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HIGH TEMPERATURE OXIDATION PROTECTION OF TUNGSTEN

*by V. Ye. Ivanov, Ye. P. Nechiporenko, L. N. Yefimenko,
and M. I. Yurchenko*

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ABSTRACT

This book is intended for specialists in the field of high-temperature materials and protective coatings. The book reviews achievements in the field of protection of tungsten and its alloys from high-temperature gaseous corrosion. Particular attention is paid to corrosion- and heat-resisting coatings. The behavior of various coatings, the materials and methods used for their production, as well as the physicochemical mechanism of their formation and protective action are examined. The authors also analyze the possible utilization of tungsten as a high-temperature structural material, the oxidation of tungsten at high temperatures, and recent achievements in the development of refractory and corrosion-resistant tungsten-base alloys.

FOREWORD

During the recent years of rigorous development of a number /3 of new branches in modern technology, which are in sharp need of materials capable of working at high-temperatures and under great mechanical loads, the possibility of using tungsten as a high temperature structural material has attracted the attention of researchers and technologists. A relative evaluation of different metals and alloys shows that tungsten is practically the only metallic material which keeps rather high mechanical strength at temperatures higher than 2000° C.

At the present, exhaustive investigations of tungsten and its alloys are being carried out in many countries of the world. However, the vast amount of experimental data which has accumulated over the last ten years is scattered over numerous literature sources and still awaits generalization. This relates in particular to such very important problems as high-temperature gaseous corrosion of tungsten, the processing of tungsten-base alloys which have improved mechanical properties and increased resistance to oxidation, and the creation of refractory protective coatings.

In our opinion, this is an opportune moment to systematize, generalize and, when possible, analyze the reports of studies carried out during the last few years, which depends to a great extent on further advances in the use of tungsten in technology. In view of the limited amount of space for this book, we avoided a detailed examination of many problems which have been treated in rather great detail in previously published monographs. Thus, having invited the attention of the reader, this short monograph is to a great extent a supplement to those others.

The authors would like to express their gratitude to Z.I. Kalashnik for his aid in formulating the draft copy, and they would like to thank the readers in advance for their critical comments on this work.

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CHAPTER I

PROBLEMS IN THE PRODUCTION OF HIGH-TEMPERATURE TUNGSTEN-BASE STRUCTURAL MATERIALS

High-temperature structural materials are absolutely necessary for the successful development of atomic and space-aviation technology. The existing heat-resisting nickel-base and cobalt-base steel and alloys are intended for prolonged utilization only at temperatures which do not exceed 1000° C. The studies directed at a search for highly resistant materials suitable for use at higher temperatures are now being conducted on a wide front. Significant advances have been achieved in developing high-temperature ceramic and metal-ceramic materials based on various high-melting compounds. Much attention has been given to graphite. However, in view of the fact that metallic materials have a large number of indisputable advantages, research studies in the field of high-melting metals and their alloys are now being conducted with the greatest intensity. /5*

Metals which melt at temperatures no lower than the melting point of chromium (1875° C) are usually referred to as refractory. This includes 12 metals in all: Cr, V, Rh, Hf, Ru, Ir, Nb, Mo, Ta, Os, Re, W. However, Rh, Ru, Ir, Os and Re are quite rare and scarcely obtainable in the quantities necessary for use as structural materials. Of the remaining refractory metals, there are four, relating to groups V and VI of the periodic table, which have the most interesting physical and mechanical characteristics - Nb, Ta, Mo and W. Table 1 shows certain properties of these metals, which are often called the "big four" metals in the literature.

Tungsten, tantalum, molybdenum and niobium have high strength over a broad temperature range (Fig. 1).

An important characteristic of the materials intended for use in aircraft is the specific strength (ratio between ultimate strength and density). A comparison of the specific strength of the "big four" high-melting metals shows that it is expedient to use niobium and molybdenum at temperatures roughly up to 1500° C, and that the /6

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* Numbers in the margin indicate pagination in the foreign text.

use of tantalum and tungsten becomes preferable at higher temperatures.

TABLE 1 PROPERTIES OF REFRACTORY METALS [1]

Properties	W	Ta	Mo	Nb
Melting point, °C	3410	2996	2610	2468
Boiling point, °C	5900	5425	5560	4927
Density, g/cm^3	19.3	16.6	10.2	8.57
Modulus of elasticity, 10^4 Kg/mm^2	3.57	1.89	3.29	1.06
Coefficient of linear expansion, $10^{-6} deg^{-1}$	4.45	5.9	5.6	7.1
Thermal conductivity, cal/(cm·sec·deg)	0.31	0.13	0.35	0.125

Tungsten has a special place among the refractory metals. In addition to its very high melting point, tungsten also has the greatest modulus of elasticity and least vapor pressure [1]. No other metal can compete with tungsten in terms of high-temperature strength [2]. At the same time, tungsten is a very abundant element in nature, and it stands only a little behind copper in this respect [1].

Since the beginning of this century, tungsten has played an exceptionally important role in technology. The fields in which this metal is used are continuously expanding. During the last two decades, the world-wide production of technical tungsten has increased sharply, and substantial progress has been achieved in perfecting the methods of obtaining and treating it. It is assumed that, if the USA maintains the current tempo in carrying out its space research program, the need for tungsten by 1970 will have increased by no less than a factor of two, compared to 1963 [3].

Tungsten is one of the elements which have been studied in great detail. The techniques used in obtaining it, the methods of processing, its properties and application are examined in greatest detail in [4-10].

A large number of problems which are very complex to science and technology must be solved in order that all the potential possibilities of tungsten as a high-temperature structural material be exploited in full. Of these problems, the primary ones /7
are: finding reliable means of protecting tungsten from high-temperature gaseous corrosion, increasing the high-temperature strength and low-temperature ductility of the metal, and developing better methods for processing and welding it.

One of the most serious disadvantages of tungsten and other refractory metals of the "big four" is the low resistance to oxidation in air at high temperatures of about 1100° C. The rate of oxidation of W, Ta, Mo and Nb in air at about 1100° is compared in Fig. 2 [9]. As can be seen, even at this relatively low temperature, tungsten oxidation takes place at a very high rate. For example, the cross-sectional area of a 10 mm diameter bar decreases roughly by 65% after 10 hours in air.

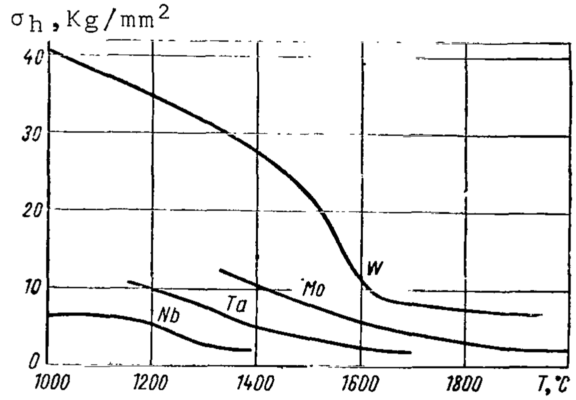


Fig. 1. Strength of Refractory Metals at High Temperatures [2] (W and Mo - in State of Strain; Ta - Recrystallized; Nb - After Deformation and Annealing for the Purpose of Eliminating Stresses).

Tungsten is used in high-temperature technology mainly in its pure form. Figure 3 shows the dependence of the strength of strained and recrystallized tungsten on the temperature; the figure was constructed according to data of various researchers [11]. The discrepancy of the values for the ultimate strength, as well as the other mechanical characteristics of tungsten, is /8 linked mainly with differences in purity and microstructure of the metal, which are determined by the methods of obtaining and processing it. The testing methods also play an important role (rate of strain hardening, dimensions and geometry of the sample, atmosphere in which the sample is tested, etc.).

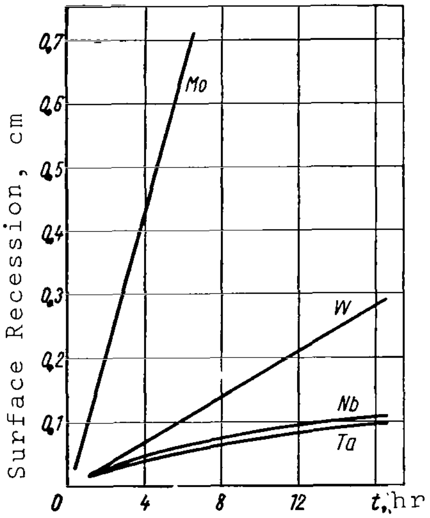


Fig. 2. Surface Recession of High-Melting Metals as a Result of Oxidation in Air at a Temperature of about 1100° C [9].

For a long period of time, powder metallurgy was practically the only method of obtaining tungsten billets and manufactured products. The methods of arc and electron-beam melting of tungsten are now being used more and more widely, since they aid in obtaining a metal of increased purity. A comparison of the properties of tungsten prepared by many different methods shows that the remelted metal has somewhat less strength but greater ductility [11-15]. The tensile strength and creep resistance depends on the grain size, and fine-grained materials have increased resistance [14]. Porosity has a negative effect on the high-temperature strength of tungsten [16].

As can be seen from Figure 3, the strength of tungsten can be greatly increased by means of cold deformation. However, the resistance of the deformed metals decreases rapidly at temperatures higher than 1200° C, where the recrystallization processes begin. We should mention that tungsten is especially softened in polygonization [17-19]. The strength which pure tungsten has at temperatures /9 higher than 1500° C is insufficient in many cases, particularly if we consider its high density (19.3 g/cm^3). Therefore, the possibility of increasing the high-temperature strength of tungsten by means of alloying is of particular interest.

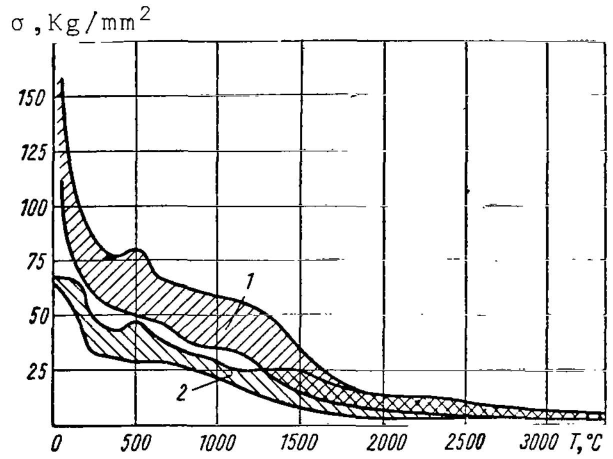


Fig. 3. Temperature Dependence of the Ultimate Tensile Strength of Tungsten: (1) Strained Metal; (2) Recrystallized.

A substantial disadvantage of tungsten is its cold brittleness. The transition of polycrystalline tungsten of technological purity from the ductile state to the brittle one usually takes place at temperatures higher than 200° C, and the transition temperatures for high-purity single crystals is within the range from -196 to -107° C [1]. The recrystallized metal has a much higher transition temperature than does the worked metal.

The problem of the cold brittleness of tungsten has been analyzed in detail in [10, 20, 21]. The ductile-brittle transition temperature (DBTT) is mainly determined by the percentage of impurities (C, O, N, H), the maximum solubility of which does not, as a sum, exceed 0.365 at.% in the metal [22], as well as the grain size and shape. The following law is observed in this regard: purification from foreign elements, size reduction /10 and deformation of a grain brings about a shift of the DBTT toward a lower temperature range. The hardly irremovable admixture of carbon has the greatest negative effect on the ductility of tungsten [10]. The ductility of tungsten also depends on the surface state of the samples: the transition temperature decreases as the perfection of the surface increases [23-25].

The cold brittleness of tungsten produces great difficulties in its processing, particularly in the fabrication of complex shapes. The principal ways in which the difficulties are overcome are the development of methods for removal of weakly soluble impurities, as well as improvements in fabrication techniques. The best results in the first direction are found in electron-beam zone melting in vacuum in combination with a special thermochemical purification from carbon [10]. Of the new methods used in obtaining semi-manufactured and manufactured tungsten products, precipitation from the gas-vapor phase is of great interest; this is accomplished by means of hydrogen reduction or thermal decomposition of volatile tungsten compounds - WF_6, WCl_6, $W(CO)_6$ [19, 26-32]. Plasma deposition seems to be a promising method for obtaining tungsten products of a complex shape [33-35]. Electric spark machining and chemical and electrochemical methods are used for fabrication techniques made of tungsten [36,37]. There have also been improvements made in methods of obtaining tungsten billes and manufactured products such as extrusion, forging, stamping, rolling, molding, heat-pressing, slip casting, etc. [38-40].

Alloying is a possible method of increasing the ductility of tungsten at low temperatures. The processing of metal-ceramic tungsten is greatly simplified with the aid of the methods of sintering in the liquid phase, or impregnation in adding to the metal such elements as Ag, Cu, Ni, Se, Ru, Th, etc., in quantities up to 15-20% [41-46]. Such materials are called "pseudo alloys". The deoxidation of tungsten is of substantial interest. The development of more ductile high-melting tungsten alloys with increased ductility is an important direction of research in the field of high-temperature material.

Alloying is an effective means of improving the corrosion resistance of metals. Many attempts have been made at producing /11 tungsten-base alloys which would have increased resistance to oxidation.

The production of heat-resisting surface layers is a promising method of protecting metals from gaseous corrosion. Substantial achievements have been made in the production of such coatings for Mo, Nb and Ta [47-51]. The most important problem is to produce reliable high-temperature strength coatings for tungsten and its alloys.

CHAPTER 2

OXIDATION OF TUNGSTEN

The study of the oxidation of tungsten is of indisputable interest both from the scientific and the technological point of view. Studies of the structural diagram of the W-O system, the kinetics of oxidation, the dependences of the nature of oxidation on the pressure, and the effects of various factors on the rate of tungsten oxidation make a substantial contribution to the construction of the general theory of oxidation of metals. On the other hand, a knowledge of the kinetic parameters and the mechanism of the reaction of tungsten with oxygen and various media and temperature ranges permits us to determine correctly the fields in which this promising metal can be used in various branches of modern technology. Moreover, this knowledge is necessary for producing high-temperature tungsten-base alloys, as well as for treating heat-resisting protective coatings. /12

However, despite its exceptionally high melting point and unique high-temperature strength, tungsten still has a limited use as a high-temperature structural material. Its low resistance to oxidation plays an important part in this situation.

Even at room temperature, tungsten begins to oxidize. At 20° C, an oxide film of thickness 60 Å is formed on the surface of the metal [52]. The oxidation of tungsten becomes substantial at temperatures higher than 600° C. A comparison of the rates of oxidation for tungsten (Figure 2) and other high-melting metals at 1100° C in air showed that tungsten is oxidized 6 times more slowly than is molybdenum, but 3 times more rapidly than are niobium and tantalum [9]. Data on the absolute rate of oxidation of tungsten at 1100° C, characterized by a recession of the metal-oxide interface for various intervals of time, are presented in Table 2.

It is completely obvious from the table that it is impossible to use tungsten in media which contain oxygen, at the temperatures, for which its utilization is justified from the point of view of specific strength. The exception is a medium with partial oxygen pressure less than 1 mm Hg, in which unprotected tungsten is oxidized at a decreased rate at temperatures close to the melting point [53]. /13

TABLE 2. RATE OF OXIDATION OF TUNGSTEN IN AIR AT 1100° C [9].

Oxidation time, min	30	60	230	500	840	950
Surface recession, mm	0.15	0.25	0.60	1.35	2.40	2.80

A large number of studies have investigated the oxidation of tungsten. Nevertheless, there is still no single opinion on the kinetics and mechanism of high-temperature gaseous corrosion of this metal. The contradictory results obtained by various researchers [9, 54-57] are to a great extent responsible for this.

The solubility of oxygen in tungsten is extremely low. According to the data of Allen et al. [58], who studied oxygen saturation of single crystals of high-purity tungsten, the solubility of oxygen at 1700° is 0.04 wt.% in all. Seigle [22] gives a value of 0.06 at.% for the maximum solubility of oxygen in tungsten (0.005 wt.%).

Inconsistent results were obtained in the studies of the diffusion of oxygen into tungsten. According to Stringer and Rosenfield [59], the activation energy of diffusion is equal to 62 kCal/mole, while Jakobs [60] obtained a value of 24 kCal/mole for the activation energy.

The coefficients of oxygen diffusion in tungsten at 1700° C which were presented in [59-60] are equal to $3 \cdot 10^{-3}$ and $1 \cdot 10^{-9}$ cm^2/sec, respectively. At the same time, Allen et al. [58] obtained $D = 3 \cdot 10^{-7}$ cm^2/sec for polycrystalline specimen, while the value of the diffusion factor in single crystals ranged from $7 \cdot 10^{-6}$ to $5 \cdot 10^{-7}$ cm^2/sec. Lee [61] analyzed the previously obtained results, and concluded that the diffusion factor at 1700° C should be on the order of 10^{-7} cm^2/sec.

A large number of oxides were detected in investigations of the phases of the W-O system: W_3O, $WO_{0.75}(W_4O_3)$, WO, $WO_{1.5}(W_2O_3)$, /14
$WO_{1.8}(W_5O_9)$, WO_2, $WO_{2.5}(W_2O_5)$, $WO_{2.66}(W_3O_8)$, $WO_{2.72}(W_{18}O_{49})$, $WO_{2.75}(W_4O_{11})$, $WO_{2.8}(W_5O_{14})$, $WO_{2.9}(W_{20}O_{58})$, WO_3 [62,63]. However, only the existence of the phases WO_2, $WO_{2.72}$, $WO_{2.9}$ and WO_3 was confirmed with sufficient reliability. The structures and lattice parameters of these phases are given in Table 3.

TABLE 3. CERTAIN PROPERTIES OF OXIDES IN THE W-O SYSTEM [62]

Formula	Color	Structure	Lattice Parameters				Oxygen Content, wt.%
			a, Å	b, Å	c, Å	β	
WO_2	--	Monoclinic	5,560	4,884	5,546	118°56′	14,82
$WO_{2.72}$	Violet	Same	18,32	3,79	14,04	115°2′	19,3
$WO_{2.9}$	Light Blue	--	12,1	3,8	23,4	95°	—
WO_3	Yellow	Monoclinic	7,28	7,51	3,83	90°	20,7

It was reported in [63] that the higher tungsten oxide (WO_3) has three modifications: a low-temperature one at -50° C, a modification at room temperature, the lattice parameters of which are given in Table 3, and a high-temperature one which has a tetragonal lattice with parameters of $a = 5.250 \pm 0.002$ Å, $c = 3.915 \pm 0.002$ Å, $c/a = 0.756$.

Multilayer scales are formed on tungsten at oxygen pressures which greatly exceed the dissociation pressure of stable oxides. In order to detect individual phases in the W-O system and to determine their phase boundaries, it is often necessary to use special investigation methods.

A detailed review concerning the W-O system is found in [56]. Individual tungsten oxides can be obtained under the conditions of controlled partial oxygen pressure. However, a method which would permit determining and regulating oxygen pressures on the order of 10^{-2} atm and below is necessary for this. The existing vacuum systems permit such rarefactions, but it is very difficult to regulate them, since even desorption of gases from the inner sur- /15
faces of a reaction chamber can bring about a substantial pressure change. A definite partial oxygen pressure in the system can be obtained by other methods, for example, by using equilibrium reactions of the following type:

$$x\mathrm{Me} + y\mathrm{H_2O} = \mathrm{Me}_x\mathrm{O}_y + y\mathrm{H_2}$$
$$x\mathrm{Me} + y\mathrm{CO_2} = \mathrm{Me}_x\mathrm{O}_y + y\mathrm{CO}.$$

These reactions were examined for the case of tungsten:

$$0{,}5\mathrm{WO_2}\,(\mathrm{sol}) + \mathrm{H_2}\,(\mathrm{g}) = 0{,}5\mathrm{W}\,(\mathrm{sol}) + \mathrm{H_2O}\,(\mathrm{g})$$
$$0{,}5\mathrm{WO_2}\,(\mathrm{sol}) + \mathrm{CO}\,(\mathrm{g}) = 0{,}5\mathrm{W}\,(\mathrm{sol}) + \mathrm{CO_2}\,(\mathrm{g})$$
$$1/13\mathrm{W_{18}O_{49}}\,(\mathrm{sol}) + \mathrm{CO}\,(\mathrm{g}) = 18/13\mathrm{WO_2}\,(\mathrm{sol}) + \mathrm{CO_2}\,(\mathrm{g})$$
$$9/32\mathrm{W_{20}O_{58}}\,(\mathrm{sol}) + \mathrm{CO}\,(\mathrm{g}) = 10/32\mathrm{W_{18}O_{49}}\,(\mathrm{sol}) + \mathrm{CO_2}\,(\mathrm{g})$$
$$10\mathrm{WO_3}\,(\mathrm{sol}) + \mathrm{CO}\,(\mathrm{g}) = 1/2\mathrm{W_{20}O_{58}}\,(\mathrm{sol}) + \mathrm{CO_2}\,(\mathrm{g}).$$

An x-ray diffraction analysis was carried out in order to identify the phases obtained. The structural diagram constructed by Speiser and St. Pierre for W-O equilibrium at a total pressure of 1 atm is shown in Figure 4. It follows from the diagram that the authors obtained the following oxides: WO_2, $W_{18}O_{49}$, $W_{20}O_{58}$ and WO_3. The same crystalline structures were determined earlier by Magneli et al. [64-70]. The melting temperature of WO_3 was equal to 1470° C, and that of WO_2 was 1700° C. The W_3O phase was also represented on the equilibrium diagram; however, there are contradictory opinions on whether or not this actually exists. In particular, the authors of [71] did not observe it. Hagg and Schönberg [72] suggested that β-tungsten is a W_3O phase. This opinion was corroborated recently in [73]. Phillips and Change [74], who heated a mixture of W and WO_3 powders for one week at 500-615° C, did not detect a W_3O suboxide, and the reaction products were a mixture of W and WO_2. The interaction of W with a H_2O-H_2 mixture at a pressure of 190 atm and 625° C for 16 hours brought about the formation of a mixture of W and WO_2. Based on these results, it was concluded that the W_3O phase is not an equilibrium one.

Gulbransen et al. [75] investigated the ranges of homogeneity for tungsten oxides. The phase boundaries of WO_2, $W_{18}O_{49}$ and $W_{20}O_{58}$ /16
oxides were determined for certain temperatures by way of measuring the vapor tension of $(WO_3)_3$ over these phases. It follows from the results they obtained that the range of homogeneity of WO_2 at 1357° C is within the interval of 1.990 - 2.000, that of $WO_{2.72}$ is within the range from 2.755 to 2.720, and that of $WO_{2.9}$ is from 2.950 to 2.888. For the $WO_{2.72}$ phase ($W_{18}O_{49}$), the phase boundaries were marked off in [76] between 2.664 and 2.766.

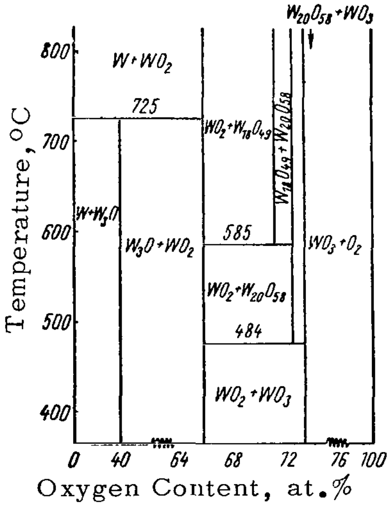


Fig. 4. Phase Diagram for Equilibrium of the W-O System for Total Pressure of 1 atm.

Phillips and Change [74] investigated the high-temperature stability of tungsten oxides and constructed a diagram of phase equilibrium in the W-O system up to 1800° C. It was found that the WO_2 phase is stable up to a temperature 1530 ± 5° C. Above this point, it dissociates into W and $W_{18}O_{49}$. The same authors reported that small quantities of Ca, Co and Sm (2-3 at.%) in solid solution stabilize the WO_2 structure at temperatures up to 1700° C. The $W_{18}O_{49}$ phase was stable at 1700° C, but the maximum temperature of $W_{18}O_{49}$ stability was not determined. It was found that the $W_{20}O_{58}$ phase is stable up to 1550° C. At higher temperatures a liquid phase is detected. It is possible that a change in the composition of this oxide up to WO_3

is the cause for the formation of the liquid phase.

A vast amount of experimental information concerning the behavior of tungsten in oxidizing media has been accumulated at the present. However, the existing information is very inconsistent. The first reason for this is the difference in materials used by the researchers, i.e., the difference in metal composition of tungsten, its structure, and its surface state. The cause of the observed discrepancies obviously could also be differences in the chemical composition, humidity and pressure of the oxidizing media.

The rate of flow of the oxidizing gas plays an important part /17 in the process of tungsten oxidation, particularly at high temperatures, where the products of tungsten oxidation are volatile and the rate of their removal from the reaction zone greatly affects the rate of oxidation of the metal. The use of imperfect methods in the earlier studies could also bring about substantial errors.

Investigations of the scale resistance of tungsten were begun in the 1920's [77]. In the earlier studies, the researchers did not pay particular attention to an examination of the mechanism of the oxidation process, and they concentrated their attention on the kinetics of the interaction between tungsten and oxygen.

A detailed investigation of the oxidation of tungsten at low temperatures was carried out by Gorbunova and Arslambekov [52]. They investigated the oxidation of tungsten films with the aid of a manometric method, while they studied the oxidation of films weighing up to 5 g with the aid of a gravimetric method. Curves for the oxidation of tungsten at 20, 30, 65 and 200° C were obtained. Even at 20° C, the thickness of the outside film on the tungsten, assuming that it consisted of WO_2, was equal to 60 Å, and at 30° C it was equal to 90 Å. These values are equal to 30 and 45 Å, respectively, if we consider the roughness of the surface. The curves of oxidation of 65 and 200° C correspond roughly to a logarithmic law. The thickness of the oxide layer at the moment when the rate of oxidation has decreased sufficiently is 230 Å at 65° C and 340 Å at 200° C. At higher temperatures (360 - 487° C) and oxygen pressure of 24 mm Hg, the change in the rate of oxidation is expressed by a parabolic curve.

The value of the activation energy for the oxidation process was found to be equal to 43.6 kCal/mole, while it was equal to 22 kCal/mole for lower temperatures. It was established that, beginning with 800° C, there is an evaporation of the oxides, which becomes substantial at a temperature of 1000° C. The energy of the evaporation process was equal to 80 kCal/mole in this case.

Two oxide layers were observed in the oxidation of tungsten: a dark blue (internal) and a yellow one. Electron-diffraction investigations showed that both oxides were close to WO_3 in composition.

Gulbransen and Wysong [78] held that the oxidation of tungsten at temperatures between 400 and 500° C obeys a parabolic low. The oxidation was carried out in oxygen at a pressure of 76 mm Hg for two hours. The activation energy for the oxidation process in this temperature range was equal to 45.65 Kcal/mole, according to [78], i.e., there was good agreement with the value obtained by Gorbunova and Arslambekov. /18

Having investigated the interaction of tungsten with the oxygen of the air for the course of three hours in the temperature range of 700 - 900° C, Dunn [77] found that the oxidation in this temperature range also followed a parabolic law. The deviations which he noted at 850 - 900° C could have been due to phase changes in the oxides.

The results of an investigation of the oxidation of high-purity tungsten in a wider range temperatures (500 - 1300° C) and of oxygen pressures (0.1 - 0.0013 atm) are found in [79]. It was established that, at temperatures of 500 - 1100° C, oxidation takes place with an increase of weight (according to the parabolic law), while at higher temperatures it takes place with a decrease of weight. In the temperature range in which the parabolic law of oxidation is observed, the velocity constants measured for long periods of oxidation were found to be greater than those in oxidation during a short period of time. Correspondingly, the activation energy for the temperature interval in which oxidation takes place according to the parabolic law was found to be equal to 44.5 kCal/mole, while that in the temperature range where the deviation from this law is observed is equal to 54.5 kCal/mole. For temperatures higher than 800° C, the evaporation of the WO_3 oxide becomes substantial, while at temperatures above 1100° C sublimation of tungsten trioxide takes place at a rate which is comparable to the rate of its formation. Therefore, in volatilization of WO_3 the surface of the sample decreases, and the rate of weight loss decreases correspondingly. Gulbransen and Andrew obtained a value for the activation energy of the process as equal to 32.5 kCal/mole for oxidation of tungsten at temperatures higher than 800° C.

An analysis of the results obtained shows that the rate of tungsten oxidation is not a simple function of the time. The adhesion of the oxide film plays an important role here. The authors of [79] considered that the reason for the change in the rate of oxidation was a cracking of the oxide layer.

The authors of [80] held a similar opinion. They also observed a deviation in the rate of oxidation from the parabolic law and its similarity to a linear law in the temperature range of 500 - - 700° C. The oxidation of pure tungsten in the temperature range 400 - 1200° C takes place according to the following law, according to their data: $\Delta P^n = k\tau$ where ΔP is the change in weight of the samples per unit surface area, τ is the oxidation time and k is constant. /19

The oxidation takes place according to a parabolic law at a temperature of 400° C (n = 2), and a protective film is formed on the metal, while the rate of oxidation is determined according to the diffusion processes. A step toward the linear law of oxidation (n → 1) begins in the range of 500 - 700° C. This can be explained by the appearance of microscopic cracks in the oxide layer. Beginning with 800° C, the linear law of oxidation is observed. In the temperature range where the linear law is observed, the rate of WO_3 evaporation is already very substantial. At 1200° C, the curves for oxidation again are close to parabolas. Obviously, such a change in the kinetics of oxidation is linked with a decrease in the surface of the samples. In opposition to the data presented in [52, 78, 79], the activation energy for oxidation obtained by Arzhanyy et al. [80] is 23.078 kCal/mole. At all temperatures, there was observed only the WO_3 oxide, which had a monoclinic lattice with parameters of a = 7.27 Å, b = 7.50 Å, c = 3.8 Å. However, the parameters of the tungsten lattice changed in dependence on the temperature of oxidation, which indicated that a tungsten layer saturated by oxygen was formed below the WO_3 oxide film. For an initial value of a = 3.31 Å, the parameter a decreased with an increase of the temperature of tungsten oxidation (for 300° C a = 3.11 Å, for 500° C a = 3.03Å, for 850° C a = 3.00 Å).

Some researchers who investigated intermediate temperatures observed a linear low of the oxidation of tungsten. For example, it was shown in [81] that oxidation by the linear law was observed at temperatures of 500 - 700° C, while it was shown in [82] that this takes place at temperatures of 600 - 850° C. The authors of [83, 84] reported that they detected laws of an intermediary type in the temperature range of 500 - 900° C.

Thus, different laws for the oxidation of tungsten were observed in the same temperature ranges. It was found that the presence of some type of law for oxidation was determined primarily by the duration of the experiment. As a rule, the researchers who /20 studied oxidation during a short period of time noted that the process took on a parabolic course, while those who studied prolonged experiments noted that the oxidation took place according to the linear law.

The oxidation of tungsten during a long period of time at temperatures of 700 - 1000° C was investigated in [85]. Oxidation was carried out in oxygen.

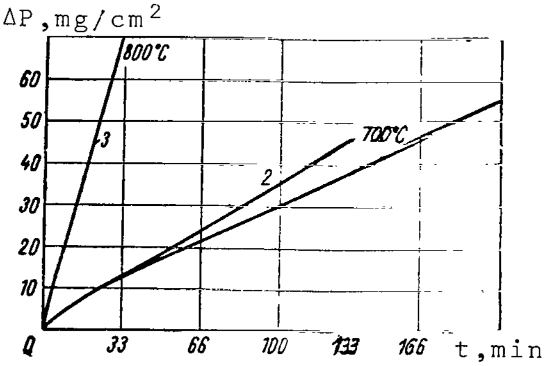


Fig. 5. Kinetics of Tungsten Oxidation at Temperatures of 700 (1,2) and 800° C (3). Curve 2 was Taken for Oxidation in a Medium of Wet Oxygen.

The purity of the metals was 99.9%. The experimental data obtained are shown in Figures 5 and 6.

The velocity constants, which relate to the parabolic law of oxidation, agree with the results of Dunn [77], who carried out experiments lasting no longer than 3 hours. The constants measured for the linear law of oxidation agree with the results of [81], the authors of which carried out oxidation of the samples for 90 hours at 700° C. It is obvious that the transition from the parabolic to the linear law was accomplished in full in this case.

Two oxide layers were observed on the oxidized samples: an outer layer of WO_3, and an inner layer whose composition was not determined. It was noticed that the thickness of the inner layer did not change with an increase of the duration for oxidation.

Using the qualitative explanation for this transition from the parabolic law of cerium oxidation to the linear one proposed in [86], Webb et al. [85] derived an equation for the oxidation of tungsten in the intermediate range. According to the authors of /21 [86] the transition from the parabolic law to the linear one takes place when one oxide converts into another by way of an addition of more oxygen. The rate of formation of the preliminary oxide is inversely proportional to its thickness, while the rate of the transition to the higher oxide is constant. The equations for the rate of growth of both layers can be written out in the following way:

$$\frac{dy}{dt} = \frac{a}{y} - b; \qquad (1)$$

$$\frac{dz}{dt} = fb, \qquad (2)$$

where y is the oxygen mass in the inner layer per unit area; z is the oxygen mass in the outer layer per unit area; f is the ratio between the amount of oxygen per gram-atom metal in the outer layer to the same value for the inner layer; a and b are constants. The total sum of oxygen per unit area is equal to the increase of mass per unit area:

$$\frac{\Delta m}{A} = y + z. \qquad (3)$$

Having integrated (1) and (2), we find that

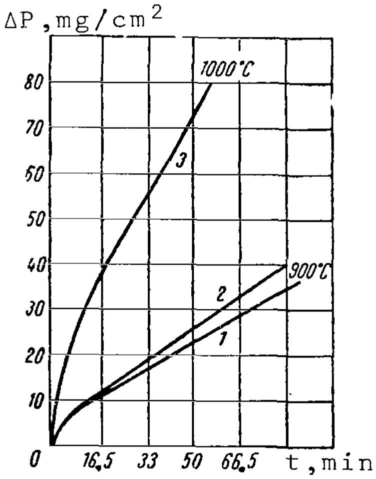


Fig. 6. Kinetics for Tungsten Oxidation at Temperatures of 900 (1,2) and 1000° C (3). (Curve 2 is Taken for Oxidation in a Medium of Wet Oxygen).

$$\ln\left(1-\frac{by}{a}\right)^{-1}-\frac{by}{a}=\frac{b^2t}{a}; \qquad (4)$$

$$z=bft. \qquad (5)$$

Having substituted (4) and (5) into (3) and having introduced the designations X = ln $(1 - by/a)^{-1}$ and Y = b^2t/a, we have the following:

$$\frac{\Delta m}{A}=\left(\frac{a}{b}\right)\ln\left(1-\frac{by}{a}\right)^{-1}+b(f-1)t=\left(\frac{a}{b}\right)[X+Y(f-1)] \qquad (6)$$

The weight increase of the tungsten samples can be calculated from this equation for any time t, and the parabolic and linear equations can be found for specified boundary conditions. Webb and his coworkers obtained calculation curves for oxidation at 700, 800, 900 and 1000° C with the aid of the equation derived.

If the inner oxide has a composition of $WO_{2.75}$, then the value of f should be equal to 1.09. However, since the actual composition of the oxide is unknown, f is assumed to be equal to 1. The calculated and experimental curves coincide well (Fig. 7).

Semmel [87] also obtained curves whose beginning part represented a straight line for the temperature range of 980 - 1370° C. However, tungsten is oxidized at 1260° C according to the parabolic law for a long time interval. According to Semmel, the decrease in rate of oxidation at 1260° C can be explained in terms of the melting of the outer oxide layer and formation of a protective film.

Thus, we can consider it established that the parabolic law for the growth of an oxide film holds during the initial stage of tungsten oxidation. For longer durations in an oxidizing medium, there is a transition from the parabolic law to the linear one, and the time of the transition depends on the temperature. There are various opinions regarding the causes for this transition. Webb et al. [85] consider that the transition is due to the formation of a layer which is smaller than the protective WO_3 oxide, and other researchers [79, 80] explain it in terms of the appearance of microscopic cracks in the layer of tungsten trioxide. The latter explanation seems to be more probable. Since the volume occupied by the oxide generally differs from the volume of the equivalent amount of metal, stresses necessarily arise on the scale if the ductile flow does not eliminate them. In certain cases, the stresses can /23
destroy the oxide film. When the volume ratio (ratio between the molecular volume of the compound and the atomic volume of the metals) is greater than one, as takes place for WO_3, compressive stresses arise in the oxide layer and bring about a transverse splitting of the layer. In this case the oxide layer loses its

protective properties and oxidation takes place according to the linear law.

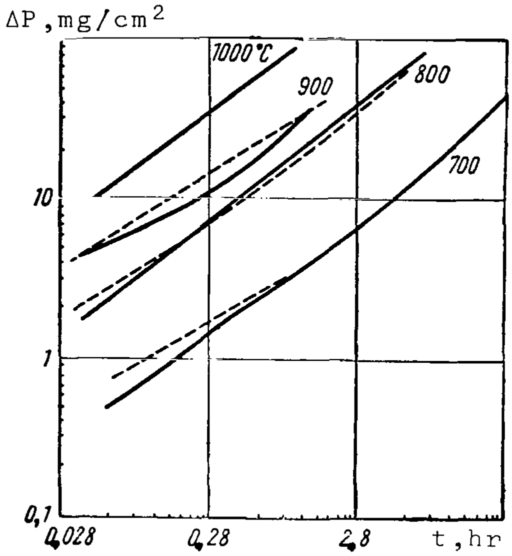


Fig. 7. Comparison of Calculated (dashed lines) and Experimental Curves for Tungsten Oxidation at 700 - 1000° C.

The stresses arising on the surface of the metal which are due to different types of processing also play an important part in oxidation. The dependence of tungsten oxidation on the type of processing of the sample surface was examined in [52, 88]. Kinetic curves for samples whose surfaces were treated by three different methods were obtained with the aid of sensitive microbalances. One type of treatment was a polishing on fine-grained emery. Another type was buffing on the same emery with subsequent electrolytic polishing. The third group of samples was subjected to preliminary oxidation. The oxide was then removed by way of hydrogen reduction at 600° C and evaporation under vacuum at 1050° C. /24

It was established that the growth of the oxide layer at temperatures higher than 300° C obeys the parabolic law of the type $x^2 = kt + C$. The value of the constant k in the case of oxide films of great thickness depends only slightly on the value of the initial surface of the samples. However, the state of the surface affects the values of the constants for the velocity and activation energy of the process. A difference in these values was observed for ground and electrolytically polished samples and, according to the authors of [52, 88], was due to the fact that in grinding there is the strain deformation along the surface and the arisal of residual stresses, as a result of which the activation energy of the oxidation process decreases. The activation energy for oxidation of electrolytically polished tungsten is equal to 46.5 kCal/mole, while that of emery-polished tungsten is 42 kCal/mole.

Similar results were obtained in a study by Gulbransen and Andrew [79], who compared the oxidation of samples which had different surface states. They investigated samples with an untreated surface, samples preliminarily annealed in hydrogen at 600° C and annealed in vacuum at 1000° C, and samples whose surfaces were subjected to electrolytic polishing and mechanical finishing. The rate of oxidation of the tungsten samples at 600° C practically did not depend on preliminary treatment of the surface by the first three methods. The difference in oxidation of electrolytically polished and mechanically finished samples was noticeable. The electrolytically polished samples, whose surfaces were not subjected to strain hardening, oxidized more slowly.

Straining of the metal, just as surface cold-hardening due to mechanical processing, accelerates oxidation so that, e.g., strained Cu, Nb, and Ti are oxidized more rapidly than the non-stained metals. This can be explained by the fact that the chemical potential of the metal is changed by the effect of straining.

I.N. Frantsevich et al. [54] studied the oxidation of strained and recrystallized tungsten specimens at 500-900° C. Cold deformation of tungsten (by 40 - 50%) was carried out under conditions of /25 discontinuous pressing on scale rings. Some of the worked specimens were annealed at temperatures exceeding the recrystalization point. The temperature range for oxidation was selected in such a way that recrystallization did not occur during the experiment. The rate of oxidation of the worked specimens was found to be higher than that of the recrystallized ones (Figures 8, 9).

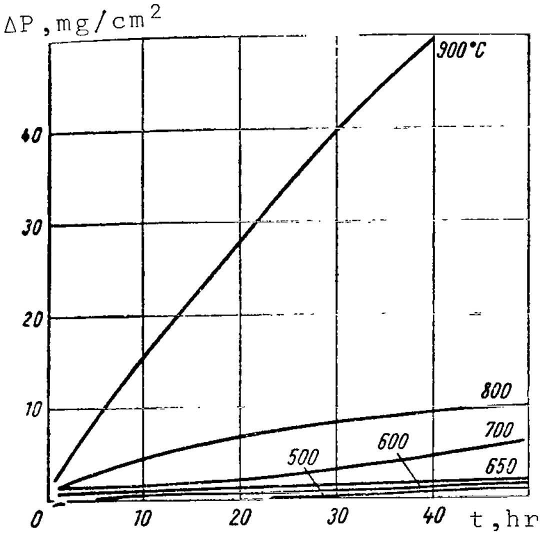


Fig. 8. Kinetics of Oxidation of Recrystallized Tungsten.

In analyzing the oxidation curve, the authors of [54] used an equation which described the process of high-temperature oxidation and which permitted a quantitative analysis in those cases when the weight of the samples decreased because of volatility or abrasion. It was shown that an increase in the constants for the rate of oxidation of worked tungsten takes place because of an increase in the number of active reaction centers. For example, in the case of oxidation at 600° C, the number of active centers per gram-atom of the metal for worked tungsten increases more than twice, compared to recrystallized tungsten. /26

In the neighborhood of 650° C, there is a break which indicates an abrupt increase in the rate of oxidation on the curve for the temperature dependence of the constants of the rate of oxidation of recrystallized tungsten (Fig. 10).

This break was also observed by other researchers at a somewhat different temperature. We can assume that the break is connected with a phase transition in the growing oxide film.

A thermochemical calculation of the heterogenous equilibrium in the W-O system was carried out for temperatures of 600 - 900° C, based on the presence of the following phases in the system: α-WO_3, γ-W_2O_5, δ-WO_2, and ε-W. On the basis of the data obtained, it was concluded that the reaction $5WO_3 + W = 3W_2O_5$ is most probable at the α-WO_3-W interface.

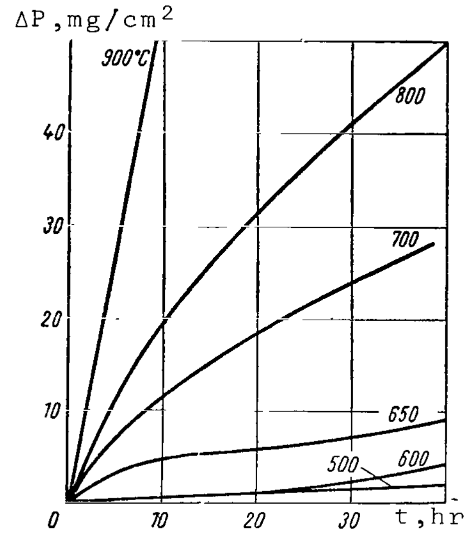


Fig. 9. Kinetics of Oxidation of Tungsten Strained by 40 - 50%.

The calculations showed that, in the temperature range of 600 - 900° C, the reaction of a transition from the γ-phase (W_2O_5) to α-WO_3 due to the addition of more oxygen ($2W_2O_5 + O_2 = 4WO_3$), as described in [82, 85], was thermodynamically impossible. /27 Consequently, the growth of the outer WO_3 layer was due to oxidation of the tungsten itself by oxygen ions scattered from without and rearrangement of the lattice from the γ-phase to the α'-WO_3 lattice during the course of oxidation.

As for the abrupt increase in the rate of oxidation of recrystallized tungsten at 650 - 700° C noted by the authors of [54], it follows from a comparison of the results for a study of the kinetics of oxidation, a thermodynamic calculation of the possible reactions and an x-ray diffraction analysis of the oxide layers that it is due to the phase conversion α-WO_3 → α'-WO_3 which takes place at these temperatures. The α-WO_3 phase has a greater concentration of anion vacancies than does the α'-WO phase, and it is observed in the entire temperature range for oxidation of strained samples. The activation energy for oxidation of worked tungsten is equal to 52.9 kCal/mole.

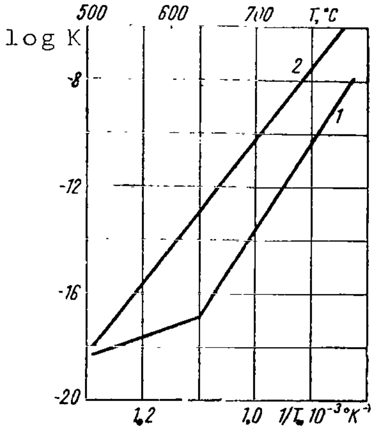


Fig. 10. Temperature Dependence of the Constants for the Rate of Oxidation of of Recrystallized (1) and Cold-Worked (2) Tungsten.

For a more complete understanding of the process of tungsten oxidation, it is necessary to study the texture of the surface layers of the metal and its effect on the rate of oxidation and the nature of the oxide film, although it is obvious that these factors have substantial significance in the case of thin films formed on the metal at a low temperatures and during short periods of oxidation. However, many researchers consider the oxide layers to be homogeneous and isotropic phases, for the sake of simplicity. This type of examination is too simplified, as was shown convincingly in works which investigated the oxidation of Cu, Fe, Zn and certain other metals. Kubashevskiy and Gopkins [55] considered that an analysis of the results obtained in investigating the effect of the texture of the metal on its oxidation showed the following facts:

1. The crystal orientation of the oxide film on the surface of the grain-oriented metal is directly linked with the orientation of the oxidizing metal. /28

2. The rate of growth of the film depends on its crystal orientation.

3. During the process of oxidation, some of the crystals in the oxide film grow more rapidly because of a more advantageous orientation.

It was reported in [89] that the following sequence in the rate of oxidation of the faces is observed: (100)>(111)>(110). The (100) face is oxidized roughly 6 times more rapidly than is the (110) face. This law was observed in single crystals of tungsten in dry oxygen at a temperature of 2050 ± 50° C and oxygen pressure of 10^{-6}atm.

According to Wagner, the oxygen pressure should not affect the rate of oxidation in the case of metals which form n-type oxides, at intermediate temperatures where the parabolic law is observed, since the number of defects on the surface of the oxide-gas interface should be insignificantly small and should not depend on the pressure change. In a substantial decrease of the oxygen pressure, the concentration of defects at the oxide-oxygen interface becomes substantial, and its magnitude depends on the temperature, pressure and affinity of the metal to oxygen. Therefore, the rate of oxidation should increase as the pressure decreases for very low pressures. All these observations refer to cases when the oxygen pressure does not exceed the atmospheric one; the effect of high pressures on the rate of oxidation of metals has not been investigated in detail. The oxidation of tungsten at high temperatures in high-velocity air flows was examined in [90, 91].

At 600 - 700° C, the oxygen pressure does not affect the process of tungsten oxidation, which forms the trioxide (WO_3), or a semiconductor of the n-type. At 750 - 850° C, the effect of the pressure is insignificant [82]. Similar data are presented in [79] where the effect of a change in oxygen pressure within the range from 0.1 to 0.0079 atm on the kinetics of tungsten oxidation at 600, 950, 1050, and 1200° C was investigated. At a temperature of 600° C, a decrease in oxygen pressure from 0.1 to 0.0132 atm increases the rate of oxidation only insignificantly.

The oxidation curves obtained in [79] are shown in Figures 11 - 14. At temperatures where WO_3 is evaporated, the dependence of the rate of oxidation on the oxygen pressure has a different character. For example, at 950° C a decrease in the pressure brings about a decrease in the rate of oxidation. It can be seen from /29 these data that the volatility of tungsten trioxide has a great effect on the velocity of the oxidation process. At a temperature of 1050° C, the oxygen pressure has a substantial effect on the course of the reaction. For an oxygen pressure equal to 0.0033 atm and below, there is a weight loss. The course of the curves for the change in weight is determined by the formation of the oxide film, the volatilization of the tungsten trioxide and its diffusion in the gas phase. The latter process is a function of the density of the atmosphere surrounding this sample.

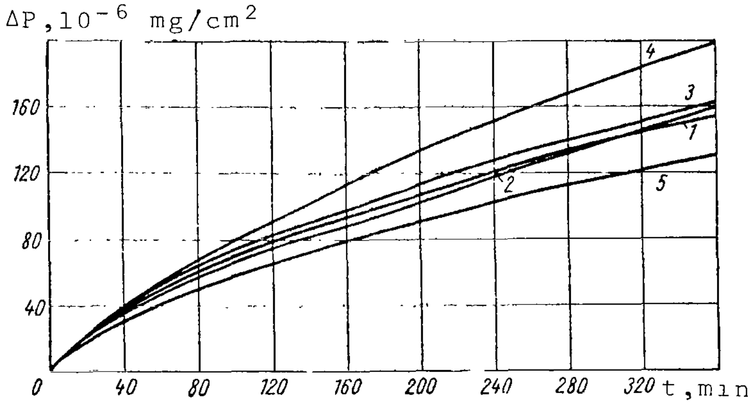


Fig. 11. Effect of Oxygen Pressure on Oxidation of Tungsten at a Temperature of 600° C: (1) 0.1; (2) 0.068; (3) 0.0355; (4) 0.0132; (5) 0.0079 atm.

At 1200° C, a weight loss of the samples is observed at all pressures while the maximum weight loss takes place at a pressure of 0.012 atm.

An attempt was made at establishing a link between the oxidation of tungsten and the temperature, time and oxygen pressure in a temperature range of 500 - 1300° C and a pressure range of 0.0013 - 20.8 atm [92, 93]. The authors suggested a method which made it possible to establish the relationship between the results [79, 82, 85], to consider the effects of the oxygen pressure on the rate of tungsten oxidation, and to obtain an equation for the rate of oxidation in a form suitable for practical use. The data concerning /31 oxidation of tungsten which were presented in [82] were subjected to analysis. According to this work, the WO_2 suboxide is formed in the initial stage of tungsten oxidation ($W + O_2 \rightarrow WO_2$), and is then converted into WO_3(WO_2 + 1/2 O_2 → WO_3) (sol.). Subsequently, there is sublimation of the trioxide by the reaction WO_3 (sol.) 1/n $(WO_3)_n$ (vap). All the reactions of the metal with oxygen can be represented by the following equation:

$$\frac{dm_{Ob}/A}{dt} = kC = kf(p), \qquad (1)$$

where $\frac{mO_b}{A}$ is the weight change per unit area due to the reaction of the metal with oxygen

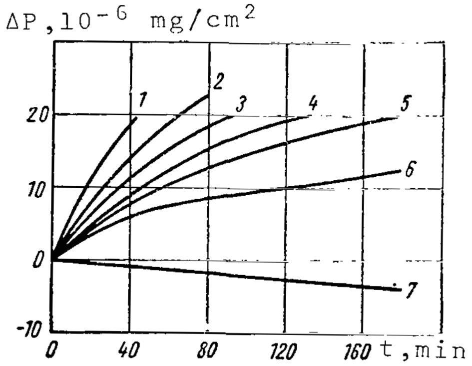


Fig. 12. Effect of Oxygen Pressure on Oxidation of Tungsten at a Temperature of 950°: (1) 0.1; (2) 0.047; (3) 0.0118; (4) 0.00528; (5) 0.0033; (6) 0.00132 atm. (7) WO_3 Evaporation.

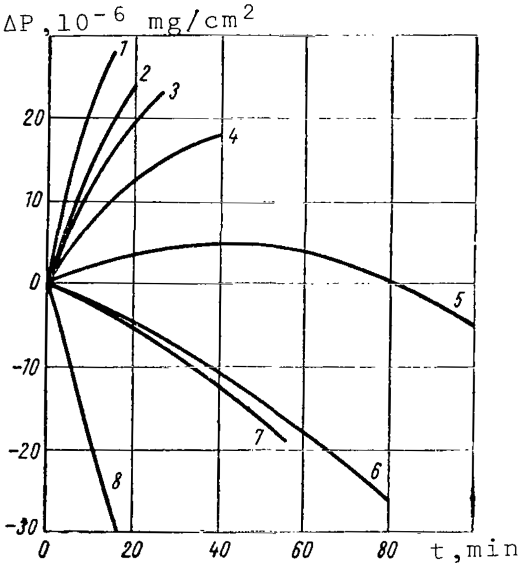


Fig. 13. Effect of Oxygen Pressure on Oxidation of Tungsten at a Temperature of 1050° C: (1) 0.1; (2) 0.0512; (3) 0.0263; (4) 0.0112; (5) 0.0066; (6) 0.0033; (7) 0.0013 atm; (8) WO_3 Evaporation. /30

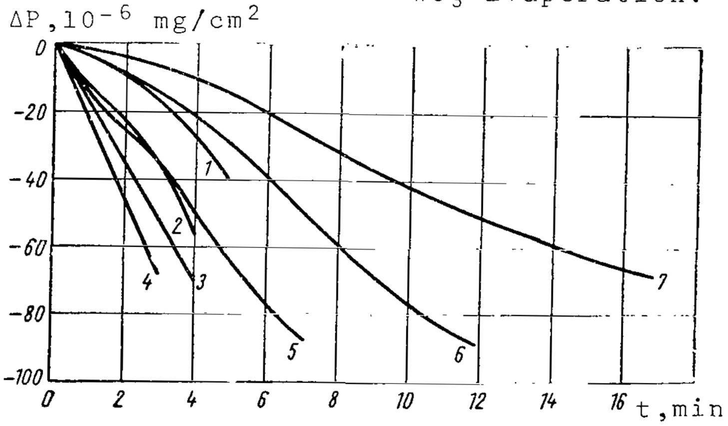


Fig. 14. Effect of Oxygen Pressure on Oxidation of Tungsten at a Temperature of 1200° C: (1) 0.1; (2) 0.047; (3) 0.025; (4) 0.012; (5) 0.0066; (6) 0.0033; (7) 0.0013 atm. /31

(g/cm^2); k is the constant of the reaction rate (sec^{-1}); C is the concentration of components controlling the rate of the reaction; f(p) is a complex pressure function which links the pressure with the concentration of components.

When the rate of the reaction is controlled by the process taking place at the phase boundary, (1) can be written out in the following way: /32

$$\frac{dm_{Ob}/A}{dt} = kC, \quad (2)$$

where C is the concentration of components at the phase boundary (g/cm^2).

In the case when oxidation is controlled by the diffusion, (1) acquires the following form:

$$\frac{dm_{Ob}/A}{dt} = \left\{\frac{D\,\Delta C\rho M_{Ob}/Me_a O_b}{2}\right\}^{1/2} \cdot \frac{1}{t^{1/2}}, \quad (3)$$

where ΔC is the difference in concentration at the oxide-oxygen and oxide-metal interfaces (g/cm^2); ρ is the density of the oxide film (g/cm^3); D is the diffusion coefficient (f^2/sec); mO_b/me_aO_b is the ratio between the weight of used oxygen and the weight of the oxide formed.

The authors of [92, 93] made the following assumptions in deriving the expression for the rate of an oxidation:

(1) The rate of WO_2 formation is controlled by diffusion, and (3) is applicable;

(2) The rate of WO_3 formation is controlled by the reaction at the phase boundary, and is expressed by (2);

(3) The rate of WO_3 sublimation is also controlled by the reaction at the phase boundary;

(4) The rate of expenditure of tungsten does not depend on the rate of WO_3 sublimation;

(5) The functions which connect the concentration to the pressure are expressed in terms of Langmuir isotherms which describe the dissociation of oxygen molecules into atoms.

Equations for the rate of formation of all the oxidation products were obtained, and the corresponding curves were constructed. The curves were compared to the experimental data obtained by

[79, 82, 85].

The equations derived agree satisfactorily with experimental data in the temperature range of 500 - 1300° C and the pressure interval of 0.00132 to 20.8 atm. For practical purposes, the rate of expenditure of tungsten due to oxidation at temperatures higher than 700° C can be determined by the following equation:

/33

$$-\frac{d\,(m_W/A)}{dt} = 5{\cdot}89\cdot 10^{6}\,e^{-\frac{12\,170}{T}}\,p^{1/2},\ \mathrm{mg/(cm^2\cdot hr)}$$

$$-\frac{dx_W}{dt} = 3{,}05\cdot 10^{2}e^{-\frac{12\,170}{T}}\,p^{1/2},\ \mathrm{cm/hr}$$

where T is the temperature, ° K, and P is the pressure, atm.

Becker et al. [94], having investigated the interaction between tungsten and oxygen at a pressure of 10^{-5} - 10^{-7} mm Hg, found that the rate of formation and evaporation of WO_3 is directly proportional to the oxygen pressure at temperatures of 927 - 1327° C, while it increases with an increase of the pressure at temperatures of 1727 - 2127° C (as a function of $p_{O_2}^{3/2}$) and decreases with a temperature increase.

Attempts were made at establishing the mechanism of the oxidation process for intermediate and higher temperatures. However, in order to establish the oxidation mechanism, in addition to a clarification of the kinetic dependences it is also necessary to know the composition and structure of the oxides formed and the nature of the defects in the metal and oxide films, which play an important role in the diffusion. Moreover, the nature and amount of defects in the lattice must be examined in dependence on the temperature and composition of the gas and admixtures.

The results of an investigation of the phase composition of the scale are presented in [95], as are data on the oxidation mechanism in the temperature range of 500 - 1300° C. Tungsten with purity of 99.8% was used as the study material. The oxidation of the specimens was carried out in drained and non-drained air and in dry oxygen. The results of the investigations showed that the samples are covered by a dark blue, thin film in oxidation of tungsten in non-drained air at 300° C. At 500° C, a layer of a gray color is formed above this film. The thickness of the layer increases with an increase of the temperature, and the color changes. At 600° C, the layer has a yellow color, and at 700° C it has a yellowish-green color; at 900° C it is green and at 1100° C it is dark green. If the oxygen takes place in drained air, all the colors of the upper layer have a yellow tinge. For temperatures up to 1200° C, the grain size in the inner layer does not exceed 10^{-4} - 10^{-5} mm. For temperatures of 1200 - 1350° C there is a substantial increase of the grain size. The layer has a very pronounced texture.

The outer layer of the scale remains fine-grained to a temperature of 1100° C, and there is also enlargement of the grains with an increase of the temperature. Investigations of the phase composition of the oxide films show that, at temperatures of 500 - 900° C, the outer layer, which the authors of [95] called α-WO_3, is close to WO_3 in chemical composition. At temperatures of 1000 - 1350° C, the structure of the outer layer changes somewhat. Therefore the authors called it α'-WO_3. The composition of the inner layer is identical to the γ-phase described by Hagg (W_4O_{11}), which has an oxygen deficiency compared to WO_3. /34

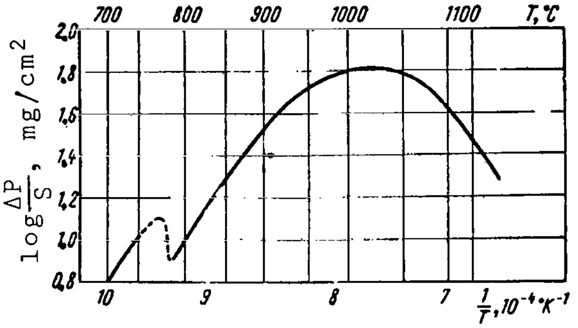


Fig. 15. Temperature Dependence of Rate of Tungsten Oxidation in the Temperature Range of 700 - 1260° C.

The graph for the temperature dependence of tungsten oxidation in the temperature range of 700 - 1260° C which was obtained by the authors of [95] is shown in Figure 15. The authors connected the change in the course of the curve at 1000° C to the arisal of the α'-phase, while the range of 750 - 800° C obviously corresponded to the break described by Hickman and Gulbranfen [96]. Having analyzed the experimental data, the authors drew the following conclusions. In oxidation of tungsten there are three oxide phases: α, α' and γ. The α and α' phases differ insignificantly and are close in composition to tungsten trioxide. The α' phase has a substantial range of homogeneity.

The rate of evaporation of the α'-phase is greater than that of the α-phase, which is expressed in the change of course of the curve at 1000° C.

The growth of the oxide layer on tungsten at temperatures higher than 750 - 800° C is determined by two processes: the diffusion of the reacting elements and the volatility of the oxides. /35 Both processes are characterized by an exponential dependence on the temperature. Therefore, their total effect on the graph of $\log(\frac{\Delta P}{S}) = f(\frac{1}{T})$ is depicted by a straight line; the change in the inclination shows that the rate of sublimation of the α'-phase changes.

Basing their arguments on Wagner's theory, V.I. Arkharov and Yu. D. Kozmanov [95] suggested a mechanism for tungsten oxidation at temperatures of 500 - 1350° C in which the adsorption and diffusion of oxygen in tungsten and the formation of the oxide phases are considered. Having analyzed the change in the structure of the oxide layer during a change in the temperature of oxidation, experiments with an inert tracer, changes in the lattice parameters in terms of the depth of the layer, and also the characteristics of the external form of the oxidized samples, they concluded that the diffusion of oxygen has overwhelming significance in the process of tungsten oxidation. The signs which would indicate diffusion of the metal, i.e., orientation of the growth in the outer layer, porousness of the inner layer, etc., were not detected [97]. Having developed a concept concerning the mechanism of reaction diffusion, particularly of the oxidation processes, V.I. Arkharov and Yu. D. Kozmanov showed in subsequent works [97, 98] that the nature of the bonding forces in the crystal lattices of the oxidation products also has an important role in the mechanism of the process. The intensification of the relative role of homopolar bonds in the compounds characterizes the intensification of the relative role of diffusion of the metalloid in the process of the reaction diffusion. Since homopolar bonds in tungsten, molybdenum, niobium and zirconium oxides are expressed rather clearly, the oxygen diffusion should play the prevailing role in oxidation of these metals.

The results of investigations which agree completely with the conclusions of V.I. Arkharov and Yu. D. Kozmanov are described in [64]. Experiments with an inert tracer in the form of a platinum spiral confirmed the primary diffusion of oxygen in tungsten oxidation for a temperature range of 500 - 900° C.

The authors of [79] considered it expedient to examine the oxidation mechanism separately for temperature ranges 500 - 600, 650 - 950 and 1000 - 1300° C, since oxidation of tungsten took place in different ways for each of these intervals.

In the temperature range of 500 - 600° C, as well as at lower temperatures, the oxidation is determined by the process of oxygen diffusion through the scale. First of all, tungsten trioxide is formed, and then the solid-phase reaction between tungsten and WO_3 results in the formation of WO_2 or other lower tungsten oxides. Such concepts almost coincide with the conclusions of V.I. Arkharov and Yu. D. Kozmanov. However, at higher temperatures there is a cracking of the oxide film, according to the authors of [79], and the rate of oxidation increases abruptly. /36

For temperatures of 1000 - 1300° C, the development of the reaction is determined by the rate at which oxygen is supplied to the reacting surface, and by the diffusion of the evaporated oxide in the gaseous phase. A change in the rate of oxidation within the temperature range of 1100 - 1200° C could be linked with the volatility of the oxides, but V.I. Arkharov and Yu. D. Kozmanov considered that the reason for the change in rate of oxidation was found in the structural transformations in oxides. Semmel [87] considered that it was the melting of the oxides. However, Semmel did not show any proof of this assumption, except for the fact that the edges of samples which had been subjected to high-temperature oxidation were rounded off.

In relation to the growing need for materials suitable for use in outer space, there have recently appeared studies in which the behavior of tungsten at high temperatures and low oxygen pressures are described.

The study of Perkins and Crooks [53], in which the oxidation of tungsten in air at pressures from 1 to 40 mm Hg and temperatures of 1300 - 3000° C is described, is of doubtless interest. The kinetics of the oxidation was examined in terms of the change in diameter of cylindrical rods that were heated by a current. The dependence of the rate of oxidation on the temperature and pressure was investigated in detail.

A strong dependence of the rate of oxidation on the pressure was observed in the range of 1300 - 1750° C. The approximate rate of oxidation in this range can be calculated with the aid of the following equation:

$$k = 14.5\, e^{-\frac{31\,500}{RT}}\, p^{0.62}\ \mathrm{g/(cm^2 \cdot min)}$$

The energy activation (Q = 31.5 kCal/mole) in this equation was obtained from a graph for the dependence of the logarith of weight /37
decrease ΔP on 1/T, which represents a straight line. The graph for the dependence of the logarithm of rate of oxidation on the pressure logarithm in this range also represents a straight line, from the inclination of which a value of n = 0.62 was determined. The value of A (constant in the velocity equation) is determined by a solution to the equation for each measured value of K. The experimentally obtained rates of oxidation differ from those calculated by ± 10%.

An increase in the rate of tungsten oxidation was observed at temperatures higher than 1750° C, while the maximum rate was observed in a temperature range of 1750 - 1800° C at low pressures.

The rate of weight loss of the oxidized metal decreases with an increase of temperature (1900 - 3000° C). At pressures lower than 15 mm Hg and temperatures higher than 2700° C, there is a certain equilibrium, and then the velocity increases with a temperature increase, apparently as the result of the evaporation of tungsten. The dependence of the rate of oxidation on the pressure at a temperature higher than 1900° C is more pronounced than that at temperatures lower than 1750° C.

It was established that the dependence of oxidation on pressure has the following characteristics:

(1) At high pressures the rate of oxidation does not depend on the pressure.

(2) At low pressures there is a linear dependence between the rate of oxidation and the pressure.

The data from an investigation of tungsten oxidation at temperatures of 1000 - 1700° C and oxygen pressures of 2 - 76 mm Hg are presented in [99]. They are compared with data for oxidation of molybdenum and carbon, which form the volatile oxides, under the same conditions. It was shown that the oxidation of tungsten takes place without the formation of an oxide film at temperatures higher than 1250° C and oxygen pressure of about 76 mm Hg, because of the volatility of WO_3. It was also established that the volatile products of tungsten and carbon oxidation can serve as a barrier preventing the diffusion of oxygen towards the surface of the samples. Because of the fact that the diffusion of oxygen through gaseous oxidation products in this case determines the rate of the process, the difference in absolute values of the rates of W, Mo and C oxidation is linked with the properties of the boundary layer of the reaction products the nature of which depends on many factors: the /38 nature of the gas, condensation temperature of the gas, etc.

In a later study, Gulbransen et al. [100] continued their investigation of the oxidation of tungsten at high temperatures (1150 - 1615° C) and low oxygen pressures (2 - 100 mm Hg).

The experiments on oxidation of tungsten at 1150° C showed that the oxidation takes place according to the linear law at oxygen pressures of 19 and 76 mm Hg, which indicates that the scale has no protective properties. A combination of various study methods permitted a determination of the amount of tungsten which enters into reaction with oxygen, its quantity in the oxide film and the amount of evaporated WO_3. It was shown that, at a temperature of 1150° C in the pressure interval under investigation, 90% of the oxygen reacting with tungsten is used in the formation of the oxide film, and 10% is evaporated in the form of WO_3.

At 1200° C and oxygen pressure of 19 mm Hg, the percentage of oxygen in the film of scale formed is less than that at 1150° C, since WO_3 is sublimated intensively. At a temperature of 1250° C and oxygen pressure of 38 mm Hg, practically all the oxygen is used for the formation of the evaporated tungsten trioxide. When the temperature reaches 1615° C and the oxygen pressure is equal to 19 mm Hg, there is a certain decrease in the rate of oxidation which is probably linked with a decrease in the area of the sample surfaces. The dependence of the rate of oxidation on the temperature has a complex character (Fig. 16). Between 1100 and 1250° C, the rate of oxidation almost does not depend on the temperature at all oxygen pressures. A substantial increase in the rate of oxidation at a pressure of 9.5 mm Hg is observed in the range of 1250 - 1350° C. Above 1350° C, the inclination of the curves decreases. The activation energy of the process in the temperature range of 1365-1615° C is equal to 14.3 kCal/mole.

The oxygen pressure has a substantial effect on the mechanism and rate of oxidation. At a temperature of 1150° C in the range of high oxygen pressures, there is a weight gain; at low pressures there is a weight loss.

A decrease in weight is observed in the temperature range of 1250 - 1615° C, and the rate of the weight decrease increases with the oxygen pressure. The effect of the oxygen pressure on the rate of the reaction is expressed by the following equation: $dn/dt = kp^{1.1}$, where dn/dt is the rate of oxidation; p is the oxygen pressure, and k is constant. /39

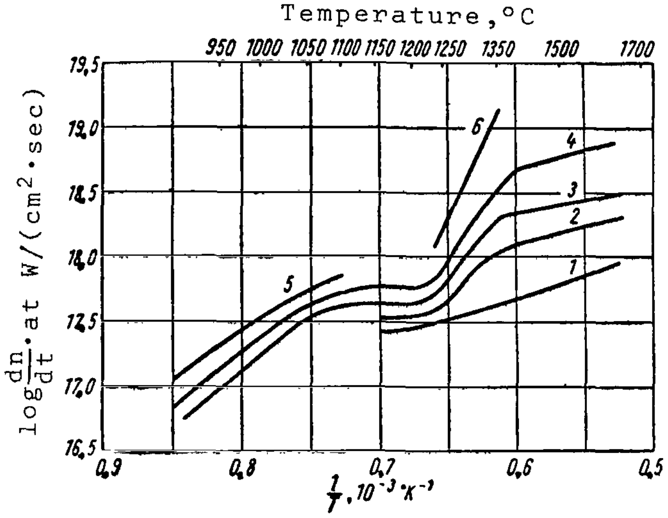


Fig. 16. Dependence of the Rate of Tungsten Oxidation on the Temperature at Oxygen Pressures of 5(1); 9.5 (2); 19 (3); 38 (4); 76 (5) and 100 mm Hg (6).

Using data on the activation energy and dependence of oxidation on the pressure, the authors of [100] derived an equation for the rate of oxidation at temperatures of 1350 - 1615° C:

$$\frac{dn}{dt} = 6{,}2 \cdot 10^{18} p^{1.1} e^{\frac{14\,300}{RT}},$$

where dn/dt is the quantity of reacting tungsten atoms per second per unit surface; p is the pressure (mm Hg); T is the absolute temperature (° K); R is the gas constant.

A comparison of the data for oxidation of tungsten, molybdenum and carbon showed that the layer of evaporated oxide over tungsten presents diffusion of oxygen toward the surface to a lesser degree than does that for molybdenum or carbon. Therefore, the rate of /40 oxidation of tungsten is higher than that for molybdenum or carbon under similar conditions. The oxidation mechanism for temperatures higher than 1300° C is similar for tungsten, molybdenum and carbon. At 1465° C and oxygen pressure of 19 mm Hg, tungsten and molybdenum oxidize at the same rate; the rate of carbon oxidation is somewhat less. At 1615° C and oxygen pressure of 38 mm Hg, tungsten oxidizes 2.5 times more rapidly than does molybdenum and 12 times more rapidly than carbon.

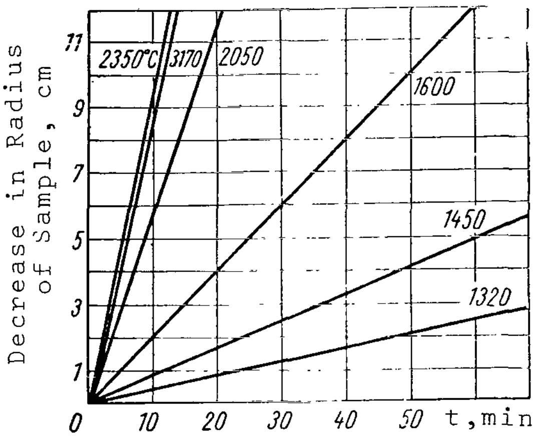


Fig. 17. Oxidation of a Tungsten Rod at Oxygen Pressure of 10^{-4} atm in Dependence on the Temperature.

The oxidation of tungsten at high temperatures (1320 - 3170° C) and low oxygen pressures (10^{-6} - 1 atm) is described in greatest detail in a study by Bartlett [101]. The oxidation was carried out in pure dry oxygen. The oxidation took place according to the linear law at all temperatures and various oxygen pressures, as is seen, for example, in Figure 17, where the oxidation of tungsten at $p_{O_2} = 1\cdot10^{-4}$ atm is shown. It is established that the rate of oxidation at temperatures higher than 2000° C does not depend on the temperature. This agrees with the data of Langmuir [102] but it contradicts the results of Perkins and Crooks [53], who observed a decrease in the rate of tungsten oxidation at temperatures higher than 2000° C.

The rate of oxidation increases in proportion to the increase /41 of oxygen pressure at pressures lower than 10^{-5} atm, while it gradually decreases with an increase of the oxygen pressure for pressures higher than 10^{-5} atm. These facts seem to indicate that the rate of oxidation at temperatures higher than 2000° C is controlled by the supply of oxygen to the surface of the samples, which was mentioned in [99, 100]. At low oxygen pressures ($p_{O_2} < 10^{-5}$ atm), the rate of oxidation can be evaluated by using the concepts in the kinetic theory of gases, on the condition that the composition of the vaporous layer over the metal surface is known.

Using a mass-spectrometric analysis, the authors of [103] found that, at temperatures above 2000° C, the principal vapor component is WO_2, although there is also a certain amount of WO_3. Considering that the reaction $W + O_2 \rightarrow WO_2(g)$ takes place on the surface, the author of [101] derived the following expression for the rate of tungsten oxidation, using the kinetic theory of gases: the rate of a decrease in the thickness of a rod at temperatures higher than 2000° C and oxygen pressures lower than 10^{-5} atm is equal to

$$x_W = \frac{\varepsilon \nu_O p_{O_2}(\infty)}{1 + \frac{\varepsilon \nu_O P_t}{k_0 \mathrm{Nu}_{AB}}},$$

where

$$k_0 = \frac{M_W D_{AB} T^{\frac{1}{2}}}{\rho_W LR} \text{and} \nu_0 = \frac{M_W}{\rho_W} \cdot \frac{1.01 \cdot 10^6 \frac{\text{dyne} \cdot \text{cm}^2}{\text{atm}}}{(2\pi mkT)^{\frac{1}{2}} N_0}.$$

Here ε is the probability of the reaction ($\varepsilon \leq 1$); M_W is the molecular weight of tungsten; ρ_W is the density of tungsten; N_0 is the Avogadro number; $p_{O_2}(\infty)$ is the pressure in the reaction zone behind the boundary layer (atm); P_t is the total pressure in the reaction zone; Nu_{AB} is the Nusselt number; T is the average gas temperature at the boundary layer; k is the Boltzmann constant; R is the gas constant; L is the characteristic dimension; D_{AB} is the diffusion coefficient; ε is a value determined from the equation $x_W = \varepsilon \nu_0 p_{O_2}$ for $p_{O_2} = 10^{-6}$ atm.

As was already mentioned, at high oxygen pressures ($p_{O_2} > 10^{-5}$ atm) the increase in the rate of oxidation with an increase of pressure decreases as a result of the fact that the evaporated WO_3 molecules form a boundary layer, which decreases the oxygen pressure on the tungsten surface. It was shown that at temperatures below /42
2000° C the rate of oxidation decreases with a decrease in the temperature for all oxygen pressures, while the activation energy of the oxidation process is equal to 42 kCal/mole, and the dependence on the pressure is expressed as $(p_{O_2})^n$, where n changes from 0.55 to 0.8.

The decrease in oxygen pressure over the surface of the metal can be significant, and this phenomenon takes place in the case of oxidation in water vapor, in carbon monoxide and dioxide, nitric oxide, etc. In this case there is not only a change in the value of the free energy for formation of the oxides as a result of the decrease in the partial oxygen pressure; there is also an interaction of the second gaseous component with the metal.

Farber [104] investigated the oxidation of tungsten in water vapor (p = 33 mm Hg) at 1300 - 1700° C, measuring the increase in resistance of rods with diameter of 0.25 mm as a measure of the wear of the metal. The decrease in cross sectional area was found to be equal to 0.02 - 0.03% per sec., and the activation energy for oxidation was equal to 14.5 Kcal/mole. At 1000° C and above, the rate of WO_3 volatilization increases in the presence of water vapors in a quantity of more than 30% (volume) because of the formation of hydroxides.

The effect of water vapors on the volatility of tungsten oxides was examined in [105, 106]. The data obtained by the authors of these studies showed that the formation of $WO_3 \cdot H_2O$ molecules was possible [107].

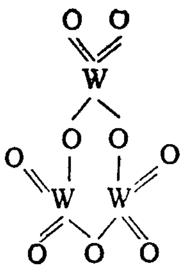
A very extensive investigation of tungsten and molybdenum hydroxides was carried out in [108]. It was shown that the heterogeneous reaction of WO_3 (sol.) + H_2O (g) = $WO_2(OH)_2$ takes place for tungsten, for which the dependence of the equilibrium constant on the temperature can be represented by the following equation:

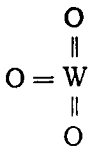
$$\log K_W = -\frac{8725}{T} + 4.10 \, (T = 1173 - 1373^\circ K),$$

where $K_W = P_{hydroxide}/P_{H_2O}$. The enthalpy and entropy for the formation of $WO_2(OH)_2$ from WO_3(sol.) and H_2O are equal to 39.9 and 18.8 kCal/mole, respectively.

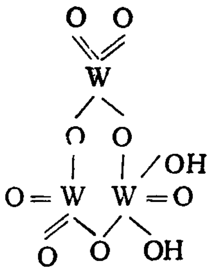
We now have the assumption that the vaporized oxide and hydroxide have the following structures:

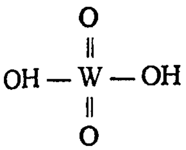
/43



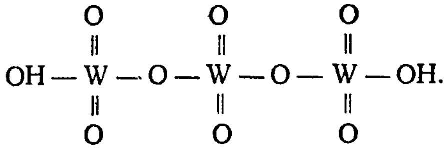


$$O=W(=O)=O$$





$$OH-W(=O)_2-OH$$



$$OH-W(=O)_2-O-W(=O)_2-O-W(=O)_2-OH.$$

In studying the interaction of tungsten with a flow of water vapor ($p_{H_2O} \simeq 1$ atm) at 1000 - 1700° C, Kilpatrick and Lott [109] also observed the formation of $WO_2(OH)_2$. They noticed that the reactions of tungsten and molybdenum with a flow of water vapor were similar. However, the lesser volatility of the tungsten oxidation products and the existence of a liquid oxide phase resulted in a situation where the rate of the process was determined by the oxidation of solid tungsten oxide WO_2 to the evaporated oxidation products $WO_2(OH)_2$ and WO_3.

In the case of tungsten oxidation in water vapors at temperatures lower than 873° C, the W_3O oxide is formed but it converts into WO_2 with an increase of the water vapor pressure (according to the author of [110]).

Speiser and St. Pierre [56] investigated the rate of transfer of tungsten oxide from the plane surface of the samples in a flow containing H_2O. The flow rates of the gas were sufficiently high for it to be unsaturated, and the rate of the loss in mass was determined by the surface reactions and not by the transfer in the gas flow. Graphs for the change in rate of evaporation of WO_2, $W_{18}O_{49}$ and WO_3 were constructed in dependence on the pressure of the water vapor. The rate of evaporation for all these oxides increased with the temperature and an increase of the water vapor pressure.

An investigation of the reaction between tungsten and nitrogen peroxide in the temperature range of 2100 - 2900° K was carried out /44
in [111] for a nitrogen peroxide pressure of $3 \cdot 10^{-9}$ - $3 \cdot 10^{-6}$ atm. The peroxide was put in a preliminarily evacuated chamber in which a tungsten filament was heated. After the disintegration of nitrogen peroxide, nitrogen and molecular oxygen were measured on a mass-spectrometer. The rate of tungsten oxidation was determined according to the change in the wire resistance for constant temperature and pressure.

It was established that the principal reactions in this process are disintegration of nitrogen peroxide and formation of $WO_2(g)$. At 2220° K and peroxide pressure of 10^{-6} atm, one thousandth of the nitrogen peroxide molecules colliding with the tungsten surface entered into the reaction and formed WO_2, while one-fiftieth of the nitrogen peroxide molecules dissociated at 2735° K and pressure of nitrogen peroxide of 10^{-8} atm. The interaction of nitrogen with tungsten can be represented in the form of several successive processes: (1) physical adsorption of nitrogen peroxide on the tungsten surface; (2) partial evaporation of adsorbed nitrogen peroxide; (3) disintegration of adsorbed molecules into nitrogen and oxygen atoms; (4) formation of molecular nitrogen and oxygen as the result of the reaction of physically adsorbed nitrogen peroxide molecules with chemisorbed oxygen atoms; (5) evaporation of chemisorbed oxygen atoms; (6) reaction of two chemisorbed oxygen atoms with tungsten as a result of which WO_2 is formed. It was established that the rate of NO_2 disintegration and the rate of WO_2 formation increase with an increase of the temperature.

For the interaction of tungsten with a flow of N_2 and N_3 gases, Hunter and Schneider [112] observed the formation of the compound $W_3N\ (_{0.95}O_{0.05})_4$ in a temperature range of 860 - 1200° C. The ratio between atoms of nitrogen and oxygen in the compound obtained was equal to 19:1, and the authors called it γ'-W_3N_4 tungsten nitride. It was established in an x-ray diffraction analysis that the compound had a cubical lattice with parameter $a = 4.122$ Å. The structure described has analogies in nitrides and oxynitrides.

Carbon monoxide and dioxide interact with tungsten and form carbides. At temperatures higher than 1200° C, CO_2 and CO cause oxidation of tungsten, whereas the corrosive interaction with CO_2 is stronger than that with CO [7].

It was reported in [113] that the oxidation of tungsten in pure carbon dioxide takes place according to the linear law. The /45 oxygen pressure in dissociation of CO_2 is rather high, and all the tungsten oxides are realized.

The oxidation of tungsten in an atmosphere containing MoO_3 vapor was described in [114]. The oxidation was investigated for temperatures of 800, 900, 1020 and 1120° C during the course of 40 minutes. The concentration of MoO_3 vapors in air corresponded to the elasticity of the saturated vapor. Oxidation in pure air was carried out for the sake of the comparison.

The oxide layer on samples which are in an atmosphere containing MoO_3 vapor does not differ from an oxide formed in air in composition or in external appearance. At temperatures of 1020 - 1120° C, the oxide film consists of two layers: the lower one is dark blue and the upper one is green for oxidation in pure air, or dark violet if the oxidation takes place in the presence of MoO_3 vapors. It was established that the outer layer is WO_2. For temperatures of 800 - 900° C, the rate of tungsten oxidation in an atmosphere containing MoO_3 vapors coincides with the rate of oxidation in pure air, while it is much less at temperatures of 1020 - 1120° C.

The decrease in the rate of tungsten oxidation in a medium with MoO_3 vapors can be explained in terms of the decrease in partial oxygen pressure in the mixture and a change in the phase composition of the oxide layer, i.e., the formation of WO_2 together with tungsten trioxide [114].

Despite the inconsistency of the data published, we can nevertheless draw the following conclusions concerning the oxidation of tungsten. It has been established reliably that the WO_2, $W_{2.72}$ $(W_{18}O_{49})$, $WO_{2.9}(W_{20}O_{58})$ and WO_3 phases exist in the W-O system. For oxidation of tungsten in air or in oxygen, the majority of researchers observed an oxide layer of a dark blue color clearly linked with a metal which was close to WO_2 in composition, as well as a yellow outer layer of WO_3. As regards the W_3O oxide, there is an opinion that it is not an equilibrium phase. For the oxidation of tungsten in media containing MoO_3 and in nitrogen peroxide, there is only formation of WO_2, while for oxidation in media containing H_2O, peroxides are formed. The properties of the oxides formed determine the rate of oxidation of tungsten and the nature of the kinetic dependences, which change during a transition from one temperature range to another.

Obviously, the oxidation of tungsten obeys a logarithmic or converse logarithmic dependence at low temperatures (up to 300° C). The oxide film formed at these temperatures is very thin, and of a single WO_2 phase. The oxidation mechanism proposed by Mott and Kabrera [55] is applicable for this temperature range. The surface state and texture of the surface layers has a substantial effect on the rate of oxidation in this case. /46

At a temperature range of 400 - 1000° C, tungsten is first oxidized according to the parabolic law, and during longer oxidation the parabolic law for the growth of the scale changes to a linear one. The time for the transition from the parabolic law of oxidation to the linear one depends on the temperature. In the transition region, where the oxidation of tungsten is not subject to either the parabolic or the linear dependence, the rate of growth of the scale layer is determined by the equation derived in [85].

Since the volume ratio for tungsten trioxide is very high (3.35), there arise stresses during the oxidation which split the film and alleviate the approach of oxygen to the metal. In this case, the parabolic law for the growth of the oxide layer changes to the linear one.

When the growth of the oxide layer takes place according to the parabolic law, the rate of oxidation is determined by diffusion in correspondence with the mechanism proposed by Wagner. In this case, two oxides are formed on tungsten: WO_2 and WO_3.

The lower oxides usually have metal conductivity, and the rate of diffusion in them is high. The lowest rate of diffusion is observed in the higher oxide, which is a semi-conductor with a deficiency of anions.

Experiments investigating the effect of oxygen pressure on oxidation showed that, in the temperature range where the parabolic law of oxidation is observed, a decrease in oxygen pressure below 1 atm does not have a substantial effect on the rate of tungsten oxidation, which corresponds to Wagner's concepts. These experiments, as well as tests with inert tracers, show that the parabolic dependence of tungsten oxidation is determined by the diffusion of O^{2-} ions through the oxide layers. For temperatures higher than 800° C, the volatility of WO_3 has a noticeable effect. Therefore, a gain in weight of the samples decreases, whereas in oxidation of tungsten at temperatures higher than 1200° C there is weight loss. /47 In this temperature range, the oxygen pressure has a great effect on the oxidation process. At oxygen pressures no higher than 1 atm in a temperature range up to 1700° C, the decrease in weight of the specimens increases with an increase of the oxygen pressure. With an increase of the temperature up to 2000° C, there is a decrease in the rate of weight loss due to the dissociation of tungsten trioxide [53].

At temperatures higher than 2000° C, there is also observed a decrease in weight of the specimens in oxidation, but it varies for different oxygen pressures. At $p_{O_2} < 10^{-5}$ atm, the rate of oxidation is proportional to the oxygen pressure, while at oxygen pressures greater than 10^{-5} atm, the rate of weight loss decreases. This dependence of the oxidation on the temperature and pressure indicates that the rate of oxidation is controlled by the supply of oxygen to the surface of the samples in this temperature range.

As was shown in [104-113], tungsten is also oxidized in gases of NO_2, CO, CO_2 and in media containing water vapor. At high temperatures the rate of WO_3 evaporation increases when there are water vapors because of the formation of hydroxides, and the resistance of tungsten to oxidation decreases.

Thus, tungsten has low resistance to oxidation because of the insufficient protective properties of the oxide films, the high rate of reaction with oxygen, and the volatility of tungsten oxides.

CHAPTER 3

STRUCTURAL TUNGSTEN ALLOYS

Tungsten is of great interest as the substrate of various alloys. /48 In searches for materials which have particular physical and mechanical properties, the structural diagrams of systems with tungsten and the majority of the elements, including the artificial metal technetium, have been investigated [63, 115 - 120]. At the present, several tungsten alloys have found usage in various branches of technology [4, 6, 7].

The use of high-melting tungsten-base alloys as high-temperature structural materials is particularly promising. It is said that the use of such alloys will be greatly expanded by 1970 [3].

It is well known that the principle criteria used in evaluating materials intended for utilization under conditions of high temperatures and stresses are their high-temperature strength, thermal stability and technological ductility. Pure tungsten has high-temperature strength. A substantial hardening of the metal is achieved by way of cold-working. However, as a result of recrystallization processes the strength of tungsten begins to drop at those temperatures for which its use is most expedient (i.e., at temperatures higher than 1500° C. A high ductile-brittle transition temperature (above 200° C) produces serious difficulties in treatments. A substantial disadvantage of tungsten is its low corrosion resistance.

The process of alloying can greatly improve the mechanical properties of tungsten. Primarily great attention has also been given to attempts at producing high-temperature tungsten alloys. However, these attempts have still not brought about substantial results. At the present, studies directed toward an increase in the high-temperature strength and low-temperature ductility of tungsten alloys, improving the methods of obtaining the alloys, and processing and welding them are being developed.

During recent years, the number of studies in the field of /49 high-temperature tungsten-base alloys has been increasing continuously. These studies are being developed intensively in the USA [9]. The Materials Advisory Board of the National Academy of Sciences of the USA has formulated target properties for high-temperature strength of tungsten alloys. For example, tungsten alloys should have ultimate tensile strength no lower than 25.2, 18.9 and 10.5 Kg/cm^2 at temperatures of 1650, 1925 and 2205° C, respectively, in combination with a specific ductility [3, 121].

Despite the fact that studies concerning the production of structural tungsten alloys on a large scale were developed relatively recently, there are already many important advances in this field. One of the most significant results is the obtainment of the high-stability "A" alloy, whose composition has still not been published. As reported by Jaffee [122], the "A" alloy has ultimate tensile strength of about 51 Kg/mm^2 at 1650° C and 42 Kg/mm^2 at 1870° C. This alloy has been included in the American refractory metal sheet rolling program. Battelle Memorial Institute has developed a ternary alloy of W-5% Re-2.2% ThO_2[1], which preserves its ductility in the form of a sheet all the way to a temperature of 40° and, at the same time, has high-temperature strength [123].

The basic principles of the increase in high-temperature strength of metals are presented in detail in the monograph [124-127]. The physicochemical theory of high-temperature strength relative to high-melting metals and alloys, particularly tungsten, are treated in recent studies by I.I. Kornilov [128-129]. Of the large number of foreign studies, those of greatest interest are [122, 130-132].

The methods used for increasing the high-temperature strength of tungsten by alloying include hardening by the formation of solid solutions and by the precipitation of finely-dispersed phases. For high-temperature stability, an increase in the recrystallization temperature has great significance in alloying. The materials intended for utilization at temperatures of 0.7 - 0.8 T_{melt} include dispersed particles of thermodynamically stable, non-volatile compounds, as well as the so-called "dopants", which guarantee obtaining a definite structure in the recrystallized state. Alloying which results in a purification from foreign admixtures and a reduction of grain size is used in order to decrease the DBTT. /50

The most complete reviews on structural tungsten alloys are found in [2, 16, 132, 137]. A great deal of data on the mechanical properties of tungsten alloys is presented in [9, 10].

Most of the tungsten alloys are now obtained by the methods of powder metallurgy. However, arc melting is beginning to be used more and more widely for this purpose.

A promising method of producing tungsten alloys is electron-beam melting. It has recently been reported that codeposition of

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[1] The compositions of the alloys are given in weight percentages. -- Author's note.

metals from the vapor-gas phase is being used in order to obtain tungsten alloys [138]. High-purity W-Re alloys of different compositions have been produced by means of simultaneous hydrogen reduction of hexafluorides of metals at temperatures of 450-700° C. It is said that a direct obtainment of various manufactured products from tungsten alloys is possible by this method.

Tungsten alloys are treated by the same methods as is the non-alloyed metal. The additional difficulties arising in processing the alloys are due to the fact that, in certain cases, higher heating temperatures are needed for the formation of the alloy, as well as a more careful control of the atmosphere. The most effective means of preliminary processing of cast tungsten alloys is hot extrusion. Ingots of W-Mo, W-Ta, W-Nb and W-Zr alloys with diameter up to 140 mm were deformed by this method [2]. Such processing methods as forging are also widely used. Different means of obtaining and processing tungsten alloys are examined in collections [38 - 40, 139 - 141].

The methods of casting and forging various details of tungsten and its alloys are being developed intensively in the USA for the needs of rocket technology: nozzle inserts, jet vanes, etc. [3, 39, 40]. In 1961, the Oregon Metallurgical Corporation produced a 110 Kg rocket nozzle of the alloy W-2% Mo by centrifugal casting [142, 143].

The same firm is testing rings made of the alloy W-15% Mo with a diameter up to 250 mm [2]. /51

The production of wires of tungsten alloys, which is widely used in radio engineering and electronics (W-ThO_2, W-Mo, W-Re), has been mastered on an industrial level [4, 6, 132], and certain alloys are also being made in the form of bars and bands with widths up to 100 mm [2]. The obtainment of sheets of tungsten alloys, for which strict requirements are imposed on the mechanical properties, is an important problem [144].

For a correct evaluation of the effect of alloying on the properties of the metal, maximally pure initial materials are needed. Many impurities, even when in the most insignificant quantities, have a substantial effect on the mechanical properties and recrystallization temperature of tungsten. A metal whose purity is far from ideal is usually used in obtaining the alloys. The impurities contained in alloying admixtures can also greatly distort the picture. Contamination of the alloys is also possible in caking or melting and in processing. The volatilization and segregation of alloying impurities and admixtures bring about deviations in the composition of the alloys obtained from the specified one, as well as heterogeneity in the moldings and ingots. Internal oxidation and carbidizing of the alloys are possible. The properties of tungsten alloys are determined to a great extent by their preceding treatment. Mechanical tests with tungsten alloys require strict standardization.

The difficulty in controlling these factors, as well as the insufficient knowledge of their effect on the properties of materials, results in substantial discrepancies and contradictions in the literature concerning the mechanical properties of tungsten alloys as well as non-alloyed tungsten.

The existing data frequently refer to materials obtained by different methods, deformed at different temperatures, and tested in the form of specimens of unlike sizes and shapes. Therefore, a comparison of the properties of tungsten alloys should be accompanied by a careful analysis of the methods used in producing and testing them.

The modern high-temperature structural tungsten alloys can be divided into the following principal classes: solid solution alloys, precipitation hardening alloys, and synthetic dispersed systems.

The alloying of tungsten by a number of metals which form substitutional solid solutions aids in attaining a substantial increase in the high-temperature strength with a relatively small decrease in the melting point and ductility. /52

The nature of the high-temperature strength of solid-solution tungsten alloys is very complex, and it is difficult to determine the relative importance of contributions from various mechanisms. The effect of ordering of solid solutions, which is observed in the alloy W-29% Mo, can be of definite significance [145]. The interaction of alloying elements with interstititial admixtures is an important factor, particularly in low alloys. The alloying admixtures can aid in purifying the metals from interstitial impurities and, consequently, in increasing the ductility. In those cases when particles of a stable, non-volatile compound are formed as a result of interaction (for example, a carbide), it is possible that there can be an increase in the strength and resistance to recrystallization.

The present concepts concerning the dislocation mechanism of solid-solution hardening are reviewed in [146]. The increase in high-temperature strength of tungsten during alloying with elements which form solid solutions is investigated in [22, 128, 129]. An interesting observation was made by Seigle [22], who showed that the dependence of hardening (determined according to the results of brief tests) of high alloys on the ratio between the atomic size of tungsten and the alloying elements is less weakly pronounced than a similar dependence on the position of the alloying elements in the periodic table. The hardening effect of metals of groups VII and VIII was found to be proportional to the group number. However, this relationship can be broken for such properties as creep-resistance and endurance, since the metals of these groups affect the recrystallization temperature of tungsten in different ways.

In view of the necessity of preserving the high melting point of alloys, the alloying of tungsten with molybdenum, niobium and tantalum is of greatest interest. As shown by Bückle [147], who carried out an x-ray diffraction analysis of all binary and ternary W, Ta, Mo and Nb Alloys, continuous series of solid solutions are realized in the system.

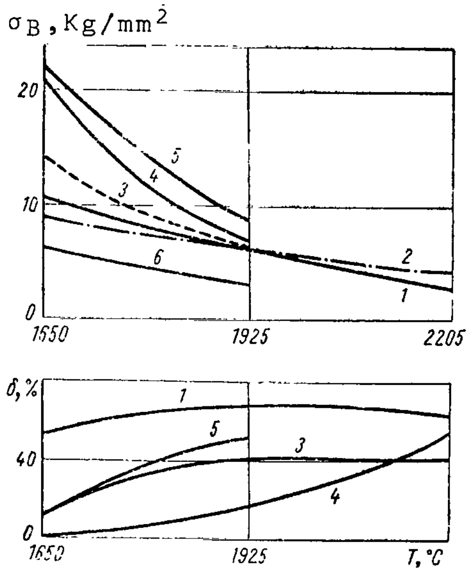


Fig. 18. Mechanical Properties of W-Mo Alloys: (1) 100% W; (2) W-0.5% Mo; (3) W-2.5% Mo; (4) W-12% Mo; (5) W-25% Mo; (6) W-70% Mo.

Of all the alloys of the solid /53 solution type, tungsten alloys with molybdenum have been examined to the greatest extent. Alloys containing from 0.5 to 50% Mo are already being produced in industry or are in the stage of being mastered [2, 132].

The resistance properties of W alloys with 0.5 - 25% Mo obtained by vacuum arc melting with a consumable electrode and strained by way of hot extrusion are examined in [13]. The results of high-temperature tensile strength tests are presented in Figure 18. Data on the strength of non-alloyed tungsten obtained and processed by an analogous method, as well as a rolled bar of an industrial W-70% Mo alloy, are also presented here for the sake of comparison.

Alloying with molybdenum in quantities greater than 2.5% guarantees a substantial hardening of tungsten at 1650° C. The W-25% Mo and W-12% Mo alloys have the greatest tensile strength at this temperature. These alloys are almost twice as strong as pure tungsten. However, /54 at higher temperatures the effect of tungsten ordering by large amounts of molybdenum admixtures rapidly weakens. Even at 1925° C, the W-25% Mo alloy exceeds pure tungsten in strength only by 25%, while the advantage of the W-12% Mo alloys decreases to the minimum. The latter alloy retains a strength which is almost equal to the strength of the non-alloyed metal all the way to 2205° C. The W-0.5% Mo alloy has somewhat greater strength at this temperature (σ_B = 4.6 Kg/mm^2).

It was reported in [2, 135, 137] that the W-Mo alloy with greatest strength at high temperatures is W-15% Mo. This alloy was selected by the "Thompson Ramo Wooldridge" firm for preparing forged pieces of rocket nozzles [2, 9]. The preliminary processing

TABLE 4. MECHANICAL PROPERTIES OF W-15% Mo ALLOYS OBTAINED BY ARC MELTING AFTER EXTRUSION [9].

Temp, °C	σ_B, Kg/mm	$\sigma_{0.2}$ Kg/mm^2	δ, %	ψ, %
1650	25.2	24.1	27.8	[illegible]
1790	17.1	16.4	34.[illegible]	80
1925	7.8	5.6	85	85
2205	3.9	2.8	125	97

TABLE 5. MECHANICAL PROPERTIES OF FORGED PIECES OF W-15% Mo ALLOYS [9].

Forged Pieces	Temp, °C	σ_B, Kg/mm^2	$\sigma_{0.2}$ Kg/mm^2	δ, %	ψ, %
Thin band	1650	26.6	25.9	22.8	55
Thickened Edge	1650	30.6	30.2	20.7	65
Thin Band	1925	8.0	6.1	68.3	71
Thickened Edge	1925	7.3	5.5	98.6	92.5

of the ingots is usually carried out by way of extrusion at a temperature of 2205° C with reduction roughly by 83%. After this the alloy is easily forged at 1095° C [2]. Table 4 gives the high-temperature mechanical properties of the W-15% Mo alloy after extrusion. The results of tests with samples sectioned from forged pieces are given in Table 5.

The average ductile-brittle transition temperature of the W-15% /55 Mo alloy after extrusion is about 270° C [2, 9]. This value is only a little above the transition temperature of nonalloyed tungsten for similar conditions of obtaining, processing and testing it. As was reported in [9], the transition temperature of this alloy decreases by 95° C after forging and annealing.

In comparing the results of investigations of the W-15% Mo alloy carried out by the "Thompson Ramo Wooldridge" firm to data on the properties of the W-12% Mo alloys obtained by Foyle [13], note the substantial deviation in the ductility of alloys which are very similar in composition. While the W-12% Mo alloys expanded at 1650° C by 1% and at 1925° C by 18%, the W-15% Mo alloy expanded at these temperatures by 27.8 and 85%, respectively.

Some mechanical properties of the alloys "OREMET-HPC 85 W-Mo" were given in [148]. This alloy, which was obtained by vacuum arc melting with a consumable electrode, contains 14-16% Mo and less than 0.010% of the admixtures C, O, Fe and Si. Products whose density is equal to the theoretical one are obtained from this alloy by way of centrifugal casting. A round bar with diameter of about 2.7 mm prepared from this alloy has the following mechanical properties at room temperature: σ_B = 114.8 - 126.7 Kg/mm^2; $\sigma_{0.2}$ = 110.6 - 122.5 Kg/mm^2; δ = 2.6 - 4.7%.

The results of an investigation of the endurance of the "BM50" alloy (W-50% Mo) at temperatures of 1100 - 2400° C are given in [149]. The alloy was obtained by the method of powder metallurgy and was subjected to "heat" drawing with reduction by 99%. The tests with samples which were prepared from a wire with diameter of 0.8 mm were carried out under vacuum. The results of the tests showed that the "BM50" alloy, whose melting point is roughly equal to 2800° C, is somewhat inferior to non-alloyed tungsten in terms of endurance. However, the difference in strength decreases with an increase of the temperature. At the same time, the alloys had higher ductility than did pure tungsten.

The endurance of the W-15% Mo and W-5% Mo alloys is shown in Figure 19.

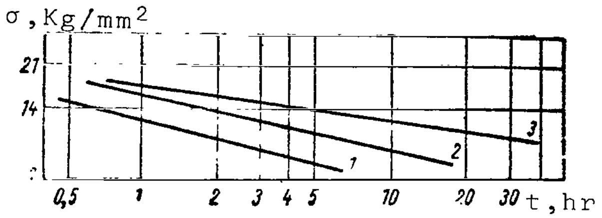


Fig. 19. Endurance of Extruded Alloys at 1650° C [9]: (1) W-5% Mo; (2) W-15% Mo; (3) W-0.52% Nb.

Semchyshen and Barr [150 - 151] evaluated the resistance properties of tungsten alloys containing various percentages of molybdenum which were melted in an arc furnace and extruded. The mechanical properties of a large number of tungsten-molybdenum alloys at high temperatures are also given in [9, 136 137]. /56

Investigations of tungsten alloys with niobium and tantalum have given very promising results. A substantial increase in the high-temperature strength is achieved in dissolving in tungsten relatively small amounts of these metals (on the order of 0.5 - 5%). For example, an alloy containing about 0.5% Nb, obtained by arc melting, has a strength of 10.5 - 12.5 Kg/mm^2 at 19.25° C [16]. At the same time, such alloys stand only a little behind non-alloyed tungsten in terms of refractoriness.

Low W-Nb alloys melted in an arc furnace were investigated by the firm "Union Carbide Metals" [9, 133, 134]. The high-temperature resistance properties of the W-0.57% Nb and W-0.88% Nb alloys strained by way of percussion extrusion and forging are shown in Table 6. There was 0.001% carbon in both alloys. The oxygen percentage in the W-0.57% Nb alloy was 0.004% and that in the W-0.88% Nb alloy was 0.018%.

Somewhat later, the same firm carried out additional tests of a tungsten alloy containing approximately 0.6% Nb [9]. An ingot of the W-0.58% Nb alloy with diameter of 100 mm was pressed out at 1870° C and then forged at 1650° C with total shrinkage by 99%. The strength limit of the alloy at 1650° C was found to be only equal to 27.6 Kg/mm^2. However, even this value is almost twice /57 greater than the strength of a forged bar made of non-alloyed tungsten.

The "Thompson Ramo Wooldridge" firm investigated the W-0.52% Nb alloy obtained by melting in an arc furnace [9]. The results of high-temperature mechanical tests of this alloy are shown in Table 7.

TABLE 6. MECHANICAL PROPERTIES OF COLD-WORKED W-0.57% Nb AND W-0.88% Nb ALLOYS [133].

Alloy	Temp, °C	σB Kg/mm²	σ0.2 Kg/mm²	δ, %	ψ, %
W-0.57% Nb	1650	42.0	≈35.0	20.0	82.0
W-0.88% Nb	1650	32.3	≈31.6	15.0	85.0
	1925	12.6	≈ 5.3	31.0	98.0

TABLE 7. STRENGTH PROPERTIES OF W-0.52% Nb ALLOYS AFTER EXTRUSION.

Temp, °C	σB Kg/mm²	σ0.2 Kg/mm²	δ, %	ψ, %
1650	[illegible]	[illegible]	32.6	80
1790	15.8	13.1	46.9	63.2
1925	9.1	5.4	55.6	64.7
2205	5.1	3.1	81,7	90

The ductile-brittle transition temperature of the W-0.52% Nb alloy in expansion is 300° C. The endurance of the W-0.52% Nb alloy in the extruded state at 1650° C is shown in Figure 19. The advantage of this alloy is obvious, compared to the W-5% Mo and W-15% Mo alloys.

Finally, tungsten alloys with niobium (up to 2%) and tantalum (up to 3.6%) melted in a vacuum arc furnace were studied in [13]. The strain hardening of the alloys was carried out by way of extrusion at 1795 - 2065° C with reduction by 87.5%. Data on the high-temperature strength of these alloys are shown in Figure 20.

In comparing the properties of the alloys which were investigated by Foyle [13], we must keep in mind that the degree of cold-hardening can differ substantially becuase of strain hardening taking place under different conditions. Of all the tungsten-niobium alloys, W-1.3% Nb has the greatest strength. The materials tested included alloys which contained 0.5 and 0.6% Nb, for which the values of the ultimate strength of 24.5 and 20.4 Kg/mm^2 were obtained at 1650° C. /58

Thus, although the essential hardening aspect of 0.5 - 0.6% Nb admixtures is obvious, the subsequent tests did not confirm the exceptionally high strength of the W-0.57% Nb alloys at 1650° C which was noted in the first study of the "Union Carbide Metals" firm. It is

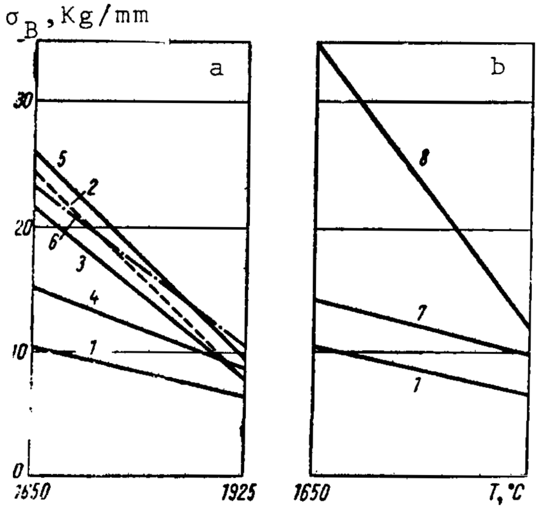


Fig. 20. Strength Properties of W-Nb(a) and W-Ta(b) Alloys: (1) 100% W; (2) W-0.5% Nb; (3) W-0.75% Nb; (4) W-1% Nb; (5) W-1.3% Nb; (6) W-2% Nb; (7) W-1.6% Ta; (8) W-3.6% Ta.

possible that this value (σ_B = 42 Kg/mm^2) was the result of some type of peculiarity in the method of obtaining the alloy. It is maintained in [16, 131] that the effect of precipitation hardening can be observed in such low tungsten alloys of the solid solution type in some cases, because of the reaction taking place during their obtainment. It is most probable that the carbides are hardening phases.

Of all the tungsten-tantalum alloys evaluated in [13], the alloy with maximum strength was that containing 3.6% Ta. At 1650° C, this alloy was much stronger than the W-Mo and W-Nb alloys, having ultimate tensile strength equal to 35 Kg/mm^2. Although the strength of this alloy decreases rapidly with an increase of temperature, as with other W-Mo, W-Nb and W-Ta alloys, it was found to be strongest even at a temperature of 1925° C, having ultimate strength of 11.8 Kg/mm^2. /59

Wilson and McKinsey [152] investigated high binary and ternary tungsten alloys with niobium and tantalum obtained by arc melting. The high-temperature resistance of the alloys was evaluated according to the results of measurements of the hardness at 1480 and 1595° C. The alloys in which there was about 50 at.% of the alloying admixture (50 wt.% Ta or 34 wt.% Nb) had greatest hardness in both binary systems. At 1595° C, these alloys, which had hardness of H_V = 80 - 115 Kg/mm^2 under a load of 1 Kg, were 2 - 3 times harder than non-alloyed tungsten. Of the alloys with equivalent concentrations of alloying elements, the W-Ta alloys were hardest.

Among the ternary alloys of the W-Nb-Ta system, there are also a large number of compositions whose hardness at high temperatures exceeds 100 Kg/mm^2. The hardness of the ternary alloys at 1480 and 1595° C depends mainly on the total percentage of alloying admixtures, and the ratio between the percentage of Nb and Ca plays only a secondary role. The ternary alloys of the following compositions were selected for determining the high-temperature tensile strength properties: W-1% Ta-3% Nb W-5% Ta-15% Nb, W-8% Ta-32% Nb, W-30% Ta-15% Nb. It was assumed that the ultimate strength of some of these alloys at 1595° C exceeds 28 Kg/mm^2 [9].

Westgren et al. [153] carried out an investigation of binary, ternary and quaternary solid-solution alloys of the W-Ta-Mo-Nb system. Binary tungsten-tantalum alloys were used for the substrate of the complex alloys, and admixtures of 6 or 12% molybdenum and niobium were added to them. The alloys were obtained by vacuum arc melting with a consumable electrode. The total percentage of impurities (C, O, N, H) did not exceed 0.01 at.%. The strain hardening of the alloys was carried out by way of hot extrusion with shrinkage by 67%.

Of all the tungsten-tantalum alloys, the W-50% Ta one has greatest hardness at room temperature (H_V = 406 Kg/mm^2 under a load /60 of 1 Kg). The introduction of 12% Nb increases the hardness of tungsten and high tungsten alloys more greatly than does alloying with the same amount of molybdenum. For a simultaneous introduction of 6% Nb and 6% Mo, the increase in hardness is proportional to the effect of a 12% admixture of each of these separately. The hardness of the alloys increases greatly as a consequence of cold working in extrusion (for example, H_V for a W-50% Ta alloy after extrusion increases up to 535 Kg/mm^2). After annealing during the course of one hour at 1925° C, the hardness of the strained alloys decreases, approaching the initial one. Thus, the recrystallization temperature of the alloys obviously does not exceed 1925° C.

Mechanical tests at 1650° C were carried out under vacuum on samples with a diameter of 3.2 mm and effective length of 12.7 mm. The results of the tests are shown in Table 8.

TABLE 8. TENSILE STRENGTH PROPERTIES OF W-Ta-Mo-Nb ALLOYS AT A TEMPERATURE OF 1650° C.

Normal Composition, wt.%				State of Alloy**	σ_B, Kg/mm^2	δ, For Length at 12.7mg, %	ψ, %
W	Ta	Mo	Nb				
100	—	—	—	1	9,8	74	99
100	-	—	—	2	9,8	60	99
75	25	—	—	1	44.8*	<1	—
50	50	—	—	1	44,8	4	8
88	—		12	1	35,0	4	<1
68	20		12	1	33,6*	4	—
44	44		12	1	37,8	7	13
44	44	—	12	2	35.7	6	6
88	—	12	—	1	17.5	47	93
68	20	12	—	1	42.7	10	13
68	20	12	—	1	46,9	16	23
44	44	12	—	1	39,9	5	<1
88	—	6	6	2	43,4*	6	—
68	20	6	6	1	37,8*	<1	—
44	44	6	6	1	39,2	<1	<1
44	44	6	6	2	35,0*	2	—

*Destruction took place along the thickened part of the sample.
** State of alloys: 1 - after extrusion; 2 - after 5 hours of a creeping test under a stress of 4.9 Kg/mm^2.

The effect of alloying elements on the high-temperature /61 strength of tungsten is basically similar to the effect on its hardness at room temperature. The most substantial hardening is achieved in alloying tungsten with tantalum. Niobium is a very effective hardener. However, the admixing of niobium into W-Ta alloys does not increase their strength. Alloying of W-Ta alloys with molybdenum yields good results. The maximum ultimate strength at 1650° C (σ_B = 46.9 Kg/mm^2) was obtained for a W-20% Ta-12% Mo alloy. At the same time, the ternary W-Ta-Mo alloys have the best combination of strength and ductility. The strength of tungsten and high W-Ta alloys also greatly increases by admixing 6% Mo and 6% Nb.

According to the results of the tests carried out, it is impossible to determine precisely the nature of the effect of alloying elements on the ductility of tungsten. Although the general tendency for a decrease in ductility is obvious, the values of the relative expansion and contraction of different alloys change within a very wide range. Parameters of the extrusion process which are not controlled affect the ductility of alloys to a certain extent.

The high values for the strength of alloys in the W-Ta-Mo-Nb system can be explained mainly in terms of hardening due to the formation of a solid solution. Cold-working has only a secondary role. There was not observed precipitation of any phases.

The results of this study show that alloying tungsten with the indefinitely soluble high-melting metals of the "big four" aids in increasing the strength at 1650° C up to 35 - 45 Kg/mm^2, i.e., roughly by a factor of 4.

Investigations of single crystals of tungsten alloys with molybdenum, niobium and tantalum which were begun recently are of great interest. Ye. M. Savitskiy et al. [154, 155] were the first to obtain single crystals of the W-Mo and W-Nb alloys by way of electron-bombardment zone melting. The single crystals have a good combination of strength and ductility. This can be explained mainly in terms of purification from foreign admixtures. The mechanical properties of single tungsten crystals with different crystallographic orientation and tungsten alloys are shown in Table 9.

TABLE 9. MECHANICAL PROPERTIES OF SINGLE CRYSTALS OF NONALLOYED TUNGSTEN AND SOME TUNGSTEN ALLOYS AT ROOM TEMPERATURE [154, 155].

Alloy	Orientation	σ_B, Kg/mm^2	δ, %	ψ, %	H_μ, Kg/mm^2	Bending angle degree
100% W	(110)	102	0	0	-	-
--	(110)	100	11	100	336	-
--	(111)	117	0	0	-	-
W-3% Mo	-	72	-	-	-	90
W-1.5% Nb	(100)	110	0	0	350	-

The properties of single crystals of tungsten alloys with 0.25 and 4% Ta obtained by electron-bombardment melting with a "floating" zone were also studied in [156, 157]. The recrystallization temperatures of these alloys are 220 - 230° C higher than that of strain-hardened single crystals of pure tungsten. The effect of carbonization and heat processing on the mechanical properties of single crystals of W-0.35% Ta and W-3.90% Ta alloys was examined in [158, 159].

We can assume that vanadium should be an effective hardener of tungsten, since it forms continuous series of solid solutions both with tungsten and the remaining metals of the "big four" [22, 160, 161]. There is very little information in the literature on tungsten alloys with vanadium. Seigle [22] reported that there is an increase in the hardener at room temperature on the average by 0.3 - 1.3% in forged alloys of W-32 at.% V and W-21 at.% V per 1 at.% V (1.1 - 4.7 Kg/mm^2).

It was noted in [9] that some properties of binary W-V alloys which contain up to 9.3% V have been investigated by Semchyshen and Barr. For equivalent (in weight) percentages of alloying elements, the W-V alloys exceeded W-Ta and W-Nb alloys in hardness at 878° C.

Obviously, the high-temperature strength properties of tungsten alloys with chromium have not been investigated in detail. It is well known that high tungsten alloys of W-Cr have very great hardness at room temperature [4, 162]. Kieffer et al. [160] carried out a qualitative investigation of the processability of tungsten alloys with 1, 3 and 5% Cr. Coarse-grained alloys obtained by arc melting are poorly strained, but the processability of fine-grained caked alloys is somewhat better. /63

Several studies have treated tungsten alloys with titanium, zirconium and hafnium. The corresponding structural diagrams show that the solubility of the metals in tungsten is limited [163 - 165]. The "Union Carbide Metals" firm investigated the effect of small additions of Ti and Zr on the mechanical properties of extruded and forged tungsten obtained by arc melting at 1650 and 1925° C [9, 133]. The results of tests of W-0.07% Ti and W-0.12% Zr alloys are given in Table 10.

TABLE 10. HIGH-TEMPERATURE MECHANICAL PROPERTIES OF WORKED W-0.07% Ti* AND W-0.12% Zr ALLOYS [133].

Alloy	Temp. °C	σ_B, Kg/mm^2	σ_S, Kg/mm^2	δ, %	ψ, %
W — 0,07% Ti	1650	11,9	≈ 9,8	36,0	98,0
	1925	9,1	≈ 5,6	37,0	98,0
W — 0,12% Zr	1650	33,7	≈28,8	16,0	39,0
	1925	10,5	≈ 7,7	49,0	98,0

*These values are also given for the W-0.005% Ti alloy in [9]

It is obvious from these data that small additions of titanium (up to 0.07%) do not greatly improve the high-temperature strength properties of tungsten, even when there is 0.003% C. Alloys with a higher percentage of titanium and carbon were not investigated. We should mention the substantial loss of titanium in the process of melting the alloys.

Alloying with zirconium greatly increases the ultimate strengths and yields of tungsten at 1650° C. However, roughly as alloys with small additions of niobium, the W-0.12% Zr alloy rapidly softens with an increase of the temperature. Nevertheless, the ultimate strength of the alloy at 1925° C is 60-80% greater than that of non-alloyed tungsten.

The mechanism of tungsten hardening by small additions of zirconium is still unclear. In all probability, the high strength of the W-0.12% Zr alloy at 1650° C is linked with an increase of the recrystallization temperature, which permits use of the cold-working effect [130]. While non-alloyed tungsten is completely recrystallized in the process of testing at 1650° C, the tungsten zirconium alloy maintains the structure acquired in cold-working to some extent. In the W-0.12% Zr alloy, there was 0.010% O_2 and 0.001% C. Apparently, in addition to strain hardening and solid-solution hardening, the strength of the alloys can be increased by way of interaction of zirconium with the impurities [22, 130]. /64

As was reported in [9], the properties of tungsten alloys containing up to 3.8% Zr and 3.6% Hf have been investigated. For identical weight percentages of the alloying admixtures, the W-Hf alloys were inferior in hardness to the W-Zr alloys at 870 and 1650° C. Zirconium and hafnium increased the hardness of tungsten at the temperatures more effectively than did C, Nb or Ta. According to the data of [166], the production of hafnium in tungsten obtained by arc or electron-beam melting greatly increases the ultimate tensile strength and creeping limit at temperatures higher than 1375° C. In this case, tungsten with hafnium admixtures has higher heat resistance than tungsten alloys with tantalum, niobium or rhenium. It was mentioned in [121] that the strength of solid solutions of W-Zr and W-Hf at 1650° C was higher than 25 Kg/mm^2. However, additional alloying is necessary in order to preserve the effect of hardening at higher temperatures.

Contradictory results were obtained in investigating tungsten alloys with cobalt. Ratliff et al. maintained that the addition of 1 at.% Co decreases the hardness of cast tungsten at room temperature by 3.6%, whereas Semchyshen and Barr observed an increase in hardness by 34% [22]. It is possible that the reason for this contradiction is the interaction of cobalt with dissolved impurities, which is most probable with Ratliff's unreduced alloys. Measurements of the hardness of W-Co alloys containing up to 2.7% cobalt at 870 and 1650° C show that cobalt is a more effective hardener than are zirconium, hafnium vanadium, niobium and tantalum [9].

In dissolving other metals in tungsten, the hardness is intensified with an increase of the concentration of alloying elements and is usually accompanied by a decrease in ductility. However, in alloying tungsten and other high-melting metals of the group VIA with rhenium, there is a substantial improvement of the low-temperature ductility as well as an increase of strength and retardation of the recrystallization process. /65

A detailed structural diagram of the W-Re system was constructed by Ye. M. Savitskiy et al. [167]. The variation of the diagram published by Dickinson and Richardson [168] agrees well with the results of [167]. There is a wide range of solid solutions of rhenium in tungsten in the W-Re system. An exhaustive survey of this system is contained in [169].

The extraordinary effect of rhenium on the mechanical properties of tungsten was first noted by Gich and Yuz [170]. These authors established that alloys containing 25 - 35% Re, which are easily deformed at temperatures on the order of several hundreds of degrees, have greatest ductility. The softening of the W-Re alloys at increased temperatures took place much more slowly than did that of non-alloyed tungsten. It was established that tungsten-rhenium alloys are capable of being strain-hardened not only by slipping but also by twinning. The results of Gich and Yuz were subsequently confirmed by Jaffee et al. [171] and a number of other researchers [172].

An extensive study concerning alloys containing rhenium, particularly tungsten ones, is found in a work by Ye. M. Savitskiy et al. The results of this study, as well as numerous foreign investigations, are generalized in a monograph in [169].

Even when 5% Re is added, there is a substantial decrease in the hardness of cast tungsten. The alloys in which the rhenium percentage is close to the solubility limits (20 - 30%) have an optimum combination of strength and ductility, improved technology and weldability.

The recrystallization of W-20% Re and W-30% Re alloys obtained by arc melting or by the powder metallurgy method and deformed with total reduction by 85 - 90% begins at temperatures of 1500 - 1550° C. The mechanical properties of W-25% Re and W-30% Re alloys are given in Table 11. The tests were carried out on sheet metals of thickness 0.7 - 1.0 mm and effective length 50 mm under vacuum of 10^{-3} mm Hg. /66

TABLE 11. MECHANICAL PROPERTIES OF CAST TUNGSTEN ALLOYS WITH RHENIUM IN BRIEF EXPANSION [169, 173].

Alloy Compositions (wt.%)	Melting Point ° C	Alloy Composition*	Test Temperature, °C	σ_B, Kg/mm^2	δ,%
W—25% Re	3100	1	20	119	2
		2	20	271	—
		2	1500	30	6,7
		2	1800	15.9	9.0
W—30% Re	3000	1	20	140	—
		2	20	272	—
		2	1500	34.1	7.0
		2	1800	14.3	5.6

*1-annealed; 2-strained

The values given in [171, 174] for the ultimate strength of a wire of the W-30% Re alloy are 2.25 times greater than those obtained by Ye. M. Savitskiy et al. [169, 173] in tests of sheet metals.

The high-temperature strength of W-Re alloys containing 20 - 30% Re is much greater than the strength of non-alloyed tungsten. The alloys also have higher ductility, both in the cold-hardened and in the recrystallized state. The ductile-brittle transition temperatures of recrystallized W-25% Re and W-30% Re alloys are 120 and 50°, respectively, while the transition temperature of pure tungsten after recrystallization is equal to 400° C [169]. The mechanical properties of W-Re alloys are examined in greater detail in [169, 171-179].

The high strength of W-Re alloys can be explained mainly by the hardening during formation of the solid solution. Saturated solid solutions can also be hardened by dispersed σ-precipitation phases (Re_3W_2). The causes for this increase in ductility have not as yet been finally clarified. The effect of rhenium on the ductility of tungsten is examined in greatest detail in [122, 169, 172, 179, 180]. Booth, Jaffee and Salkovitz [180] consider that the principal factors bringing about the increase in ductility are the changes in the nature of the relationship between the stress and the rate of recession movement, the solubility of the impurities, the surface energy, electron structure, strain mechanism due to the development of the twinning process, etc. /67

It is well known that single crystals of pure tungsten are ductile at room temperature and even at negative temperatures [1, 10, 16, 58, 154, 155]. As for the other metals of the VIA group - Mo and Cr, very small amounts of impurities have a substantial effect on the brittleness of polycrystal tungsten. Seigle [22] maintains that the maximum solubility of oxygen, carbon and nitrogen in tungsten is 0.06, 0.03 and 0.005 at.%, respectively. It is shown in [181] that an increase in the purity of single crystals of tungsten by way of an increase in the number of electron-bombardment meltings brings about an increase in the ductility. It is assumed that impurities dissolved in metals of the VIA group segregate at grain boundaries, recessions, and point defects [122, 179, 182, 183]. There are various opinions concerning the mechanism of embrittlement of tungsten, molybdenum and chromium by these admixtures [10, 183]. It is possible that the embrittlement effect is linked with precipitation of oxycarbonitride phases along the boundaries of and inside the grains, by the arisal of strained microvolumes in which the formation of cracks is made easier, by the development of Cottrell atmospheres around the recession, etc. An increase in the ductility of tungsten should be the result of purification from foreign admixtures. A possible way of removing the oxygen is its volatilization in a composition of Re_2O_7 during the melting of the alloys [17]. According to Jaffee et al. [172, 179], an increase in the ductility of W, Mo and Cr in alloying with rhenium is linked with a decrease in the solubility of the impurities. This assumption was based on a theory of Robins [182], who maintained that a decrease in the solubility of impurities can be expected in alloying metals of the VIA group with metals of groups to the right in the periodic table, because of the electron interactions due to the tendency to preserve the optimum value for the ratio between valence electrons per atom and the coordination number. Although there are no direct experimental proofs of the /68 correctness of this assumption, the development of the twinning process observed in tungsten-rhenium alloys can be compared to the phenomenon of the increase in number of twins for an increase in the purity of single tungsten crystals [181]. However, the ductility effect of rhenium can also be explained by the increase in solubility of the impurities [180]. A detailed analysis of all these factors at the present level is given in [180].

Carrying out a fractographic investigation of tungsten and the alloys W-3% Re and W-5% Re, Gilbert [184] noted that the effect of rhenium on the ductility of tungsten was closely connected with its effect on the grain size.

There are several works in which the ternary alloys of W-Mo-Re are investigated. The structural diagram of this system shows that it has a wide range of solid rhenium solutions in tungsten and molybdenum in it [185]. The minimum percentage of rhenium for which the W-Mo-Re alloys can be plastically deformed, not only by slipping but also by twinning, is roughly 20 at.% [185].

The results of an investigation of the properties of W-Mo-Re alloys are given in [186]. Ingots were hammered and rolled with summary shrinkage by more than 90%. An increase in the percentage of rhenium in the alloys with a constant ratio between the percentage of tungsten and molybdenum brings about an improvement in the ductility and strength. Of all the alloys with constant percentage of rhenium, those which have more tungsten have the best mechanical properties. In view of the deficiency of rhenium, its percentage in alloys must be reduced to the minimum. Thus, considering the above, the ternary solid solutions which are close to the twinning boundary, in whose composition there is no less than 20 at.% Re for percentages of rhenium and molybdenum (at.%) in the ratio 1:1, are most promising. The mechanical properties of certain W-Mo-Re alloys are given in Table 12.

Alloys of W-Mo-Re which are worked with reduction by 90% begin to recrystallize at temperatures of 1450 - 1550° C. Rhenium alloying greatly decreases the ductile-brittle transition temperature of W-Mo alloys. Tests with ternary alloys after the formation with 70%-shrinkage and recrystallization annealling at 1600° C showed that the transition temperature of these alloys in bending is within /69 the range of 50 - 200° C. The W-11% Mo-22% Re alloy has the lowest transition temperature.

TABLE 12. MECHANICAL PROPERTIES OF TERNARY W-Mo-Re ALLOYS IN EXPANSION [169, 173, 186].

Percentage of alloying elements, wt.%		Melting Point °C	State of Alloy *	Test Temperature ° C	σ_B, Kg/mm^2	δ, %
Mo	Re					
20	40	2700	1	20	125	0
			2	20	185	—
			2	1500	21	13.5
			2	1800	11.8	22
15	29	2700	1	20	98	2
			2	20	129	—
			2	1500	26	7.2
			2	1800	9.3	6
24	31	2500	1	20	90	6
			2	20	113	—
			2	1500	24	8.0
			2	1800	8.6	15
34	33	2650	1	20	92	10
			2	20	124	—
			2	1500	21.1	7.0
			2	1800	9.3	8.5

*1-annealed; 2-strained

The mechanisms of hardening and increasing ductility of the ternary W-Mo-Re alloys and the binary W-Re and Mo-Re alloys are basically very similar. Detailed information on the properties of W-Mo-Re alloys is given in [169, 173, 176, 177, 185, 188].

Ternary tungsten alloys with tantalum and rhenium have also been studied. There is a wide range of ternary solid rhenium solutions in tungsten and tantalum in the W-Ta-Re system [169]. Alloys of the type W-4% Ta-8% Re have the optimum mechanical properties, [9, 189].

A large number of studies have treated the possibility of decreasing the rhenium content in tungsten alloys or replacing it completely by some other metal. Positive results in the first direction are achieved by using tungsten containing different im- /70
purities as the substrate of the tungsten alloys. This type of metal is used widely in electro-vacuum industry [179, 190, 191].

The searches for rhenium substitutes are described in [172, 179]. It was shown that additions of metals of the platinum group bring about the development of twinning in tungsten [162]. Ratliff et al. [179] studied low (up to 10 at.%) binary tungsten alloys with metals of groups VII and VIII: Mn, Se, Co, Ni, Ru, Rh, Pd, Re, Os, Ir and Pt. The greatest effect of decreasing the hardness of cast tungsten is observed in adding admixtures of the following elements (in order of increasing effectiveness): Re, Os, Ru, Pt and Ir. The compositions of these alloys, as well as data on their hardness, are given in Table 13.

TABLE 13. SOFTENING OF CAST AND METAL-CERAMIC TUNGSTEN IN Re, Os, Ru, Pt and Ir ALLOYING

Percentage of Alloying Elements, at.%	Cast Annealed Alloys		Cermet Alloys	
	H_V, Kg/mm^2	ΔH_V	H_V, Kg/mm^2	ΔH_V
0	343	—	383	—
5Re	293	50	308	75
0.87Os	304	39	331	52
0.83Ru	304	39	—	—
0.62Pt	315	28	—	—
0.3Ir	316	27	334	49

The W-Os and W-Ir cermet alloys included in Table 13 are not inferior to the W-Re alloys in terms of processability. The ductile-brittle transition temperature of tungsten alloyed with 5 at.% Re decreased in the annealed and recrystallized state by 35 and 105° C, respectively. The additions of Os, Ir and Re increased the temperature for the beginning of recrystallization of tungsten up to 1500 - 1600° C. Iridium and rhenium had an identical effect on the grain size reduction of recrystallized tungsten.

The production of precipitation hardening alloys is an important direction in increasing the high-temperature strength of tungsten. The data in the literature concerning alloys of this type are still not very numerous. However, they do show that, at very high temperatures, these alloys are more promising than hard alloys. The finely-dispersed particles of the precipitating phases greatly increase the recrystallization temperature and strength characteristics, without showing any substantial negative effect on the ductility. In some cases, there is even observed an improvement in the deformability of the materials together with an increase in high-temperature strength.

The alloys of refractory metals containing the intermetallic phases of elements which form substitional solid solutions are generally very brittle. Therefore, the alloys in which the second phase is the product of interaction of the alloying metals with elements forming solid solutions, particularly carbon, are of greatest interest.

A detailed review of the mechanisms of hardening by finely-dispersed particles is found in [192]. The problems relating to the hardening of tungsten by this method are examined in [128].

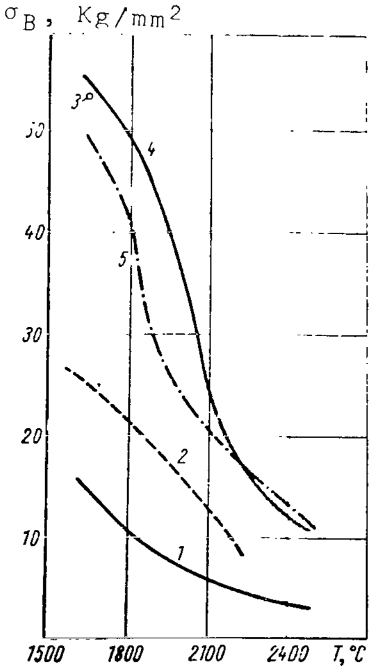
The firm "Climax Molybdenum" studied cast low-tungsten alloys with niobium, zirconium and hafnium, to which carbon or boron was added in order to obtain the effect of precipitation hardening [121]. The compositions of the alloys, their hardness, and the temperatures at which there was 100% recrystallization after one hour of annealing are given in Table 14.

TABLE 14. COMPOSITION, HARDNESS AND RECRYSTALLIZATION TEMPERATURE OF ALLOYS INVESTIGATED BY THE "CLIMAX MOLYBDINUM" FIRM [121].

Percentage of Alloying Elements, wt.%					Hv* Kg/mm^2	Recrystallization Temperature ° C
Zr	B	Hf	Nb	C		
0.07	0.004	—	—	—	483	1925
0.48	—	—	—	0.048	480	2595
—	—	0.19	—	0.027	538	2540
—	—	1.18	—	0.086	521	2540
—	—	—	1.42	0.005	—	—
—	—	0.23	1.41	0.012	—	—
0.44	—	1.22	—	0.095	512	2650

*After forging at 1480° C with 63.1 - 76.5%-shrinkage.

The alloys were processed by way of extrusion and forging, while only the alloys W-0.07% Zr-0.004% B, W-0.48% Zr-0.048% C and W-1.18% Hf-0.086% C could be rolled with sufficient compaction. /72



Hammered rods of these three alloys were subjected to a resistance test at high temperatures. The results of the tests, which are given in Figure 21, show that the high-temperature resistance of the alloys is several times greater than the resistance of non-alloyed tungsten. In general, the W-0.48% Zr-0.048% C and W-1.18% Hf-0.086% C alloys are two of the most highly resistant tungsten alloys known to the present. At temperatures of 1650 and 1925° C, the strength of the W-0.48% Zr-0.048% C alloy is equal to 54.6 and 43.6 Kg/mm^2, respectively, which is a record value. It was reported in the subsequent work of this firm [193] that the

Fig. 21. Strength Properties of Precipitation Hardening Tungsten Alloys: (1) 100% W; (2) Strength Level of Tungsten Alloys as Given by the Materials Advisory Board; (3) W-0.07 Zr-0.004%B; (4) W-0.48% Zr-0.048%C; (5) W-1.18% Hf-0.086% C.

forged alloy W-1.42% Nb-0.005% C also has high strength.

The maximum values for ultimate strength at temperatures higher than 1925° C which were obtained in [121] for worked alloys were the following: 23.8 Kg/mm^2 at 2205° C; 14.7 Kg/mm^2 at 2480° C; 4.6 Kg/mm^2 at 2760° C. These values are the highest published to this date for tungsten alloys. However, it is not mentioned in this study precisely which alloy is being discussed.

The tests with recrystallized alloys carried out in [193] /73 showed that the W-1.18% Hf-0.086% C alloy is strongest at temperatures higher than 1925° C.

The W-0.48% Zr-0.048% C and W-1.18% Hf-0.086% C alloys in the melted and recrystallized states were also tested for endurance at temperatures of 1650, 1925 and 2205° C [121]. Figure 22 gives the results of the tests, represented in the form of the dependence of stress on the Larson-Miller parameter.[2] The endurance of the alloys was 3 - 4 times higher than that of non-alloyed tungsten, and 2 - 3 times higher than that of solid solutions of W-Nb, W-Zr and W-Hf with small percentages of alloying elements. The advantage of the W-Zr-C and W-Hf-C alloys becomes more noticeable at higher values of the Larson-Miller parameter (high temperatures and long durations), which is obviously linked with an increase of the recrystallization temperature of the alloys. Obviously, the high resistance of these alloys is the result of the combined effect of the mechanisms of hardening in the formation of a solid solution and precipitation hardening.

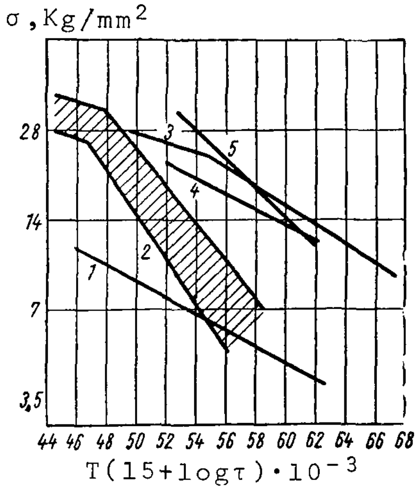


Fig. 22. Endurance of Alloys: (1) 100% W; (2) Low-Alloy Solid Solutions of W-Nb, W-Zr and W-Hf; (3) W-048% Zr-0.048% C (forged); (4) W-0.48% Zr-0.48% C (recrystallized); (5) W-1.18% Hf-0.086% C (forged).

The ductile-brittle transition of the W-0.48% Zr-0.048% C and W-0.07% Zr-0.004% B alloys is observed in the same temperature interval as for non-alloyed tungsten.

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[2] The Larson-Miller parameter is $T(C + \log \tau)$, where T is the test temperature, τ is the time before destruction, C is constant. Based on the experimental results, a value of 15 was selected in [121] for the constant C. - Author's note.

Dickinson and Friedman [194] patented tungsten alloys containing 0.01 - 2.0% Hf, Zr or Ti and 0.004 - 0.05% C. These alloys have ultimate strength of 17.5 - 51.1 Kg/mm^2 at 1650° C, and they preserve good ductility at low temperatures. It was reported in [195] that the ultimate strength of the worked alloy W-0.195% Hf-0.017% C at 1925° C is 43.75 Kg/mm^2. /74

An attempt at increasing the strength of solid high-tungsten alloys by precipitation hardening in adding small amounts of carbide forming elements and in increasing the percentage of carbon gave interesting results [196]. A binary alloy containing about 10 - 12% Nb was selected as the reference point; as was shown earlier [153], this alloy has very high strength.

Small ingots of W-Nb alloys with additions of V, Zr, and C were obtained by vacuum arc melting with a consumable electrode and were extruded with 67%-shrinkage during heating roughly up to 2200° C. The results of the tests, which are given in Table 15, show that small amounts of V, Zr, and C admixtures, which guarantee precipitation of the carbide phase, strengthen W-Nb alloys to a great extent. At 1925° C, the W-Nb-V-Zr-C alloy exceeds the W-Nb alloy in strength roughly by a factor of 2, and it exceeds non-alloyed high-purity tungsten by a factor of 6.

TABLE 15. MECHANICAL PROPERTIES OF THE ALLOYS W-Nb, W-Nb-Zr-C AND W-Nb-V-Zr-C AT 1925° C.

Composition of Alloy, wt.%	σ_B,Kg/mm^2	δ for Length of 12.7 mm, %	ψ, %
100W*	5,6	52	99
W — 10,2Nb — 0,005C . . .	18,9	<1	<1
W — 10,7Nb — 0,14Zr — 0,19C	34,3	42	64
W — 12,6Nb — 0,29V — 0,12Zr — 0,07C	39,9	43	52

*The properties of high-purity tungsten remelted by electron bombardment are given for the sake of comparison.

As a result of one hour of annealing at 1925° C, the W-Nb-alloy is completely recrystallized, while the recrystallization of the alloys W-Nb-Zr-C and W-Nb-V-Zr-C is less than 50%. /75

The introduction of the finely-dispersed carbide phase also greatly increases the ductility of solid W-Nb. The reasons for this phenomenon have not been explained in full. Obviously, grain size reduction could play a great role here.

Apparently, materials of this type include the forged alloy W-3.10% Mo-0.04% Zr-0.001% C. Sheets of this alloy with thickness of 1.3 mm have ultimate strength equal to 38.5 and 9.5 Kg/mm^2 at 1650 and 1925° C, respectively [197].

It was reported in [198] that the alloy W-25% Mo-0.11% Zr-0.05% C has ultimate strength of 51.5 Kg/mm^2 at 1425° C.

The synthetic dispersed systems obtained by the method of powder metallurgy are the most important class of refractory tungsten alloys. The use of the term "alloys" for such materials is conditional, since they are actually a mechanical mixture of tungsten and various high-melting compounds. The materials of this type, which are sometimes called "precipitation strengthened" alloys, are in many respects close to precipitation hardening alloys in terms of their properties. The basic difference is the nature of the microstructure. In a precipitation strengthened alloy, in contrast to a precipitation hardened one, each particle of the second phase is surrounded by several grains of the matrix having various orientations. Therefore, the theory explaining the effect of strengthening regular precipitation hardening alloys are generally not applicable for synthetic dispersed systems.

The high-temperature strength of these materials, which contain compounds with high dissociation energies and low solubility in the metallic matrix in the strengthening phases, is very high. At the same time, dispersed admixtures of a number of refractory compounds decrease the ductile-brittle transition of tungsten to a great extent.

There are various opinions in the literature concerning the mechanisms of the effect of synthetically introduced phases on the properties of tungsten [133, 157, 179, 192, 199]. Obviously, impurities along the grain boundaries increase the recrystallization temperature and decelerate the growth of the grains, controlling their size and shape. The creep resistance also increases, due to the fact that the impurities prevent slipping along the grain boundaries. /76

Even about 50 years ago, it was found that admixtures of thorium oxide guaranteed distortion resistance and increased the strength of a tungsten wire at temperatures greatly exceeding the recrystallization temperature of the metal. The techniques used in producing "non-slack" tungsten filaments are described in detail in [4, 6]. Some aspects of hardening tungsten by this method are examined in [16, 200, 201].

A systematic investigation of the effect of high-melting oxides (ThO_2, ZrO_2, SiO_2, MgO, HfO_2, Al_2O_3, UO_2), nitrides (TiN, ZrN, HfN, TaN) and carbides (HfC, TaC, Ta_2C) on the recrystallization of cermet tungsten sheets was carried out by Jaffee et al. [202]. The introduction of 1% ThO_2 (in combination with the volatile admixture of 0.2 - 0.5% Na_2O during sintering), 0.12 - 3.2% ZrO_2 and 0.75% ZrN (decomposing during sintering) was found to be most effective.

These additions increase the primary recrystallization temperature of tungsten by 200° C. Secondary recrystallization of W-ThO_2-Na_2O was not accomplished even after 1 hour of annealing at 2600° C. The grains remained extended and oriented parallel to the rolling direction.

The mechanical properties of W-ThO_2 alloys, or so-called "thoriated tungsten" have been studied most extensively. At the present, American industry is producing thoriated tungsten with 0.5 - 2.0% ThO_2, not only in the form of wires but also as rods and bands [2, 132].

The alloys which contain 1 - 2% ThO_2 have optimum mechanical properties. The high-temperature strength of these alloys is much greater than that of non-alloyed tungsten. For example, the W-2% ThO_2 alloy has ultimate strength equal to 7 Kg/mm^2 at 2420° C, while pure tungsten has such strength only at 1925° C [134]. The results of mechanical tests of the alloys W-1% ThO_2 and W-2% ThO_2 carried out by different authors are given in Tables 16 and 17.

TABLE 16. HIGH-TEMPERATURE MECHANICAL PROPERTIES OF THE W-2% ThO_2 ALLOY [133]

Test Temperature, °C	σ_B, Kg/mm^2	σ_S, Kg/mm^2	ψ,%
1370	29.5	≈28.8	74.0
1480	27.4	≈26.7	38.0

The discrepancy in the values for the ultimate strength of the W-2% ThO_2 alloy at 1370° C could be due to different reasons, the most important of which is a difference in the degree of dispersion of the ThO_2 impurities and in the degree of hard working. Recrystallized W-ThO_2 alloys are much weaker than deformed ones [157, 199].

TABLE 17. STRENGTH OF THORIATED TUNGSTEN AT HIGH TEMPERATURES [137]

Alloy	Test Temperature °C	σ_B, Kg/mm^2	Alloy	Test Temperature °C	σ_B, Kg/mm^2
W — 1% ThO_2	1370	34.1	W — 2% ThO_2	1370	24.9
	1650	26.0		1650	20.7
	1925	19.7		1925	18.7
	2205	9.8		2205	12.3

The positive effect of additions of ThO_2 on the high-temperature strength of tungsten is illustrated by Figure 23 [16], where the endurance of the W-2% ThO_2 alloy is compared to that of the non-alloyed metal.

"Westinghouse" carried out an investigation of the high-temperature mechanical properties of W-Ta-C alloys [9, 16, 133]. The alloys which contained about 0.4% TaC had maximum resistance. According to the data of [133], the mechanical properties of W-0.4%

TaC at 1370° C are such: $\sigma_B = 47.1$ Kg/mm ; $\sigma_S \approx 39.4$ Kg/mm^2; $\psi = 42.0\%$. It was reported in [16] that an addition of 0.35% TaC increases the resistance of tungsten at 1370° C up to 42 Kg/mm^2. Mayleuth and Ogden [137] reported that the W-0.38% TaC alloy has a resistance of 36.2 and 21.8 Kg/mm^2 at 1370 and 1650° C, respectively. Thus, despite certain discrepancies in the data, the effect of increasing the resistance of tungsten by small additions of TaC is obvious.

The results of vacuum tests for the endurance and creep resistance of the W-0.38% TaC alloy are given in Figure 24 [9]. The endurance of this alloy at 1480° C is several times higher than that of tungsten with 2% ThO_2. /78

Tungsten hardening with tantalum carbide at 1350 - 1550° C is more effective than that with thorium oxide. However, the resistance of W-TaC alloys decreases rather rapidly with an increase in the temperature, while the resistance of the W-ThO_2 alloy is higher than that of pure tungsten, even at temperatures exceeding 2200° C. Tantalum carbide is easily reduced by tungsten trioxide and it looses carbon, while ThO_2 has high stability all the way to 2650° C [157].

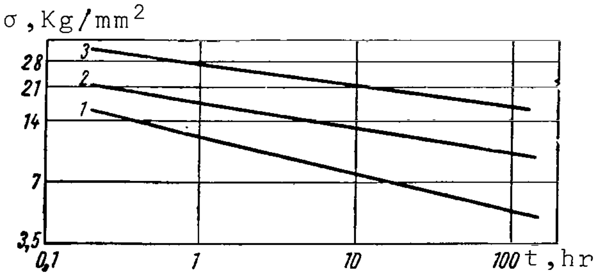

Fig. 23. Endurance of Non-Alloyed Tungsten and W-2% ThO_2: (1) 100% W at 1480°C; (2) W-2% ThO_2 at 1480°C; (3) W-2% ThO_2 at 1370°C.

G.S. Pisarenko, et al. [15] determined the mechanical properties of the alloy W-0.05% NbC. This alloy has ultimate strength at 1525, 1725 and 2025° C which is roughly equal to 35, 12 and 7 Kg/mm^2, respectively, and the relative expansion of the alloys at these temperatures changes from 8 to 55%.

The alloys W-0.5% HfO_2, W-Ta_2O_5, and W-1% HfN were also investigated in [9, 157, 203, 204]. There was no substantial increase in resistance at 1480 and 1650° C in adding 0.5% HfO_2 [9]. It was noted in [205] that the addition of 1% W_2B to tungsten powder before sintering does not change the mechanical properties at room temperature. However, there is a certain increase in resistance after annealing at 1000° C. An addition of 1% W_5Si_3 increases the resistance of the rolled metal, but the strength decreases after high-temperature annealing [205]. It is probable that tungsten boride and silicide decompose during the sintering process. /79

The effect of synthetically produced dispersion phases on the ductility of tungsten is of particular interest. The dependence of the expansion of high-purity tungsten and W-1% ThO_2 alloys in the recrystallized state on the temperature which was obtained by

King and Sell [199] is shown in Figure 25.

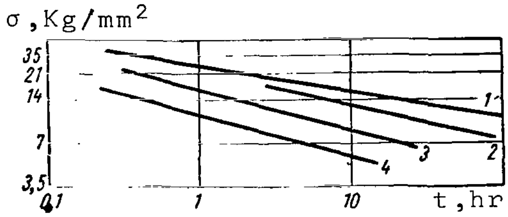

Fig. 24. Endurance and Creep Resistance of the Alloy W-0.38% TaC at 1480° C; (1) Decomposition; (2) Deformation by 3%; (3) Deformation by 1%; (4) Deformation by 0.5%.

It can be seen that, at temperatures lower than 1500° C, the alloy is inferior to non-alloyed tungsten in terms of ductility. At temperatures higher than the greatest expansion range, the alloy is somewhat more ductile than pure tungsten. An increase in the ductility with an increase in the rate of deformation and a tendency for the ductility to decrease with an increase in temperature which King and Sell observed in the high-temperature range were explained in terms of the formation of pores and vacancies at the grain boundary, as well as at the sub-boundaries inside the grains, the probable mechanism for which was the condensation of vacancies from the matrix.

The ductile-brittle transition temperature of the W-2% ThO_2 alloy during expansion was determined in [16]. An alloy deformed by 80% was tested after removal of the stresses by annealing for 30 minutes at 1500° C. It was found that the transition of the W-2% ThO_2 alloys to the brittle state occurs at the same temperatures for recrystallized tungsten. A certain decrease in the ductility of tungsten during addition of ThO_2 was noted in [2]. However, Jaffee et al. [202] found that dispersed particles of the compounds enumerated in Table 18 decreased the transition temperature of worked tungsten by 60-80° C. /80

The greatest effect of decreasing the transition temperature of recrystallized tungsten is observed in adding ThO_2 or ThO_2 + NaO_2 (by 75 - 90° C), as well as ZrO_2 (by 40 - 80° C). Just as pure tungsten, the recrystallized alloys have a much higher transition temperature than do the worked ones. In this case, the following law is

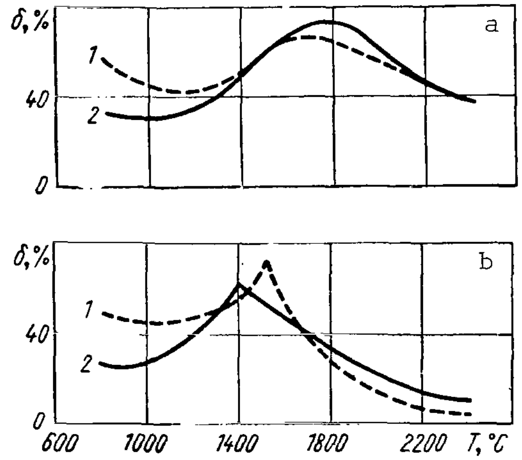

Fig. 25. Ductility of Tungsten (1) and the Alloys W-1% ThO_2 (2) for Rates of Deformation: $3.3\cdot\cdot10^{-2}$ sec^{-1} (a); and $8.4\cdot10^{-5}$ sec^{-1} (b).

usually observed: the smaller the grain of the recrystallized material, the lower its transition temperature.

The alloys W-ThO_2 and W-ZrO_2 with percentage of oxides up to 8 vol.% were investigated in [179] (the alloy also contained an admixture of 0.2% Na_2O, which affected the grain shape). The alloys had good processability. It was established that an increase in the percentage of oxides from 1 to 8 vol.% brings about a decrease /81 in the ductile-brittle transition temperature during bending, together with an increase in the recrystallization temperature and a grain size reduction. The transition temperature depends on the heat treatment. The alloys W-8 vol.% ThO_2 (85° C) and W-8 vol.% ZrO_2 (90° C) had the lowest transition temperature after one hour of annealing at 1300° C. It is interesting that the transition temperature is dependent to a great extent on the volume of the oxide phase, and not on a determination of which oxides were added to the metal.

TABLE 18. EFFECT OF ADMIXTURES OF REFRACTORY COMPOUNDS ON TRANSITION TEMPERATURE OF DEFORMED TUNGSTEN DURING BENDING (RATIO BETWEEN LEAST PERMISSABLE BENDING RADIUS AND THICKNESS OF SAMPLE EQUAL TO 10)

Content of Admixture, %	Transition Temperature, °C
0 (non-alloyed tungsten). . . .	230
1.0ThO_2	160
0.60ZrO_2	150; 170
0.56TiN	160
0.75ZrN	150
1.50TaC	170

The authors of [179, 202] explained the results they obtained in terms of the fact that finely-dispersing particles of thermodynamically stable, volatile oxides, preventing the growth of the grains in sintering, rolling and high-temperature annealing, aid in the formation of a structure consisting of small expanded grains with boundaries of irregular shapes. The size and shape of the grain have a very substantial effect on the ductility of tungsten. The coarse-grained, recrystallized structures, for which the surface area of the grains per unit volume is minimum, are most brittle. A size reduction and deformation of the grain increases the expanse of the grain boundaries, which results in a spreading of the impurities segregated on them (or the precipitating of oxycarbonitride phases) over a large area. It is well known that strongly-deformed fine-grained tungsten, e.g., a thin layer obtained by powder metallurgy, usually has maximum ductility.

The mechanism of the effect of ThO_2 and ZrO_2 on the ductility of tungsten was examined in detail in [179]. It was assumed that the dispersed particles of the inactive oxide preventing movement of dislocations during annealing guaranteed that fine-grained structures of recrystallized materials be obtained. The ThO_2 and ZrO_2 particles can prevent expansion of microscopic particles, and /82 can also act as sources of recession production.

The results examined above show that the production of synthetic dispersed systems, mainly oxide ones, can pave the way for interesting possibilities in improving the mechanical properties of tungsten. It was held in [206] that these materials should surpass regular precipitation-hardening alloys in high-temperature creep resistance, due to the high-thermal stability of the strengthening phases. The synthetic dispersed tungsten-base systems which have been developed to the present are still inferior to precipitation hardening alloys in terms of high-temperature strength since, obviously, the regular methods of powder metallurgy do not permit obtaining dispersed structures which are optimal from the point of view of the mechanisms of precipitation hardening. The results obtained in investigations of the material Ni-2% ThO_2 (the so-called "TD-nickel"), which is prepared by powder metallurgy with the aid of the method of chemical coprecipitation, are very interesting, since they make it possible to control to a great extent the size of the ThO_2 particles, their distribution in the nickel matrix and, thus, the obtainment of intrinsically dispersed, and not aggregate structures [207]. We can assume that the use of such technology for producing precipitation-hardened tungsten-base alloys will eventually increase their resistance characteristics to a great extent.

Attempts were made at improving the mechanical properties of tungsten by way of combining such methods as "doping" and rhenium alloying. The "dopants" (admixtures of salts or metal oxides) which are usually added to WO_3 before reduction are used in the electric light-bulb industry for obtaining "non-slack" tungsten filaments. In contrast to inert or non-volatile oxides of the type ThO_2, the "dopants" are evaporated during preparation and utilization of the filament, thus guaranteeing the formation of a stable structure formed by long grains with indented boundaries extended along the axis of the wire during the process of secondary recrystallization. Investigations of the effect of such admixtures were described in [4, 6, 208].

Cermet alloys containing 1 - 20% Re, for which tungsten of type 218 was used as the substrate (with an admixture of potassium silicotungstate and aluminum chloride), were investigated in [190]. It was found that the addition of the admixture resulted in alloys having optimum properties for small percentages of rhenium (3 - 5%). These alloys were much superior in mechanical properties to pure tungsten and low tungsten W-Re alloys, as well as W(218). The alloys W(218)-3% Re and W(218)-5% Re, which were tested in the form of a wire with diameter of about 0.2 mm, were characterized by an increased structural stability and resistance at high temperatures. The most important result was that these alloys had very high ductility at room temperature when in the recrystallized state. While W(218) and the alloy W-3% Re were brittle after annealing at 2850° C, the expansion of the alloys W(218)-3% Re and W(218)-5% Re was 9.0 and 11.5%, respectively, after annealing at 3000° C. /83

Taylor [191] studied the mechanical properties of a crystallized bar made of tungsten with an admixture, as well as the same with addition of 3% Re. The alloy was stronger than tungsten with admixtures at all temperatures (1400 - 2900° C), but inferior to it in terms of high-temperature ductility. The addition of 3% Re decreased the hardness of tungsten at room temperature.

The mechanisms which determine the properties of such materials are still unknown. Obviously, they are linked with the nature of the combined effect of rhenium and admixtures on the processes of formation of the structure of recrystallized tungsten.

Ratliff et al. [179] investigated the effect of alloying tungsten with rhenium, osmium or iridium (up to 58 at.%) and adding particles of thorium oxide (up to 8 vol.%) on the DBTT and on the deceleration of the grain growth. The metals and ThO_2 were added in the following combinations: 5 at.% Re-2 vol.% ThO_2, 5 at.% Re-4 vol.% ThO_2, 0.87 at.% Os-8 vol. % ThO_2 and 0.3 at.% Ir-8 vol.% ThO_2. All the alloys contained an additive of 0.2% Na_2O. The ternary alloys with Os or Ir which were annealed for one hour at 1200° C had the least transition temperature, roughly equal to 75° C. The transition of the alloys W-5 at.% Re-2 vol.% ThO_2 and W-5 at.% /84
Re-4 vol.% ThO_2 in the annealed state took place roughly at 150 and 80° C, and that of the alloys in the recrystallized state was 245 and 225° C, respectively. (The transition temperature of the alloys was determined from the ratio between the minimum bending radius and the thickness of the sheet sample, as equal to 8).

Further investigations of such alloys [123, 209 - 211] showed that the alloy W-5 at.% Re-4 vol.% ThO_2 (W-5% Re-2.2% ThO_2) has the best combination of properties. Industrial tungsten powder with alkali silicate additives was used for obtaining this alloy. The mechanical properties of sheets of this alloy were such at room temperature: σ_B = 135.1 Kg/mm , σ_S = 127.4 Kg/mm , δ = 6% [209]. A perfection of the methods used in processing the alloy W-5% Re-2.2% ThO_2 (use of strong annealing in rolling) aided in increasing its ductility. At a temperature of 0° C, the sheets of the alloy with thickness of 1.0 mm had δ = 12% and ψ = 18% [212], and they preserved their ductility in extension all the way to -40° C [123]. This alloy also had high ductility in the recrystallized state [211]. At the same time, it had high-temperature strength. Recrystallization of the alloy during one hour of annealing took place at 2000° C, and the ultimate strength at 1650° C was equal to 25.6 Kg/mm^2 [209]. The methods for adding ThO_2, which are now being perfected [210, 211], have a substantial effect on the structure and properties of this alloy.

The fractographic investigations in [212, 213] gave interesting results which permitted that certain assumptions be made concerning the role of ThO_2 in the alloy W-5% Re-2.2% ThO_2. It was found that ThO_2 particles are deformed during rolling into plates with thickness of about 1000 Å, which, apparently, represent oriented single crystals to a certain extent. It was assumed that, as a result of a difference in rates of deformation of the matrix and ThO_2 additions during rolling, internal cracks parallel to the plane of the sheet arise around the plates formed and subsequently prevent the growth of the cracks which extend across the sample and usually bring about destruction.

Data on some properties of tungsten alloys with 2% ThO_2 and 5-24% Re are given in [214]. The alloy W-24% Re-2% ThO_2 preserve high ductility after recrystallization. The alloys in which rhenium is added are less ductile but their deformability is nevertheless much higher than that of thoriated tungsten. At the same time, a wire of these alloys has much greater resistance to high-temperature creeping than does a wire of an alloy containing 24% Re. /85

"Westinghouse" studied the resistance properties of the alloys W-25% Re-1% ThO_2 and W-25% Re-1% HfN at temperatures up to 2400° C [215]. The results of these tests have still not been published.

White [216] applied the method of precipitation hardening to alloys which did not contain rhenium. Although the alloy W-20% Ta-12% Mo-5 vol.% ThO_2 obtained by way of hot pressing was not subjected to resistance tests, it was noted that the introduction of ThO_2 greatly increased its high-temperature stability.

In addition to their regular alloys, the so-called "composite" tungsten-substrate materials are being used more and more widely in space technology. This holds true for example, for cermets of the type W-25% Cr-15% Al_2O_3 [217] or W-BeO [218], as well as the pseudo alloys of the type W-Ag (porous tungsten matrix impregnated with silver), which are used for preparing non-cooled rocket nozzles [219], particularly for the "Polaris" rockets [91].

The data given show that various alloying methods guarantee a substantial increase in the high-temperature strength of tungsten (Fig. 26).

Obviously, for temperatures lower than 2000° C, it is most expedient to use solid solution alloys of the system W-Ta-Mo-Nb. The advantage of such alloys as W-12% Nb and W-15% Mo becomes even more obvious when we compare them to non-alloyed tungsten, based on the specific strength. For temperatures exceeding 2000° C, the precipitation-hardening alloys and synthetic dispersed systems are most promising. Unfortunately, there is too little data in the literature on such very important characteristics of tungsten alloys as creep resistance and endurance.

Substantial advances were also made in developing alloys which have improved low-temperature ductility. The most interesting alloys are of the type W-Re-ThO_2, which combine ductility with relatively high-temperature strength.

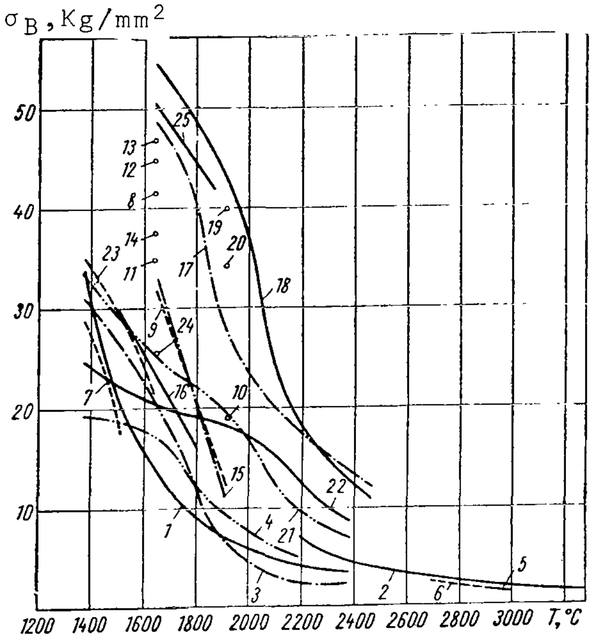

Fig. 26. Resistance of Tungsten Alloys at High Temperatures: /86

No.	Alloy Composition, wt.%	Method of Obtaining and Processing	Literature Source
1	100% W	Powder Metallurgy; hammered bar	[2]
2	100% W	Powder Metallurgy; deformed sheets	[2]
3	W-10% Mo W-25% Mo	Powder Metallurgy; hammered bars	[2]
4	W-15% Mo	Arc-Melting	[2]
5	W-20% Mo	Electron-bombardment melting; Annealing for 1 hour at 1205°C	[2]
6	W-30% Mo	Electron-bombardment melting; Annealing for 1 hour at 1205° C	[2]
7	W-50% Mo	Powder Metallurgy; hammered bar	[2]
8	W-0.57% Nb	Arc-Melting; extrusion and forging	[2] /87
9	W-0.88% Nb		[2]
10	W-10.2% Nb	Arc-melting; extrusion	[196]
11	W-12% Nb	Same	[153]
12	W-25% Ta W-50% Ta	Same	[153]

Continuation

No.	Alloy Composition, wt.%	Method of Obtaining and Processing	Literature Source
13	W-20% Ta-12% Mo	Same	[153]
14	W-20% Ta-6¢ Mo-6% Nb	Same	[153]
15	W-0.12% Zr	Arc-melting; extrusion and forging	[2]
16	W-25% Re	Arc-melting; deformed sheets	[169,173]
17	W-1.18% Hf-0.086% C	Arc-melting; forging	[121]
18	W-0.48% Zr-0.048% C	Arc-melting; forging	[121]
19	W-12.6% Nb-0.29% V-0.12% Zr-0.07% C	Arc-melting; extrusion	[196]
20	W-10.7% Nb-0.14% Zr-0.19%C	Same	[196]
21	W-1% ThO_2	Powder metallurgy; hammered bar	[2]
22	W-2% ThO_2	Same	[2]
23	W-0.38% TaC	Powder metallurgy; forging and annealing for 30 min at 1600° C	[2]
24	W-5% Re-2.2% ThO_2	Powder metallurgy; deformed sheets	[209]
25	Alloy "A"		[122]

The reserves for increasing the resistance and ductility of tungsten alloys are far from exhausted. Further investigations of alloys of new compositions are necessary, as are improvements in the methods of obtaining them (for example, using chemical means of adding precipitated phases) and processing them (particularly heat treatments), etc. The use of reinforced filaments is a promising method in solving the problem of increasing resistance. It was reported in [20] that the reinforcement of tungsten by ZrO_2, Y_2O_3, ThO_2, HfB_2 and TaC filaments increases its strength by a factor of 4 - 18.

Investigations of the mechanisms of strengthening and plastification of tungsten in alloying have principal significance. /88

An extensive study was carried out for the purpose of producing tungsten alloys which have increased resistance to high-temperature oxidation. The results of these studies are examined in reviews [54, 57, 221 - 224].

Obviously, there are still no tungsten-base alloys which combine satisfactory mechanical properties with resistance to oxidation at temperatures above 1500° C. Possibly, the only exception is the synthetic dispersed systems containing 10 vol.% Al_2O_3, MgO or ThO_2, which were developed by White [90], and whose resistance to oxidation at 1600 - 2500° C is almost one order higher than that of non-alloyed tungsten. The mechanical properties of these materials were not defined, and it was only mentioned that they have a structural stability. However, based on the data given in [9, 179], it can be considered that the content of oxides in these alloys is higher than the optimum one from the point of view of precipitation hardening.

The problem of increasing the resistance of tungsten to oxidation by way of alloying is exceptionally difficult, mainly because of the high volatility of WO_3 at temperatures above 1100° C. There is no general approach to a solution for this problem. It is considered that positive results can be obtained by way of adding elements capable of forming stable, non-volatile oxidation products. The effectiveness of this method is illustrated by a comparison to the effect of having chromium, which forms an oxide film of Cr_2O_3 and Nb, introduced into the composition of a stable tungstate [224]. For an identical percentage of admixtures (at.%), the W-Nb alloys oxidize almost two times slower than do W-Cr alloys. Only for a percentage of about 50 at.%, for which the formation of a solid Cr_2O_3 film is possible, does chromium guarantee a stronger deceleration of oxidation than niobium.

Very interesting results were obtained for tungsten alloys with tantalum and niobium, which are also promising in terms of their mechanical properties. The rate of oxidation of the alloy W-50% Ta at oxygen pressure of 0.21 atm is determined by diffusion through the oxide layer all the way to a temperature of 1460° C [222]. The oxide formed on the alloy is described by the formula $Ta_{10}W_8O_{49}$, and it has a much lower vapor pressure than does WO_3. The protective properties of a $Ta_{10}W_8O_{49}$ film have also been confirmed by the fact that the rate of oxidation does not depend on the pressure in a certain interval. The alloys W-10% Ta and W-25% Ta have a lower resistance to oxidation. /89

Alloying with niobium in quantities up to 25 - 30%, which results in a change of the structure of the oxide layer, also decreases the weight of tungsten oxidation by a factor of 3 - 4 at temperatures of 1200 - 1300° C [225, 226]. It was maintained in [152] that some ternary W-Ta-Nb alloys are 10 times superior to non-alloyed tungsten in high-temperature strength at 1200° C. The oxidation of these alloys is described by a parabolic law. The alloy W-24% Nb-10% Ta was patented as having increased strength properties in combination with good resistance to oxidation at 1095° C [227].

The kinetics and oxidation mechanism of binary and ternary tungsten alloys with tantalum and niobium are examined in detail in [54, 57, 152, 222, 225, 226, 228, 229].

Systematic investigations of the effect of various admixtures on tungsten oxidation at relatively low temperatures were carried out by Andes and Heckel (Ti, Zr, V, Nb, Ta, Cr, Mo) [225], and by I.N. Frantsevich and R.F. Voytovich (Ti, Zr, Nb, Ta, Fe, Co, and Ni) [228].

The principal results obtained in [225] are given in Figure 27. The alloys were tested for 5 hours at a temperature of 1200° C in an air current.

It was found in [228] that none of the alloying elements, except Fe and Co, have an advantageous effect on the resistance of tungsten to oxidation at temperatures of 500 - 900° C. The decrease in rate of tungsten oxidation for cobalt alloying can be explained by the formation of a complex oxide CoW_4, which makes oxygen diffusion difficult.

Ternary tungsten alloys with Ti, Zr, V, Nb, Ta, Cr and Mo in various combinations were also investigated in [225]. In addition to the W-Nb-Ta alloys, the alloys of W-Cr-Ti, W-Nb-Ti and W-Ta-Ti also had increased resistance to oxidation.

The alloys W-(20-40%)Cr-(1-25%)Ti [230], W-(4.8 - 24.8%) Nb- /90
(7.5 - 27.5%)Ti [231] were patented as resistant to oxidation at 1200° C, the alloys W-(15 - 18%) Nb-20% Ta-(2 - 5%) Ti [227] as resistant at 1095° C, the alloys W-10% Nb-30% Cr-10% Fe and W-20% Nb-20% Cr-10% Fe [232] as heat resistant at 1040° C.

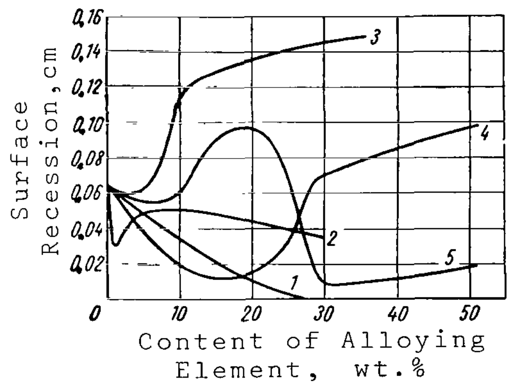

Fig. 27. Effect of Alloying Admixtures of Cr (1), Ti (2), Mo (3), Nb (4) and Ta (5) on Tungsten Oxidation [225].

It was suggested in [224] that titanium stabilizes the niobium and tantalum tungstates formed and thereby increases the high-temperature strength of W-Nb and W-Ta alloys. However, it was reported in [229], in which the alloys W-Nb-Ti were investigated in a wide range of compositions, that additions of titanium have a negative effect on oxidation of W-Nb alloys at temperatures above 1200° C.

The data on the effect of rhenium on the heat resistance of tungsten are contradictory. It is held in [190] that additions of 1 - 20% Re decrease the rate of tungsten oxidation at 650° C in air by a factor of 6 - 7. The effect of decelerating high-temperature tungsten oxidation by rhenium alloying was also mentioned in [233]. At the same time, R.F. Voytovich and V.A. Lavrenko [234] showed that the W-5% Re alloy oxidizes 5 times more

rapidly at 800° C than does non-alloyed tungsten. The oxidation /91
of the W-20% Re alloy is also greatly accelerated at temperatures higher than 700° C (Fig. 28).

There are data concerning a situation where a certain increase in the resistance of tungsten to oxidation at high temperatures is achieved by way of hafnium alloying [233].

It was reported in [235] that the alloy W-10% Cr-1% Pd has increased resistance to oxidation. The alloy was tested in cyclical heating up to a temperature of about 1400° C. A protective Cr_2O_3 film was formed on the surface of the alloy. An addition of palladium brought about the self-healing ability found on the oxide layer.

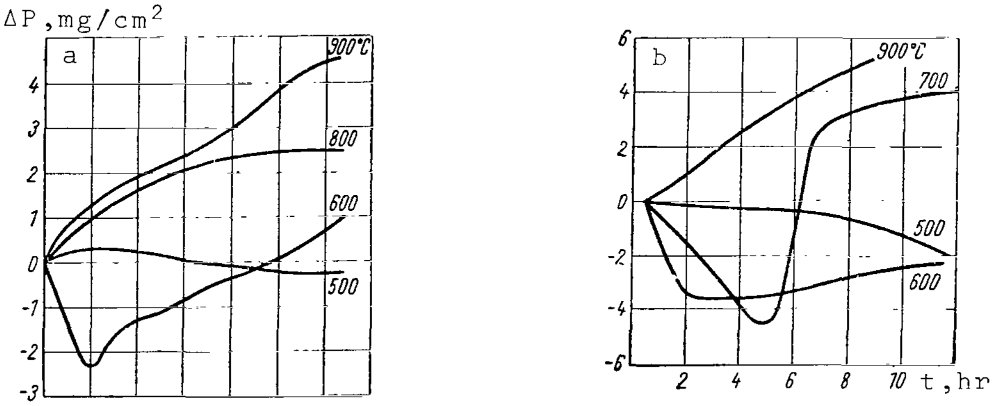

Fig. 28. Kinetics of Oxidation of Recrystallized (a) and Worked (b) W-20% Re at Various Temperatures.

B.K. Opara and N.P. Zhuk examined the oxidation of tungsten with admixtures of 0.7 - 5.0% ThO_2 and 1% La_2O_3 [236]. It was found that the introduction of the precipitation phases worsened the high-temperature strength of the metal at temperatures of 700-900° C. An increase of the percentage of ThO_2 in the W-ThO_2 alloys brought about an acceleration of the oxidation.

As was mentioned above, it was found in [90] that the alloy W-10 vol.% ThO_2 has a resistance to oxidation which is 3 times higher at temperatures of 1600 - 2500° C than that of pure tungsten, for velocities of air currents up to 41.5 m/sec. This is connected with the formation of the liquid oxide phase on the surface of the samples, which prevents WO_3 volatilization. At temperatures above
2500° C, the liquid film is blown off by an air current, which /92
results in a certain decrease in heat resistance. Attempts at stabilizing the liquid oxide phase by way of adding to the W-10 vol.% ThO_2 alloy admixtures of 10% Ta and 15% Ta + 5% Zr did not give substantial results. Somewhat better results were obtained in testing alloys of W-10 vol.% Al_2O_3 and W-10 vol. % MgO, on which

liquid oxides were also formed. The first of these alloys was found to be most heat-resistant. The temperature dependence of the rate of oxidation of these alloys is shown in Figure 29.

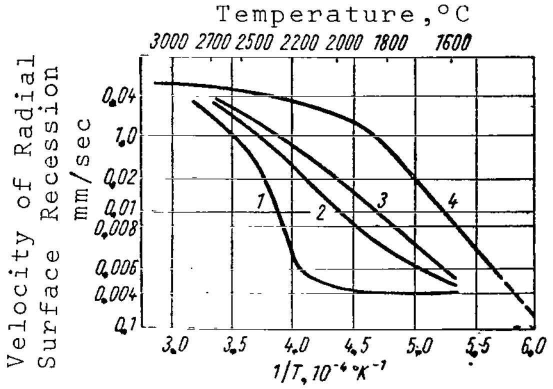

Fig. 29. Dependence of Rate of Oxidation of the Alloys W-10 vol.% Al_2O_3 (1); W-10 vol.% MgO (2); W-10 vol.% ThO_2 (3); 100% (4) on Temperature. The Tests Were Carried Out for an Air Current Velocity Equal to 23.2 m/sec.

The liquid oxide phase is formed on the alloys because of an interaction of WO_3 with dispersed refractory oxides. The increased resistance of the W-10 vol.% Al_2O_3 alloy can be explained by the fact that the least amount of tungsten trioxide is found on this alloy in the liquid oxide layer formed.

We should mention that, despite the substantial deceleration of tungsten oxidation by admixtures of refractory oxides, the absolute values for the rate of oxidation remain very high.

Structural tungsten-substrate alloys which have a rather high resistance to gaseous corrosion at temperatures where their use is most expedient have still not been produced. The increase in the high-temperature strength /93 achieved by way of alloying is usually not very high and is almost always (except for the alloys W-Nb, W-Ta and, possibly, W-ThO_2) accompanied by a substantial decrease in the melting points and a worsening of the mechanical properties. Nevertheless, investigations in the field of highly-resisting tungsten alloys should be continued, since in certain cases (for example, in media with a decrease in oxygen pressure) the resistance to oxidation achieved can be sufficient. Moreover, in using combined alloy-protective coating systems, it is desirable to have the alloy which is most resistant to oxidation as the substrate in order to prevent catastrophic destruction of the product in the case of a flaw on the coating. It is possible that the addition to the composition of the alloys of special components spreading over the coatings during the process of their utilization would aid in increasing the durability of the protective coating.

Studies on the production of structural tungsten alloys which could be used at high temperatures without protective coatings encounter great difficulties. The alloys on which stable, nonvolatile solid or liquid oxidation products having protective properties are formed are most interesting, as are materials of the type W-Ag and W-Cu. Tests with tungsten impregnated with silver or copper under the conditions of flight at supersonic speeds and at low altitudes showed that these materials have better resistance to oxidation at temperatures higher than 2400° C than does the pure metal [91].

For progress in the field of producing high-temperature tungsten-base alloys, we need studies which would provide a deeper understanding of the mechanisms of the processes of high-temperature oxidation, as well as the laws of the effect of various alloying elements on these processes.

CHAPTER 4

PROTECTIVE COATINGS FOR TUNGSTEN

The problem of protecting tungsten from oxidation was raised /94 at the very beginning of this century, when that metal began to be used in electrotechnical industry. The first patents for protective coatings for tungsten were issued in the 1920's [237]. However, large-scale works on the production of heat-resisting coatings for tungsten and other refractory metals were started only at the beginning of the 1950's in relation to the sharp need for the newest type of high-temperature structural materials in aircraft and rocket technology.

At the present, in the USA alone more than 100 industrial firms and scientific centers [238] are occupied with the production of high-temperature protective coatings, of which roughly half are working on the production of heat-resisting coatings for high-melting metals [239, 240].

Coated refractory metals are widely used in the structures of reentry vehicles, e.g., the "Asset" (rocket aircraft with triangular wing) and "Dyna-Soar" (rocket aircraft X-20) [241 - 243].

The need for using coatings in order to protect surfaces which are exposed to aerodynamic heating is clearly illustrated in the following example [242]. Under conditions close to the real conditions of the return of a soaring spacecraft into the dense layers of the Earth's atmosphere (temperature of 1650° C, pressure of 5 mm Hg, air speed of about 300 m/sec, flight duration of one hour), the surface recession of a leading edge made of tungsten reaches 8 mm as a result of oxidation.

The problems of developing protective coatings for reentry systems are examined in detail in [244].

It is also expedient to use coated refractory metals in preparing non-cooled nozzles of rockets operating on solid, liquid and nuclear fuel [242]. The possibility of using them in the small altitude-control rockets is considered in [241].

The most important field in which coated refractory metals are /95 used is nuclear technology, particularly the nuclear reaction systems of spacecraft [51, 241, 242].

There are promising outlooks in the use of refractory metals with protective coatings in regular high-temperature technology: the use of coated tungsten and molybdenum as heaters can aid in the development of resistance furnaces operating in oxidizing media at temperatures on the order of 2000° C [245]. At the present, the production of coatings which guarantee protection of tungsten from oxidation at temperatures all the way to 2750° C is one of the basic problems in the field of heat-resisting coatings [241].

It does not seem possible to obtain a "universal" coating capable of reliable protection of tungsten in various media and in a wide temperature range. The requisite working characteristics (mechanical and corrosion) of the tungsten-protective coating system are determined by the specific application for which the given system is developed.

The properties of a coating and the general metal-coating system depend mainly on the properties of the material of the coating, as well as the method by which it is deposited on the surface.

The following are included in the basic requirements imposed on materials to be used as high-temperature protective coatings: refractoriness; high resistance to oxidation; thermal stability; low volatility; self-healing ability; low diffusion coefficients of the components of the gaseous medium, the tungsten and the alloying elements in the coating material; low diffusion coefficient of the material of the coating in tungsten; absence of low-melting eutectic and brittle intermetallic compounds in the system tungsten-substrate-coating material; good adhesiveness with the tungsten substrate; high-temperature strength; agreement of the thermal expansion coefficient of the coating material and the tungsten substrate; deformability; resistance to erosion and mechanical impact.

In some cases, such characteristics of the coating material as emissivity, thermal conductivity and electrical resistivity also have great significance.

None of the known materials satisfy all the enumerated requirements at the same time. Therefore, the selection of the material for the coating is mainly determined by the parameters of the medium in which the metal is proposed to be used. /96

The method of applying the coating plays a significant role; it should guarantee high-density, flawless coatings which have strong adhesion to the entire surface of the substrate. The substrate and coating should not be contaminated during the applications. The metal substrate should not be heated up to temperatures exceeding the recrystallization point in order to avoid a sharp worsening of the mechanical properties. The method should make it possible to apply a coating of uniform thickness on a product of a complex shape and of large dimensions under industrial conditions.

At the present, a large number of diverse methods has been developed for applying protective coatings on refractory metals and alloys. The methods most widely used are electrolytic deposition, plating, precipitation from the vapor-gas phase, diffusion saturation, flame and plasma spraying, submersion in a melt, electrophoresis, dross smearing with subsequent sintering or welding, vacuum metallizing, etc.

The selection of a method is basically dictated by the properties of the coating material, the dimensions and geometry of the coated product, and the conditions under which the coating is to be used.

Detailed reviews of the materials used for high-temperature coatings and the methods of applying them are found in [246 - 250].

The metallic substrate and the protective coatings should be considered as a single system. In the ideal case, the metal-coating system should combine the mechanical properties of the substrate with the high-temperature strength of the coating material. However, under the real conditions found in producing high-temperature protective layers for the surfaces of high-temperature metals, the properties of both composite parts of the system, as a rule, change as a result of their interaction.

The nature of the effect of high-temperature coatings on the /97
mechanical properties of high-melting metals is a problem of basic importance.

There are very little data in the literature concerning the mechanical properties of coated tungsten. The effect of some coatings on the strength and plasticity of a forged tungsten bar was investigated by Johnson et al. [251]. The results they obtained are given in Table 19.

TABLE 19. MECHANICAL PROPERTIES OF A FORGED TUNGSTEN BAR WITH VARIOUS COATINGS *

Test Conditions	Temperature ° C	σ_B Kg/mm^2	$\sigma_{0.2}$ Kg/mm^2	δ for length 20 mm,%	ψ, %
Without Coatings, in a mixture of air and nitrogen	20	114	82.5	0	0
	1095	26	23	16.0	92.5
	1370	20.8	20	10.7	56.9
	1370	24	22.5	13.5	96.5

continuation, Table 19

Test Conditions	Temperature °C	σ_B Kg/mm^2	$\sigma_{0.2}$ Kg/mm^2	δ for length 20 mm %	ψ,%
With chromium coatings, in air.	20	43.5	—	—	—
	1095	20.5	19	—	—
	1095	28	—	12.5	58.0
	1370	23	21.5	9.9	55.0
	1370	23	21.5	16.0	48.5
With a chromium and rhodium coating, in air	20	31	—	0	0
	1095	20	17.5	10.0	9.0
	1095	27.5	—	20.0	65.9
	1370	23	22	6.0	58.0
	1370	24	23	17.9	76.5
With a coating of type "W-2" (thickness of 0.13 mm)**, in air.	20	10.5	—	0	0
	1095	26.5	—	18.8	74.0
	1095	26.5	—	17.5	63.0
	1370	22	21	17.7	95.3
	1370	21.15	21	18.0	96.3

*The samples were kept at the test temperature for 30 minutes before the test.

** "W-2" is a silicide coating modified by chromium [246].

It can be seen from the table that all the tested coatings decrease the strength of tungsten at room temperature to a great extent. It does not seem to be possible to determine the nature of the effect of the coatings on the low-temperature ductility of tungsten according to these data. The metal substrate can have a substantial effect on the properties of the coating. Having spread /98 through the coating, the components of the coated alloy can change the characteristics of the protective surface layers. As a result, a coating which protects the pure metal very well can be completely unsuitable for protecting an alloy with this metal as the base. We also know of cases when the addition of some type of component into the composition of the alloy brought about an increase in the durability of the coating.

Unfortunately, there has not been sufficient attention paid to an investigation of the physicochemical mechanisms of the interaction of tungsten with various materials, or to a theoretical analysis of the problems of producing heat-resisting coatings for tungsten.

The development of standarized methods for testing the coatings is an important problem. At the present, coatings are generally tested under conditions which imitate the specific conditions under which they will be used. The test methods are described in detail in [252]. It is very difficult to predict the behavior of coatings during a change of the test parameters. While the dependences of the durability of the most promising coatings on the temperature and on the test time have been studied rather well, the effect of such factors as pressure, heat flux, composition of the gaseous medium, temperature gradients, mechanical stresses, etc., remains practically unknown. The results obtained in tests with coatings depend to a great extent on the size and shape of the sample, the thickness ratio between the coating and the substrate, the method of heating during testing, the rate of heating and cooling, and other characteristics of the method used. The properties of the coatings can change substantially even during an insignificant modification of the application method. All these circumstances complicate a comparison of the results obtained by different researchers.

Despite the fact that great attention has been given to investigations of methods of protecting tungsten from high-temperature oxidation, there is a very limited amount of information on the properties of protective coatings in the literature. Of the survey studies, the most interesting are [242, 246, 253]. /99

Judging by the data in the literature, the present development of coatings for tungsten is still in the laboratory stage. The average lifetime of the best coatings does not exceed 40 hours at 1650 ° C, 10 hours at 1870 - 1925° C and 2 hours at higher temperatures [254].

The existing high-temperature coatings for tungsten can be divided into the following basic classes: metal, oxide, cermet and coatings of solid metal-like and intermetallic compounds.

The principal advantage of metal coatings is their ductility. Moreover, such coatings generally have good adhesion with tungsten because of the formation of intermediate diffusion zones on the surface of the metal-coating interface. However, few metals have a sufficiently high resistance to oxidation at increased temperatures. Even at temperatures of about 1400° C, platinum and rhodium are relatively heat-resistant [246].

Such methods as electrolytic deposition, plating, and flame or plasma spraying are generally used for applying metal coatings on tungsten. Electrolytic deposition has been best mastered; its basic advantage is that the deposition process takes place at low temperatures. Various methods of applying galvanic coatings on tungsten are examined in [247, 255 - 257].

Galvanic chromium and nickel coatings guarantee effective protection of tungsten at relatively low temperatures (900 - 1200° C), and deposition of alternating layers of chromium and nickel give best results [246].

The optimum total percentages of chromium and nickel in such coatings are approximately 22 and 78%, respectively.

Reaction Motors developed a coating which consists of Au + (Ni - Cr) [246]. At temperatures of 1095 - 1375° C, this coating guarantees protection of tungsten for 500 hours. A coating consisting of molybdenum disilicide and the alloy Ni - Cr also has such heat resistance [246]. However, the durability of these coatings rapidly decreases at higher temperatures.

The coatings of alloys Ni-Si-B-Cr, Ni-Si-Cr-B-W, Ni-Cr-P and /100 Ni-Si-B developed by Reaction Motors and Wall Colmonoy protect tungsten in the temperature range of 1095 - 1375° C for 1 - 200 hours [246]. The maximum temperature at which it is possible to use the alloys as protective coatings is determined by their fusion or transition to unprotected oxidation.

Coatings of the alloy Al-Si are described in [246, 258]. These coatings are obtained by way of immersion of tungsten products into melts at temperatures of 1000 - 1300° C. During oxidation in air, a protective layer consisting of Mullite or sillimanite is formed on the surface of the alloys. Coatings made of Al-Si alloys sustain prolonged heating in air at temperatures of about 1400° C.

Coatings made of the metals of the platinum group are also used for protecting tungsten from high-temperature oxidation. Platinum and rhodium are of greatest interest, since they have rather high resistance in oxidizing media [246, 259].

Bückle [260] found that a covering made of platinum with thickness of 20 μm protects a tungsten sample at 1250° C for 30 min. Withers [247] gave data on the high-temperature strength of platinum coatings obtained by way of electrolytic deposition from melted cyanides. A covering with thickness of about 127 μm protected tungsten from oxidation at 1650° C for 5 hours.

American Machine and Foundry developed platinum and platinum-rhodium alloy coatings (of the type Pt-30% Rh) [246]. The lifetime of such coatings at 1650° C is 5 - 10 hours, while disintegration usually takes place because of the presence of point defects.

Rhodium coatings were investigated at New York University [198, 261, 262]. The surface layers of rhodium with thickness from 5 to 75 μm were obtained by electrolytic deposition from an aqueous sulfate bath. Such coatings increase the maximum possible temperature at which tungsten can be used in oxidizing media by at least 550° C [198].

The production of intermediate layers between the tungsten substrate and the protective rhodium layer contributed to a further increase in the high-temperature strength. Re, Cr and Si were used as /101 the materials for the intermediate layers [262]. Coatings consisting of layers of Cr, Si, Cr and Rh applied in sequence have the best protective properties [198, 261]. The layers were obtained by the electrolytic method (Rh) and by way of deposition from the vapor-gas phase (Cr, Si). Subsequently, there was diffusion annealing in a protected atmosphere, during which process the rhodium coating was fused. The chromium and potassium layers were applied as a diffusion barrier and were used for improving the adhesion of the coating to the substrate [261]. Moreover, the chromium and potassium affected the characteristics of the outer protection layer.

A tungsten wire with such a coating heated by an electric current disintegrates after one hour at 1640° C, or 20 minutes at 1650° C [198, 261]. The formation of low-melting eutectic and brittle intermetallic compounds does not permit the use of such coatings at higher temperatures for prolonged periods of time.

Thus, platinum and rhodium coatings can satisfactorily protect tungsten from oxidation in air at temperatures all the way up to 1650° C. The possibility of using the metals of the platinum group in order to protect tungsten at higher temperatures was analyzed in [246, 263]. The melting points of platinum and rhodium are lower than 2000° C. This, in itself, greatly decreases the value of these metals as materials for high-temperature coatings. Moreover, oxides of the metals of the platinum group are very volatile at the temperatures of greatest interest. The temperature dependence of the rate of weight decrease of Ru, Rh, Ir and Pt in oxidation which was obtained in a study Krier and Jaffee [259] is shown in Figure 30.

An essential disadvantage of coatings of noble metals is the high rate of interdiffusion of tungsten, platinum and rhodium. According to the data in [263], the total thickness of the diffusion zone in W-Pt and W-Rh systems reaches 110 - 200 and 60 - 90 μm, respectively, after one hour of annealing at a temperature of 1700° C, and the thickness of the intermetallic phases formed in this case is equal to 8 and 14 - 20 μm. The solid solutions and intermetallic compounds obtained as a result of diffusion are characterized by brittleness and low heat-resistance [246].

The development of barrier layers preventing interdiffusion of tungsten and the coating materials is very important in this regard. It was reported in [264] that rhenium, ruthenium and iridium layers prevent diffusion of tungsten most effectively. /102

There are almost no quantitative data on the diffusion of oxygen in metals of the platinum group. We can assume that oxygen has a high diffusion mobility in platinum and rhodium [246]. However, Dickinson et al. [263] noted that the penetration of oxygen through coatings made of metals of the platinum group is not a factor of primary importance.

The substantial difference in the thermal expansion coefficients of tungsten and of the metals of the platinum group can bring about a break in the continuity of the coatings during abrupt changes in the temperature regime [246].

Use of the recently developed hafnium-tantalum alloys could be very promising in protecting tungsten from high-temperature oxidation. These alloys preserve their resistance to oxidation at temperatures higher than 2200° C and, at the same time, have high ductility at room temperature. The properties of corrosion-resistant Hf-Ta alloys were examined in detail in [265].

The protective oxide film which is formed in oxidation of alloys containing 20 - 30% Ta consists mainly of a high-temperature tetragonal modification of HfO_2 stabilized by tantalum oxide. This oxide film has good adhesion to alloys, low volatility and high resistance to thermal and mechanical shocks. /103

The alloy Hf-27% Ta has maximum resistance to oxidation [265]. Tests at a temperature of 2095° C which were carried out with the aid of an oxyacetylene blowpipe showed that the oxidation of this alloy takes place according to the parabolic law for the first 10 - 15 min, and then almost linearly (Fig. 31).

A substantial increase in the resistance of the alloy Hf-27% Ta is achieved by adding molybdenum admixtures. It was found that, besides the alloy Hf-27% Ta, Hf-20% Ta and Hf-20Ta -2% Mo are very perspective [266].

The Hf-Ta alloys can be applied on tungsten by way of plating, plasma spraying, simultaneous deposition from the

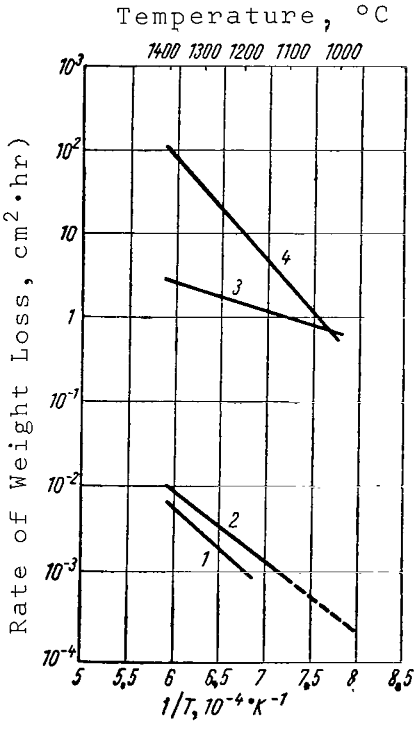

Fig. 30. Dependence of Rate of Weight Decrease of Metals of the Platinum Group: Rh(1); Pt(2); Ir(3) and Ru(4) in Oxidation in Air on the Temperature.

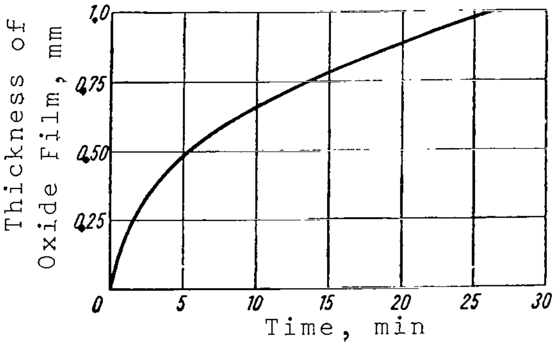

Fig. 31. Kinetics of Oxidation of Hf-27% Ta Alloys at a Temperature of 2095° C.

vapor-gas phase, etc. As mentioned in [265], plating guarantees very strong adhesion of the Hf-27% Ta alloy to tungsten. The Hf-Ta alloys were also applied on tungsten products by way of plasma spraying and in the form of slurry [267]. It was found that these alloys can be used as high-temperature coatings. However, there /104 are no data on the heat-resistance of coatings of Hf-Ta alloys on tungsten.

In [51, 254, 268], it was reported that coatings of tin alloys with aluminum have been used for protecting tungsten. At first, coatings made of Sn-25% Al and Sn-50% Al were developed for the purpose of protecting tantalum in the alloy Ta-10% W [246, 269]. These coatings can be applied by dipping, the slurry method, deposition, etc. The protective effect of coatings of this type is obviously due to the formation of an oxide film of Al_2O_3. The characteristic aspect of layers of Sn-Al alloys is the arisal of the liquid phase in them at the working temperatures. In all probability, it is precisely the presence of the liquid phase which causes the self-healing ability of these coatings. As mentioned in [51, 266], the lifetime of a coating made of an Sn-Al alloy on tungsten is 8 hours at 1375° C and 1 hour at 1895° C. The tests were carried out with the aid of an oxyacetylyne blowpipe. The temperature was measured by an optical pyrometer. During the entire test at 1375° C, there were signs of intergranular corrosion of the tungsten [51].

Refractory oxides are most stable in high-temperature oxidizing media. The possibility of using them as materials for high-temperature coatings is very interesting. The properties of high-melting oxides are examined in [246, 270, 271]. The characteristics of the oxide materials are given in Table 20.

TABLE 20. PROPERTIES OF REFRACTORY OXIDES [246]

Characteristics	Al_2O_3	BeO	CeO_2	Cr_2O_3	HfO_2	MgO	SiO_2	ThO_2	Y_2O_3	ZrO_2
Type of lattice	Hex.	Hex.	Cub.	Hex.	Monoclinic*	Cub.	Hex.*	Cub.	Cub.	Monoclinic*
Melting point, °C	2045	2570	2645	2340	2805	2800	1730	3200	2410	2685
Density, g/cm^3	3.98	3.01	7.13	5.21	9.68	3,58	2.32	9,69	4,84	5,56
Thermal conductivity at 1205° C cal/(cm·sec·degree)	0.013	0.041	—	—	—	0,013	—	0.005	—	0.005
Emissivity at 1205° C	0.35	0.42	—	—	—	0,28	0.65	—	—	0,45
Bending strength at 20°C, Kg/mm^2	24.5	17.5	—	—	14.0	10.5	10.85**	8,4	—	14.0

*Has crystalline modifications.
**Vitreous SiO_2.

In selecting the materials for the oxide coating, it is necessary to know the precise composition of the effective medium, particularly its humidity. For example, beryllium oxide, which has relatively low vapor pressure, can interact with water vapor at a temperature higher than 1650° C and thereby form a volatile hydroxide. /105

There are very little experimental data on the volatility of high-melting oxides. The results of measurements of the vapor pressure of some oxides at a temperature of 1730° C are given in Table 21.

TABLE 21. VOLATILITY OF OXIDES AT A TEMPERATURE OF 1730° C [246].

Material	Vapor Pressure, atm
Al_2O_3	$5{,}7 \cdot 10^{-6}$
BeO	$\approx 1{,}2 \cdot 10^{-7}$
MgO	$\approx 5 \cdot 10^{-6}$
ThO_2	$1{,}3 \cdot 10^{-10}$
ZrO_2	$\sim 10^{-6}$

Many high-melting oxides are inert, in relation to tungsten, up to very high temperatures. The maximum temperatures at which there is no substantial chemical interaction in tungsten oxide systems for 10 - 100 hours are given in Table 22 [246].

We should mention that data of such a type are indefinite, as a rule, since there is usually only a qualitative evaluation of the interaction. The media in which they are produced can greatly affect the results of such tests.

TABLE 22. MAXIMUM TEMPERATURES AT WHICH USE OF VARIOUS OXIDES CONTACTING TUNGSTEN IS POSSIBLE [246].

Oxide	Temperature, °C	Oxide	Temperature, °C
Al_2O_3	1980	ThO_2	2280
BeO	2100	TiO_2	1800
Cr_2O_3	1800	Y_2O_3	1980
HfO_2	2100	ZrO_2	1900
MgO	1980	$MgAl_2O_4$	1980
SiO_2	1600		

/106 The method of slurry application with subsequent sintering or fusion is usually used in order to apply oxide coatings on high-melting metals.

Horsfall [272] used high-temperature enamel in order to protect tungsten bars with diameter of 3.2 mm and length of 300 mm. The samples were heated by an electric current in order to anneal the enamel. The enamel coating adhered well to the tungsten surface and guaranteed satisfactory protection from oxidation for ten minutes at 1315° C. The composition of the enamel slurry was such: 9 parts by weight of $ZrO_2 \cdot SiO_2$; 1 of Al_2O_3; 0.5 of Co_3O_4; 0.02 of $H_2MoO_4 \cdot H_2O$ and 0.3 of dextrose.

A ceramic coating which protected tungsten from oxidation for 10 hours at 1650° C was developed by Bergeron et al. [273]. Before

the application of the coating, the samples, which were made of wires with diameter of about 0.8 mm, were carefully degassed by way of a brief warmup at temperatures of 1650 - 2095° C in a vacuum of $5 \cdot 10^{-5}$ mm Hg. A slurry of the following composition was then applied on the samples: 35 parts by weight of frit; 65 of zirconium, 4 of loam, 0.25 of bentonite and 45 of water. The frit consisted of 81% SiO_2, 2% Al_2O_3, 13% B_2O_3, 4% Na_2O. The coating was caked in a vacuum of $2 \cdot 10^{-5}$ mm Hg at temperatures of 1035 - 1425° C. The final fusion was carried out in a nitrogen atmosphere. Rather dense and solid coatings were obtained after a heating for 2 minutes at a temperature of 1565° C and nitrogen pressure somewhat exceeding 1 atm. The thickness of the coating was 0.15 - 0.20 mm. The samples were tested in a vertical muffle furnace heated by a gas burner. During the test at 1650° C, crystallization of the mono- /107
clinic zirconium oxide ZrO_2 was observed. We should mention that the temperature of the samples was measured by an optical pyrometer. Therefore, it could actually be much higher (up to 1735 - 1760° C). The mechanism of disintegration of the coatings was obviously linked with a gradual migration of oxygen towards the surface of the metal-coating division on which various tungsten oxides were formed: WO_2, $W_{18}O_{49}$, $W_{20}O_{58}$ and WO_3.

Flame and plasma spraying are widely-used methods of applying coatings of high-melting oxides. Some properties of Al_2O_3 coatings obtained by these methods are given in Table 23.

TABLE 23. PROPERTIES OF Al_2O_3 COATING [274]

Characteristics		Type of coating	
		flame	plasma
Coefficient of thermal expansion, $10^{-6}deg^{-1}$	at 25—300°C	53	55
	at 25—600°	66	69
	at 25—1000°	70	73
Thermal conductivity, Kcal/(m•hr•deg)	at 25°	0,15	0,21
	at 300°	0,20	0,28
	at 1000°	0,42	0,59
Total porosity, %		8	6
Density, g/cm^3		3,33	3,35
Real density, g/cm^3		3,60	3,66

As can be seen from the table, the coatings obtained by way of plasma spraying have less porosity than do the coatings applied by a flame torch. Moreover, the plasma coatings have increased strength of adhesion to the metals. A detailed review of the use of the method of plasma deposition for obtaining high-temperature coatings is found in a study by L.N. Usov and A.I. Borisenko [274].

Krier and Blocher [242] reported that a ThO_2 coating applied by a plasma jet guarantees protection of tungsten at a temperature of 2205° C for 0.3 hours. The test was carried out in air at a pressure of 20 mm Hg. Solar is developing coatings made of ThO_2 /108 and HfO_2 [275].

It was reported in [276] that thick reinforced oxide coatings applied on tungsten by way of smearing withstood tests imitating the re-entry of a spacecraft into the dense layers of the Earth's atmosphere, for which the temperature of the surface reached 2760° C. The lifetime of thin oxide coatings obtained by way of plasma deposition was 10 minutes at a temperature of 2480° C in a static air medium [276].

Oxide coatings obtained on tungsten by way of caking and fusion or by way of deposition have substantial disadvantages. As a rule, such coatings are characterized by a very low strength of adhesion to the substrate. An agreement between the coefficients of thermal expansion is an important factor determining the protective properties of coatings under the conditions of rapid changes in the temperature regime. Data on the thermal expansion of a number of oxides are given in Table 24, from which we can see that only zirconium has a thermal expansion coefficient at 25 - 1500° C which is sufficiently close to the thermal expansion coefficient of tungsten.

The possibility of using oxide coatings obtained by the methods of flame and plasma spraying is limited to a great extent by their porosity, which is usually 5 - 10%. When there is such porosity, the coating cannot serve as a sufficiently effective barrier preventing the penetration of oxygen to the metal surface.

The disadvantages of coatings applied in the form of slurry is that very high temperatures are required for their caking or fusion. Recrystallization of the tungsten is possible during these processes.

The complex oxide coatings developed by the firm "Thompson Ramo Wooldridge" are promising [51, 224, 240, 242, 277 - 286]. These coatings are applied on tungsten by way of successive precipitations under vacuum of layers of titanium, zirconium or yttrium, as well as zirconium alloys with boron and silicon alloys with tungsten in various combinations. Subsequently, there is diffusion annealing in a medium of wet hydrogen or in powders of Se_2O_3, ZrO_2 and SiO_2, during which there is regulated oxidation of the coatings. A dense oxide film which has good protective properties is formed /109 on the surface of the coatings during the process of high-temperature oxidation in air. The thickness of the coatings is 75 - 100 μm. Such coatings are characterized by high strength of adhesion to the tungsten substrate.

The best results were obtained in testing coatings whose composition in the oxidized state is described by the following: (Si-W)-O, Ti-Zr-(Si-W)-O and Ti-(Zr-B)-(Si-W)-O. There is no specific information on the compositions of these coatings. It is assumed that the oxide phase formed on the coating of Ti-Zr-(Si-W)-O is close in composition to tungsten orthosilicates WSi_2O_7, in which part of the silicon atoms are replaced by titanium and zirconium

TABLE 24. THERMAL EXPANSION OF TUNGSTEN AND REFRACTORY OXIDES [246]

Material	Temperature Range, °C	Thermal Expansion, %	Material	Temperature Range, °C	Thermal Expansion, %
W	25—500	0.215	ZrO_2 (Monoclinic)	25—500	0.31
	25—1000	0.465		25—1000	0.74
	25—1500	0.75		25—1050	0.79
	25—2000	1.07	HfO_2 (Monoclinic)	25—500	0.26
	25—2500	1.45		25—1000	0.57
Al_2O_3	25—500	0.36		25—1500	0.93
	25—1000	0.83		25—1700	1.08
	25—1500	1.37	ThO_2	25—500	0.41
BeO	25—500	0.36		25—1000	0.92
	25—1000	0.88		25—1500	1.50
	25—1500	1.52		25—1700	1.75
	25—2000	2.19	$ZrO_2 \cdot SiO_2$	25—500	0.18
MgO	25—500	0.61		25—1000	0.45
	25—1000	1.33		25—1500	0.78
	25—1500	2.23			
	25—1800	2.82			

atoms [242]. Some data on the high-temperature strength of coatings of this type applied to samples of sheet tungsten are given in Table 25. The samples were heated in a high-temperature air furnace. During the testing at 1650°C, the samples were cooled off to room temperature every 5 hours, and at higher oxidation temperatures they were /110 cooled off every hour.

TABLE 25. HEAT RESISTANCE OF COATINGS DEVELOPED BY THE FIRM "THOMPSON REMO-BULDRIDGE" [240].

Coating	Temperature, °C	Average Endurance, Hr.	Maximum Endurance, Hr.
(Si—W)—O	1650	30—40	47
	1815	20—22	22
	1895	10—12	15.5
	1925	6—7	7.5
	1980	0.2	0.5
Ti—Zr—(Si—W)—O	1650	30—40	72
	1815	20—22	26
	1895	14—16	17.5
	1925	9—10	15
	1980	0.5	1.5
Ti—(Zr—B)—(Si—W)—O	1815	20—22	22
	1895	15—16	16.5
	1925	6—7	7.5
	1980	0.5	0.5

As can be seen from the Table, these coatings have good protective properties at high temperatures. However, it was noted in [51] that, at a temperature of 870°C, their average endurance decreases roughly down to 2 hours.

The coatings (Si-W)-O and Ti-Zr-(Si-W)-O were also tested under conditions of decreased air pressures [284]. At temperatures of 1870-1925°C and constant pressures below 15 mm Hg, there was partial disintegration of the coatings. During tests in an air current with velocity of 610-855 m/sec (dynamic pressure of 16-20 mm Hg), layers of (Si-W)-O and Ti-Zr-(Si-W)-O protected tungsten from oxidation and erosion in a temperature range of 1595-1870°C.

The mechanical properties of sheet tungsten with coatings of (Si-W)-O and Ti-Zr-(Si-W)-O were determined in [276, 283, 284] at temperatures up to 1815°C. Obviously, the certain worsening of the mechanical characteristics was linked, not with a negative effect of the coating itself, but with the heating of tungsten up to high temperatures during the process of obtaining the protective layers [276].

Tests of tungsten with coatings of (Si-W)-O and Ti-Zr-(Si-W)-O /111
in the state of strain under loads reaching 20% of the yield points showed that, at a temperature of 1840°C, the coatings preserved their protective properties completely [284].

Coatings of this type were applied on the linings of nozzles of small rocket engines [240]. A tungsten lining with a Si-W coating obtained by simultaneous deposition is shown in Fig.32. The tests which were carried out gave encouraging results.

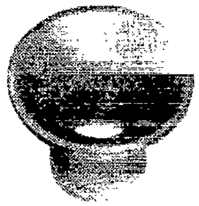

Fig. 32. Tungsten Nozzle Insert With Si-W Coating.

A certain increase in the high-temperature strength of the coating of (Si-W)-O was achieved by way of plasma deposition of the surface layers from mixtures of titanium nitride and boron nitride [284]. Such coatings guaranteed a brief protection of tungsten from oxidation at a temperature of 2040° C.

We should mention that in some studies the coatings developed by Thompson Ramo Wooldridge were classified not as oxides but as modified silicide coatings [9, 51, 241, 276, 287].

The diffusion of oxygen in various oxide materials was investigated with the purpose of evaluating the possibility of using high-melting oxides in producing coatings which protect tungsten for long intervals of time at temperatures above 2000°C.

It was reported in [280] that, at a temperature of 2000°C, only Al_2O_3 and, possibly, MgO have sufficiently low coefficients of oxygen diffusion to serve as effective barriers against a penetration, for a thickness of the coatings not exceeding 250 μm.

Smith et al [289] studied the diffusion of oxygen and stabilized 4% CaO in zirconium and hafnium oxides and in pure thorium oxide. The porosity of the materials was 5%. However, the effect of penetration of gas through the pores was insignificant because the pores were isolated.

The permeability constants (product of permeability times thickness) for $Zr_{0.92}$, $Ca_{0.08}$, $O_{1.92}$, $Hf_{0.86}$, $Ca_{0.14}$, $O_{1.86}$ and ThO_2 at /112 oxygen pressure of 25 mm Hg and temperatures of 1100-2050"C are expressed in the following way, g/(cm·sec):

$$P_{ZrO_2}\cdot l = 7.8\cdot 10^{-2}\exp\left[-\frac{55\,700}{(RT)}\right],$$

$$P_{HfO_2}\cdot l = 0.2\exp\left[-\frac{58\,500}{(RT)}\right],$$

$$P_{ThO_2}\cdot l = 4.65\cdot 10^{-3}\exp\left[-\frac{46\,100}{(RT)}\right].$$

The penetrability of ZrO_2 and HfO_2 is proportional to the square root of the oxygen pressure. The dependence of the ThO_2 penetrability on the pressure changes with a temperature change.

High rates of oxygen diffusion in high-melting oxides are a serious obstacle to the development of high-temperature protective coatings. It is possible that certain complex oxides have somewhat better properties.

Metal-ceramic coatings are developed mainly for the purpose of overcoming such characteristic disadvantages of oxide materials as low strength of adhesion to the tungsten substrate and unsatisfactory thermal stability. It is desirable to use solid cermets in those cases when high erosion-resistance is required, in combination with high-temperature strength.

Cermet coatings are usually applied on tungsten by methods of plasma spraying or simultaneous electrolytic and electrophoretic deposition. In obtaining coatings by the method of combined electrodeposition to the regular bath used in electrolytic deposition, particles of a ceramic material with dimensions up to 40-50 μm are introduced and sustained in suspension by interspersion.

Cermet coatings which consist of mixtures of metal-substrate and high-melting oxides are of great interest. When coatings in which the percentage of the ceramic component gradually increases with a withdrawal away from the metal surface are applied on tungsten, we can expect increases in the strength of adhesion and thermal stability due to the fact that the transition layers have intermediate /113 properties. Heat resistance of such coatings should be provided by the outer layer of the refractory oxide.

This principle was used by Buckle [260], who obtained oxide coatings on high-melting metals by way of sintering. The coatings which included layers of mixtures of metal-substrate and oxides in their composition had increased strength of adhesion.

It was noted in [275] that coatings obtained by way of plasma spraying which have a constant percentage of W and HfO_2 stabilized by 5% Y_2O_3 protect tungsten for 5 minutes at temperatures of 1980-2315°C under conditions of heating with an oxyhydrogen burner.

A coating made of the cermet $W-HfO_2-SrZrO_3$ was developed for the purpose of protecting tungsten nozzles of liquid-fuel rockets [290]. Test startups of the engines showed that this coating sustains a thermal stress arising during the initial heating and guarantees protection of tungsten from oxidation. Solar developed coatings of $W-ThO_2$ cermets [264]. The percentage of thorium oxide gradually increased from 10% on the surface of the base-coating division to 90% on the outer surface. These coatings, which were obtained by plasma spraying, were found to be promising in terms of protecting rocket noses made of tungsten, which are heated during re-entry into the dense layers of the atmosphere up to 2760°C.

Cermets of other types are also used as the materials of protective coatings. Coatings which are obtained by simultaneous electrolytic and electrophoretic deposition and which consist of Ni, Cr, Pt, Rh, and Co-W and Al_2O_3, ZrO_2, SiO_2, $MoSi_2$ alloys in various combinations protect tungsten from oxidation for approximately 15 hours at 1375°C [253]. The endurance of coatings made of chromium and various solid metal-like compounds or oxides in oxidizing media is 5-20 minutes at temperatures exceeding 1925°C [246].

Some data on the heat resistance of cermet coatings applied on tungsten by way of simultaneous electrode deposition are given in Table 26.

TABLE 26. PROTECTIVE PROPERTIES OF CERMET COATINGS [291]. /114

Material of Coating	Temperature, °C	Endurance, min	Coating Thickness, μm
$Cr-ZrB_2$	2205	10	75
$Pt-Rh-ZrB_2$ . .	2870	1	500—750
$Cr-HfO_2$	2620	5	125

Bartlett [292] reported that coatings made of the cermet $Cr-ZrB_2$ protect tungsten from oxidation at a temperature of 2125°C for

30 min. Cermet coatings have very high erosion resistance. However, their protective effect in high-temperature oxidizing media is usually comparatively brief.

Tungsten forms a number of high-melting solid metal-like compounds (carbides, borides and silicides). Some of them have high-temperature strength and erosion-resistance. The possibility of using these compounds as the materials of high-temperature protective coatings is of great interest. The properties of tungsten carbides and borides are given in Table 27.

TABLE 27. PROPERTIES OF TUNGSTEN CARBIDES AND BORIDES [248, 293].

Material	Lattice Type	Melting Point °C	Density (x-ray) g/cm^3	Micro-Hardness kg/mm^2	Thermal Coefficient of Linear Expansion (0-1200°C), $\alpha \cdot 10^6$
W_2C . . .	Hex.	17,34	2730	1780	3,84
WC . . .	Hex.	15,77	2870	923	5,2
W_2B . . .	Tetr.	16,72	2770	2420	—
α-WB . . .	Tetr.	16,0	2400	3700	—
W_2B_5 . . .	Hex.	13,1	2300	2660	—
WB_4 . . .	Tetr.	8,40	—	2663	—

Different variations of the method of diffusion saturation are usually used for obtaining coatings made of high-melting tungsten compounds.

The authors of [248, 294] obtained precipitated tungsten-substrate carbide coatings by rotating the samples in holders filled with lamp black. /115

It was established that the coatings consist of two layers: a W_2C layer bordering the metal and a thin outer WC layer. The thickness of the W_2C layer increased abruptly with an increase of the time and temperature of carbidization, while the WC layers grew very slowly. The boundary between the W_2C layer and the metal was continuous, which confirmed the conclusions drawn in [295] concerning the absence of a substantial difference in the rate of carbon diffusion along the grain boundaries of polycrystalline tungsten compared to the rate of diffusion through the grain.

According to the authors of [248], this type of boundary between W_2C and W was one of the reasons for the relatively poor adhesion of the carbide layers to the metal substrate. Moreover, the weak adhesion was due to a substantial difference in the specific volumes and coefficients of thermal expansion of W and W_2C. Layers whose thicknesses did not exceed 50-70 μm had satisfactory adhesion to the substrate.

Thin radial cracks penetrating toward the substrate were observed in the W_2C layers. The microhardness of the W_2C layers obtained at a temperature of 1900°C was 1650-1780 Kg/mm^2. A determination of the weight and thickness of these layers in dependence on the time showed that, at all temperatures of carbidization (1600-1900°C), the kinetics of the process corresponded to the parabolic law. The activation energy of carbon diffusion in tungsten was found to be equal to 104 ± 9.200 Kcal/mole.

A.P. Epik et al. [296] carried out an investigation of the high-temperature strength, wearing qualities and chemical stability of diffusion tungsten-substrate carbide coatings which were obtained by the method described in [248, 297, 298]. Tungsten samples with the carbide coatings were oxidized at temperatures of 600-1000° C. It was established that the carbidized tungsten samples oxidized more rapidly than did the pure metal, which agreed with the results of [299]. Table 28 gives data on the weight change of carbidized and pure tungsten in oxidation.

TABLE 28. RESULTS OF HEAT-RESISTANCE TESTS OF CARBIDIZED TUNGSTEN /116

MATERIAL	Weight Gain (mg/cm^2) at Various Temperatures		
	600°C	700°C	800°c
W	6	15	27
Carbidized W	2.4	22	100

The low heat resistance of tungsten carbides can be explained by the fact that gaseous oxides CO and CO_2, which disintegrate the scale and decrease its protective properties, are formed together with the tungsten oxides.

Data on the wearing qualities of carbidized tungsten are of interest. The tests for resistance to abrasion were carried out according to the method described in [296, 300]. The results obtained indicated that carbide coatings increase the resistance of tungsten to abrasion by a large factor.

There are data which indicate that coatings consisting of tungsten carbide and 8% cobalt, as well as coatings made of tungsten carbide in combingation with aluminum oxide, have the best protective properties [54].

Protective coatings made of tungsten borides are characterized by very high hardness. Some of them are resistant to oxidation at temperatures up to 1370°C [54].

The boronizing of tungsten in a powder mixture of amorphous boron and 3% NH_4Cl was described in [294]. A single-phase coating consisting of W_2B was obtained as a result.

A.N. Minkevich [301] studied the boronizing of tungsten and other metals in various media: (1) in a bath consisting of melted borax and about 40% boron carbide; (2) in a boron powder under vacuum at a pressure of $5 \cdot 10^{-4}$ mm Hg; (3) in a boron carbide powder under vacuum; (4) in a borax melt (electrolytic boronizing). The saturation of tungsten by boron took place at 1100-1500°C.

The diffusion layer on the tungsten consisted of W_2B, WB and W_2B_5. The layers obtained were found to be very resistant to wear. A test on an Amsler machine for 2 hours under a load of 50 Kg showed that the boronized layers on the tungsten lost 0.0175 g/m^2 in weight, while the cemented steel layer (30XGT) lost 0.046 g/m^2.

The process of tungsten boronizing was described in [248]. The /117
tungsten samples were put in a powder of 84% boron carbide and 16% borax and were annealed for 1-8 hours at 1100-1400°C. Two layers were formed on the tungsten as a result of the annealing: an inner layer which was close in composition to W_2B, and an outer one ($WB + W_2B_5$). Analagous data on the composition of the layers were obtained in [301, 302]. The micro-hardness of the inner layer, which was obtained at the maximum saturation temperature, was 2326-2460 Kg/mm^2, and that of the outer layer was 1960-2150 Kg/mm^2.

An investigation of the kinetics of the process of boronizing of high-melting metals showed that the increase in thickness of the diffusion layer and the weight gain of the samples were expressed by a parabolic dependence. The activation energy for diffusion and the temperature dependence of the coefficient of diffusion for boron in tungsten were determined according to the method described in [294, 295], and were equal to: $Q = 64$ kCal/mole, $D = 1.48 \exp(-32{,}000/T)$.

The oxidation of tungsten samples with boride coatings was investigated in [296] for temperatures of 600-1000°C. The method by which the coatings were obtained is described in [248]. The samples of tungsten with boride coatings had greater heat resistance than did pure tungsten (Table 29).

TABLE 29. HEAT RESISTANCE OF BORONIZED TUNGSTEN

Material	Weight Gain (mg/cm^2) at Various Temperatures			
	600°C	700°C	800°C	900°C
W	6	15	27	
Boronized W	0.3	4	20	55

The silicides of refractory metals are most advantageous as high-temperature materials. The production of protective surface layers made of molyblenum disilicide aids in increasing the maximum working temperature of molyblenum in oxidizing media up to 1800-1900°C [47, 242, 245, 246, 270, 287]. Silicide coatings have also been used successfully for protecting tantalum and niobium [242, 246, 253, 276].

The silicides of the transition metals are similar in their physicochemical properties to carbides, nitrides and borides. However, in contrast to the carbides and nitrides, they are not interstitial phases, since the ratio between the atomic radius of the silicon and the atomic radii of metals forming silicides greatly exceeds Hagg's ratio (0.59) and is almost always close to one, e.g., for tungsten disilicide $\frac{r_{Si}}{r_W} = 0.84$ [303]. Formation of the substitutional phases takes place under this condition. /118

Tungsten silicides were first obtained at the end of the last century by way of fusing together tungsten and silicon [303]. Subsequently, there were other means of obtaining silicides developed, the principal ones of which are now the methods of powder metallurgy.

Kieffer et al. [304] investigated the phases in the W-Si system [304]. They used samples prepared by the method of hot extrusion for the experiments. A structural diagram of the W-Si system (Fig. 33) was constructed on the basis of the results of a thermal analysis, as well as metallographic and x-ray diffraction analyses; this diagram was subsequently confirmed by Blanchard and Cueilleron [305], who investigated materials prepared by arc melting in a hydrogen atmosphere. The compounds W_3Si_2 and WSi_2 were detected in the W-Si system, and they melted without decomposition at temperatures of 2320 and 2165°C, respectively. It was found later that the compound which was identified as W_3Si_2 is more correctly represented by the formula W_5Si_3 [303, 306, 307].

It was suggested in [308] that there is a lower silicide W_3Si in the W-Si system which is isomorphous Mo_3Si and which relates to the structural type $\beta = W$. This phase was observed after annealing siliconized tungsten samples in air at a temperature of 1700°C. However, more careful investigations of tungsten siliconization in powders of WSi_2 and W_5Si_3 showed that the previous conclusions concerning the W_3Si phase were erroneous [309]. It was found that the errors in the x-ray diffraction analysis were due to the closeness of the values for the periods $c_{W_5Si_3} \approx 0.5a_{W_5Si_3} \approx a_x$ (a_x is the lattice parameter of the assumed W_3Si compound, calculated on the assumption that the Mo_3Si and W_3Si phases are isomorphous).

There are three eutectice in W-Si systems. The eutectic temperatures are equal to: 1400 ± 5°C (WSi_2-Si), ~2060°C (WSi_2-W_5Si_3) /119
and ~2250°C (W-W_5Si_3).

The principal properties of tungsten silicides are shown in Table 30.

It was shown in [304] that tungsten disilicide has high-temperature strength. The WSi_2 samples were prepared by the method of hot extrusion. The oxidation was carried out in air in a Tamman furnace at a temperature of 1500°C. The heat resistance of WSi_2 can be explained in terms of the formation of a vitreous SiO_2 film which has the self-healing ability.

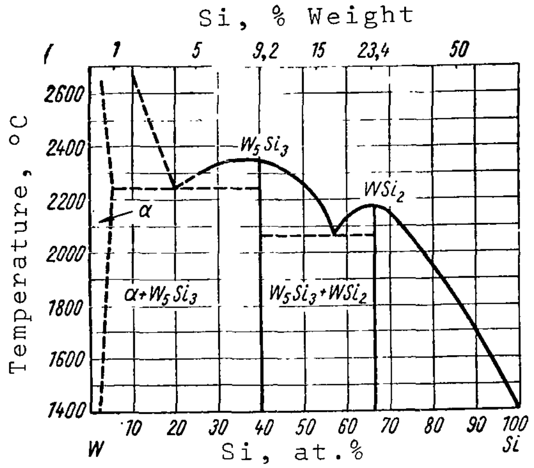

Fig. 33. Structural Diagram of W-Si System.

A mechanism for the formation of a protective film on silicides for 2 basic cases was proposed in works [248, 303] by Kieffer and Benesovskiy. In the first case, a volatile oxide of a metal (WO_3, MoO_3) is formed in oxidation of the the silicide, and, after this oxide is removed, there remains on the surface a film consisting mainly of SiO_2. As the remnants of the volatile oxides are removed, the film becomes more and more dense and preserves its protective properties roughly up to a temperature of 1800°C. At higher temperatures, the SiO_2 film collects into drops and strips the silicide surface. The oxidation of molybdenum and tungsten disilicides is of such a nature.

In the oxidation of silicides of metals which form non-volatile /120 oxides, a protective silicate layer arises only at definite temperatures and certain ratios between the percentages of SiO_2 and the oxide of the metal ($TiSi_2$), or a porous scale which has low strength of adhesion to the substrate is formed ($TaSi_2$, $NbSi_2$, $ZrSi_2$, $CrSi_2$).

The results of investigations of the high-temperature corrosion resistance of tungsten silicides obtained by the methods of powder metallurgy are given in [248, 303, 304, 310].

G.V. Samsonov and S.V. Dudova [303] constructed isotherms for the oxidation of WSi_2 and disilicides of certain other metals at temperatures of 500-1100°C. According to these authors, the disilicides decompose in the following way in order of decreasing resistance to oxidation at temperatures of 800-1000°C: $MoSi_2 > NbSi_2 > TiSi_2 > TaSi_2 > FeSi_2 > CoSi_2 > CrSi_2 > ZrSi_2 > WSi_2$.

However, this ordering of the high-temperature strength of disilicides contradicts the data of Kieffer [304] and Campbell [311], who found that isomorphous $MoSi_2$ and WSi_2 compounds have roughly identical resistance to oxidation.

The low heat resistance of tungsten disilicide observed by the authors of [303] can possibly be explained in terms of the imperfection of these samples, which were obtained by the method of hot extrusion. It is well known that there is partial contamination of samples with carbon during hot extrusion using graphite molds. It is difficult to obtain sufficiently dense and poreless samples

TABLE 30. PROPERTIES OF TUNGSTEN SILICIDES [293].

Characteristics	W_5Si_3	WSi_2
Silicon Content, wt.%	10.1	23.4
Structure	Tetragonal	Tetragonal
Lattice Parameters:		
a, Å	9.605	3.218
c, Å	4.964	7.896
c/a	0.52	2.454
Melting Point, °C	2320	2165
Density, g/cm^3	12.21	9.25
Heat of Formation, kCal/mole	46.5	22.4
Specific Electrical Resistivity, OM·cm		12.5
Transition Temperature of Superconducting State, °K	2.84	<1.2
Coefficient of Thermal emf, Z/deg		+0.2
Work Function, eV		3.38
Compressive Strength Ultimate, Kg/mm^2:		
at 20°C		126.9
at 1000°C		59.5
Microhardness, Kg/mm^2 (under load 50 G)	770	1074
Interaction with Mineral Additives	Interacts only with Lydrofluoric acid	Interacts only with Lydrofluoric acid
Interaction with Melted Alkalies	Decomposes	Decomposes

of the compounds which have strictly stoichiometric compositions /121
by this method. The presence of impurities and the porousity of the materials have an effect on the oxidation process and, as was shown in [312], can result in disintegration of the samples during oxidation in the range of low temperatures. This disintegration of WSi_2 samples obtained by methods of powder metallurgy was also observed in [310], where it was shown that the reason for this phenomenon, besides the porosity, could be a deviation from a stoichiometric composition.

Fitzer [313] first detected the phenomenon of low-temperature decomposition during oxidation of $MoSi_2$ samples prepared by the method of hot extrusion. He found that the molybdenum disilicide samples decompose during the course of several hours at temperatures of 400-600°C. The decomposition products were a loose powder of a greyish-white or greenish-yellow color. An x-ray diffraction analysis of this powder showed only molybdenum disilicide. A metallographic analysis showed that individual $MoSi_2$ grains were surrounded by the products in the ratio 1:3, as was a lower molybdenum oxide.

Using the external analogy with low-temperature decomposition of tin, Fitzer called the decomposition of molybdenum disilicide the "pest". /122

It was shown in [310] that WSi_2 samples obtained by way of caking in hydrogen at a temperature of 1550°C first increase in volume during oxidation in a low-temperature range, and then decompose, converting into a yellow powder. Tungsten disilicide was detected in the composition of this powder; this indicated that the decomposition took place until there was complete oxidation of the sample. The author of [310] confirmed that the resistance of the samples increases with an increase of the caking temperature, i.e., with an increase in the density and an increase in the percentage of silicon in the disilicide.

Decomposition of WSi_2 during oxidation in air is also observed when the disilicide is used as a protective coating for tungsten [261]. However, the decomposition of the coating should not be confused with the decomposition of isolated samples, since the metal substrate has a substantial effect on the state of the surface layer.

The phenomenon of oxidation decomposition of WSi_2 was examined in [312], where samples obtained by various methods were studied. It was shown that the decomposition takes place in a temperature range of 700-1000°C. The principal cause of the disintegration, obviously, was the presence of pores and cracks. Poreless WSi_2 samples obtained by the method of vacuum siliconization were not destroyed.

The general characteristic aspect of high-melting compounds subjected to the "pest" is brittleness and decreased (compared to the high-temperature range) resistance to oxidation. The oxide films formed at low temperatures do not have the ability to cover the surface defects or isolate the material from an oxidizing medium. As a rule, the oxidation products are nonvolatile at the temperatures of the "pest" and accumulate in the pores and cracks. The formation of the oxide is accompanied by an increase in volume, sometimes by a factor of 2-3, which brings about the arisal of internal stresses, by the effect of which there is a rapid growth of the cracks and, ultimately, disintegration of the materials.

In the case of high-melting compounds on metals, this effect can be deepened by the penetration of isolated cracks to the metal substrate. The intensive oxidation of the metal can accelerate decomposition of the coating. /123

Flawless homogeneous samples of high-melting compounds, the density of which is close to theoretical, do not decompose in the low temperature range. The rate of decomposition of porous materials, which depends mainly on the imperfectness of the sample, can also change in dependence on the purity and degree of homogeneity of the material, its stoichiometry, and the composition of the gaseous atmosphere. Intercrystalline oxidation and strengthening of the grain boundaries can make a substantial contribution to the "pest" phenomenon. It is doubtless that individual aspects of the "pest" phenomenon of high-melting compounds of various types can vary.

The oxidation decomposition of WSi_2 and other solid metal-like and intermetallic compounds in the low-temperature range can obviously be prevented or weakened in the following manner: decrease of the defects in the material; increase in their purity and degree of homogeneity; alloying of materials which increase their ductility and bring about the formation of oxide films with increased protective properties or critical temperatures; production of gas-proof protective layers on the surface of the manufactured product.

It was shown in a number of studies that the vacuum method of siliconization of metals is very advantageous; it allowed for obtaining both single-phase isolated samples of silicides and coatings of various thicknesses on metals and alloys [314, 324]. The basic advantage of this method is that silicides of very high purity and density can be obtained.

The kinetics and mechanism of oxidation in air of tungsten silicides obtained by the method of vacuum siliconization have been examined in [312, 325, 327].

A tungsten foil (99.95% W) with thickness of about 0.1 mm and a high-purity silicon powder (99.92%) were used for obtaining single-phase samples of tungsten disilicide. Difussion annealing was carried out at temperatures of 1200-1350°C in a vacuum furnace, where a small molybdenum bath with tungsten samples covered with silicon powder was placed. Diffusion of silicon in tungsten took place during the isothermal annealling process and silicide phases were formed. Samples containing only one WSi_2 phase could be obtained during prolonged periods of annealing. An additional soaking in silicon was necessary for homogenization of the samples. /124

The data of an x-ray diffraction analysis of the plates obtained indicated that a tungsten disilicide with the following lattice parameters was formed: $a = 3.2147 \pm 0.0001$ Å; $c = 7.8297 + 0.0003$ Å. The microhardness of the samples obtained was found to be equal to 1400 Kg/mm^2, while the hot-pressed tungsten disilicide samples had a microhardness equal to 1057-1090 Kg/mm^2 [303].

The high-temperature strength of WSi_2 was studied in air in a temperature range of 600-1800° C [325, 326]. The oxidation took place in furnaces with silicon carbide heaters and in a high-temperature furnace with molybdenum heaters protected by a coating of molybdenum disilicide.

We should make a distinction between the three temperature ranges in which the oxidation of tungsten disilicide takes place in different ways, and for which specific mechanisms for the formation of oxide films are characteristic. The existence of these ranges is linked with the properties of WO_3. Tungsten trioxide begins to evaporate substantially at temperatures of 900 - 1000°C, and its vapor pressure reaches 1 atm at 1350°C. Silicon dioxide is also formed during oxidation of WSi_2. The composition and protective properties of the oxide films are determined by the volatility of WO_3.

Irregular oxidation of the suface of the samples is observed during the initial test period at temperatures of 650-1000°C. A compact oxide film is formed during prolonged soakings. The dependence of the weight increase of the samples is described by formulas of the following types:

$$W = kt^m$$

(W is the weight change per unit surface, mg/cm^2; t is the time of oxidation, min; k and m are constants). The kinetics of WSi_2 oxidation in this particular range can be seen in Figure 34.

At higher temperatures (1150-1250°C), there is observed a weight loss of the samples, since WO_3 evaporates intensively, while the SiO_2 film formed does not have sufficient protective properties. Thus, two processes occur simultaneously; increase in weight of /125 samples due to the formation of non-volatile silicon oxide SiO_2 and decrease in weight due to the evaporation of the tungsten oxide WO_3. It is obvious that the process of evaporation of tungsten trioxide in this temperature range is predominant. A metallographic and x-ray diffraction analysis confirms that there are layers of crystalline silicon dioxide SiO_2 (cristobalite).

From the point of view of using tungsten disilicide as the material of heat-resisting coatings, the temperature range of most interest is that in which a protective film of amorphous silica is formed on the surface of the disilicide (1300-1800°C). At these temperatures, there is observed an increase in the weight of the samples, while the rate of oxidation is very low and roughly equal to that of molybdenum disilicide.

The investigations carried out in [325, 326] permit us to represent the mechanism of WSi_2 oxidation in this temperature range in the following way. During the initial oxidation period, oxides of the metal and of silicon are formed on the surface of the disilicide. During the formation of the solid film, some of the WO_3 dissolves in SiO_2 and a vitreous protective layer is formed. Subsequently, the access of oxygen to the surface of the disilicide is practically eliminated, and the rate of oxidation is determined by the rate of diffusion with the oxide layer. The disilicide expands below the SiO_2 film, and the lower silicide is formed $WSi_2 \rightarrow W_5Si_3 + Si$. The liberated silicon interacts with oxygen, which brings about a gradual increase in the thickness of the silica layer. Tungsten

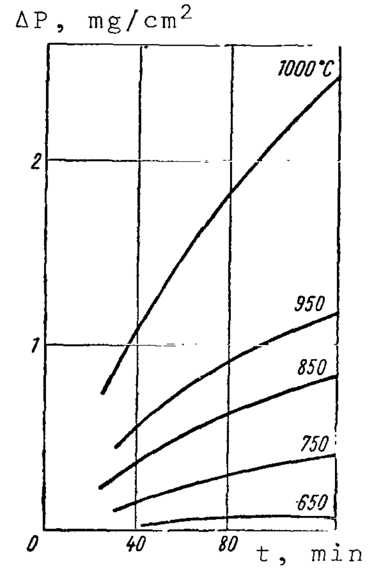

Fig. 34. Kinetics of Oxidation of Tungsten Disilicide in Air at Temperatures of 650-1000°C.

trioxide is formed during the initial observation period, and it takes place in the formation of the protective film: /126

$$2WSi_2 + 7O_2 \rightarrow 2WO_3 + 4SiO_2.$$

After the formation of the film, the diffusion through it and the reaction with formation of the lower silicide have a determinantal value. The existing experimental data do not permit us to draw any definite conclusions concerning the diffusion of components of the ternary system W-Si-Othrough the oxide film.

Thus, tungsten disilicide can be used for protecting a metal from high-temperature oxidation. The most valuable property of WSi_2 as the material of coatings is the self-healing ability in a vitrous protective SiO_2 film.

The brittleness of tungsten disilicide and the continuous diffusion process occurring during utilization in the conversion of the disilicide to the lower silicide at the metal-coating interface limits the possibilities of using WSi_2 coatings to a certain extent.

As was already mentioned, the principal factor determining the high-temperature strength of coatings is agreement between the coefficients of thermal expansion of the coating and the substrate. A theoretical analysis of the stresses arising in coatings due to a difference in the coefficients of thermal expansion shows, that, in using brittle materials as coatings, it is desirable that the coefficient of thermal expansion of the coating be lower than that of the substrate [237]. Otherwise, tensile stresses arise on the coatings during cooling, and can bring about cracking.

The results of an investigation of the effect of stresses arising because of a difference in the coefficients of thermal expansion on the imperfection of silicides layers on molybdenum are presented in [328], in which it is shown that cracking of the $MoSi_2$ layers is due to the fact that the silicide has a higher coefficient of thermal expansion than does molybdenum.

In using WSi_2 coatings for protecting tungsten, where the coefficient of thermal expansion of such coatings is roughly equal to $8.9 \cdot 10^{-6} deg^{-1}$ [329], there is a similar ratio for thermal expansions [246]. /127 Therefore, the durability of silicide coatings on tungsten is much lower in cyclical heating than under isothermal conditions.

Several methods of applying silicide coatings on refractory metals and alloys have been developed to the present. One of the best methods is the above-mentioned vacuum siliconization. Activating substances which accelerate the formation of silicide layers but, at the same time, contaminate the coatings and decrease their protective properties do not take part in the process of siliconization under vacuum.

The kinetics and mechanism of the siliconization process of refractory metals in vacuum were examined in [314-324], in which it was shown that the mechanisms of vacuum siliconization of Mo, Ta and W are basically identical.

The reactive diffusion in the W-Si system was investigated in [317]. It was shown that, in the siliconization of tungsten under vacuum of 10^{-5} mm Hg at temperatures of 1150-1350°C, saturated samples interact mainly with the vapor phase of silicon. The role of contact with solid silicon is secondary, since the area of the contact surface of the sample with the powder silicon is small, compared to the total area of the sample. The layers of silicide phases formed as the result of diffusion annealing arise in sequence from the lower silicide to the higher ones:

$$W + Si \rightarrow \text{sol. solut. Si in } W \rightarrow W\ Si_3 + Si \rightarrow WSi_2.$$

The disilicide is the principal component of the diffusion zone for a long period of annealing. In the W-Si system, there is primary diffusion of silicon through the silicide phases, i.e., the reaction of the formation takes place at the boundary with the metal. This can be seen in the presence of a texture of orientation correspondence in the layer of the silicides W_5Si_3, preservation of the relief of the initial surface of the metal on the surface of the silicide samples, the change in the shape of the samples from square to cross-shaped, and the closeness of the silicide layers to the metal.

As was shown in [322], isolated silicide phases grow according to the parabolic law. A deviation from this law is observed only in the initial state of the process, when the rate of formation of /128
silicide phases is greater than the rate of their diffusion growth. This can be explained by the fact that the rate of formation of the silicide phases is connected with the rate of the reaction on the surface, and the latter depends on the temperature, heat of formation of the compound, structure of the substrate, etc. The rate of growth of the diffusion layer is determined by the diffusion factor, which can be found from the kinetics of the growth. For this it is necessary to know the change in concentrations according to the thicknesses of the layers.

The siliconization in a section of silicon in which contacts of the sample where the silicon was eliminated was investigated in order to clarify the role of the vapor phase, the process of chemisorption, and the decomposition of the compounds in the general process of siliconization [319]. The investigation was carried out at temperatures of 1200 and 1250°C and residual pressure of 10^{-5} mm Hg. The obtained curves for the dependence of the thickness of the layers of tungsten silicides on the saturation time corresponded to the parabolic law (Fig. 35).

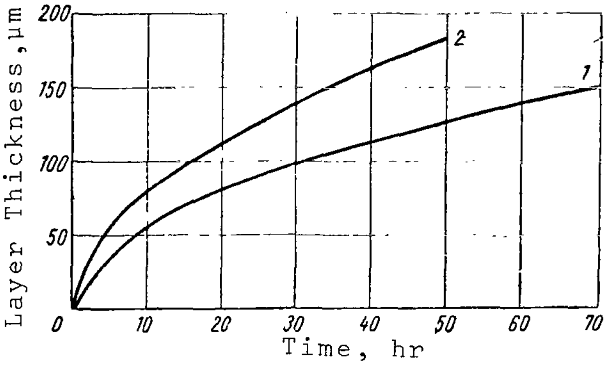

Fig. 35. Kinetics of Siliconization of Tungsten in a Section of Silicon at Temperatures of 1200°C (1) and 1250°C (2).

The disadvantage of the method of vacuum siliconization is the low speed of the process. Experiments on the siliconization of metals under the conditions of a temperature gradient between the saturated sample and the silicon were carried out in [319] for the purpose of investigating the possibilities of increasing the speed of vacuum siliconization. It was found that, in the case of the presence of a temperature gradient (the temperature of the sample was lower than the temperature of the silicon source), the rate of siliconization increased. This indicated that, during the siliconization of the metal in the silicon powder, when the sample and silicon were at identical temperatures, some of the silicon evaporated from the surface of the sample. The evaporation brought about a decrease in the rate of siliconization. /129

One of the most widely used methods of siliconization is saturation from the vapor-gas phase. The silicide coatings are obtained by hydrogen reduction of silicon haloids on the hot surface of a covered sample. Campbell et al. [311] obtained silicide layers by using the following reaction:

$$\mathrm{Me} + \mathrm{SiCl_4} + \mathrm{H_2} \rightarrow \mathrm{MeSi} + \mathrm{HCl}.$$

In order to obtain a coating consisting of WSi_2, the process was carried out at temperatures of 1100-1800°C and total pressure in the reaction zone equal to 1 atm. Fitzer [330] showed that the siliconization of tungsten in an atmosphere of $SiCl_4 + H_2$ at temperatures of 1000-1200°C also produces coatings which consist mainly of tungsten disilicide.

Subsequently, the method of siliconization in a medium of $SiCl_4 + H_2$ was improved many times. The authors of [331, 332] proposed a circulation method of siliconization, which can be distinguished by the repeated use of hydrogen chloride. An increase in the speed of the process and economy of materials are thus achieved.

The coatings can be obtained very rapidly by using the method of siliconization in a glow discharge in a medium of $SiCl_4 + H_2$ at a temperature of 1000°C [333]. Experiments showed that, for the optimum siliconization regime (pressure in the reaction chamber of 40 mm Hg, flow rate of gases no more than 0.5 l/min) the rate of siliconization in a glow discharge exceeds the rate of normal siliconization by the chloride method by a factor of 3.

The methods of siliconization of metals in solid powder mixtures have been widely used. Besides silicon, the composition of the mixture usually includes inactive admixtures, such as aluminum oxide or chamotte, which prevents the caking of silicon and its nearness to the surface of the metal. Siliconization can also be accomplished in powders of ferrosilicon or silicon carbide [334]. For activators of the diffusion in the gaseous /130
phase, NH_4Cl or NaF are included in the composition of the mixtures. In the USA, this method of applying the coatings is called "pack cementation" [247, 261, 335]. Pack cementation can be carried out in an inert or reducing atmosphere and under vacuum.

The results of an investigation of the effect of various admixtures on the process of tungsten siliconization in powder mixtures are given in [261]. It was established that Al_2O_3 does not affect the siliconization process, and NaF admixtures were found to be more effective than other haloids. High-quality coatings were obtained in siliconization in mixtures of silicon with 10% NaF and 5% NH_4Cl at temperatures of 1010-1065° C. The rate of tungsten siliconization under such conditions increased to a great extent, and the thickness of the coatings reached 380μm after 4-8 hours.

According to the data in [336] the disilicides are the principal components of the diffusion layers in siliconization of Ti, Nb, Ta, Cr, Mo and W in a powder of silicon with activating admixtures. The activation energy for diffusion of silicon in these metals was found to be less than that for boron or carbon. According to the authors of [336], these data can well be explained by assuming that the factor determining the activation energy of the process is the ionization potential of the diffused metalloid, and not its ionic radius.

It was shown in [337] that the growth of a WSi_2 coating on tungsten during siliconization in a powder mixture of Si and NaF takes place according to the parabolic law. The activation energy is equal to 25 kCal/mole. The temperature dependence of the rate of formation of the coatings is expressed by the following equation:

$$l_{WSi_2} = 0.96 \exp\left[-\frac{25\,000}{RT}\right] \ (\mathrm{cm \cdot min^{-1/2}}).$$

The method of silicification in the quasi-liquified layer is widely used in the USA [247, 338, 339]. This method is used on an industrial scale. The advantages of siliconization in a quasi-liquified layer are the increased rates of growth of the layer and /131 economy of the process. The rapid heat transfer and heating continuity characteristic of this method permit its usage for applying coatings on large structures of varying forms. The device used for siliconization of high-temperature metals in quasi-liquified layers is represented schematically in Figure 36 [247].

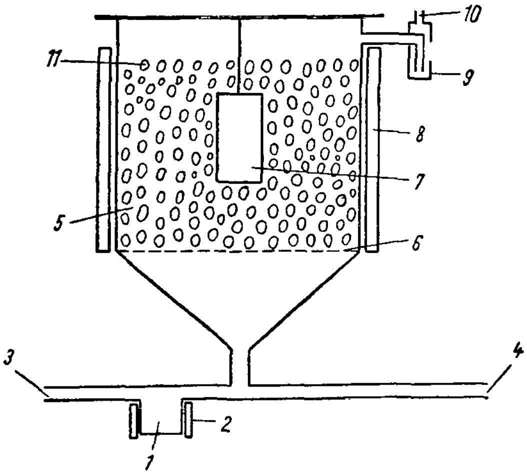

Fig. 36. Schematic Diagram of Device Used for Siliconization of Metals in a Quasi-liquified Layer: (1) Haloid supply; (2) Heater; (3) Carrier Gas Supply; (4) Liquifying Gas supply; (5) Liquified Region; (6) Grid Providing Uniform Distribution of Gas Flow; (7) Coated Detail; (8) Heater; (9) Trap; (10) Gas Outflow; (11) Liquified Particles of Coating Material.

The silicon particles are converted into a quasi-liquified state by way of penetration of a gaseous mixture of iodine and nitrogen in a vertical column, where the coated structure is also placed. The rising gases react with silicon and transfer it onto the structure. The processes which take place in applying the coating are described by the following reactions:

$$Si + 2I_2 \rightarrow SiI_4,$$

$$2SiI_4 + Me \rightarrow MeSi_2 + 4I_2.$$

Silicide coatings can be obtained by way of siliconization from the liquid phase. Coatings of satisfactory quality are obtained in dipping tungsten products into melts containing copper and 10-30% (weight) Si [340]. The obtainment of silicide coatings on tungsten by an electrolytic method is described in [341]. The manufactured products were dipped in a melt of an alkaline fluoride with an addition of 0.5-50 mol.% alkaline fluorosilicate, having a temperature of 600-800° C. Silicon rods were the anode and the coated detail was the cathode. /132

Investigations of the high-temperature strength of tungsten protected by silicide coatings are described in [51, 242, 246, 253, 261]. It was shown in [261] that a coating made of tungsten disilicide with a thickness of about 30 μm applied on a tungsten wire with diameter of 2 mm by way of siliconization in a solid-phase bath containing 10% NaF and 5% NH_4Cl protects the metal from oxidation in air at a temperature of 1815° C for 10 hours. It was found that the disilicide was decomposed and a lower silicide W_5Si_3 was formed at the boundary between the coating and the metal during its usage. A thin protective layer of SiO_2 was formed on the surface of WSi_2 layer. The principal cause of the disintegration of the coating was point defects, which appeared in the SiO_2 film during the initial stage of the formation of the vitreous layer due to the presence of local contamination. Self-volatilization of these defects did not take place because of the intensive self-healing of tungsten trioxide.

At higher temperatures, the endurance of the coatings decreases substantially. At 2000° C the silicide coatings protect a tungsten wire for 30 min [258].

The factors determining the upper effective temperature limits and endurance of silicide coatings on tungsten are the presence of eutectics between WSi_2 and W_5Si_3, melting and exaporation of the protective oxide film diffusing in the oxide film, and the reaction between the coating and the substrate. As was noted in [263], it is very difficult to determine the melting point of the oxide layer, even if we assume that it consists of pure silicon dioxide SiO_2. The viscosity of SiO_2, which permits the usage of silicide coatings at temperatures higher than the melting point of silicon dioxide (1730° C), is of great significance. The loss of SiO_2 due to evaporation is the reason for the decrease in thickness of the oxide film and preservation of the effective period of the coating.

Dickinson et al. [263] suggested that the loss of SiO_2 could take place as a result of simple evaporation and formation of volatile SiO in the reaction of silicon dioxide with the silicide on the surface of the oxide film-silicide interface. Bubbles of SiO passing through the viscous SiO_2 layer could destroy the coating. The durability of the silicide coating at high temperatures depends mainly on the thickness of the applied WSi_2 layer, since the process of diffusive decomposition of WSi_2 at the coating-metal interface /133 takes place during its utilization and is accompanied by the formation of a lower silicide W_5Si_3.

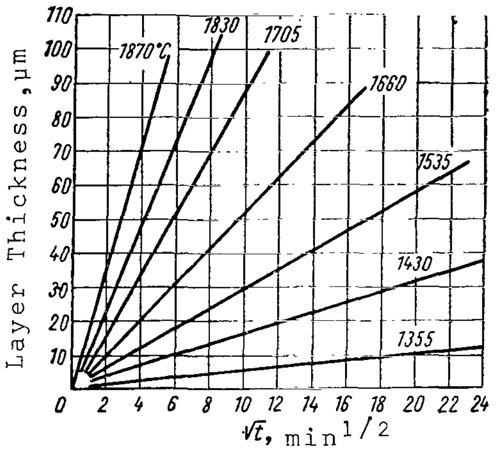

Fig. 37. Kinetics of the Growth of a W_5Si_3 Layer During Heating of Siliconized Tungsten.

An investigation of the diffusion in the WSi_2 system was carried out by Bartlett et al. [342]. Tungsten samples with a WSi_2 coating were annealed in nitrogen. The thickness of the coating was 60μm.

The kinetics of the growth of the W_5Si_3 phase before the disappearance of the WSi_2 phase is described by a parabolic dependence (Fig. 37). After the disappearance of the disilicide layer, the growth of the lower silicide is abruptly decelerated. The activation energy for the growth of the W_5Si_3 phase is 43 kCal/mole.

In examining the processes of decomposition of the higher silicide and formation of the lower one, the authors of [342] derived equations which aid in calculating the rate of decomposition of the WSi_2 phase and the rate of growth of the W_5Si_3 phase. The growth of the W_5Si_3 layer is determined by the following equation: /134

$$\frac{dx_{W_5Si_3}}{dt} = \frac{16}{21}\left(\frac{M}{\rho}\right)_{W_5Si_3} \frac{D_{W_5Si_3}\,\Delta c_{W_5Si_3}}{X_{W_5Si_3}}$$

Integration of this equation gives an expression for the change in thickness of the W_5Si_3 layer with time:

$$X_{W_5Si_3} = \left[\frac{32}{21}\left(\frac{M}{\rho}\right)_{W_5Si_3} \tilde{D}_{W_5Si_3}\,\Delta c_{W_5Si_3}\right]^{1/2}\cdot t^{1/2},$$

where $X_{W_5Si_3}$ is the thickness of the W_5Si_3 layer; $\left(\frac{M}{\rho}\right)_{W_5Si_3}$ is the ratio between the molecular weight and density of W_5Si_3; $D_{W_5Si_3}$ is the total diffusion coefficient in the W_5Si_3 phase; $\Delta c_{W_5Si_3}$ is the difference in concentrations at the boundaries of W_5Si_3 phase; t is the time.

Substituting the values of $\left(\frac{M}{\rho}\right)_{W_5Si_3}$ into this equation and comparing it to the graph of Arrhenius for the growth of the W_5Si_3 phase, we can represent the product of the total diffusion coefficient times the difference in concentrations by the following expression:

$$(\tilde{D}_{W_5Si_3}' \cdot \Delta c_{W_5Si_3}) = 2.95 \cdot 10^{-1} \exp\left(-\frac{Q}{RT}\right)\left(\frac{cm^2}{sec}\right)\cdot\left(\frac{mole}{cm^3}\right),$$

where Q=86 kCal/mole, which is twice grater than the experimental activation energy for the growth of the W_5Si_3 phase.

The expression obtained by the authors of [342] for the rate of growth of the W_5Si_3 phase was derived on the assumption that there is simultaneous diffusion of silicon and tungsten. However, the same researchers held later that the rate of silicon diffusion in the silicide phases is great, while the diffusion of tungsten is insignificant [337]. This was shown with the aid of experiments with an inert tracer of ZrO_2. Similar conclusions were drawn in [317].

Since a disilicide coating converts rapidly at high temperatures into a layer of the lower silicide during its usage, an investigation of the high-temperature strength of W_5Si_3 is of definite interest. /135 Such an investigation was carried out in [327]. The method of obtaining single-phase W_5Si_3 samples differed somewhat from the methods of obtaining tungsten disilicide. The difference was that the tungsten siliconization under vacuum took place, not in a silicon powder, but in a WSi_2 powder. The properties of the W_5Si_3 samples obtained in [327] are shown in Table 31. The characteristics of samples obtained by the method of hot extrusion are also given in the table for the sake of comparison [303, 343].

TABLE 31. SOME PROPERTIES OF THE LOWER TUNGSTEN SILICIDE.

Lattice Parameters		Density, g/cm^3		H_μ under a load of 100 G, Kg/mm^2	Litera -ture Source
a, Å	c, Å	Calculated	Experimental		
9.614	4.964	14.52	13.75±0.35	1290	[327]
9.645	4.969	14.55		770	[303]
9.615	4.964	14.52			[343]

The experiments which were carried out showed that the high-temperature strength of W_5Si_3 in air at temperatures of 500-1000° C is much inferior to that of the disilicide. If the change in weight per unit area after WSi_2 oxidation for one hour at 950° C is +0.8 mg/cm^2, then this value is equal to +20 mg/cm^2 for W_5Si_3 at 900° C. After a rather brief period of oxidation, the W_5Si_3 samples begin to decompose, as can be seen in Figure 38, and the time for decomposition depends on the temperature. The decomposition of the

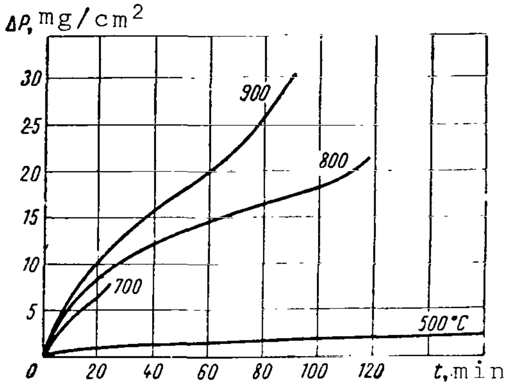

Fig. 38. Kinetics of W_5Si_3 Oxidation in Air at Temperatures of 500-900° C.

samples is linked with intercrystalline oxidation, which results in an accumulation of oxides along the grain boundaries, formation of cracks, and breaking-off of isolated grains. The segments of the curves for oxidation before decomposition of the samples represent parabolas.

The phase composition of the oxides formed was established with the aid of an x-ray diffraction and metallographic analysis (Table 32.)

Individual experiments /136 on the oxidation of W_5Si_3 samples at high temperatures (about 1200° C) for which a protective film of amorphous silica is formed on the tungsten disilicide showed that such a film is not observed on the W_5Si_3 surface. Obviously, the amount of silicon entering into composition with the lower silicides is insufficient for its formation.

TABLE 32. PRODUCTS OF OXIDATION OF THE LOWER TUNGSTEN SILICIDE.

Oxidation Temperature, °C	Results of Metallographic Analysis *	Results of x-ray iffraction nalysis
500	1. Dark blue layer	γ-WO_3
	2. Yellowish-green layer	Mixture of α-WO_3 and SiO_2 (α-tridymite)
600-900	1. Dark blue layer	γ-WO_3
	2. Yellow layer	Mixture of α-WO_3 and SiO_2 (α-tridymite)
1000	1. Dark blue layer	γ-WO_3
	2. Bright yellow layer	Mixture of α-WO_3 and SiO_2 (α-tridymite)
	3. White layer	SiO_2 (α-tridymite)

*The numbering of oxide layers begins from the substrate.

Silicide coatings have high-temperature strength at air pressures close to atmospheric. /137 There is very little information on the effect of pressure on the properties of silicides. It was noted in [91] that, at air pressures higher than 45 atm and temperatures above 1945°C, a diffusion coating WSi_2 ("Durak" type) does not guarantee tungsten protection. The behavior of silicide coatings on tungsten at decreased oxygen pressures is obviously similar to the behavior of $MoSi_2$ coatings. The authors of [246] gave data concerning the fact, at partial oxygen pressures lower than 5 mm/Hg, the oxidation of molybdenum disilicide is substantially accelerated. This is connected with the fact, that under conditions of high temperatures and low oxygen pressures, there is no formation of a protective SiO_2 layer, but a volatile silicon monoxide is formed.

A SiO_2 film obtained by preliminary oxidation of the silicide coating in air evaporated during subsequent heating under vacuum, and the protective properties of the coating decrease abruptly. In this case, two porcesses can take place simultaneously: evaporation of SiO_2 and decomposition of SiO_2 with the formation of SiO. As was shown in [263], a Langmuir equation can be used in order to evaluate the speed of these processes. Attempts at improving the high-temperature strength and ductility of tungsten disilicide were described in [344, 345]. Alloying admixtures of B, Cr, Fe and Al were added for this purpose. A partial replacement of silicon atoms by boron atoms brings about the formation of stable ternary phases. However, there is no substantial improvement of the high-temperature strength in this case.

A ternary compound of $W(Si, Al)_2$ which had a hexagonal lattice was detected in the system W-Si-Al. For aluminum content less than 13 at .%, there was no rearrangement of the tetragonal lattice, while the aluminum entered into the disilicide lattice and formed a solid interstitial solution [346, 347].

Identification of the oxidation of tungsten disilicide alloyed with aluminum at temperatures above 1700°C is of particular interest. In this temperature range, we can expect improvements in the heat resistance of WSi_2 due to an increase in the refractoriness of the oxide layer in the addition of aluminum oxide to SiO_2. The formation of high-temperature complex oxides $3Al_2O_3 \cdot 2SiO_2$ (mullite) and $Al_2O_3 \cdot SiO_2$ (sillimanite), having melting points of 1900 and 1810°C, respectively, is also possible. /138

An investigation of the effect of molybdenum disilicide on the high-temperature strength of WSi_2 is described in [304]. Alloys of WSi_2-$MoSi_2$ prepared by the method of hot extrusion were tested in an air current at a temperature of 1500° C for 4 hrs. It was established that admixtures of molybdenum disilicide increase the heat resistance of WSi_2. The best results were obtained in tests of materials containing 40-60% (weight) $MoSi_2$.

There are also data which indicate that WSi_2 - $NbSi_2$ alloys have increased heat-resistance in a temperature range of 1000-1200°C, [348]. Materials containing about 19.9 at .% Nb are most resistant to oxidation. N.V. Dokukina and F.I. Shamray maintain that an oxide layer which is formed on materials containing 18-24 at .% Nb and which consists of β Nb_2O_5 and SiO_2 is more dense, and has more adhesion to the substrate, than oxide films formed on non-alloyed WSi_2.

Krier and Blocker [242] reported that they developed a coating consisting of modified WSi_2 which protected tungsten from oxidation at a temperature of 1815°C for 30 minutes, for a thickness of 150 µm. The composition of the coating was not given. Prolonged protection of tungsten from oxidation at 1090-1480°C was guaranteed by a coating modified with boron [349].

A silicide coating of the type "W-2" modified with chromium guarantees protection of tungsten in an air current at a temperature of 1425°C for 1.5 hours [253]. For an alloy of W-50% Mo, the endurance of this coating is 60 hours at 1480°C [246]. An increase in the protective properties of silicide coatings when various modifiers are added to their composition is linked mainly with an increase in the ductility of the disilicide, a decrease in the difference of coefficients of thermal expansion for WSi_2 and W, and a change in the composition of the protective oxide film.

The endurance of the silicide coating can be improved by way of applying on the surface gas-proof ceramic layers. As mentioned in [245], to increase the effective temperature and endurance of /139 siliconized tungsten heaters on the surface of a silicide coating it is cecommended that high-melting enamels consisting of combinations of such high-enthalpy oxides as BeO, ThO_2, HfO_2, MgO, ZrO_2, CaO and others be applied.

Bergeron et al. [273] applied a ceramic coating which had best protective properties in application directly on the surface of tungsten across WSi_2 layers. This combined coating (WSi_2 and enamel) protected tungsten for several minutes at 1930°C. However, the zirconium dioxide entering the enamel composition interacted with the SiO_2 film formed on the disilicide, which worsened the properties of the coating. This was also mentioned in a study by Goetzel and Landler [261], in which it was shown that a ZrO_2 layer applied across WSi_2 layers by way of plasma spraying decreases the heat-resistance of the silicide coating.

The endurance of silicide coatings on tungsten might be greatly increased by way of producing diffusion barriers which decelerate the process of redistribution of the silicide phases. However, the high chemical activity and diffusion mobility of silicon produced exceptional difficulties in work in this direction.

Intermetallic tungsten compounds can be of definite interest from the point of view of high-temperature strength. It is well known that some beryllides and aluminides of high-temperature metals have very great high-temperature strength, due to the formation of thin protective films consisting mainly of BeO or Al_2O_3 [246, 350]. The diffusion coatings of these compounds are used for protecting tantalum and niobium [242, 246, 253, 269, 276].

The existence of three compounds in the W-Be system was established: WBe_2, WBe_{12} and WBe_{22} [351, 352]. It was reported in [271] that the tungsten beryllides WBe_2, WBe_{12} and WBe_{22} have a relatively low high-temperature strength in air. The surface recession of these materials under oxidation for 100 hours at a temperature of 1595° C exceeds 50 μm.

Pentecost [246] gave data on the high-temperature strength of a beryllide alloy whose composition is described by the formula "WBe_5". For 100 hours of oxidation at 1260° C, the specific weight gain of WBe_5 samples having a density equal to 93% of the theoretical one was 5.1 mg/cm^2. The surface recession of the alloy, calculated /140 according to the results of thermographometric measurements, did not exceed 15 μm.

There is no data on the properties of beryllide coatings on tungsten. In general, the principal factors which limit the use of beryllides as coating materials are the high values of their coefficients of thermal expansion and the rapid diffusion of beryllium in high-melting metals [246].

A large number of intermetallic compounds was observed in the W-Al system [353]. Apparently, the high-temperature strength of tungsten aluminides was not investigated.

According to the data of Krier and Blocher [242], they developed a binary aluminum coating which protected tungsten from oxidation for 2.5 hours at a temperature of 1925°C. The tests were carried out with the aid of an oxyacetylene blowpipe.

Such high-melting compounds as SiC, Si_3N_4, TiB_2, ZrB_2-$MoSi_2$ alloys, and certain other materials of this type can also be used for protection of tungsten [51, 54, 246].

It was noted in [91] that tungsten with a ZrB_2 coating obtained by flame spraying was tested under the conditions of a flight at supersonic speeds and low altitudes. The tests were carried out for 5 sec. The coating decelerated the oxidation process somewhat at low heat fluxes. However, at surface temperatures higher than 1945° C and pressures above 45 atm, the coating disintergrated at a catastrophic rate. At the present, there are many tungsten alloys which have much better mechanical properties than does non-alloyed tungsten. However, coatings are being developed for pure tungsten. There is only scattered information on the application of a rhodium coating on a wire of thoriated tungsten [262] and a silicide coating of the type "W-2" on an W-50%Mo alloy [246]. We should keep in mind that, in applying any type of coating on various tungsten alloys, its properties can change substantially, mainly because of the interspersion in the metal-coating system. It is possible that special alloying of highly-resistant tungsten alloys by components /141 which do not worsen the mechanical properties of the substrate and which have an advantage effect on the protective properties of the coating will aid in obtaining materials which have increased high-temperature strength and thermal stability.

As can be seen from the data presented, coatings of the metals of the platinum group protect tungsten satisfactorily from oxidation for relatively long periods of time at temperatures up to 1600- 1650°C, while at temperatures up to 1900-1950°C it is coatings of tungsten disilicide and oxide coatings of the type Ti-Zr-(Si-W)-O (which sometimes also relate to silicides) modified by metallic admixtures. At even higher temperatures, a brief protection of tungsten is achieved with the aid of coatings made of high-temperature oxides and cermets.

The problem of guaranteeing prolonged protection of tungsten from oxidation at temperatures higher than 2000°C still remains unsolved.

An experimental investigation of factors determining the effectiveness of high-temperature protective coatings for tungsten was carried out by General Telephone and Electronics [263, 354, 356]. Some of the conclusions drawn from this investigation are given in [224, 242, 246, 263, 276, 356]. The protective properties of the coatings depend mainly on the valotization of the material of the coatings due to evaporation or oxidation, the interaction of the coating with the substrate, diffusion through the oxide film, etc.

The high-temperature materials which form protective films of such oxides as ThO_2, HfO_2 or ZrO_2 during the process of oxidation are the most advantageous ones for high-temperature strength coatings proposed to be used at temperatures above 2000° C. In searches for such materials, General Telephone and Electronics investigated the following system: W-Hf-O, ZrN-ThN-O, Zr-Th-O, Zr-N-O, Zr-Y-O, Hf-Y-O, W-Hf-Re-O, etc. However, they obviously still have not succeeded in finding materials on which slowly-growing high-melting oxide films having self-healing ability could be formed. It is possible that the formation of such films can be found in the presence of the liquid phase in the coating. The systems Al-Sn-Cr and Al-Sn-La were investigated for this purpose. However, the results of these studies have still not been published. /142

We should mention that a substantial obstacle to the production of coatings which preserve the protective properties at temperatures above 2000°C is the high rate of oxygen diffusion in high-temperature oxides [288, 356, 357].

For a successful development of high-temperature coatings, it is necessary, first of all, to conduct fundamental investigations of the kinetics and mechanism of such processes as diffusion, oxidation and evaporation of the most promising materials.

CONCLUSION

The efforts of numerous researchers have brought about substantial progress in the study of tungsten oxidation and the effect of alloying on its mechanical and corrosion properties. There have also been significant achievements in the development of coatings to be used for protecting the metal from high-temperature oxidation. A vast amount of experimental data has been accumulated, and much has been done to explain the physiochemical mechanisms of various processes which determine the behavior of tungsten under high-temperature conditions. /143

A great deal of attention has been given to high-temperature oxidation of tungsten. The oxidation of tungsten has been investigated in a wide range of temperatures (from room temperature up to the melting point) and oxygen pressures.

Investigations of the kinetics of oxidation have shown that non-alloyed tungsten cannot be used at temperatures higher than 700° C without protective coatings in media which have partial oxygen pressures. However, for air pressures lower than 1 mm Hg, the rate of tungsten oxidation decreases substantially, which in some cases permits its usage in the fabrication of components to be effective for short periods of time.

The low resistance of tungsten to high-temperature oxidation is due mainly to the volatility of the oxides formed.

The data in the literature concerning oxidation of tungsten are inconsistent in part. An explanation of the causes for the inconsistencies and a construction of a single concept concerning the properties of tungsten oxides, the kinetics, and the mechanism of the oxidation processes are the principal tasks of the future research.

Tungsten alloying makes it possible to obtain materials which have exceptionally high-temperature strength. Several high-melting alloys have been developed whose short-time tensile strength exceeds 40 Kg/mm^2 at 1600° C and 20 Kg/mm^2 at 2000° C. Substitutional solutions, hardened by dispersed particles of precipitated carbide /144 phases, are the most resistant of all the existing alloys. Synthetic dispersed systems of the type $W\text{-}ThO_2$ also have high strength.

In all probability, the high-temperature strength of tungsten alloys can be greatly improved by perfecting the methods of obtaining and processing them. The obtainment of tungsten alloys which combine high-temperature strength and improved low-temperature ductility presents much greater difficulties. A decrease in the ductile-brittle transition temperature is observed in alloying tungsten with rhenium. Admixtures of Os and Ir guarantee a certain improvement in the ductility of tungsten. However, Re, Os and Ir are rare and expensive metals, and the possibilities of using them are very limited. Low tungsten alloys with rhenium and noble metals of group VIII containing dispersed admixtures of high-melting inert oxides are of great interest in this respect. The use of tungsten with alkali-silicate precipitates as the base of W-Re alloys gives interesting results.

Apparently, a promising possibility for improving the low-temperature ductility of tungsten is its deoxidation, which has yet not been studied as it should be. Rare-earth elements are good reducers for other metals of group VI (molybdenum and chromium).

As for the mechanisms of the effect of dissolved elements and dispersed phases on the resistance properties of tungsten, there are many ambiguities here. The construction of a physicochemical theory of tungsten alloying is a constant condition for rapid progress in the development of structural tungsten alloys.

Tungsten alloys which have high resistance to oxidation at temperatures above 1200° C have still not been obtained. Moreover, an alloying which brings about an increase in scale resistance usually results at the same time in a substantial decrease in the melting point and a worsening of the mechanical properties of the alloys. The most substantial increase in the resistance of tungsten to oxidation at high temperatures is achieved by way of adding elements and compounds which aid in the formation of stable tungstates or liquid oxide phases, on the surface of the alloys, which prevents intensive volatilization of the oxide of the metal. There is no theory which /145 holds for the development of scale-resistant alloys with bases of metals forming volatile oxides.

An interesting possibility of obtaining alloys which have increased resistance to high-temperature oxidation is based on the use of the effect of internal oxidation. By programmed formation of the alloy in media which have specific temperatures and partial oxygen pressures, we can obtain multilayer oxide structures in the zone close to the sample surface which have high protective properties for a corresponding selection of the components.

At the present, there are several types of heat-resisting coatings which provide an increase in the temperature limit to prolonged utilization of tungsten and oxidizing media up to 1600° - 2000° C. The diffusion coatings of tungsten disilicide are among the most promising. The principal problems which must be solved in order to and the use of silicide coatings are a prevention of their low- perature decomposition, an increase in the heat resistance at mperatures of 1700 - 2000° C, and improvement of their protective operties under conditions of high temperatures and decreased oxy- pressures. The endurance of silicide layers on tungsten can be eatly increased by way of modifying them with admixtures which in- rease the ductility of tungsten disilicide and improve the protec- ve properties of the surface oxide film. The working characteris- cs of silicide coatings can also be improved by applying layers various enamels on their surface.

At temperatures higher than 2000° C, coatings made of high-temperature oxides and cermets guarantee brief protection of tungsten from oxidation. A selection of the materials of coatings to be used at temperatures of 2000° - 3000° C is very limited. High-melting xides of the type ThO_2, HfO_2, ZrO_2 and various oxides of complex composition are of greatest interest here. Methods must be developed which make it possible to obtain poreless coatings of these compounds. Detailed investigations of the kinetic and physicochemical mechanisms /146 of the interaction of high-temperature oxides with tungsten, diffusion phenomena in high-melting oxides, and ternary structural diagrams of the type W-Th-O, W-Hf-O, and W-Zr-O should play an important role n the development of high-temperature coatings.

Liquid-phase coatings which have the self-healing ability an be of definite interest. In this case, there are no dif- culties linked with the brittleness of high-melting oxides and poor rrespondence between their thermal expansion and the thermal ex- ansion of tungsten.

At temperatures of about 3000° C, the use of porous tungsten im- egnated with silver, as well as combined materials of other types, s most promising.

At the present, heat-resisting tungsten alloys are being developed, as a rule, without a consideration of their compatability with heat-resisting coatings. In developing coatings, it is often not considered that they will be applied, not on pure tungsten, but on tungsten alloys which have perfected mechanical properties. The most fruitful method of producing high-temperature structural materials on a tungsten substrate is a combined development of heat-resisting alloys and high-temperature coatings.

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