PRINCIPLES OF HEAT-RESISTANT ALLOYING

E. V. Vasil'eva and D. A. Prokoshkin

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The heat resistance of metals can be increased by different methods – alloying of the solid solution; formation of dispersed intermetallic phases, carbides, and nitrides; creation of a network of secondary phases; plastic deformation; heat treatment; etc. Of major importance in the strength of a system are the properties of the matrix, the solid solution. Of special importance is the hardening of the solid solution of refractory metals used as structural materials at high temperatures.

Many investigators have noted an inflection on the curves of hardness, strength, elasticity, creep rate, and other properties of pure metals at temperatures of 0.4-0.5 T_{melt} [1]. The variation of the creep rate with temperature has a distinct inflection, pointing to a change in the mechanism of the process. The energetic parameter of creep at temperatures above 0.5 T_{melt} is close to the value of the activation energy of self-diffusion of the respective metal. Thus, one can conclude that self-diffusion has a controlling influence on creep [2]. This has been confirmed by tests of many metals and has the character of established law.

It is considerably more difficult to analyze the creep of alloys, since we do not have adequate studies of the principles of the influence of alloying elements on the strengthening and weakening of solid solutions at high temperatures. At present the principles of alloying heat-resistant alloys are based on the physicochemical properties and valence of the components, the ratio of atomic radii, the number of components, heterogeneity of the structure, and other factors.

However, we still lack adequate studies of the physicochemical interactions of components in the solid solution and the influence of alloying elements on the fine structure and strength of the system at different temperatures.

To explain the creep mechanism of alloys it is necessary to determine the influence of alloying elements on the diffusion mobility and creep and the relationship between these phenomena in different systems.

According to G. V. Kurdyumov [3], the diffusion mobility of metals depends on the strength of interatomic bonds and the structure. In approximating the strength of interatomic bonds one ordinarily uses the physical characteristics – the melting point, the heat of fusion, the heat of sublimation, mean square amplitude of the fluctuation of compressibility, elastic constant, etc. There have been numerous attempts to determine the energetic parameter of the diffusion of metals from these characteristics [4-8].

The existence of these dependences points to the determining role of interatomic bonds in the diffusion of metals and therefore its parameter can to some extent be used for the characteristic of the strength of alloys in the range above 0.4-0.5 T_{melt}.

We have analyzed the variation of the self-diffusion of metals with temperature from a new aspect, examining the data on the self-diffusion of 14 metals obtained in more than 50 investigations and plotting them as a function of homologous temperatures, i.e., the diffusion temperature in reference to the melting point (Fig. 1). In such a comparison the metals are to a certain extent in similar physicochemical states in reference to the thermal mobility of atoms and interatomic bonds.

Shown in the diagram are the experimental points obtained by the isotopic method. It should be noted that in determining the self-diffusion coefficient by the isotopic method the original work of

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The Institute of Metallurgy of the Academy of Sciences of the USSR and the section on physical chemistry and technology of inorganic materials held a jubilee scientific meeting April 4-6, devoted to the 50th Anniversary of the Great October Socialist Revolution, in which prominent metal scientists of the USSR reviewed the heat resistance of metals and alloys. One of these reports is published here – Editor. Institute of Metallurgy of the Academy of Sciences of the USSR; Bauman MVTU. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No.8, pp.2-7, August, 1967.

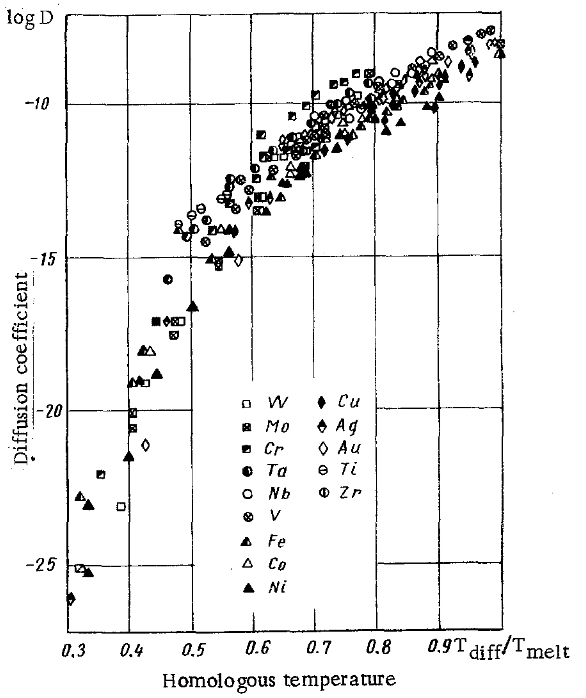

Fig. 1. Temperature dependence of self-diffusion of metals.

P. L. Gruzin [8], A. A. Zhukhovitskii [9], V. M. Golikov [10], and others has been of great importance.

More than 300 points are plotted on the diagram and, despite the different experimental conditions, purity of the materials, and methods of chemical analysis of the diffusion layers, the data obtained lie in a narrow band with little deviation. Thus, one can assume the self-diffusion coefficients of bcc, fcc, and hcp metals at homologous temperatures are quite similar. This dependence can be considered as the homologous diffusion rule.

Approximation of the temperature dependence of the self-diffusion coefficient on the Minsk-2 computer gave an equation of a cubical parabola:

$$-\log D = 9 + 43(1 - T_{diff}/T_{melt})^{2.8}$$

Analysis of Fig. 1 makes it possible to state the following:

1. The self-duffusion rate of different metals near the melting point is approximately the same, which depends on the close values of the interatomic binding energy. P. L. Gruzin's statement that the self-diffusion coefficient of metals near T_{melt} is approximately 10^{-8} cm^2/sec [7] has had numerous confirmations.

2. The self-diffusion rates of different metals at 0.4-0.5 T_{melt} have very similar values. Thus, the recrystallization temperature of pure metals established by A. A. Bochvar as 0.4 T_{melt} is functionally related to the homologous diffusion rule and consequently with the atomic interactions of metals.

3. The self-diffusion constant and interatomic bonds of bcc, fcc, and hcp metals have close values at homologous temperatures, which is important for the explanation of the high-temperature properties of metals.

If we compare the self-diffusion coefficients of certain refractory metals at 1100°C (~ 0.5 T_{melt}) we find that these metals can be divided into two groups – one group (molybdenum, tantalum, tungsten) with a diffusion mobility below that of niobium, and the other above it. A great deal of research has been done on the interdiffusion of metals, but the results are contradictory.

In our study of the interdiffusion of pairs of metals in groups IVa, Va, and VIa we found a rule which is definitely correlated with the homologous diffusion rule. The samples were carefully polished, clamped in pairs in a vise, and heated in vacuum for 20, 50, 100, and 200 h at 1100, 1300, 1500, and 1800°C. After cooling, microsections of the joints were prepared for metallographic and spectral analysis.

Provided that each pair of samples is subjected to the same conditions of temperature, time, and mutual contact, it is evident that the depth of penetration of atoms of each pair of metals in contact is determined by the rate of interdiffusion. The results of chemical analysis of the diffusion layers by the microspectral method in the Kamek apparatus are given in [11] for niobium paired with the metals of groups IVa, Va, and VIa.

The analysis showed that the depth of penetration of titanium and zirconium into niobium is substantial, while the depth of penetration of tungsten, tantalum, and molybdenum is small, which conforms with the homologous diffusion rule. Lowest of all the depths of penetration was that of tungsten, which has a very low self-diffusion coefficient at 1300°C, while the depth of penetration of niobium into tungsten is considerably greater.

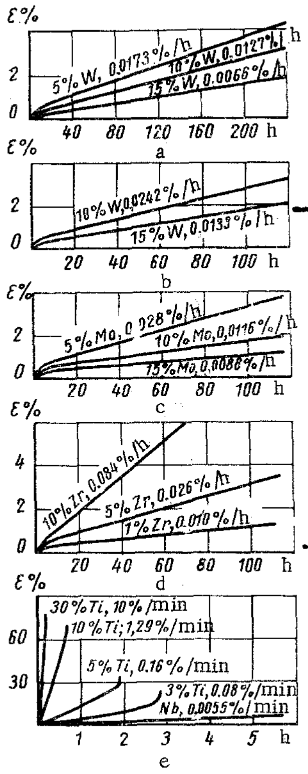

Fig. 2. Creep curves of alloys. a) Nb-W, 1100°C, 16 kg/mm^2, after extrusion; b) same, after annealing 5 h at 1500°C; c) Nb-Mo, 1100°C, 12 kg/mm^2, after annealing 5 h at 1400°C; d) Nb-Zr, 1100°C, 8 kg /mm^2; e) Nb-Ti, 1300°C, 6 kg/mm^2.

These results lead to the conclusion that the diffusion mobility of metals in solid solutions conforms with the homologous diffusion rule. Metals with lower melting points and, consequently, lower strength of interatomic bonds, manifest higher diffusion mobility at the same temperature. On the contrary, metals with higher melting points have lower diffusion mobilities. From this we conclude that it is possible to evaluate the strengthening and weakening influences of alloying elements on the basis of the ratio of their melting points.

It is interesting to consider the principles of the influence of alloying elements on the creep rate of the solid solutions formed in heat-resisting alloys. Niobium is very promising as a base-solvent, since its high plasticity permits alloying with a wide variety of components. With metals of groups IVa, Va, and VIa niobium forms continuous solid solutions at high temperatures, which also favors investigation of the rule at any degree of alloying.

For the investigation of the influence of alloying elements on creep the alloys of niobium with metals of groups IVa, Va, and VIa were melted in an arc furnace with consumable electrodes. The alloys were extruded and subjected to creep tests at 1100-1300°C in both the deformed and annealed conditions.

Figure 2, a and b, shows the creep curves of the Nb-W alloys. The higher the tungsten content, the lower the creep rate. Tungsten has the highest melting point of the metals and, as can be seen in Fig. 1, its diffusion mobility at 1100°C is the lowest. The low diffusion mobility of tungsten atoms remains in the niobium alloy [12] and predetermines the decrease in the creep rate of the alloy. The atomic radius of tungsten (1.40) is 4% smaller than that of niobium (1.45), which has comparatively little effect on the properties of the alloys.

Figure 2c shows the creep curves of Nb-Mo alloys. The melting point of molybdenum is considerably lower, and the diffusion mobility at 1100°C higher, than that of tungsten. Nevertheless, molybdenum strengthens niobium, reducing the creep rate. This is apparently due to the strengthening of the interatomic bonds and the reduction of the diffusion mobility of the system induced by molybdenum (more refractory than niobium), in conformity with the homologous diffusion rule and the results obtained on the interdiffusion of niobium and molybdenum. The atomic radius of molybdenum (1.39) differs from that of niobium by 4%, and therefore the size factor has no significant influence.

Testing temperature, °C	Creep rate (%/min) at 10 kg/mm^2			
	Nb	Nb + 1% V	Nb + 5% V	Nb + 15% V
1200	0.035	0.05	0.1	0.21
1300	0.418	0.530	0.865	1.56

In the table we give the creep rates of annealed niobium-vanadium alloys under a stress of 10 kg /mm^2 at 1200-1300°C. In contrast to molybdenum and tungsten, vanadium has a high diffusion rate compared with niobium, as was shown in the interdiffusion experiments [13], and thus weakens the interatomic bonds. Vanadium weakens niobium and increases the creep rate under the conditions investigated, thus confirming the rule of the dependence of the weakening influence of alloying elements on the melting point. The atomic radius of vanadium (1.34) is 8% smaller than that of niobium. Nevertheless, the size factor has no decisive influence on the creep rate under these temperature conditions; the diffusion process is the decisive factor. At temperatures below $0.5\,T_{\mathrm{melt}}$ the size factor has a notable influence. Thus, vanadium increases the heat resistance of niobium at 850°C [13].

The influence of zirconium is similar to that of vanadium. Figure 2d shows the creep rates of niobium alloys with 1, 5, and 10% Zr at 1100°C under a stress of 8 kg/mm^2. The creep rate increases with the zirconium concentration, in conformity with the higher diffusion rate of zirconium as compared with niobium. The atomic radius of zirconium is 10% bigger than that of niobium. The influence of the size factor is particularly notable at low zirconium concentrations.

Comparing zirconium and vanadium, which have very similar melting points, one notes their different effects on the resistance of niobium solid solutions. Vanadium, with an atomic radius smaller than that of niobium, has a greater influence on the properties of the solid solution than zirconium. Here appears the strong "disturbing" influence on the lattice and binding strength of the element with a smaller atomic radius. At testing temperatures above $0.5T_{\mathrm{melt}}$ of niobium the diffusion mobility of the alloying element is the decisive factor, in conformity with the homologous diffusion rule.

Titanium is a very low-melting alloying element. By comparison with niobium it has a very high diffusion mobility, which induces notable weakening. Figure 2e shows the creep rate of Nb-Ti alloys at 1300°C under a stress of 6 kg/mm^2.

As would be expected, titanium substantially weakens niobium, the creep rate increasing with the titanium concentration. The size factor in this case has no substantial influence, since the atomic radius of the solvent and solute is the same.

The results of the experiments lead us to the following conclusions.

Tungsten, with the highest melting point, strengthens the interatomic bonds the most, reduces the diffusion mobility correspondingly, and greatly reduces the creep rate. Tantalum and molybdenum have similar effects.

The opposite effect is obtained by alloying niobium with metals with a lower melting point and correspondingly higher diffusion mobility. The creep rates of the alloys increase regularly with decreasing melting points of the alloying element, particularly in the alloys with titanium.

On the basis of the data given here we can formulate an important principle of heat-resistant alloying which makes it possible to appraise the strengthening or weakening influence of elements on the heat resistance of solid solutions by the ratio of the melting points of the alloying element and the basic component.

In systems with the same or nearly the same structures of the components (bcc and fcc) alloying the solid solution with elements which have a higher melting point increases the heat resistance (decreases the creep rate) of the solid solution and, on the contrary, low-melting components reduce the heat-resistance properties. In this case the alloy has a similar structure.

The rule is confirmed by the data on the properties of heat-resistant alloys based on tungsten, tantalum, molybdenum, niobium, chromium, zirconium, titanium, etc.

It is indicated in the literature that strengthening depends on the electron concentration or on the different valences of the interacting elements.

The influence of the valence has been established for transition metals of groups I-VI in the first, second, and third long periods, in which the increase in binding energy is proportional to the valence of the elements. But in passing from one period to another this rule breaks down, since the strength of interatomic bonds increases with the atomic number in each group at the same valency.

It was found in [14] that trivalent aluminum dissolved in monovalent silver reduces the strength of the interatomic bonds. Both metals have the same crystal lattice and atomic radius, thus excluding the size and structural factors.

Monovalent copper increases the diffusion mobility of divalent nickel [15] and decreases that of trivalent aluminum. In addition, it is well known that divalent zinc, cadmium, and mercury increase the diffusion mobility and correspondingly weaken the interatomic bonds in solid solutions of copper, silver, and gold. Thus, the use of simple valency for evaluating the strengthening or weakening influence of elements leads to ambiguous results.

On the other hand, the melting point and diffusion mobility of metals are definitely related to the strength of interatomic bonds and can be used to formulate the principle of heat-resistant alloying of metals on the basis of the ratio of the melting points of the solvent and solute.

This principle of alloying makes it possible to select alloying components to obtain the necessary heat-resisting properties. It is of particular value for the development of alloys based on refractory metals, for which strengthening of the solid solution is one of the fundamental means of increasing the heat-resistance properties at high working temperatures.

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