

Surface tension of [001] tilt boundaries in tin in the vicinity of transformation of special $\Sigma 17$ boundaries into general boundaries

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The temperature dependences of the ratio of the surface tensions of special and general grain boundaries σ_s/σ_g were determined from the shape of triple junctions between special and general boundaries. The investigation was carried out on [001] tilt boundaries in tin in the misorientation angle interval $\varphi = 25.5-30^\circ$ at temperatures from $0.85T_m$ to the melting point T_m . It was found that the temperature dependences $\sigma_s(T)$ for boundaries with misorientation angles $26.5-29.5^\circ$ had kinks due to transformation of these special $\Sigma 17$ boundaries into general boundaries of the $\Sigma 1$ type on increase in temperature. A study was also made of the orientational dependence of the surface tension of boundaries with $\pi = 26.5-29.5^\circ$ at $T \approx 0.97T_m$ deduced from the shape of the thermal etching channel at the point of emergence of a boundary on the outer surface. The orientational dependences of the mobility of boundaries with $\varphi = 26-29.5^\circ$ were determined at six temperatures in the range $(0.94-0.98)T_m$. The results obtained made it possible to plot the line of the $\Sigma 17-\Sigma 1$ transition using the temperature and misorientation angle as the coordinates. This line was described well by assuming a dislocation structure of the special grain boundaries.

Our aim was to investigate in detail the thermodynamic properties of one of the special boundaries in tin in the range of misorientation angles and temperatures where one would expect a general boundary phase transition.

EXPERIMENTAL METHOD

Grain boundaries with misorientation angles close to the special values can, in principle, in various structural modifications (see Sec. 2). If the temperature dependences of the thermodynamic characteristics of a boundary in different modifications intersect below the melting point, boundaries with a special structure are transformed into boundaries of the general type. In the case of first-order phase transitions such temperature dependences [for example, the temperature dependence of the surface tension $\sigma(T)$] could exhibit a kink, whereas in the case of second-order transitions they should exhibit an inflection.

We investigated the temperature dependence of the ratio of the surface tension σ_1 of tilt boundaries with misorientation angles $25.5-30^\circ$ near the special angle 28.07° ($\Sigma 17$) to the surface tension of boundaries of the general type with misorientation angles $30-32^\circ$ lying outside the range of exist-

tence of the $\Sigma 17$ special boundaries. This ratio was determined from the shape of a triple junction consisting of one special boundary and two identical boundaries of the general type (Fig. 1). The misorientation angle of the general boundaries was determined from the condition $\varphi_2 = \varphi_3 = (90^\circ - \varphi_1)/2$ applicable to the [001] boundaries. Samples with triple junctions were grown by the method of directional crystallization in an argon atmosphere of the OSCh grade in a boat of specially pure graphite from tin with anomalous impurity concentration below 10^{-6} at T_m . Figure 2a shows schematically a tricrystal with a triple junction. After growth a sample with a triple junction was cut as shown in Fig. 2b and after chemical polishing in an $\text{HNO}_3-40\% \text{ HF}$ solution it was placed in a high-temperature attachment of an optical microscope. Annealing took place in an argon atmosphere of the OSCh purity grade and temperature was kept constant to within $\pm 0.5^\circ\text{C}$. Successive anneals shifted the triple junction as shown in Fig. 2b. Since $\sigma_s = \sigma_g = \sigma_g$, a special boundary with $\sigma_s = \sigma_g$ always remained plain. The angle at the vertex of a triple junction was determined with a micrometric eyepiece. The distances h and l (Fig. 2b) were determined. The ratio of the surface tensions was found from $\sigma_s/\sigma_g = \sigma_1/\sigma_2 = \sigma_1/\sigma_3 = 2 \cos [\arctan (l/2h)]$. The magnification was selected so that the measurements of h and l were made far from the junction where the boundaries with σ_2 and σ_3

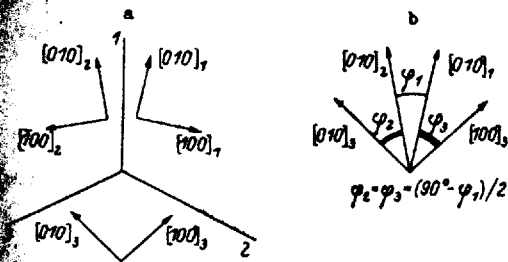


FIG. 1. Crystallography of triple junctions consisting of [001] tilt boundaries used to determine the temperature dependences of the relative surface tension σ_1/σ_g . Junctions consist of one special boundary (denoted by 1 and characterized by a misorientation angle φ_1) and two identical general boundaries [2 and 3, $\varphi_2 = \varphi_3 = (90^\circ - \varphi_1)/2$]. The special boundary is represented as passing through the (100) plane of the lattice of $\Sigma 17$ incident sites.

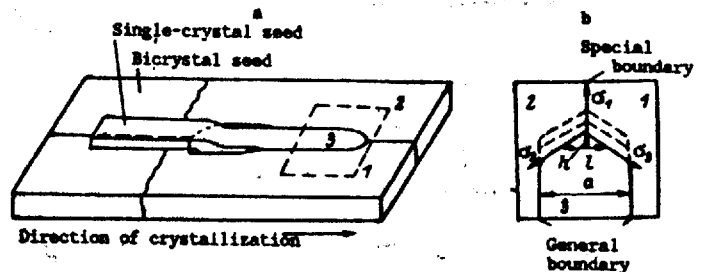


FIG. 2. Samples with triple junctions: a) schematic representation of the growth of a tricrystal; b) successive positions of a junction in the course of determination of the temperature dependences σ_1/σ_g . Measurements were made of the values of h and l ; $a = \text{const}$.

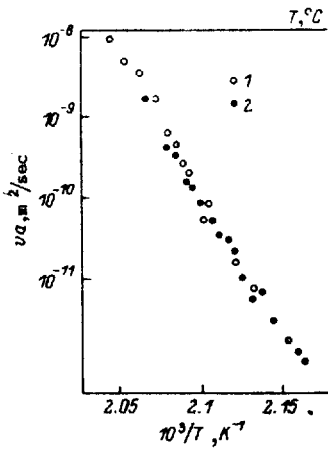


FIG. 3. Temperature dependences of the velocity of a general boundary (1) (boundary 2 or 3 in Fig. 2) and of a triple junction (2). The velocities are reduced to the same driving force. The velocity of a triple junction is governed by the mobility of general grain boundaries and it is not limited by the intrinsic mobility of a junction.

were already rectilinear and the ratio l/a did not exceed 0.1. As shown in Ref. 3, the shape of a moving triple junction was in equilibrium, i.e., it was governed by the values of σ_1 , σ_2 , and σ_3 if the velocity of a triple junction was limited by the mobility of grain boundaries and not by the mobility of a junction. The reduction in the velocity of general boundaries in a junction (Fig. 3) was entirely due to a reduction in the driving force acting on these boundaries, which decreased from $2\sigma_g/2a$ to $(2\sigma_g - \sigma_1)/2a$. Therefore, we determined the equilibrium values of the angle at the vertex of the investigated triple junction.

The geometry of the triple junctions was such that a change in the misorientation angle ϕ_1 of a special boundary altered also the misorientation angles of general boundaries $\phi_2 = \phi_3$. Consequently, we could not plot orientational dependences $\sigma_g(\phi)$ because we did not know in general how the surface tension σ_g varied. Therefore, the orientational dependence of the surface tension of tilt boundaries with $\phi = 26.5$ - 29.5° (at a temperature $0.97 T_{mp}$) was found using thermal etching channels. These channels were formed as a result of annealing in 10^{-3} Torr vacuum for 770 h. The profiles of the thermal etching channels were determined using a microinterferometer with a laser light source

at 200-300 points for each sample, which increased the precision of determination of the ratio σ_g/σ_{surf} .

As pointed out in Ref. 1, special boundaries differ from boundaries of the general type not only in respect of their structure, but also in regard of the properties. Therefore, we investigated the orientational dependences of the mobility of boundaries with $\phi = 26$ - 29.5° at different temperatures. The mobility was determined for a constant migration-driving force.

2. RESULT

We determined the temperature dependences of the ratio σ_1/σ_g for ten [001] tilt boundaries in tin with misorientation angles from 25.5 to 30° at temperatures from $0.85T_{mp}$ to T_{mp} . Figure 4 shows the temperatures of the ratio σ_1/σ_g . These dependences are arranged in increasing order of the misorientation angle ϕ . The first two temperature dependences (a and b) are almost perfect straight lines and the ratio σ_1/σ_g rises, reaches its maximum at T_C , and then falls. The shape of these maxima is such that we should describe them as kinks rather than inflections of the temperature dependences of σ_1/σ_g . The temperature T_C increases on increase in ϕ , reaches its maximum at $\phi = 28.3^\circ$, which is close to $\phi = 28.07^\circ$ for the $\Sigma 17$ boundaries, and falls again. In the case of the last temperature dependence of σ_1/σ_g representing the boundary with the misorientation angle $\phi = 30^\circ$ again there are no singularities. The positions of the kinks in the temperature dependences of σ_1/σ_g is independent of the force driving a junction (Fig. 5a), of the sequence in which the temperature dependences are recorded, i.e., where the temperature is increased or reduced (Fig. 5b), and of the misorientation angles of the general boundaries in a junction (Fig. 5c).

It follows that the position of T_C corresponding to the kinks in the temperature dependences of σ_1/σ_g is governed only by the misorientation angle of the special boundaries with σ_1 and is independent (within the limits of the experimental error and in the investigated range of the parameters) of other thermodynamic, geometric, and kinetic (transport) factors. The presence of kinks in the temperature dependences of σ_1/σ_g means, in our opinion, that at the temperature T_C a special boundary of the $\Sigma 17$ type is transformed into a general boundary. The curves in Fig. 4 agree well with the hypothesis of a first-order phase transition. Figure 6 shows the dependence of the kink

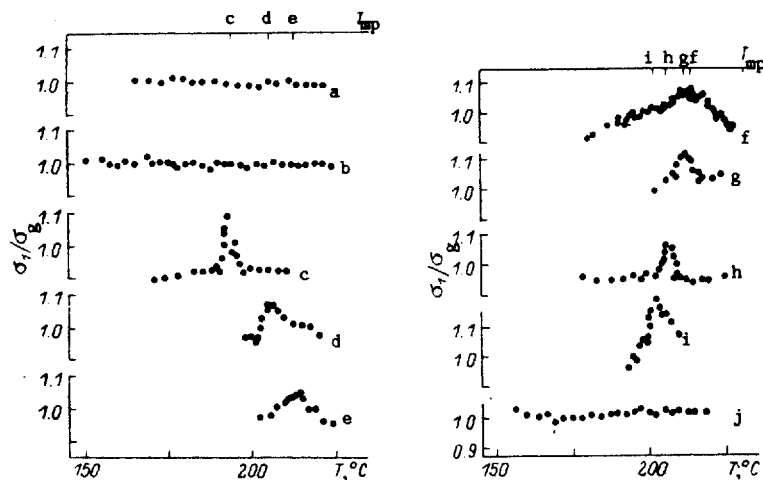


FIG. 4. Temperature dependences of the ratio of the surface tension σ_1 of special boundaries to the surface tension of general boundaries $\sigma_2 = \sigma_3 = \sigma_g$. Misorientation angle ($^\circ$): a) 25.5; b) 26.0; c) 26.5; d) 27.0; e) 27.7; f) 28.2; g) 28.5; h) 29.0; i) 29.5; j) 30.0.

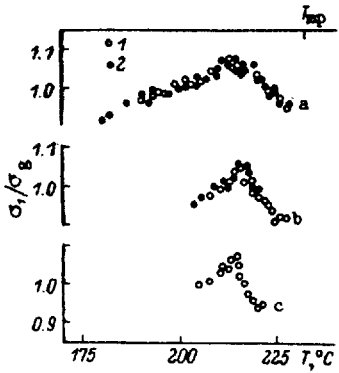


FIG. 5. a) Temperature dependence of σ_1/σ_g (Fig. 4) for $\phi = 28.2^\circ$ plotted for different driving forces on $a_1/a_2 = 2.2$. b) Temperature dependence of σ_1/σ_g measured during consecutive increase (1) and consecutive reduction (2) of temperature in the case when the misorientation angle was $\phi = 28.2^\circ$ corresponding to the (120) plane of the coincident-site lattice. c) Same temperature dependence as in Fig. 5b, but for $\phi_2 \neq \phi_3$, $\phi_2 = 23^\circ$, and $\phi_3 = 39^\circ$.

temperature T_c on the misorientation angle of the grain boundaries. The thin vertical lines in Fig. 6 represent the range of temperatures in which a given boundary behaves as one of the general type. We have thus plotted a line separating the range of existence of the $\Sigma 17$ special boundaries from boundaries of the general type. This produces a nearly symmetric bell-shaped curve with its vertex line at $\phi = 28.3^\circ$ and $215 \pm 2^\circ\text{C}$ ($0.97T_{mp}$).

We also investigated the orientational dependence of the surface tension σ_1 at $T_1 = 213 \pm 2^\circ\text{C}$, slightly below the peak of the bell-shaped curve in Fig. 6: this surface tension was deduced from the shape of the thermal etching curves. The dependence obtained is shown in Fig. 7. It is in the form of a nearly horizontal line with two points that do not fit this line. It is clear from the phase

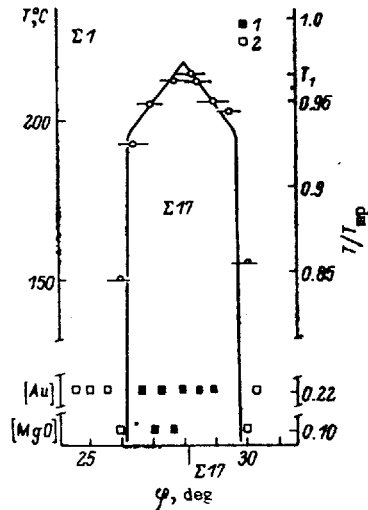


FIG. 6. Phase equilibrium line of the $\Sigma 17$ special boundaries and the $\Sigma 1$ general boundaries in tin, plotted using the temperatures T_c (Fig. 4). The lower part of the figure gives the published data on the structure of special $\Sigma 17$ twist boundaries in gold at $T/T_{mp} = 0.2$ (Ref. 4) and in magnesium oxide at $T/T_{mp} = 0.1$ (Ref. 5): 1) network of secondary grain-boundary dislocations is observed; 2) diffraction by primary grain-boundary dislocations is observed.

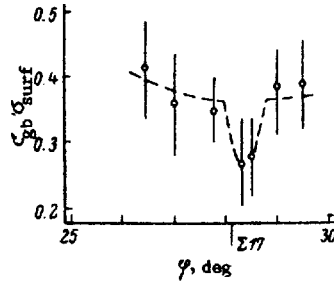


FIG. 7. Orientational dependence of the surface tension of [001] tilt boundaries in tin σ_{gb} found by measuring the angle at the vertex of a thermal etching channel at the point of emergence of grain boundaries on an outer surface. Here, σ_{surf} is the surface tension of a free (001) surface; $T = 0.97T_{mp}$.

diagram in Fig. 6 that these two points lie precisely in the range of existence of the $\Sigma 17$ special boundaries. Therefore, the surface tension σ_g of the $\Sigma 17$ special boundaries at less than the surface tension of the general boundaries σ_g at the temperature in question. The value of σ_g is almost independent (within the limits of the experimental error) of the misorientation angle ϕ . If the kinks in the temperature dependences of the surface tension σ_1/σ_g are indeed associated with the transformation of the $\Sigma 17$ special boundaries into those of the general type, then this transformation should also destroy the special properties of the boundaries. For example, the difference between the mobilities of the special and general boundaries should disappear. Therefore, we determined the orientational dependences of the reduced velocity of migration v_a of boundaries with the misorientation angles $\phi = 26-29.5^\circ$ at different temperatures (Figs. 6 and 8). We plotted in Fig. 8 the dependences of v_a on the misorientation angle ϕ . These orientational dependences exhibited discontinuities of the reduced velocity and in the range of existence of the $\Sigma 17$ special boundaries the reduced velocity of the boundaries was higher than outside this range. The positions of the discontinuities of the reduced velocity were independent of the migration-driving force a .

We thus established that the orientational dependences of the surface tension of the boundaries

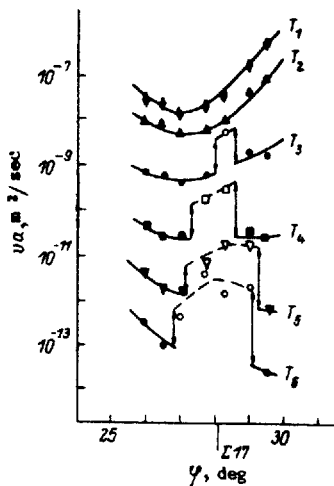


FIG. 8. Orientational dependences of the reduced velocity of [001] tilt boundaries in tin with the misorientation angles from 26 to 29.5° , obtained at various temperatures T ($^\circ\text{C}$): 1) 221; 2) 219; 3) 213; 4) 208; 5) 204; 6) 200.

deduced from the thermal etching channels and the orientational dependences of the velocity of migration of boundaries at different temperatures were in satisfactory agreement with the phase diagram in Fig. 6.

3. DISCUSSION OF RESULTS

The results of our investigations of the temperature and orientational dependences of the surface tension and of the velocity of migration of {001} tilt boundaries in the tin near the $\Sigma 17$ misorientation are, in our opinion, evidence of a phase transition transforming the $\Sigma 17$ special boundaries into those of general type. The nature of the temperature dependences of the surface tension σ_1 allows us to assume that this is a first-order phase transition. The boundaries lying close to the coincidence misorientation have a lower energy than the boundaries of the general type⁶ and their properties (mobility,^{7,8} grain-boundary diffusion parameters,^{9,10} and mechanical characteristics¹¹) are very different from properties of boundaries of the general type.

The structure of the special grain boundaries differs from the structure of the general boundaries: they consist of parts of a special boundary with the $\phi = \phi_c$ structure separated by grain-boundary dislocations. At some value of the misorientation angle close to the special value

$$\varphi = \varphi_c + \Delta\varphi$$

we can expect in principle two different structures of the boundary: that consisting of primary dislocations with the period d_1 described by

$$d_1 = d_1(\varphi = \varphi_c + \Delta\varphi) = b_p / [2 \sin(\varphi/2)]$$

or of regions of a special boundary with the periodicity

$$d_{1s} = d_1(\varphi_c) = b_p / [2 \sin(\varphi_c/2)],$$

separated by secondary grain-boundary dislocations with the period

$$d_2 = d_2(\Delta\varphi) = b_p / [2 \sin(\Delta\varphi/2)],$$

where b_p is the lattice Burgers vector and $b_c = B_p/\sqrt{\epsilon}$ is the Burgers vector of secondary grain-boundary dislocations. The actual definite which is formed is that which has a lower free energy. When $\Delta\phi$ is increased the energy of a wall of secondary dislocations increases and at some definite value of $\Delta\phi$ there is a change in the type of the boundary structure. Such a change in the structure should, in our opinion, alter the nature of the phase transition. The special-general phase transition may be induced also by a change in temperature, since the free energy of the less ordered general boundaries decreases more rapidly on reduction in temperature than does the free energy of special boundaries. As already pointed out, the nature of the temperature dependences of the surface tension of the investigated grain boundaries allows us to assume that the $\Sigma 17$ - $\Sigma 1$ transition is of the first order. We shall consider the thermodynamics of such a transition and using the concept of the dislocation structure of grain boundaries we shall plot the equilibrium line of the $\Sigma 17$ and $\Sigma 1$ phases using T and ϕ as the coordinates.

We shall consider equilibrium between two grain-boundary phases in the one-component system. At the transition point the chemical potentials of the atoms μ_1^S and μ_2^S are the same in the two phases:

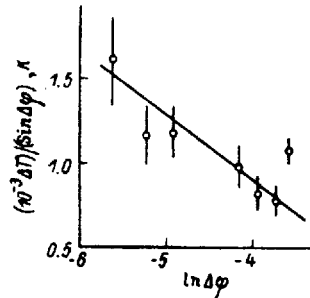


FIG. 9. Comparison of the $\Sigma 17$ - $\Sigma 1$ equilibrium line (points) and the predictions of the dislocation model at the transition temperature T_c (continuous line). Here, ϕ is the misorientation angle; $T = 220^\circ\text{C} - T_c$.

$\mu_1^S = \mu_2^S$. The grain-boundary phase equilibrium curve is governed by the surface along of the Clausius-Clapeyron equation. If the variables are σ and T , then

$$\left(\frac{d\sigma}{dT}\right)_l = -\frac{\Delta(\partial\mu^S/\partial T)_S}{\Delta(\partial\mu^S/\partial\sigma)_T},$$

$$\left(\frac{d\sigma}{dT}\right)_l = \frac{\Delta S^S}{\Delta A}.$$

It therefore follows that the first-order phase transition of a grain boundary is accompanied by an abrupt change in the entropy ΔS^S and in the specific area ΔA occupied by one mole of the substance in the boundary. If we consider boundaries with different misorientation angles ϕ , then the equilibrium temperature of the phase transition varies with the misorientation angle as follows:

$$\left(\frac{dT}{d\phi}\right)_l = -\frac{\Delta A}{\Delta S^S} \left(\frac{d\sigma}{d\phi}\right).$$

A change in the misorientation angle of a special boundary by $\Delta\phi$ gives rise to a wall of secondary grain-boundary dislocations with the period d_2 . The energy of a tilt boundary then increases by $\Delta\sigma$, which is given by

$$\Delta\sigma = \left(\frac{Gb_p^2}{4\pi(1-\nu)}\right) \sin \Delta\varphi \left(1 + \ln \frac{b_p}{2\pi r_0} - \ln \Delta\varphi\right).$$

Here, r_0 is the cutoff angle, and G and ν are the elastic moduli. We then find that

$$\Delta T = -\frac{\Delta A}{\Delta S^S} \left[\frac{Gb_p \sin \Delta\varphi}{4\pi(1-\nu)} \left(1 + \ln \frac{b_p}{2\pi r_0} - \ln \Delta\varphi\right)\right].$$

Figure 9 shows our dependence $T_c(\phi)$ plotted in the form of the dependences $(\Delta T / \sin \Delta\phi) - (\ln \Delta\phi)$. The intercept on the abscissa can be used to find r_0 : $r_0 \approx 1.9b_p$. Therefore, we find that the width of the cores of secondary grain-boundary dislocations is twice their Burgers vector. This is in agreement with the concept of greater width of the cores of grain-boundary dislocations is twice their Burgers vector. This is in agreement with the concept of greater width of the cores of grain-boundary dislocations.¹² The angle $\Delta\phi^*$ at which the cores of the grain-boundary dislocations merge can be estimated from the condition $d_2 = 2r_0$, and we then find that $\Delta\phi^* \approx 17^\circ$.

The slope of the straight line in Fig. 9 can be used to determine the value of $\Delta A / \Delta S^S$. If $G = 18 \text{ GPa}$ (Ref. 13), $\nu = 0.330$ (Ref. 13), and $b_p = a/\sqrt{17} = 7.8 \text{ nm}$, we find that $\Delta S^S / \Delta A = 0.04 \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. The value of $\Delta S^S / \Delta A$ can also be estimated from general thermodynamic considerations which yield $\Delta S = L/T_0$. Melting of tin requires $L_m/T_0 = 14 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ (Ref. 13) and we have

$\Delta A = \Delta V_m V_{mol}/a = 7 \cdot 10^2 \text{ m}^2/\text{mol}$ (Ref. 13). We therefore obtain $\Delta S^S/\Delta A = 2 \cdot 10^{-2} \text{ J} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. It therefore follows that the value of $\Delta S^S/\Delta A$ obtained in our experiments for the $\Sigma 17-\Sigma 1$ transition is an excellent agreement with the estimates obtained for a typical "bulk" phase transition.

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- ¹ L. S. Shvindlerman and B. B. Straumal, *Acta Metall.* **33**, 1735 (1985).
- ² A. N. Aleshin, S. I. Prokofyev, and L. S. Shvindlerman, *Scr. Met.* **19**, 1135 (1985).
- ³ A. V. Galina, V. E. Fradkov, and L. S. Shvindlerman, Preprint [in Russian], Institute of Solid State Physics, Academy of Sciences of the USSR, Chernogolovka (1985).
- ⁴ T. Y. Tan, S. L. Sass, and P. W. Balluffi, *Philos. Mag.* **31**, 575 (1975).

- ⁵ C. P. Sun and R. W. Balluffi, *Philos. Mag. A* **46**, 49 (1982).
- ⁶ G. Hasson, J. Y. Boos, I. Herbeuval, M. Biscondi, and C. Goux, *Surf. Sci.* **31**, 115 (1972).
- ⁷ E. M. Fridman, Ch. V. Kopetskii (Kopezky), and L. S. Shvindlerman, *Z. Metallkd.* **66**, 533 (1975).
- ⁸ D. M. Molodov, B. B. Straumal, and L. S. Shvindlerman, *Scr. Met.* **18**, 207 (1984).
- ⁹ B. B. Straumal, L. M. Klinger, and L. S. Shvindlerman, *Acta Metall.* **32**, 1355 (1984).
- ¹⁰ A. N. Aleshin, B. S. Bokshstein, A. L. Petelin, and L. S. Shvindlerman, *Metallofizika* **2**, No. 4, 83 (1980).
- ¹¹ Y. T. Chou, B. C. Cai, A. D. Romig Jr, and L. S. Lin, *Philos. Mag. A* **47**, 363 (1983).
- ¹² H. Gleiter, *Scr. Met.* **11**, 305 (1977).
- ¹³ *Properties of Elements* [in Russian], Metallurgiya, Moscow (1985).

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