

THE COLD BRITTLENESS THRESHOLD OF
REFRACTORY METALS

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UDC 669.15'29:620.16.4

Interstitial elements are considered the most harmful impurities in refractory metals of groups VA and VIA [1-5]. As a general rule, with increasing amounts of interstitial impurities the ductile-to-brittle transition temperature rises sharply, the resistance to impact loading decreases, and the technological properties are impaired.

Some investigators [2, 3] have concluded that all the refractory metals of groups VA and VIA are ductile at low temperatures when the concentration of interstitial elements (C, N, O, H) does not exceed the solubility limit at the testing temperature; an increase of the concentration of interstitial elements to the solubility limit at high temperatures also promotes strong embrittlement.

Thus, all interstitial impurities (as solute or second phase) are equally harmful for metals of groups VA and VIA. To prevent brittleness of these metals at low temperatures it is recommended that the interstitial impurities be eliminated.

However, a more detailed analysis of the experimental data cited in the review [3] and elsewhere [6-11] indicates that there are other reasons for the embrittlement of refractory metals of group VIA.

Let us examine the results on the effect of interstitial elements on the low-temperature properties of VA metals, leaving hydrogen aside, since the variation of its solubility in these metals with temperature differs sharply from that of the other interstitial elements.

Figure 1 shows the variation of the ductile-to-brittle transition temperature of niobium and vanadium with the concentrations of oxygen, nitrogen, and carbon.

The variation of the ductile-to-brittle transition temperature with the impurity concentration differs for each interstitial element. In niobium the sharpest increase in the transition temperature is induced by nitrogen, which has a relatively low solubility at low temperatures (see Table 1). Oxygen, which has a higher solubility than nitrogen at low temperatures, induces a smaller increase of the transition temperature.

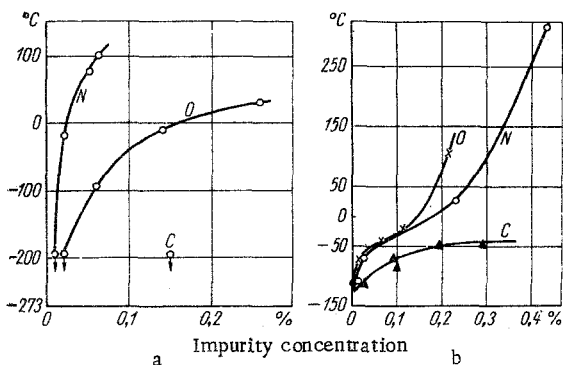


Fig. 1. Variation of cold brittleness with the concentration of oxygen, nitrogen, and carbon [3]. a) Niobium; b) vanadium.

Carbon, which is practically insoluble in niobium at temperatures near 20°C, has almost no effect on the cold brittleness temperature. The binary alloy Nb + 0.035 C (wt. %) melted in an electric arc furnace has a relative reduction in section of 50% at 200°C [6]. The presence of a small amount of carbide in niobium impairs only its capacity for plastic deformation at 20°C.

In vanadium the solubility of carbon at low temperatures is approximately an order higher than in niobium and is close to the solubility of oxygen and nitrogen; carbon raises the transition temperature to approximately the same extent as oxygen or nitrogen.

Thus, the ductile-to-brittle transition temperature of VA metals is increased only by those interstitial elements whose solubility in the solid state at low temperatures is a measurable value.

TABLE 1

Solvent	Solubility, wt. %	Limit solubility in solid state, wt. %	Source of data
Oxygen			
V	0,5 (1500° C)	1,25	[19]
Nb	0,25 (775° C); 1,0 (1100° C)	—	[12]
Ta	0,09 (500° C); 0,5 (1500° C)	0,7	[15]
Cr	0,03 (1350° C)	—	[12]
Mo	0,008 (1500° C)	0,012	[16]
W	0,005 (1700° C)	—	[3, 12]
Nitrogen			
V	1,0 (500° C); 1,0 (1500° C)	—	[12]
Nb	0,1 (500° C); 0,4 (1500° C)	2,5	[3]
Ta	0,2 (200° C); 0,7 (1600° C)	1,06 (2200° C)	[18]
Cr	0,028 (1000° C); 0,26 (1400° C)	4,0	[12]
Mo	0,002 (1500° C)	0,012	[16]
W	$0,19 \cdot 10^{-4}$ (1600° C)	$0,38 \cdot 10^{-3}$ (2400° C)	[12]
Carbon			
V	0,2 (1000° C)	~0,7 (1650° C)	[12, 34]
Nb	0,0025 (500° C); 0,05 (1500° C)	0,8	[17]
Ta	0,02 (1500° C)	0,42 (2600° C)	[13]
Cr	0,006 (500° C); 0,32 (1500° C)	—	[12]
Mo	0,001 (500° C); 0,03 (1650° C)	0,15 (2100° C)	[20]
W	~0,008 (1800° C)	0,06 (2600° C)	[20]

For niobium and tantalum [3, 7] these elements are oxygen and nitrogen; for vanadium they are oxygen, nitrogen, and carbon.

Analysis of the cold brittleness-interstitial impurity concentration curves indicates that the sharpest increase of the ductile-to-brittle temperature is in the region of solid solutions. The increase is less significant beyond the solubility limits for any of the elements. When the solubility of the interstitial element in metals of a given group is low (carbon in niobium) the ductile-to-brittle transition temperature for metals of group VA hardly increases. In this respect the effect of interstitial elements on the properties of refractory metals of group VIA at low temperatures is characterized as follows:

1. The influence of interstitial elements on the cold brittleness temperature of the metals is most harmful when they are in solution.
2. In the form of isolated particles of second phase the interstitial elements have a negligible influence on the cold brittleness temperature.
3. The ductile-to-brittle transition temperature of metals depends on the concentration of interstitial elements and follows Kurnakov's rule in the same manner as other properties.
4. The ductile-to-brittle transition temperature must be very sensitive to the structural condition of alloys. On quenching to the solid solution it must be higher than in slow cooling, leading to heterogenization of the structure.

All these statements can be applied as well to refractory metals of group VI, since the principles of the variation of the properties of metallic alloys with the composition that were found by N. S. Kurnakov are general for all alloys.

The solubility of interstitial elements in metals of group VI at low temperatures is infinitesimally small. Alloys of tungsten, molybdenum, and chromium containing a small amount of carbon, nitrogen, and oxygen should, in the equilibrium condition, have almost the same ductile-to-brittle transition temperatures as the respective basic components, i.e., the effect of these impurities on the cold brittleness temperature of metals of this group should be very slight (approximately the same as in the Nb—C system).

However, the experimental data show that the cold brittleness temperature of cast molybdenum increases very sharply with increasing amounts of oxygen and depends very little on the concentration of other elements. An increase of the cold brittleness temperature (by about 150°C) when the carbon concentration was increased from 0,004 to 0,008% has been noted in cold worked metal [9].

The transition temperature of chromium is raised substantially by nitrogen and carbon [8, 10, 11, 21-23], while oxygen has almost no effect. Nitrogen sharply increases the transition temperature of polycrystalline chromium only in the cold worked and quenched conditions; when chromium is cooled in the furnace, nitrogen has no effect [8, 23].

In a study of the effect of interstitial elements on the low-temperature properties of single crystals and polycrystalline aggregates of tungsten it was found [24] that the transition temperature depends more on the grain boundaries than on nitrogen, oxygen, or carbon impurities.

Thus, the cold brittleness temperature of VIA metals is not strictly dependent on the concentration of interstitial elements. In addition, its variation with the heat treatment follows Kurnakov's rule.

This serves as the basis for the assumption that impurities of most interstitial elements do not have a direct influence on the plastic properties of refractory metals of group VIA. The negative influence of small quantities of them on the cold brittleness temperature of tungsten, molybdenum, and chromium is indirect and is the result of the presence of other impurities that also determine the properties of VIA metals at low temperatures.

It is considered that the embrittlement mechanism of refractory metals of group VIA is of the adsorption type [3-5, 25]. According to data in [3-5], the main participants in adsorption enrichment of the grain boundaries are interstitial elements, since their atoms have a high diffusion mobility by comparison with the atoms of substitution elements.

Their segregation in the grain boundaries around crystallites results in shells of hardened solid solution consisting of atoms of the base metal and the interstitial elements that block the movement of dislocations and thus lead to brittle fracture of the metals [4]. However, atoms of interstitial elements are not independently adsorbed in the grain boundaries [26], which was confirmed in [27, 28]. Substitution elements are the main participants in adsorption enrichment of the intergranular boundaries. The segregation of interstitial elements in the grain boundaries of polycrystalline materials, as was shown in an investigation of the brittleness of grains of intermetallic compounds [29, 30], can occur only under certain favorable conditions — in the presence of impurities with a high chemical activity toward the interstitial elements. The statement in [4] that shells of hardened solid solution consisting only of interstitial atoms and atoms of the base metal are formed around grains of refractory metals of group VIA gives rise to doubts.

The first shells of solid solution to form in the grain boundaries of these metals should be formed from atoms of the base metal and the substitution elements existing in it. The latter, in the case of an elevated chemical activity toward interstitial elements as compared with the base metal, can act as a sort of "internal getter" [3] and promote additional complication of the chemical composition of these shells.

The interstitial elements in metals of group VIA can be considered as associated impurities, the concentration of which depends not so much on the limits of their solubilities in the solid solution as on the concentration of substitution elements that interact with them. This pertains to oxygen and nitrogen, the basic components of the atmosphere, with which all metals come in contact to one degree or another during metallurgical processing.

The effect of the purity of the metal on the amount of solute oxygen has been shown in the case of iron [32]. In very pure iron, obtained by zone melting, oxygen is almost insoluble; in contaminated iron, obtained by the electrolytic method, the solubility is quite measurable.

Intercrystalline internal adsorption of impurities, as is well known, can occur in any metal, including metals of group VA. However, it was found in [32] that the plastic properties of VA metals after annealing at temperatures of intensive development of intercrystalline internal adsorption not only do not decrease but even increase.

The reason for such a difference in the metals of groups VA and VIA is the difference in the solubilities of interstitial elements, particularly oxygen and nitrogen. In view of the exceedingly slight solubilities of these elements in chromium, tungsten, and molybdenum at low temperatures, the atoms of these metals are almost incapable of retaining the atoms of interstitial elements around them. Therefore, when atoms of interstitial elements penetrate into the depth of these metals (into intercrystalline areas) they interact with atoms of impurity elements and are strongly held by electrostatic attraction.

The solubility of oxygen and nitrogen in metals of group VA is far higher than in metals of group VIA. For this reason the atoms of nitrogen and oxygen penetrating into these metals are distributed evenly throughout the body of the grain and are held in that position by the atoms of the base metal. As the result, the grain boundaries in metals of group VA are enriched only in impurities of substitution elements. Therefore, no significant change in the low-temperature properties of VA metals is observed even at relatively high

impurity concentrations in intercrystalline transition zones. The fact that a large volume of the body of the grains is free of them even promotes an increase of ductility.

It should be noted that under favorable conditions such impurities can conduct oxygen and nitrogen into the bulk of the metal and promote embrittlement of refractory metals of group VA.

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* Source unclear in Russian original [Publishers].