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EFFECT OF IMPURITY ELEMENT SUBSTITUTION ON THE FAILURE BEHAVIOR OF A W–Ni–Fe ALLOY

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As is known, a failure crack is capable of propagating in a jumplike fashion, i.e. with periodically repetitive retardation and subsequent rapid shift at almost suppressed plasticity [1].

Fractographic studies [2] of single- and polycrystalline fractures of metal specimens of a bcc lattice showed that such crack motion corresponds to formation, on the failure surface, of regions characteristic of slow crack growth below a critical dimension followed by their propogation in an avalanchelike fashion. In the region of rapid crack movement, the inhomogeneity of previous plastic deformation and structural defects, so-called notches, play an important role. The study conducted in [3] on samples of different notch types led to observation of a distinct tendency for acceleration of crack displacement according to increase of notch sharpness.

The probability of notch formation in materials, i.e. regions of high local deformation, depends particularly on the technique of production, which causes possible inhomogeneities in impurity, structure, composition, and distribution.

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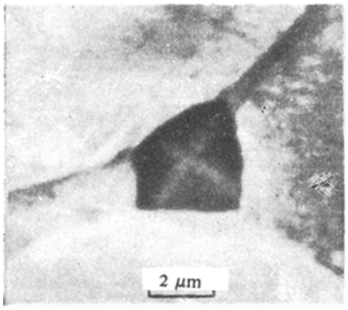

Fig. 1

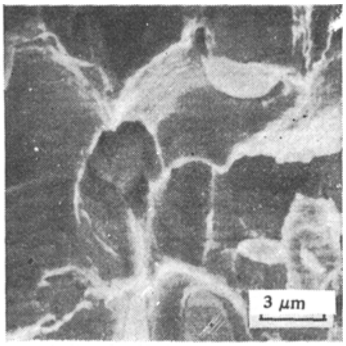

Fig. 2

Fig. 1. Structure of inclusions. Scanning electron microscope representation illustrated by reverse electrons.

Fig. 2. Deformation and failure behavior of material containing nonmetallic inclusions.

The present work is devoted to study of the content, shape, size, and chemical composition of nonmetallic inclusions and substitutional impurity segregation in a W–Ni–Fe alloy, as well as their effect on failure behavior of this alloy. We studied metallographic polished sections and fracture surfaces of specimens of this alloy after tests by standard tensile methods. We used a tensile rate of 1 mm/min in the temperature interval 77 to 273°K. We also studied specimens after three-point bending tests under a static load in the temperature interval 77 to 273°K, including recording of plots.

In industrial practice, the starting material for tungsten production is the trioxide, whose degree of purity is determined by the scheme of raw-material processing. According to [7], WO_3 contains (by mass) up to 0.09% of impurities. According to extent of removal in the tungsten production process, these can be placed in the following sequence: As, P, KCl, and Ca. Associated with tungsten are K, Si, Al, Fe, and Mo [5, 6].

The nickel and iron used for preparation of the alloy are powders or compounds (carbonates, nitrates, and oxides) and contain (by mass) up to 1.09% of impurities.

In performing the present work, we prepared alloys of 90% W, 7% Ni, and 3% Fe using commercial tungsten anhydride, iron oxide, carbonyl nickel, and powders of the latter metals. We conducted the investigations by quantitative metallographic analysis, x-ray fluorescence microanalysis, and scanning electron microscopy with simultaneous qualitative microanalysis of chemical composition.

Sample metallographic analysis indicated that the method and conditions of producing the alloy charges affects the size and shape of inclusions. In an alloy whose charge was produced by joint reduction of oxygen-containing compounds as components, the inclusions have a spherical shape and a size not greater than 10 μm (Fig. 1a). In an alloy prepared from separately reduced powders, we noted inclusions in the form of spheres, polyhedra, and shapeless formations up to 45 μm in size.

The particles analyzed in the alloy are distinguished not only in shape, but also by chemical composition (Table 1). Comparison of the chemical x-ray fluorescence data (Table 1) and the metallographic analyses (Fig. 1 and 2) gives reason to consider that the inclusions in the alloy are inhomogeneous in composition and represent complex oxides of the system with multiphase structures.

The results obtained do not contradict known reports on the nature and content of impurities in tungsten [4, 8]. The compositional inhomogeneity, multiphase character, and dimensions of the inclusions are determined by the valence of the chemical compound comprising each impurity in the tungsten (tungsten anhydride). They are also determined by interaction with themselves and with charge components during the various stages of alloy production.

The nonmetallic inclusions, whose specimen volume content varies from 0.1 to 0.4%, are distributed in the grains and at the boundaries of structural compounds.

TABLE 1. Chemical Composition of Nometallic Inclusions in a W-Ni-Fe Alloy

Mass fraction of elements (%)								Comments
Na	Al	Si	Ca	Ti	Fe	Ni	W	
5,61	9,48	19,48	12,77	3,00	1,81	3,56	0,82	Alloy charge prepared by mixing and joint reduction of oxygen-containing alloy component compounds
3,22	5,08	18,57	21,81	15,94	1,48	0,88	1,66	
2,72	4,20	8,97	20,91	12,25	0,61	1,20	3,60	
2,88	4,25	8,67	22,38	19,04	0,61	1,28	2,40	
4,52	11,19	18,93	9,56	10,08	0,00	0,00	0,3	Charge prepared by mechanical mixing of metallic alloy component powders
1,36	11,68	21,1	10,15	2,56	0,1	0,1	0,00	
0,00	0,00	46,74	0,00	0,00	0,00	0,00	0,00	
0,00	9,43	22,06	23,65	0,92	0,06	0,22	0,00	
0,00	3,39	21,02	19,78	1,18	0,00	0,01	0,00	
0,23	0,20	0,49	0,24	0,25	0,38	4,75	68,56	

The shape, size, chemical composition, and consequently properties of the nonmetallic inclusions, and also their distribution in the alloy bulk, substantially affect the deformation and failure behavior. One of the distinguishing characteristics of composite materials (to which the alloy under study belongs) is a microscopically inhomogeneous deformation character [9, 10]. In a heavy W–Ni–Fe alloy, with a structure comprised of refractory compounds dispersed as spherical particles, the deformation inhomogeneity is caused by the variable thickness of the binder between the grains of the refractory compound.

Deformation inhomogeneity is aggravated by nometallic inclusions, whose properties sharply differ from the properties of the matrix. They lead to irregular occurrence of deformation at all temperatures and are sources of microscopic failure [11].

As known [11, 12], inclusions impede dislocation motion, elevating the level of elastic stress. The relaxation of stress in our alloy can occur either by local plastic flow or by failure. This depends on the location of inclusions in the material bulk (at a boundary for a refractory compound binder), on the relation between properties of the inclusions and the structural compounds, and also on the time–temperature loading conditions. Nonmetallic inclusions distributed in the binder, characterized by a weak adhesive bonding with the matrix, behave as pseudopores. Relaxation of elastic stresses exceeding the fluidity limit occurs by crack formation along the surface break of the matrix, i.e., at an inclusion. Cavities grow due to dissolution of dislocations in them, attested by the microphotograph of a cavity wall with the slip bands emanating at its surface (Fig. 2).

Inclusions in the refractory phase grains and at interphase boundaries lead to grain failure. Such inclusion behavior, as known [2], is possible only when the inclusion strength is close to theoretical. The source of grain failure in a refractory phase can be inclusions with a shear strength of at least $E_W/30$, where E_W is the elastic modulus of tungsten [2]. Figure 3a shows the structure of a refractory grain whose failure was initiated by nonmetallic inclusions having no noticeable region of slow crack growth. At the same time, it is clearly seen from Fig. 3b that the slow crack growth zone (~3 μm) precedes the brittle transcrystallite grain failure of the refractory compound. This has a characteristic flowing fracture.

We conducted a comparative study of the region of microcrack growth (plastic arrest) for tungsten single crystals of (010) orientation. This was done according to Griffith's equation, modified by Orovani and Irvin. The data on crack surface energy temperature dependence and fracture stress were derived from [16]:

$$\sigma_F = [2E\gamma_E/\pi(1-\nu^2)c]^{1/2}, \tag{1}$$

where γ_E is the effective formation energy per unit of surface, equal to 6.3 and 65 J/m^2 at 77 and 295°K, respectively; σ_F is the failure stress, equal to 0.5 GPa at 295°K; E is the tungsten elastic modulus, equal to 395 GPa; and K is Poisson's ratio, equal to 0.29.

According to the study performed, c is the region of plastic arrest where the critical crack size is 73 μm at a temperature of 295°K. If it is assumed that the failure stresses of single-crystal tungsten [13] and tungsten-based single-crystal grains in the W–Ni–Fe alloy

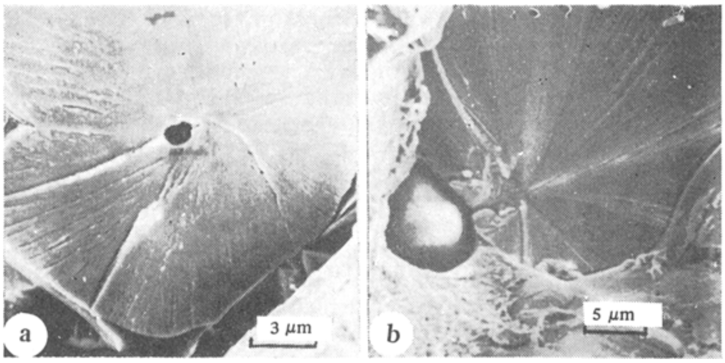

Fig. 3. Fracture of a refractory phase grain initiated by a nonmetallic inclusion (a) without formation of slow crack growth; (b) with formation.

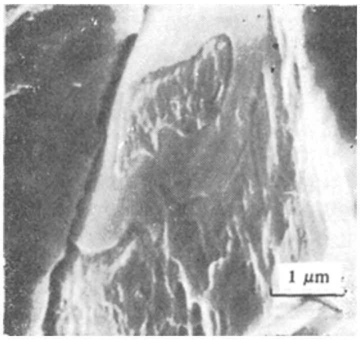

Fig. 4. Intercrystallite binder failure with an impurity atom film at the grain boundary.

are nearly the same, the difference obtained (3 and 73 μm) attests that the particle and tungsten-based grain surfaces are powerful stress concentrators, substantially alleviating the conditions for nucleation of a brittle crack.

We also evaluated the critical crack size from Eq. (1) for conditions realized at 77°K. In this process, $\gamma_E = 6.3\ \mathrm{J/m^2}$ [15] $\sigma_F = 2.25$ GPa [14], and c is equal to 0.7 μm. The result obtained agrees with the fractographic analysis data, attesting that refractory grains fail at 77°K without formation of noticeable regions of plastic crack growth.

A crack fracturing tungsten can penetrate into the binder. Such a transition is linked with the increase in effective surface energy of the refractory failure phase to the γ binder (Ni-based solid solution), since crack motion at the binder is accompanied by local plastic deformation. This is possible with further increase of applied load [2, 15].

As known [1], intergranular boundaries are effective barriers to crack movement only during growth of a grain substantially below the critical crack size. This situation and the study performed above thus enable it to be concluded that the grain diameter of the refractory phase should not exceed the size of the plastic crack arrest zone. For refractory grains exceeding the critical crack size tests at a given temperature, or for conglomerated grains of mutually close crystallographic orientation, the crack length increases, its surface energy is reduced, and its motion is accelerated. During this process, the kinetic energy of crack motion may prove sufficient to fracture the binder layer between the refractory grains without increasing the applied stress.

Impurity segregation at boundaries can lead to reduction of the fracture energy and to formation of notches. As was already recalled, nonmetallic inclusions contain Na, Ca, Si, Al, Ti, Fe, and W. These elements, together with Mo, Cr, S, etc., are localized, according to the qualitative x-ray fluorescence data, along the boundaries of the principal structural constituents in the form of segregations, films, and other formations. To explain why Ni-based solid solution boundaries are enriched with these elements, we conducted a special evaluation of the molybdenum impurity concentration at the surface of grains originating during uniform segragation at a set temperature.

The molybdenum concentration was calculated from the Mak-Lin's equation [2, 16]:

$$C_B = \frac{C_0 \exp\left(-\frac{F}{kT}\right)}{1 + C_0 \exp\left(-\frac{F}{kT}\right)}. \qquad (2)$$

Here C_0 is the molybdenum concentration in a grain; F is the binding energy between an impurity atom and boundary:

$$F = -kT_m \ln\left[\left(\frac{\partial C_L}{\partial T}\right)\left(\frac{\partial C_S}{\partial T}\right)^{-1}\right], \qquad (3)$$

where T_m is the solvent melting temperature; C_L and C_S are the equilibrium impurity concentrations in the liquid and solid state, respectively; and k is Boltzmann's constant.

We calculated the energy assuming that a high-angle boundary has a quasiliquid structure and that impurity distribution between the grain and boundary is analogous to that obtained from the phase diagram [17]. We established that a binary Ni–Mo solid solution grain boundary can contain up to 32-37% Mo (by mass) at temperatures of 1173 to 1573°K.

The presence of sulfur at Ni-based grain boundaries agrees with known literature data on sulfur segregation in nickel of different purities, containing from 0.0005 to 0.01% S (by mass) [18, 19]. According to these data, the sulfur concentration at boundaries varies from 20 to 40%, rising with increase of annealing time.

Evidently, the segregations and impurity atom films also explain the intercrystallite failure observed at fractures along the binder grain boundaries (Fig. 4).

CONCLUSIONS

The substitutional impurity element composition and content of nonmetallic inclusions in a W–Ni–Fe alloy are affected by their content in the charge starting components. These include salts and oxides or metallic powder components in a state controlled by the corresponding production conditions.

The nonmetallic inclusions in the alloy consist of multicomponent oxides distributed in the bulk as particles of different shape. Their content ranges from 0.1 to 0.4%.

Some impurity elements tend to form segregations and films at Ni-based solid solution grain surfaces. This is the binder of a W–Ni–Fe alloy.

During the alloy deformation process, nonmetallic binder inclusions, characterized by weak adhesive bonds with the matrix, play a role of pseudopores, absorbing slip bands.

Substitutional impurity elements tending to formation of segregations (Mo, S, etc.) lead to brittle intercrystallite failure.

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