alloys at 1200°F.</i> JOM, Vol. 3, April 1951, p. 331.
	738.	McMullin	<i>Arc Melting of Mo-Cr-Fe Alloys.</i> TASM, Vol. 46, 1953, p. 799.
Mo-Cr-Ti	739.	Elliott et alii	<i>System Titanium-Chromium-Molybdenum.</i> JOM, Vol. 5, 1953, p. 1544.
Mo-Mn-Ti	740.	Elliott et alii	<i>System Titanium-Manganese-Molybdenum.</i> JOM, Vol. 6, 1954, p. 228.
Mo-Cr-Co	741.	Rideout & Beck	<i>Survey of Portions of the Chromium-Cobalt-Nickel-Molybdenum Quaternary System at 1200°C.</i> NACA TN 2683, April 1952.
Mo-Nb-Ta, Mo-Nb-W, Mo-Ta-W	742.	Bückle	Ref. 14.

4.2 Impurity Effects and Analysis

4.2.1 Effects (see also Section 4.5.6)

Oxygen	743.	Platte	<i>Welding of Mo.</i> Ref. 572, p. 151.
	744.	Spacil & Wulff	<i>Effects of O₂ - N₂ - C on the Ductility of Wrought Molybdenum.</i> Ref. 572, p. 262.
	745.	Jaffee	Ref. 572, p. 334. (Effect of O ₂ on the tensile properties of Mo and Alloys).
	746.	Lawthers	<i>The Effect of Testing Atmosphere on the Properties of Mo-base Alloys.</i> AIME Conference, Cleveland, 16 April 1957.
	747.	Perry	<i>Effective Heat Treatment of Mo.</i> Metal Progress, February 1954, p. 75. (Influence of the annealing temperature).
	748.	Olds	<i>Effects of O₂ - N₂ - C on the Ductility of Cast Mo.</i> JOM, February 1956, p. 150.
	749.	Maringer	<i>Effects of O₂ on Mo.</i> JOM, March 1954, p. 365.
	750.	Martin	<i>Annealing of Point Defects in Mo.</i> Acta Metallurgica, 1957, p. 371. (Effect at 140-180°C).

	751.	Peiffer	<i>Concerning the Mechanism of Resistivity Recovered Observed in Cold-Worked Molybdenum. TAIME, Vol.212, October 1958, p.647. (Study of the effect of impurities O_2 - N_2 - C on the variation of resistivity at 145°C).</i>
Nitrogen	752.	Spacil	Ref.744.
	753.	Tury	<i>Effect of Molecular Nitrogen on Mo at High Temperature. Nature, 1936, p.531.</i>
	754.	Olds	Ref.748.
	755.	Maringer	<i>Effects of O_2 in Mo. JOM, February 1952, p.149.</i>
Carbon	756.	Spacil	Ref.744.
	757.	Olds	Ref.748.
	758.	Speiser	Ref.611.
	759.	Bas	<i>Carburization of Mo from a Gaseous Phase. Helvetica Physica Acta, June 1956, p.231.</i>
Miscellaneous	760.	Spacil	Ref.744.
	761.	Bruckart & Jaffee	<i>High-Temperature Properties of Molybdenum-Rich Alloy Compositions made by Powder Metallurgy Methods. Symposium on Metallic Materials for service at Temperatures above 1600°F. ASTM Special Technical Publication No.174, 1955, p.111. (Influence of additions of Ti, TiO_2, ZrO_2, Zn. Dispersed oxide strengthening phase).</i>
	762.	-	<i>The Effect of Selected Rare Earth Addition on the Removal of Interstitials. University of Denver, NASW-8, 8 May 59. (Additions of Ce - La - Y - YB - Gd - Lu - hardness measurements on cast buttons).</i>
	763.	-	<i>Calculations for Reactions of Cr, Mo with O_2, N_2, H_2, C, S. Rand Corporation Report R-108, February 1954.</i>

4.2.2 Analysis

General Review	764.	Mallett	Ref.110.
	765.	Fassel	Ref.321.
	766.	Niebuhr	Ref.111.
Gas	767.	Mallett	<i>Determination of Gases in Mo. Ref.572, p.365. (Oxygen: evaluation of methods - results of comparative studies; Hydrogen: difficulties with concentrations of about 1 ppm; Nitrogen: evaluation of methods).</i>
	768.	Mallett	<i>Vacuum-Fusion Analysis for Mo. TASM, Vol.46, 1954, p.375. (Methods for O_2 and N_2-accuracy).</i>

	769.	McDonald	<i>Vacuum Fusion Analysis</i> . Analytical Chemistry, October 1955, p.1632. (Determination of O_2 by the iron bath method).
	770.	-	Compte rendu du Congrès International de Spectroscopie de Lucerne, 12-18 September 1959. To be published.
Oxygen	771.	Codeil	Ref.118.
	772.	Durand	Ref.120.
Miscellaneous	773.	Kiess	<i>Series in the Arc Spectrum of Mo</i> . US Bureau of Standards, V - 19, 1923, p.113.
	774.	Bush	<i>Analysis of Binary Mo Alloys</i> . Analyst, 1955, p.536.
	775.	Pepkowitz	<i>Precision Determination of Low Concentrations of C</i> . Analyst, 1954, p.1022.
	776.	Dyck	<i>Spectrographic Analysis of Mo Metal Powder</i> . (Metallic elements). Analytical Chemistry, Oct. 59, p.1640.

4.3 Diffusion (see also Sections 4.5.4 and 4.5.5)

777.	Harwood	Ref.572, p.448 (Diffusion Mo-Cr, Mo-Ni, Mo-Cr-Ni).
778.	Schwöpe	<i>Investigation on the Mutual Diffusion of Various Elements and Mo</i> . BMI Report AS 53-022, 15/10/53.
779.	Zima	<i>Some High-Temperature Oxidation Characteristics of Nickel with Chromium Additions</i> . TASM, Vol.49, 1957, p.924. (Diffusion Ni-Cr at 1100°C).
780.	Byron	<i>Diffusion of Cobalt in Molybdenum</i> . JES, 102, January 1955, p.38.
781.	Shewmon	<i>Marker Movements in Ti-Mo - Diffusion Couples</i> . Acta Metallurgica, September 1955, p.452.
782.	Samuel	<i>Diffusion of Cr and other Elements</i> . Transactions of the Institute of Metal Finishing, 1954, p.153.
783.	Wahlin	<i>The Transmission of H_2 through Metals</i> . JAP, December 1951, p.1503.
783a.	Gordon et alii	<i>Intermetallic Compounds in the System Molybdenum-Beryllium</i> . JOM (TAIME), Vol.3, August 1951, p.637.

4.4 Behaviour in Gaseous Medium at Elevated Temperature

(Further information is contained in Section 4.2.1 and Section 5.7 of Part IV).

4.4.1 General

784. Northcott Ref.570, Ch.8, p.157. (General survey).
785. Harwood *Oxidation Behaviour*. Ref.572, Ch.19, p.420.
786. Kubaschewski Ref.144. (Basic general information - p.1, 156. Mo - p.171, 187).
787. Healey *Physical and Chemical Adsorption of Gases on Mo*. Journal of Physical Chemistry, February 1953, p.178.
788. Andersson *On the Crystal Structure of MoO_3* . ACS, 1950, p.793.
789. Kubaschewski *Metallurgical Thermochemistry*. Pergamon Press, 1951. (Vapour pressure of MoO_3).
790. Berkowitz *Mass Spectrometric Study of Mo Oxide Vapour*. Bulletin of the American Physical Society, 26/4/56, p.202.
791. Hägg *Recent Structure Investigation of Oxygen Composition of Mo*. Reviews of Pure and Applied Chemistry, December 1954, p.235.
792. Hägg & Magnéli *X-Ray Studies on Molybdenum and Tungsten Oxides*. Arkiv für Kemi, Mineralogi och Geologi, Vol.19A, 1944, No.2. (Study of the oxides of Mo).
793. Kihlberg *On the Thermal Decomposition of Mo Trioxide*. ACS, 1955, p.471.
794. Staskiewicz *Heat of Formation of Mo Oxides*. Journal of the American Chemical Society, 1955, p.2987.

4.4.2 Oxygen and Air

	<i>Metal</i>	<i>T(°C)</i>	<i>Pressure</i>	<i>Remarks</i>
795.	Nachtigall. Ref. 544.	Mo un- alloyed	200-600 air 1 atm	
796.	Gulbransen. <i>The Kinetics of Oxide - Film Formation</i> . Transactions of the Electrochemical Society, 1947, p.594.	"	300-450 O ₂ (0.1 - 0.01 0.001 atm	parabolic law

		Metal	T(°C)	Pressure	Remarks
797.	Lustman. <i>Oxidation of Mo in Air</i> . Metal Progress, 1950, p.629.	Mo un-alloyed	600-860	air	
798.	Mosher. <i>The Kinetics of the Oxidation of Mo</i> . M.S. Thesis, Ohio State University, 1953.	"	-	-	
799.	Simnad. <i>Kinetics and Mechanisms of the Oxidation of Mo</i> . JOM, 1955, p.1011.	"	-	-	
800.	Bartlett. <i>Oxidation of Mo in Air</i> . TAIME, April 1958, p.280.	"	760-1205	air	Effect of speed and direction of air stream
801.	Semmel. Ref.556.	"	980-1370	air	
802.	Ham. Ref.586.	binary alloys	600-940	still and moving air	Effect of 20 of the principal metal elements
803.	Gleiser. <i>Symposium on Basic Effects</i> . ASTM, Vol.65, Special Publication 171, 1955. <i>Properties of Oxidation Resistant Scales</i> . Ohio State University, Feb.1955, OTS/PB 119.850.	binary ternary	900-940 940-1100	air air	Mo-Ni and Mo-Cr Mo-Ni-Si and Mo-Cr-Si
804.	Rengstorff. <i>Search for Oxidation Resistant Alloys of Mo</i> . JOM, Feb.56, p.171.	binary and ternary	980-1100	air	55 alloys of Mo-Ca, Mo-Ni-Co, Mo-Cr-W, Mo-Cr-Ti
805.	Hickman. <i>Oxide Film Formed on Metals and Binary Alloys</i> . AIME Technical Publication 2483, Dec.1948,	binary	300-700	air	binaries with W - Ni - Co - Cr

		Metal	T(°C)	Pressure	Remarks
806.	Kessler. Arc Melted Mo-Cr Alloys. TASM, 1950, p.1008.	binary Mo-Cr	815-980	air	Effect of the addition of Be
807.	Lawthers. Ref.746.	-	-	-	

4.4.3 Miscellaneous

808. Friedman *High Temperature Durability of Mo in Oxygen-Deficient Combustion Gases*. Jet Propulsion, 1954, p.187. (Unprotected Mo resists about 100 hr. at 1430°C in certain combustion gases).

4.5 Protective Coatings

4.5.1 General Papers

809. Harwood *The Metal Molybdenum*. ASM, Office of Naval Research, 18/9/56, Chapter 18, p.408. (Begley: *Jet - Turbine Uses*). Chapter 19, p.420-461. (Harwood: *Protection against Oxidation*). (Oxidation behaviour - coating requirements and evaluation methods - Mo - base alloys - self-regenerative scales - ceramic - MoSi₂ - clad metal coatings - sprayed metal - electroplated coatings - diffusion coatings - chromizing - other methods).
810. Jaffee *Report on Mo*. MAB, February 1959. (Protection against oxidation - General up-to-date survey).
811. Blanchard *Oxidation Resistant Coatings for Mo*. WADC TR 54-492 (Parts I & II, 1955).
812. Bückle *Molybdenum Alloys and their Protection against Oxidation*. La Recherche Aéronautique, November 1957, p.35. (Present position - the alloys - protective coatings - detailed study of each type - advantages and drawbacks - present applications - future developments).
813. - *Metal Progress*, November 1958, p.82 (Turbine of G.E.C. working at 1100°C with buckets in Mo-Ti protected by five coating layers).
814. Freeman *Molybdenum for High Strength at High Temperature*. Jet Propulsion, February 1958, p.138. (Specifications - general assessment - comparative results for different types for oxidation tests, thermal shock, mechanical shock and erosion).
815. Northcott *Protective Coatings*. Ref.570, p.174.

816. Mac Loud *Molybdenum*. Metal Progress, Aug. 1958, p. 75. (General survey - practical tests of the G.E.C. on blades and wheels at 800-1,120°C).
817. - *Mo in Aeronautics*. Metal Industry, 6/9/57. (General survey - practical tests by Westinghouse at 980-1100°C on blades with mechanical cladding with nickel alloy).
818. Bartlett Ref. 800. (From 760-1,200°C, effect of ambient conditions).
819. Harwood *Protecting Mo at High Temperature*. Materials and Methods, December 1956, p. 85.
820. Blanchard *Oxidation Resistant Coatings for Mo*. Materials and Methods, February 1956, p. 180.
821. Jaffee *Protective Coating Systems for Mo*. Fabrication of Mo, ASM, 1959, p. 119.
822. Herzig *Protecting Mo from Oxidation*. Metal Progress, Oct. 55, p. 109.
823. Levinstein *Coating Development and Evaluation*. Fabrication of Mo, ASM, 1959, p. 186.
824. Oxx *A Liquid Phase Coating for Mo*. TAIME, June 1960, p. 541.
825. Bartlett *Coatings for Protecting Mo from Oxidation*. DMIC, 6 Mar. 1959, ASTIA AD-210-978.
826. Bartlett *Coatings for Protecting Mo from Oxidation*. DMIC TR 109 (PB 15-1064).
827. Gleiser *Basic Effects of Environments on Scaling of Metals at Elevated Temperature*. ASM Publication 171, 1955.
828. Parke *Molybdenum, a New High Temperature Metal*. Metal Progress, July 1951, p. 81. (Protection by cladding - SiO₂ - ceramic - electroplating alloy additions).
829. Beck *Coatings on Mo*. Metal Industry, 21 Jan. 55, p. 43.
- 829a. Chao *Recent Progress in Protective Coatings for Mo*. JLCM, December 1960, p. 426.
- 829b. Klopp Ref. 196c.
- 829c. Doane *Oxidation Resistant Coatings for Mo*. WADC TR 54-492, Part III, April 1957.

4.5.2 Silicides

830. Beidler *The Formation of Molybdenum Disilicide Coatings on Molybdenum.* JES, January 1951, p.21.
831. Kieffer & Benesovsky *Warm- und Zunderfeste Sinterwerkstoffe.* ZM, Vol.42, 1951, p.97. (Sintered carbides + ceramic + silicides).
832. Kieffer *Beitrag zum System Molybdän-Silizium.* ZM, Vol.43, 1952, p.101.
833. Fitzer *Siliconizing of W and Mo.* Monatshefte für Chemie, 1952, p.81.
834. Nowotny Ref.728.

4.5.3 Alloys

835. Rengstorff Ref.804. (Test at 980 and 1090°C - effect of Cr-Ti - W - Ni - Co - Ca, etc. 55 arc melted binary or ternary alloys).
836. Gleiser Ref.827.
837. Kessler *Arc Melted Mo-Cr Alloys.* TASM, 1950, p.1008. (Study of oxidation at 1200 - 1800°F) (650-980°C).
838. Bartlett *Alloys Mo-Ni.* TAIME, Aug.1958, p.458. (Developed by sintering practical difficulties).
839. Rendall et alii *The Forgeability, Creep Strength, and Ductility of Mo and Some of its Alloys.* JIM, Vol.82, 1953-54, p.345.

4.5.4 Diffusion Coatings

840. Leadbeater *Oxidation Resistance of Diffusion Coatings.* Metal Treatment, 1954, p.309, 387. (Diffusion coatings with Al-B-Be-Cr-Si-Ti-Zr-V, etc.)
841. Leadbeater *Oxidation Resistance of Diffusion Coatings.* Product Finishing, May 1955, p.70.

4.5.5 Cladding

842. Bruckart & Jaffee *Cladding of Molybdenum for Service in Air at Elevated Temperature.* TASM, Vol.44, 1952, p.181. (Cladding with Ni, Inconel, Stellite, hastelloy).
843. La Chance *Cladding of Mo by Rolling.* TASM, 1956, p.595. (Ni, Inconel - steels or Ni, miscellaneous - tests at 1,000°C).
844. Bruckart *Cladding of Mo for Service in Air.* TASM, 1951, p.176.

- 845. - *Gold Protects Mo.* Battelle Technical Review, August 1956, p.14.
- 846. Bruckart *Molybdenum Alloys and Protection by Cladding.* Rand Corporation publication, 25/4/50.
- 847. Durst *A New Development in Metal Cladding.* JOM, Vol.8, 1956, p.328.
- 848. Lomas *Nickel-Clad Mo.* Machinery, 1953, p.965.

4.5.6 *Sprayed Metals*

- 849. Mansford *Sprayed and Diffused Metal Coatings.* Metal Industry, 14 Nov.58, p.413. (Alloys Fe Al Cr - Kanthal - Sischromal ...).
- 850. Herzig *Protecting Mo from Oxidation.* Metal Progress, 1955, p.109.
- 851. Blanchard Ref.811, Parts I, II, III, 1954-57.

4.5.7 *Electro-plated Metals*

- 852. Safranek *Electro-Deposits of Cr and Ni* (alone or in alternate layers). Revue du Chrome Dur, September 1958, and Technical Proceedings, AES Convention, June 1956, p.105.
- 853. Runck *Electroplated Coatings of Ni and Cr on Mo* (one or multiple layers). JES, Feb.1957, p.74.
- 854. Couch *Protection of Mo at High Temperatures.* JES, August 1958, p.450. (Cr + Ni coatings).
- 855. Couch *Ni-Al Coatings on Mo.* JES, August 1953, p.485. (Coatings of Cr-Ni-Al).
- 856. Taylor *Composite Coatings of Cr and Ni.* JES, September 1955, p.244 c.
- 857. Harwood *The Protection of Molybdenum against High-Temperature Oxidation. (A Survey of the Problem and Progress).* Proceedings, American Electroplaters' Society, Vol.43, 1956, p.78.
- 858. Faust Ref.187. (Methods and baths).
- 859. Vaaler *Introductory Plating Studies.* BMI Report 813, 1953. (Ni).
- 860. Korbelak *Plating on Mo.* Plating, 1953, p.659, 1126. (Electro-deposition methods).
- 861. Beck *Coatings on Mo.* Metal Industry, 21 Jan.55, p.43. (Deposits of Al-Si-B - operating methods - properties) (Baths of melted salts).
- 862. Beck *Use of Ni-Al Alloys Coatings for Protection of Molybdenum.* JES, Sept.59, p.783.

863. Beach Ref. 184.
864. Hansen *Adherent Electroplating on Mo.* Metal Finishing, October 1953, p. 76.
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PART IV*

APPLIED RESEARCH

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APPENDIX

NOTES AND ABBREVIATIONS USED IN PARTS III & IV

Notes

** Systems of which a complete knowledge, in relation to the material under consideration, is regarded as interesting.

* Systems, a knowledge of which appears useful.

a,b,c etc. after a number indicates only that the reference was added at a later stage, i.e. after the numbering of the references had been completed.

ABBREVIATIONS

ACS	Acta Chemica Scandinavica
AIME	American Institute of Metallurgical Engineers
ASM	American Society of Metals
ASME	American Society of Mechanical Engineers
ASST	American Society for Steel Treating
ASTM	American Society for Testing Materials
BMI	Battelle Memorial Institute
DMIC	Defense Metals Information Center (Battelle Memorial Institute)
JAP	Journal of Applied Physics
JES	Journal of the Electrochemical Society
JIM	Journal of the Institute of Metals
JLCM	Journal of Less Common Metals
JOM	Journal of Metals
MAB	Materials Advisory Board (US)
MIT	Massachusetts Institute of Technology
NACA	National Advisory Committee for Aeronautics
OSR	Office of Scientific Research (US)

TAIME	Transactions of the American Institute of Metallurgical Engineers
TASM	Transactions of the American Society of Metals
TASME	Transactions of the American Society of Mechanical Engineers
UKAEA	United Kingdom Atomic Energy Authority
USAEC	United States Atomic Energy Commission
WADC	Wright Air Development Center (US)
WADD	Wright Air Development Division
ZAC	Zeitschrift für Anorganische und Allgemeine Chemie
ZK	Zeitschrift für Kristallographie
ZM	Zeitschrift für Metallkunde

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