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ANALYSIS OF THE INFLUENCE OF TEMPERATURE AND DEFORMATION ON THE STABILITY OF THE GRANULAR STRUCTURE OF ALLOYS CONTAINING SECOND-PHASE PARTICLES

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Analysis of the influence of thermal, mechanical, and electromagnetic actions on the stability of the granular structure of dispersion-hardened alloys with a uniform distribution of incoherent mobile particles of constant radius has been performed. It has been shown that of all parameters describing the process of interaction between the grain boundary and particles, only the relative mobility μ is a function of temperature. An expression for the relative mobility, universal for all metals, has been obtained in the approximation in which the particles in the crystal matrix participate in the diffusion motion according to the Geguzin model (volume flow mechanism). It has been shown that the influence of the test temperature on the relative mobility μ and, therefore, on the stability of the granular structure is determined by the ratio of the activation energy of grain-boundary migration H to the activation energy of particle motion Q.

One possible way of increasing the heat resistance of alloys is by dispersion-hardening — the introduction of "inert disperse second-phase particles uniformly distributed in the metal volume" [1]. Disperse particles in the metal matrix retard the formation and growth of new grains in the recrystallization process. This makes it possible to preserve the prolonged workability of materials up to $(0.9–0.95)T_{\text{melt}}$ and make them resistant to cyclic loads.

Heat resistance of an alloy is achieved by preserving the fine-graininess of the structure at high working temperatures. It is essential that the thermal, mechanical, and electromagnetic actions activate no grain growth in a dispersion-hardened alloy. The influence of these external factors on the granular structure stability can be tested in an experiment. However, such an experiment will require considerable material and time expenditures. In this connection, forecasting of the stability of the granular structure of dispersion-hardened alloys based on an adequate physical model of the process is of particular importance. Thus, in [2], for dispersion-hardened alloys with a uniform distribution of incoherent particles of constant radius, the dragging condition for the migrating grain boundary with allowance for the diffusion motion of particles was obtained in an approximation in which the grain boundary is curred around particles and planar between particles (Fig. 1). This condition is based on the general thermodynamic principle that the free energy of a system decreases in the spontaneous irreversible isothermal process of recrystallization: $dF < 0$. Consequently, an energy barrier appears in the path of motion of the grain boundary to retard the recrystallization process: $dF = \delta A + \gamma dS - GdV \geq 0$. As a result of mathematical manipulations, Marvina et al. [2] came to the following form of the criterion for the dragging of the grain boundary by particles in the process of recrystallization:

$$b\pi^2\nu^{2/3}\gamma^2\mu \sin^2 2\varphi + 2\pi b\nu^{2/3}\gamma (1 - \cos\varphi)(G + \pi r\gamma\mu \sin 2\varphi)/r + \\ + G\left[\pi r\gamma\mu \sin 2\varphi - (1 - \pi b\nu^{2/3} \sin^2\varphi)(G + \pi r\gamma\mu \sin 2\varphi)\right] \geq 0 , \quad (1)$$

where $b \approx 0.3527$.

In the literature, a large number of models of the interaction between the grain boundary and the second-phase particles under recrystallization have been proposed [3–6], but none of them explicitly describes the influence of the test temperature on the stability of the granular structure of the alloy. It is easy to see that the major thermody-

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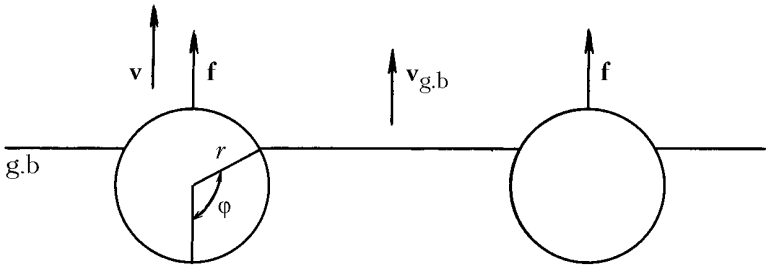

Fig. 1. Local configuration of particles and grain boundary during its migration (grain boundary: curved around particles and planar between particles) [2].

namic parameter — temperature — is also absent from the criterion for the dragging of the migrating grain boundary by particles (1). Criterion (1) describes the condition for the dragging of the migrating grain boundary by second-phase particles by the following parameters: ν, φ, r, G, γ, μ. In [7], the temperature dependence of these parameters was considered. In particular, it was shown that the analysis of the influence of temperature on the stability of the granular structure of dispersion-hardened alloys is reduced to the consideration of the temperature dependence of the relative mobility $\mu = M/M_{g.b}$.

The diffusive motion of the second-phase particles in a dispersion-hardened alloy can be described by the Geguzin model (volume flow mechanism) [8]. According to this model, the particles can move relative to the matrix crystal lattice at a rate $\mathbf{v} = \frac{3}{2\pi}\alpha\frac{D\omega\mathbf{f}}{kTr^3}$. Using the literature expressions for the particle mobility $M = \mathbf{v}/\mathbf{f}$ [8] and for the self-diffusion coefficient of matrix atoms $D = nl^2 \exp\left(-\frac{Q}{kT}\right)$ [9], one can reduce the equation for the particle mobility to the form $M = \frac{3}{2\pi}\alpha\frac{\omega}{kT}\frac{nl^2}{r^3}\exp\left(-\frac{Q}{kT}\right)$. Taking into account the expression for the grain-boundary mobility $M_{g.b} = \frac{nl\omega}{kT}\exp\left(-\frac{H}{kT}\right)$ [10], we obtain the formula for the relative mobility:

$$\mu = \frac{3l}{2\pi r^3}\exp\left(\frac{H-\mathbf{Q}}{kT}\right) = \frac{3l}{2\pi r^3}\exp\left[\left(\frac{H}{\mathbf{Q}}-1\right)\frac{\mathbf{Q}}{kT}\right]. \quad (2)$$

It should be noted that when particles are moving by the volume-flow mechanism the activation energy of the particle motion Q is the activation energy of the self-diffusion of the matrix atoms. Comparison of all activation-energy values of the self-diffusion of metals measured directly by isotopic methods [9] shows that for thirteen face-centered cubic metals the dimensionless ratio $q = Q/kT_{melt}$ is within the range of 15.5 (Au)–20.9 (Pb). Three hexagonal (Mg, Cd, Tl_α) and four transition volume-centered cubic metals (V, Nb, Mo, Fe_α) also fall within this range. The mean for them is $q = 17.7$; usually $q = 18$ is taken. In view of the foregoing, expression (2) can be reduced to a form that permits obtaining temperature dependences of the relative mobility μ, universal for all metals, for the particle motion by the volume-flow mechanism:

$$\mu = \frac{3l}{2\pi r^3}\exp\left[\left(\frac{H}{\mathbf{Q}}-1\right)\frac{q}{\theta}\right]. \quad (3)$$

Let us analyze the dependence of the relative mobility μ on temperature and the relative activation energy H/Q by formula (3). The migration activation energy H is highly sensitive to the type of boundaries and the content of impurities. If we compare it to the self-diffusion activation energy Q, we see that for different boundaries in different metals [9] $H/Q = 0.2$–2.8. Low values of the activation energy of grain-boundary migration H and, consequently, of the ratio H/Q are observed in pure metals. The larger the impurity content, the higher the value of the relative activation energy H/Q. Therefore, in real industrial alloys the range of H/Q values is much narrower. The diffusive motion of particles produces a marked effect on the process of interaction of the grain boundary with particles only at

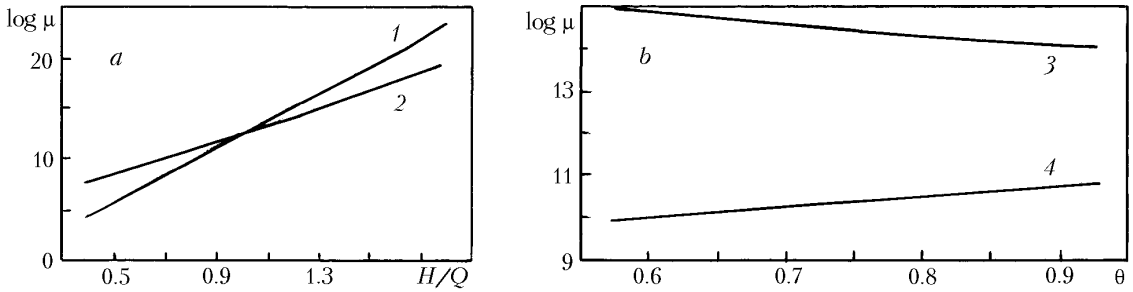

Fig. 2. Influence of the relative activation energy H/Q (a) and similar temperature θ (b) on the relative mobility μ: 1) θ = 0.6; 2) 0.95; 3) H/Q = 1.2; 4) 0.8. μ, m^{-2}.

high temperatures $T > 0.5T_{melt}$. At such temperatures, heat-resistant alloys are used. In this connection, it is reasonable to calculate the function log μ(H/Q) by formula (3) in the range of values $0.4 \le H/Q \le 1.8$ at two values of a similar temperature: $\theta_1 = 0.6$ and $\theta_2 = 0.95$.

As is seen from Fig. 2a, the relative mobility μ increases with H/Q at all temperatures. It should be noted that μ can increase both with increasing particle mobility M as a result of the change in the mechanism controlling the motion of these particles or a decrease in their radius ($M \sim r^{-3}$) and with decreasing mobility of the grain boundary $M_{g.b}$ as a result of its dragging by impurities and second-phase particles. Expression (3) was obtained taking into account that particles are moving according to the Geguzin model (volume flow mechanism) [8] with no change in the mechanism of their motion, and the chemical composition of impurities remains unaltered. Therefore, at a constant radius of particles and an invariable chemical composition of the alloy the factor affecting the increase in μ will be a decrease in $M_{g.b}$ due to the dragging of the grain boundary by impurities that segregate mainly along the grain boundaries. Consequently, at one and the same temperature in a more impure alloy the migration of the grain boundary will be slower: $M_{g.b}$ will be lower and the relative mobility μ higher than in the pure material. According to criterion (1), with increasing μ the granular structure stability increases. Therefore, the impurities contained in a dispersion-hardened alloy retard the grain growth. However, the introduction of "dangerous" impurities (in nickel alloys this is sulfur) can lead to a decrease in the specific energy of grain boundaries and an increase in their brittleness.

Figure 2b shows the dependence log μ(θ) calculated by formula (3) in the range of similar temperatures $0.6 \le \theta \le 0.95$ at two values of H/Q. At H/Q = 1.2, the relative mobility μ decreases with increasing temperature θ, whereas at H/Q = 0.8 it increases. Consequently, the influence of temperature on the relative mobility μ and, therefore, on the stability of the granular structure of an alloy containing second-phase particles is defined by the ratio H/Q, i.e., its activation parameters.

Substituting expression (3) into the thermodynamic criterion for the dragging of the grain boundary by particles (1), we analyze the dependence of stability of the granular structure of dispersion-hardened alloys on the similar temperature θ and the relative activation energy H/Q. At constant values of γ, r, ν, φ, G, the expression on the right side of Eq. (1) is a function of only two arguments: $F(\theta, H/Q)$. Let us calculate this function in the range of values $0.4 \le H/Q \le 1.8$; $0.6 \le \theta \le 0.95$. For analysis, we will use a dispersion-hardened alloy having the following parameters: γ = 0.728 J/m^2; $r = 4 \cdot 10^{-8}$ m; ν = 0.03 (Ni–HfO_2 [11]). Let us consider the motive force of the process of grain-boundary migration G to be constant and equal to $1.2 \cdot 10^6$ J/m^3. As follows from Eq. (1), at such values of G and different ratios H/Q, both the dragging of the grain boundary by particles and its separation from the particles are possible. It should be noted that the value of $G = 1.2 \cdot 10^6$ J/m^3 falls within the experimental range of maximum values of the motive force of migration ($G = 1 \cdot 10^6$–$1.55 \cdot 10^7$ J/m^3) at which, in the Ni–HfO_2 alloy, dragging of the grain boundary by particles was observed [11]. Let us take the angle of the grain-boundary flow by a particle to be equal to $\varphi = 45^o$ (Fig. 1).

The calculation of the function $F(\theta, H/Q)$ characterizing the stability of the granular structure of the dispersion-hardened alloy in accordance with the thermodynamic criterion (1) is given in the form of a contour graph in Fig. 3a (the values of the function $F(\theta, H/Q)$ on the graph are given on a logarithmic scale). Analysis of Fig. 3a shows that the values of this function can be subdivided into two regions: I, where $F(\theta, H/Q) < 0$, which corresponds to the

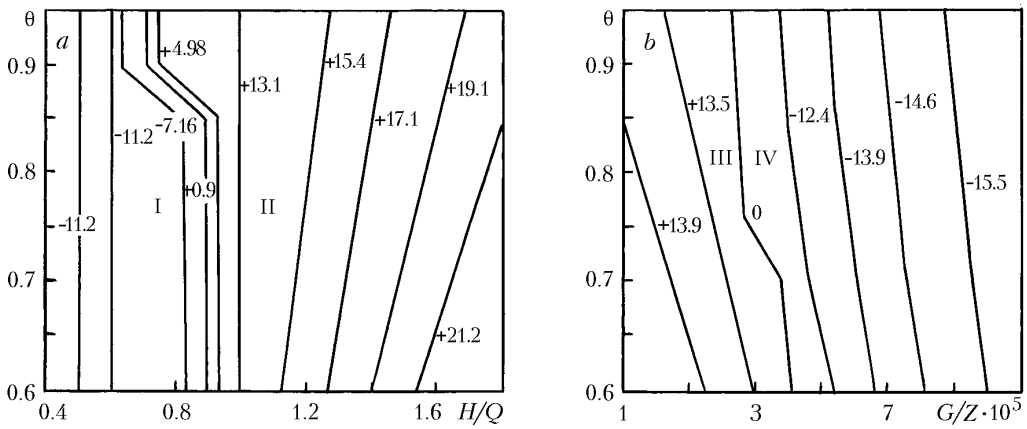

Fig. 3. Function F and stability of the grain boundary of the dispersion-hardened Ni–HfO_2 alloy in accordance with (1) versus the similar temperature θ and the relative activation energy H/Q (a) and versus θ and the dimensionless motive force of grain-boundary migration G/Z (b). Regions I and IV of negative values of the functions $F(H/Q, \theta)$ and $F(G/Z, \theta)$ correspond to the separation of the grain boundary from particles; regions II and III of positive values of these functions correspond to the joint motion of the particle and the grain boundary. F, H^2/m^4.

separation of the grain boundary from the particles, and II, where $F(\theta, H/Q) \geq 0$, i.e., the migration rate of the grain boundary is limited to the particle velocity. At low values of H/Q and a high migration motive force of $G = 1.2 \cdot 10^6$ J/m^3, the grain boundary separates from the particles and freely migrates in the volume of the basis material (Fig. 3a, region I). The dragging of the grain boundary by particles at given values of γ, r, v, G occurs at $H/Q \geq 0.9$ (Fig. 3a, region II).

From Fig. 3a it is also seen that the influence of the test temperature on the stability of the granular structure is defined by the ratio H/Q. The test temperature practically has no effect on the stability of the granular structure of the alloy at $H/Q = 0.4$–0.6, since the respective values of μ calculated by formula (3) lie in the range of values of $\mu = 10^7$–10^9 m^{-2}. In [2], it was shown that the structure stability increases with increasing relative mobility μ at $\mu > 10^{12}$ m^{-2}. At a relative activation energy of $H/Q = 0.6$–1.0 an increase in the temperature leads to an increase in the stability of the granular structure of the alloy. This is likely to be due to the increase in the relative mobility μ (Fig. 2b, curve 4) and, consequently, in the particle mobility M compared to the grain-boundary mobility $M_{g.b}$. The above quality is consistent with the results of the experiment [12], where in the copper matrix separation of the migrating grain boundary from the slow-moving Al_2O_3 particles and at the same time joint migration of the boundary with mobile SiO_2, GeO_2, and B_2O_3 particles were registered.

In alloys containing impurities in large quantities, $H/Q > 1$, grain-boundary migration occurs slowly and the structure is fairly stable. In this case, as the graph (Fig. 3a) shows, with increasing test temperature the stability of the granular structure will decrease. At high motive forces this may lead to a disturbance of the granular-structure stability with increasing test temperature, which was precisely registered under experimental conditions [10]. It should be noted that at a relative activation energy $H/Q < 1$ the granular-structure stability, i.e., the value of the function $F(\theta, H/Q)$, increases with increasing temperature, while at $H/Q > 1$ it decreases. In the second case, however, at a constant motive force of grain-boundary migration G the alloy will be more stable and for the grain boundary to separate from the particles a motive force higher than in the first case will be needed.

For an alloy with particles moving by the volume-flow mechanism having a relative activation energy $H/Q > 1$, the stability of the granular structure may be disturbed both with increasing test temperature and with increasing motive force of grain-boundary migration. To obtain a motive force universal for all metals caused by a certain external factor, it is expedient to represent it in the dimensionless form of G/Z. An increase in G, while an alloy is in use, can be caused by any one of several different factors: elastic deformation (the limiting value of $G/Z = 10^{-18}$) or plastic deformation ($G/Z = 10^{-4}$), irradiation ($G/Z = 10^{-4}$), action of electric ($G/Z = 10^{-8}$) or magnetic (G/Z

= 10^{-9}) fields, and temperature gradient (at grad $T = 10^5$ K/m $G/Z = 10^{-10}$) [9]. If several motive forces G_i are acting simultaneously, then the resulting motive force is $G = \Sigma G_i$. The influence of external factors may increase by several orders of magnitude the migration motive force G caused by the proper boundary tension ($G/Z = 10^{-6}$) and provoke grain growth.

Figure 3b illustrates the dependence $F(G/Z, \theta)$ for the grain-boundary migration in an alloy with the following parameters: $\gamma = 0.728$ J/m^2; $r = 4 \cdot 10^{-8}$ m; $\nu = 0.03$; $H/Q = 1.1$ (Ni–HfO_2) [11]. It is seen that the values of the function $F(G/Z, \theta)$ decrease with increasing temperature θ and motive force of grain-boundary migration G. The limiting value of the dimensionless migration motive force of the grain boundary G/Z for the given dispersion-hardened alloy, at which the granular boundary stability will not be disturbed at all operating temperatures, is $G/Z = 3.5 \cdot 10^{-5}$. If we take into account that the motive force caused by the proper boundary tension is $G/Z = 10^{-6}$, then for the external factors affecting the alloy while in use $G/Z = 3.4 \cdot 10^{-5}$. Consequently, the given alloy will preserve the fine-grained structure even under a small plastic deformation ($G/Z = \rho l^2/2$ [9]) with the density of the dislocations introduced under deformation $\rho = 7.5 \cdot 10^{14}$ m^{-2}. Thus, such a graph will help to calculate the working temperature range and the allowed values of deformation and other external factors for a particular dispersion-hardened alloy. The application of the temperature dependence of the relative mobility (3) to the thermodynamic criterion of stability of the granular structure of dispersion-hardened alloys (1) [12] can be used in practice for developing dispersion-hardened alloys with given properties.

CONCLUSIONS

1. For dispersion-hardened alloys with a uniform distribution of incoherent particles of constant radius, whose diffusive motion occurs by the volume-flow law (Geguzin model), the dependence (universal for all metals) of the relative mobility μ on the similar temperature θ, the activation energy of grain-boundary migration H, and the activation energy of motion of particles Q and their radius r has been obtained.

2. It has been shown that the influence of temperature on the stability of the granular structure of an alloy containing second-phase particles is defined by the ratio H/Q, i.e., its activation parameters. At a relative activation energy $H/Q < 1$ the granular-structure stability increases with increasing temperature, and at $H/Q > 1$ it decreases. In the second case, however, the alloy will be more stable, and for the grain boundary to separate from the particles a grain-boundary-migration motive force G higher than in the first case will be needed.

3. The stability of the granular structure of a dispersion-hardened alloy increases with increasing relative activation energy H/Q at all temperatures. Since low values of the grain-boundary-migration activation forces and, consequently, of H/Q as well are observed in pure metals and high values are observed in metals and alloys containing impurities in large quantities, the presence in a dispersion-hardened alloy of impurities retards grain growth. Therefore, the action by small impurities is an important way of "constructing an alloy."

4. For an alloy with a relative activation energy $H/Q > 1$, whose particles are moving by the volume-flow mechanism, the granular-structure stability can be disturbed with both increasing test temperature and increasing grain-boundary-migration motive force. The application of the temperature dependence of the relative mobility (3) to the thermodynamic criterion of stability of the granular structure of dispersion-hardened alloys (1) [2] makes it possible to calculate the working temperature range and the allowed values of deformation and other external factors for a particular dispersion-hardened alloy.

NOTATION

D, self-diffusion coefficient of matrix atoms, m^2/sec; dF, change in the free energy of the system, J; dS, change in the grain-boundary area as a result of bending, m^2; dV, increment of volume "swept up" by the grain boundary during its migration, m^3; $\mathbf{f}$, force of interaction of an individual particle with the grain boundary (Zener force), H; G, motive force of grain-boundary migration, J/m^3; $-GdV$, decrease in the free energy of the system due to the "sweeping" of nonequilibrium defects in the matrix volume dV, J; H, activation energy of grain-boundary migration, J; H/Q, relative activation energy; k, Boltzmann constant, J/K; l, interatomic distance, m; $M_{g.b}$, grain-boundary mobility, m^3/(sec·H); M, particle mobility, m/(sec·H); n, atomic oscillation frequency, sec^{-1}; Q, self-diffusion activation

energy of matrix atoms (activation energy of particle motion by the volume-flow law), J; r, particle radius, m; T, temperature, K; T_{melt}, melting temperature of metal matrix, K; $\mathbf{v}$, particle velocity, m/sec; $\mathbf{v}_{g.b}$, grain-boundary velocity, m/sec; Z, shear modulus of metal matrix, Pa; α, coefficients of the order of unity depending on the particle shape and grain-boundary structure; δA, elementary work done by the system during particle motion, J; φ, angle of the grain-boundary flow by a particle; γ, grain-boundary energy per unit of surface area, J/m^2; γdS, increase in the grain-boundary free energy caused by a change in its area dS as a result of bending, J; $\mu = M/M_{g.b}$, relative mobility, m^{-2}; ν, volume concentration of particles; $\theta = T/T_{melt}$, similar temperature; ρ, density of dislocations introduced by deformation, m^{-2}; ω, atomic volume, m^3. Subscripts: g.b, grain boundary; melt, melting.

REFERENCES

1. K. I. Portnoi and B. N. Babich, *Dispersion-Hardened Materials* [in Russian], Metallurgiya, Moscow (1974).
2. L. A. Marvina, V. B. Marvin, V. R. Karib'yants, and I. V. Neupokoeva, Prediction of stability of the granular structure of dispersion-hardened alloys under collective crystallization, *Nauka Proizvodstvu*, No. 4(42), 33–35 (2001).
3. L. A. Marvina and V. B. Marvin, *Diffusion Processes and Degradation of the Structure in Metals* [in Russian], Dal'nauka, Vladivostok–Blagoveshchensk (1996).
4. L. A. Marvina and V. B. Marvin, Conditions for the dragging of migrating grain boundary in an alloy with particles under primary recrystallization, *Fiz. Metal. Metalloved.*, **88**, No. 5, 11–20 (1999).
5. E. Rabkin, Zener drag in the case of anisotropic grain boundary energy, *Scr. Materialia*, **39**, No. 12, 1631–1637 (1998).
6. B.-N. Kim and T. Kishi, Finite element simulation of Zener pinning behavior, *Acta Materialia*, **47**, No. 7, 2293–2301 (1999).
7. N. V. Selivanov and I. V. Neupokoeva, On the influence of high temperatures on stability of the granular structure of dispersion-hardened alloys, *Vestn. AGTU*, No. 1(20), 31–34 (2004).
8. Ya. E. Geguzin and M. A. Krivoglaz, *Motion of Macroscopic Inclusions in Solid Bodies* [in Russian], Metallurgiya, Moscow (1971).
9. M. A. Shtremel', *Strength of Alloys* [in Russian], Pt. 1, MISSIS, Moscow (1999).
10. S. S. Gorelik, *Recrystallization of Metals and Alloys* [in Russian], Metallurgiya, Moscow (1985).
11. V. A. Kulikov, N. M. Zaitseva, Yu. N. Kolobov, and L. S. Bushnev, *Structure and Properties of Dispersion-Hardened Strengthened Nickel Alloys* [in Russian], TGU, Tomsk (1986).
12. M. F. Ashby and R. H. Centamore, The dragging of small oxide particles by migrating grain boundary in copper, *Acta Materialia*, **16**, No. 7, 1081–1088 (1968).