Physics of the Solid State, 2024, Vol. 66, No. 4

01,08,15

Removal of impurities, defects and non-equilibrium quasi-particles from fine grains of amorphous alloy crystallites

© *S.V. Terekhov*

Donetsk Institute of Physics and Technology named after A.A. Galkina,
Donetsk, Russia

E-mail: svlter@yandex.ru

Received March 26, 2024
Revised March 26, 2024
Accepted March 29, 2024

Thermodynamic aspects of removal of foreign components from the fine grain of the crystalline phase of an amorphous alloy, the adsorption capacity of the crystallite boundary and the effect of the impurity type on the formation of a new layer for fractal and topological changes in the internal energy of atoms on the interphase surface are considered. The conditions of purification of fine grains are determined for ideal and interacting phases of an amorphous alloy. The paper shows that the positivity of the phase-mixing energy contributes to the formation of islands of the same type of particles. A change of the chemistry of the formed crystalline shell and the surface activity of impurities can result in the formation of layered structures.

Keywords: spherical fine grain, non-equilibrium, adsorption, segregation of impurities, surface tension.

DOI: 10.61011/PSS.2024.04.58191.69

1. Introduction

Amorphous, hierarchically structured and other similar alloys belong to non-equilibrium systems where locally equilibrium regions can be formed. Phenomena and processes at the external and internal boundaries of regions have a significant impact on the performance of materials and products made from them. In particular, the accumulation of impurities [1–5]:

– alters the mechanical and electromagnetic properties [6–9] of nanostructured [1,3] and *k*-component [2,4] alloys;

– results in degradation of the properties of materials exposed to radiation [5];

– reduces the performance of mechanisms [10,11];

– facilitates grain refining under severe plastic deformation [12,13] or the occurrence of phase instability [14].

A variety of approaches are used for analytical description of the impurity atom surface diffusion [15–20]. For instance, the study of bimetallic nanoparticles [20] showed the formation of a „core-shell" nanostructure when one of the components is displaced onto the nanoparticle surface. It should be noted that a component characterized by a lower value of surface tension moves to the surface. The challenge of describing the formation and stability of such structures is related to their non-equilibrium state.

A new derivation of the Butler equation [22] was proposed in Ref. [21] using the subregular solution model. The segregation in polycrystalline grains with a size up to 100 nm was evaluated for the core of a nanoparticle in the form of an unlimited impurity source. A similar problem needs to be solved for a spherical nucleus of a crystalline phase in an amorphous medium, but with a limited source of impurity atoms. It should be noted that the combination of atomistic and thermodynamic approaches in numerical modeling of the Au$-$Ag system [23] predicts the effect of formation of a layered structure, weakly expressed inside the core and clearly manifested on its surface. Moreover, it is necessary to distinguish the segregation layer from the layer of a new incipient phase at the boundary of the nanoparticle [19]. The interlayer increases in size over the time, and the thickness of the segregation shell reaches a constant threshold value. It is attributable to local alterations of the properties of the alloy at the interphase boundary.

An abnormal kinetics of the growth of the nucleus of a new phase is observed when an impurity particle moves along the surface of the crystallite because of the decrease of the characteristic energy of the system (Weissmuller effect [24]). The total energy of the grain boundaries decreases in a pure metal because of the absorption of smaller grains by large grains. The presence of impurities can result in the zeroing of the boundary energy because of the segregation of minor components, which results in the stabilization of the grain size [13,25,26]. The impurity concentration decreases at the interphase boundary if the grain size decreases [17].

The diffusion coefficients and segregation energies of impurity atoms differ in *k*-component alloys so the kinetics of impurity displacement at grain boundaries can become significantly non-monotonic. This is attributable to the fact that the diffusion coefficient of the impurity along the boundary significantly exceeds its value in the volume of the phase [20]. The segregation of impurities in grains with a size equal to at least a certain critical value in the case of binary alloys results in an ideal purification of the grain volume from an impurity component, even at sufficiently low temperatures [27].

Reduction of concentration of impurity at the fine grain boundary is well described using the regular solution model [20,28]. The grain refinement causes a phase transition shift towards lower temperatures at its boundary if the segregating atoms interact with each other [29]. Grain refinement to nanoscale sizes due to severe plastic deformation generates a large number of non-equilibrium boundaries, which prevents further grain refinement [20] and increases the segregation capacity of the alloy [27]. It should be noted that the expansion of the segregation layer stabilizes the non-equilibrium grain boundaries [20].

The following processes occur at the interphase boundary of a growing grain:
– formation of a new layer of the nucleus through the diffusion supply of atoms from an unlimited amorphous matrix;
– adsorption-desorption of particles;
– displacement of impurity atoms and quasi-particles from the grain volume to the boundary;
– diffusion wandering of adatoms;
– fractality of the energy landscape of the boundary, etc.

In view of the above problems, the purpose of this work is to determine the thermodynamic properties of a spherical crystal phase nucleus and its boundary in an amorphous alloy, to clarify the role of adsorption and the type of system components for the formation of an interfacial area.

2. Non-equilibrium states and purification of fine grains

Binary amorphous alloys are the most suitable objects for studying the patterns of phenomena and processes in a disordered environment because of their low impurity content. External impacts (isothermal annealing [30], severe plastic deformation [31], etc.) on such an alloy result in its crystallization with the formation of stable spherical nuclei when their radius exceeds a certain threshold value. However, the interphase surface of the crystallites is unstable and non-equilibrium, since various kinds of inhomogeneities, defects, and impurity atoms are displaced onto it from the nucleus volume.

Let's distinguish three non-equilibrium states of a grain:

1) weakly non-equilibrium (linear relationships between thermodynamic quantities) — the system can be approximated by a set of locally equilibrium regions according to Prigozhin [32]. Thermodynamic characteristics in them depend on the space-time arguments, and the potentials of thermodynamic fields smoothly change in case of the transition from region to region;

2) strongly non-equilibrium (nonlinear relationships between thermodynamic quantities) — even the local ergodicity is interrupted [33], the state can be described only using nonlinear kinetic equations;

3) states far from thermodynamic equilibrium — currents are produced both along the boundary and across it with the formation of dissipative structures in addition to various streams [34]. It is necessary to use a kinetic-dynamic approach for modeling the phenomena and processes.

Fine grains of the crystalline phase occupy small areas that quickly reach local equilibrium. Since Prigozhin's principle is applicable to the weakly non-equilibrium state of a spherical nucleus of a crystalline phase in an infinite amorphous medium, we consider a quasi-system of 4 ideal phases with volume fractions x_i $(i = 1-4)$: ordered (phase 1), impurity (phase 2), „void phase" [33] (phase 3) consisting of cavitons [34] (from Italian „cavitá" — cavity, void) and amorphous parent phase (phase 4). Subelements components are the components of phases, for example, grains of crystallites are taken as such for the crystalline phase.

Phase 1 is formed by atoms of the crystallizing component and contains a small amount of impurities, point defects, non-equilibrium inhomogeneities and cavitons displaced onto the interphase surface. Phase 2 is formed by a combination of impurity atoms and imperfections of the crystal lattice. Phase 3 mainly consists of cavitons, the volume fraction and quantity of which significantly exceed the volume fraction and quantity of atoms. Phase 4 is an equivalent of „a frozen" liquid in which the number of cavitons is comparable to the number of atoms, so the region is in a disordered state. The volume fractions of the phases x_i $(i = 1-4)$ are related by an obvious ratio

$$\sum_{i=1}^{4} x_i = 1, \tag{1}$$

We will use a cell-based approach like in Ref. [35] to describe the thermodynamic properties of grain. The volume of the crystallite is divided into cells of varying sizes, each of which contains one of the subelements of a particular phase. This approach results in the close packing of the with atoms, quasi-particles and cavitons. The chemical potentials of μ_i of subelements of ideal phases (phases that do not interact with each other) are determined by the formulas

$$\mu_i(P, T, t) = \mu_{i0}(P, T, t) + \beta^{-1} \ln x_i(T, t), \tag{2}$$

$\mu_{i0}(P, T, t)$ — standard values of chemical potentials for each phase, P — pressure, T — temperature, k_{B} — Boltzmann constant, $\beta = (k_{\mathrm{B}}T)^{-1}$. The independence of the values (2) from the spatial variable means that the phases are considered isotropic and homogeneous.

The expression for the Gibbs energy density is obtained by excluding the volume fraction of phase 1 from consideration using (1) and using (2)

$$g = \sum_{i=1}^{4} \mu_i x_i = h - sT, \tag{3}$$

where

$$h = g_1 + \sum_{i=1}^{4} g_i x_i$$

— Helmholtz energy density,

$$g_1 = \mu_{01},\ g_i = \mu_{0i} - \mu_{01}\ (i = 2\ldots4),\ s = -k_\mathrm{B}\sum_{i=1}^{4} x_i \ln x_i$$

— entropy density. Fine grains of the crystalline phase are purified when the characteristic function reaches a minimum of (3) according to the arguments $i = 2\ldots4$. In other words, the reaction of displacement of phases $i = 2\ldots4$ from a fine crystallite take place when the following equalities are reached

$$x_I/x_1 = \exp(-\beta g_i) = K(P, T). \qquad (4)$$

(4) shows that an increase of the values of g_i results in a decrease of the volume fractions of phases $i = 2{-}4$ in the fine grain. From a chemical point of view, the equality (4) describes the reaction of displacement of the subelements of the phase i $(i = 2\ldots4)$ from the fine grain of the crystalline phase. The value $K(P, T)$ determines the reaction constant at given pressure P and temperature T.

3. Phase interaction and transition of inhomogeneities to the boundary

A significant number of random variables are known to be subject to the normal distribution (Gauss–Laplace law [36]), the discrete equivalent of which is the Bernoulli distribution. Let us assume that the probability p_i that the phase subelement i has energy ε_i is described by the Boltzmann formula

$$p_i = \exp(-\beta\varepsilon_i). \qquad (5)$$

Then the probability W of placement of phase subelements in cells taking into account permutations N_i $(i = 1\ldots4)$ of identical subelements of the same grade is calculated according to the Bernoulli's theorem [36]

$$W = \Big(N!\prod_{i=1}^{4} p_i^{N_i}\Big) \Big/ \prod_{i-1}^{4} N_i!, \qquad (6)$$

here $N = \sum_{i=1}^{4} N_i$. The grain free energy density f per subelement is equal to

$$f = -\big(\theta \ln W\big)/(VN)$$
$$= \sum_{i=1}^{4} \varepsilon_i x_i + \theta \sum_{i=1}^{4} x_i \ln x_i = u - sT, \qquad (7)$$

where V — system volume, $x_I = N_i/N$, $\theta = k_\mathrm{B}T$, $u = \sum_{i=1}^{3} \varepsilon_i x_i$ — internal energy. Depending on the type of functions ε_i, the obtained relations can describe: a regular solution (only pair-phase interactions are taken into account), a subregular system (functions ε_i depend not only on pair interactions, but also on triple interactions) [37–39], etc. In the case of a regular solution, the chemical potentials of the subelements of the phases (2) are equal to

$$\mu_I = \big(\partial f/\partial x_i\big)_{V,T,x_j \neq x_i} = \mu_{i0} + \sum_{j=1}^{4} Q_{ij} x_j + k_\mathrm{B}T \ln x_i, \qquad (8)$$

where Q_{ij} —parts of the long-range order phase interaction potentials averaged over the system volume. The Gibbs energy density (3) reaches an extreme in the variable x_k $(k = 2\ldots4)$ taking into account the equalities (1) and (8) when the following ratio is fulfilled

$$\mu_1 + Q_1 x_1 = \mu_k + Q_k x_k, \qquad (9)$$

where $Q_1 = Q_{11} - Q_{1k}$, $Q_k = Q_{kk} - Q_{k1}$. The ratio (9) implicitly defines he dependence of the volume fraction x_k $(k = 2\ldots4)$ on the pressure P, temperature T and the volume fraction x_1 of the crystalline phase 1. We obtain the following by differentiating (9) by x_k $(k = 2\ldots4)$ taking into account the symmetric ratio $Q_{1k} = Q_{k1}$

$$\partial(\mu_1 - \mu_k)/\partial x_k = 2E_{1k}, \qquad (10)$$

where $2E_{1k} = Q_1 + Q_k$ is the mixing energy of phases 1 and k.

It is shown in Ref. [40] that an upward diffusion is observed when the displacement energy of two coexisting phases is positive. This means that the mutual diffusion coefficient has negative values, and particles of the same type tend to gather in one place. Therefore, if an impurity, defect, or non-equilibrium quasi-particle is displaced from the fine grain to its boundary, then they are surrounded by similar subelements, so the fine grain is purified.

4. Boundary adsorption capacity

Let's consider one nanosphere of a growing nucleus of the crystalline phase. Since its volume is divided into cells, the boundary surface also comprises L seats with areas a_i $(i = 1\ldots4)$. It should be noted that the caviton adsorption onto the nanosphere surface is equivalent to the desorption of any other subelement from the boundary, the total number of which is denoted by L, and the number of subelements of one or another type of system is denoted by L_t $(i = 1\ldots4)$. Then the following equalities are valid

$$\begin{cases} \sum\limits_{i=1}^{4} L_i = L \\ \sum\limits_{i=1}^{4} a_i L_i = aL = A \end{cases}, \qquad (11)$$

where $A = 4\pi r^2$ — the area of the spherical surface, r — the nu radius, the values $a_i L_i = A_i$ set the boundary areas occupied by the component i. It can be easily deduced from (11) that

$$L_4 = \frac{A - a_p L_p}{a_4}, \quad L = \frac{A - (a_p - a_4)L_p}{a_4}, \tag{12}$$

where

$$L_p = \sum_{i=1}^{3} L_i, \; a_p L_p = \sum_{i=1}^{3} a_i L_i, \; a_p = \sum_{i=1}^{3} a_i C_i,$$

the concentrations $C_i = L_i/L_p$ of subelements of the phases $1\ldots3$ are related to the effective concentrations of components by the equalities $C_i = c_i/c_p$ $(i = 1\ldots3)$, $c_p = L_p/L$.

The following equalities are obtained by dividing all equations (11) by L

$$\begin{cases} c_p + c_4 = 1 \\ a_p c_p + a_4 c_4 = \Gamma^{-1} \end{cases}, \tag{13}$$

here $\Gamma = L/A$ — the boundary adsorption capacity. The system (11) will take on the following form if all the equalities (11) are divided by the area of the boundary A

$$\begin{cases} \Gamma_p + \Gamma_4 = \Gamma \\ \sum\limits_{i=1}^{3} a_i \Gamma_i + a_4 \Gamma_4 = 1 \end{cases}, \tag{14}$$

where $\Gamma_I = L_i/A$ $(i = 1\ldots3)$ — adsorption of phase subelements, $\Gamma_P = \sum_{i=1}^{3} \Gamma_i$. From (13) and (14) we find

$$\Gamma = [a_p c_p + a_4(1 - c_p)]^{-1};$$

$$\Gamma_i = c_i \Gamma (i = 1\ldots3); \; \Gamma_p = c_p \Gamma; \; \Gamma_4 = (1 - c_p)\Gamma. \tag{15}$$

It is apparent from (15) that the adsorption capacity of the boundary Γ determines the Langmuir adsorption of all components of the quasi-system of phases. For instance, the adsorption of atoms, point defects, and nonequilibrium quasi-particles (except cavitons) is determined by the Langmuir isotherm formula (Figure 1)

$$\Gamma_p/\Gamma_{p0} = K c_p [1 + (K - 1)c_p]^{-1}, \tag{16}$$

where $\Gamma_{p0} = a_p^{-1}$, $K = a_p/a_4$.

The growing crystalline layer have the form of agglomerates (islands) with a low concentration of adsorbed atoms and quasi-particles ($c_p \ll 1$) and a positive mixing energy of adatoms, when each of them tends to surround itself with similar neighbors. The particles with a negative mixing energy are randomly arranged around the sphere. The layer practically covers the entire sphere of the nucleus if the concentration of atoms and quasi-particles is close to one and the growth of a new layer begins after filling this sphere. The surface diffusion in the considered cases forces the adsorbed particles to join the island or occupy more energetically advantageous positions. Therefore, the nucleating seed increases in size by the mechanism of layered growth despite the sign of the adatom mixing energy. The chemical and phase compositions of the crystallizing layers can change if the fine grain size exceeds a certain threshold value, i.e. a layered structure can form.

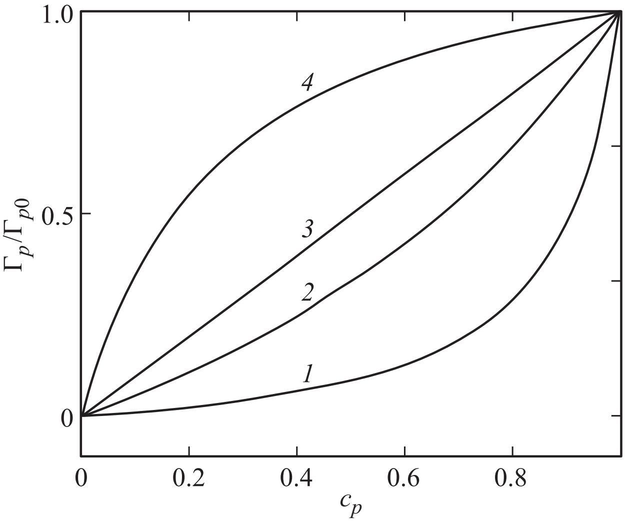

Figure 1. Langmuir adsorption isotherms with different values of the parameter K: *1* — 0.1; *2* — 0.5; *3* — 1.0; *4* — 5.0.

5. The impact of particles on surface tension

Its formation can be also caused by the impact of impurities and non-equilibrium quasi-particles on the surface tension of the layer. Impurity atoms can belong to the class of surface-active substances (SAS), surface-neutral substances (SNS) or surface-inactive substances (SIS). Particles of the first class reduce the fine grain boundary surface tension, particles of the second class do not change the fine grain boundary surface tension, particles of the third class increase it.

The growth of a spherical crystallite can be accompanied by the formation of a new monoatomic layer with fractal or topological dimensionality. Phases 1 and 2 can be considered as a combined source of atoms of crystallizing substance, impurities, defects and nonequilibrium quasi-particles since elements of phase 2 are displaced from the fine grain core to the boundary surface, and elements of phases 1 and 2 are adsorbed from phase 4. Let's apply a cell-based approach (see clause 3) to a system with the interaction of N_1 subelements of the combined phases 1 and 2, significantly exceeding the interactions of N_2 subelements of the other two combined phases 3 and 4. Additionally, we take into account the energy fractality of the boundary, i. e. the internal energy of the subelements of the combined phase is written as

$$\varepsilon_1 = Q_{11}(\Gamma_1)^{d-1}/2, \tag{17}$$

where Q_{11} — the energy parameter of the interaction of the subelements of the combined phase deposited on the boundary, Γ_1 — total adsorption of atoms, impurities, defects and non-equilibrium quasi-particles at the boundary, d — fractal similarity coefficient. The incremental free

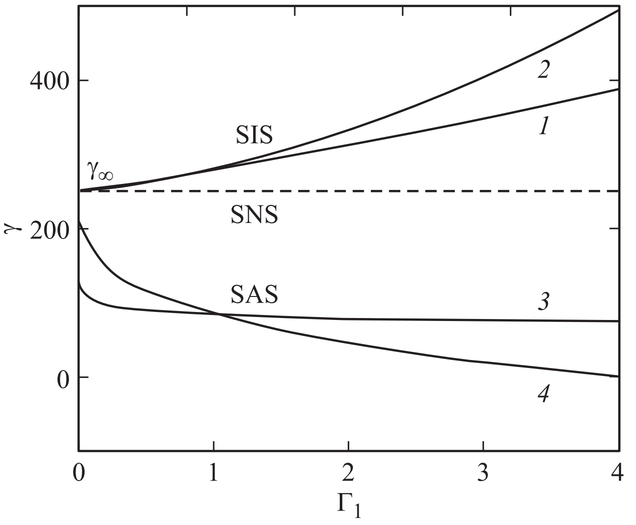

Figure 2. The dependence of the surface tension of the boundary γ on the adsorption of particles Γ_1 at $W=-30$, d: *1* — 1.1, *2* — 1.5; $W=165$, d: *3* — 0.05, *4* — 0.3.

energy of the new layer of the crystalline phase is written as

$$F_A=\gamma_\infty A+\varepsilon_1 N_1+\Delta\theta\left[N_1\ln\left(\frac{N_1}{N}\right)+N_2\ln\left(\frac{N_2}{N}\right)\right], \tag{18}$$

γ_∞ — surface tension in case of creation of a geometric surface at infinity, $\Delta\theta=k_\mathrm{B}\Delta T=k_\mathrm{B}(T-T_c)$, T_c — crystallization temperature. The surface tension is equal to (Figure 2)

$$\gamma=(\partial F_A/\partial A)_{N_1,T}=\gamma_\infty-0.5Q_{11}(d-1)(\Gamma_1)^d$$
$$+(\Delta\theta/a_2)\ln\left[(1-a_1\Gamma_1)/(1+(a_2-a_1)\Gamma_1)\right], \tag{19}$$

Figure 2 shows that the curves describe SAS with $W=0.5Q_{11}(d-1)>0$ and exponent $d<1$ and the curves describe SIS with $W=0.5Q_{11}(d-1)<0$ and $d>1$ (parameters $\gamma_\infty=250$ and $Z=\Delta\theta/a_2=-0.1$).

The principle of local equilibrium can be applied to a spherical grain if its surface is topological and has a weakly non-equilibrium state. Let's write the internal energy U of the boundary as [41]

$$U=\gamma A+S_A T+\mu L_p, \tag{20}$$

where γ —surface tension, S_A — entropy of the interphase boundary, L_p — the number of particles and quasi-particles placed at the boundary. The internal energy per unit area is equal to

$$u(s,\Gamma_p)=\gamma-iT+\mu\Gamma_p, \tag{21}$$

here $i=-S_A/A$ is the thermodynamic information. The following expression is obtained according to the Gibbs–Duhem ratio for the surface tension differential by calculating the infinitesimal change of the free energy (21) and taking into account its additivity

$$d\gamma=idT-\Gamma_p d\mu. \tag{22}$$

On the other hand, an infinitesimal change of surface tension according to the Laplace formula (for example, [42, p. 32]; [43, p. 13]) is equal to

$$d\gamma=(Pdr+rdP)/2, \tag{23}$$

wherein the differential of the radius of the nanosphere is set by the equality

$$dr=(\partial r/\partial T)_P dT+(\partial r/\partial P)_T dP. \tag{24}$$

The expression for the differential of the chemical potential of particles at the phase boundary is found from (22–24)

$$d\mu=(-d\gamma+idT)/\Gamma_p$$
$$=-(2\Gamma_p)^{-1}[r-r_0]dP+(i-i_0)dT=\omega dP-sdT, \tag{25}$$

where $r_0=-P(\partial r/\partial P)_T$, $i_0=(2\Gamma_p)^{-1}P(\partial r/\partial T)_P$, $\omega=-(2\Gamma_p)^{-1}[r-r_0]$ is the average volume per particle, and $-s=i-i_0$ is its contribution to the entropy of the boundary. This implies that the characteristic

$$i+s=i_0. \tag{26}$$

When the sum (26) is vanished ($i_0=0$), the boundary is in dynamic equilibrium and it reaches a stationary state when the right side is equal to the constant ($i_0=\mathrm{const}$). The particles are chaotized at the boundary when the right side is negative for the SIS and the particles are ordered when it is positive for the SAS. Because of the positivity of the value $\omega>0$, the partial derivative $\partial r/\partial P$ will have different values for SAS $r<r_0$ ($\Gamma_p>0$ [42]) and for SIS $r>r_0$ ($\Gamma_p<0$ [42]). The independence of the radius of the growing nucleus from pressure according to the definition of volume ω is possible only for SIS that increase surface tension.

6. Conclusion

One of the priorities of modern materials science is the creation of new alloys based on disordered media. Such alloys include, in particular, amorphous alloys with fine grains of the crystalline phase. Their amorphous matrix is reinforced with small crystallites, which makes it possible to classify such a material as composite. Experimental studies of alloys with purified grains and their boundaries demonstrate an improvement of the physical and chemical characteristics, increased thermal stability and service life of products made of such a material. Therefore, the determination of the thermodynamic conditions for purification of fine grains, the properties of their boundary surface, and the impact of particles on surface tension are urgent tasks. The use of various models is attributable both to the variety of mechanisms of growth of new layers on a spherical grain and their composition, and to the geometry of the formed boundary. The displacement of impurities, defects and non-equilibrium quasi-particles from the core of a fine grain to its boundary is described by a displacement reaction in the ideal phase model. Factoring of the interaction of subelements of phases within the framework of the cell-based model determines the role of mixing energy in the formation of islands of particles at the boundary or their chaotic distribution over the grain surface. The Langmuir isotherm defines the boundary adsorption capacity. The boundary surface tension depends on both its geometric nature and the chemical composition of the newly formed layers of the crystalline phase.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] S.V. Divinsky, S.M. Zakharov, O.A. Shmatko. Uspekhi fiziki metallov **7**, 1 (2006). (in Russian).

[2] K.D. Belashchenko, V.G. Vaks. ZhETF **112**, *2* (8), 714 (1997). (in Russian).

[3] V.M. Samsonov, I.V. Talyzin, A.Yu. Kartoshkin, M.V. Samsonov. Fizika metallov i metallovedenie **120**, *6*, 630 (2019). (in Russian).

[4] A.V. Matveev. Kondensirovannye sredy i mezhfaznye granitsy, **14**, *3*, 358 (2012). (in Russian).

[5] V.V. Slezov, O.A. Osmaev, R.V. Shapovalov. Voprosy atomnoy nauki i tekhniki **2**, 82 (2007). (in Russian).

[6] C.Y. Wong, C.R.M. Grovenor, P.E. Batson, D.A. Smith. J. Appl. Phys. **57**, *2*, 438 (1985).

[7] Y. Fujita, K. Kitakizaki, K. Masuda-Jindo. Solid State Phenomena **51−52**, 21 (1996).

[8] K. Wang, T. Xu, C. Shao, C. Yang. J. Iron Steel Res. **18**, *6*, 61 (2011).

[9] X.F. Zhang, T. Fujita, D. Pan, J.S. Yu, T. Sakurai, M.W. Chen. Mater. Sci. Eng. A **527**, *9*, 2297 (2010).

[10] V.I. Arkharov. In: Fizika hrupkogo razrusheniya. Nauk. dumka, Kiev (1976). Ch. II. pp. 44–57. (in Russian).

[11] A.V. Vasiliev, S.B. Ermakov, V.V. Karginova. Kholodil'naya tekhnika i kondicionirovanie **1**, 16 (2009). (in Russian).

[12] D.L. Beke, C. Cserháti, I.A. Szabó. J. Appl. Phys. **95**, *9*, 4996 (2004).

[13] J.R. Trelewicz, C.A. Schuh. Phys. Rev. B **79**, *9*, 094112-1 (2009).

[14] B.S. Bokstein, C.V. Kopetsky, L.S. Schwindlerman, A.N. Orlov, L.M. Klinger, D.A. Gorbunov, V.M. Ievlev, Y.M. Mishin, I.M. Razumovsky, S.Z. Bokshtein, A.N. Alyoshin, S.I. Prokofiev, B.B. Straumal, V.E. Fradkov. Structure and properties of internal interfaces in metals. Nauka, M. (1988). (in Russian).

[15] D. McLean. Granicy zeren v metallakh. Metallurgizdat, M. (1960). (in Russian).

[16] R.H. Fowler, E.A. Guggenheim. Statistical Thermodynamics. University Press, Cambridge (1939). 693 p.

[17] V.V. Slezov, L.N. Davydov, V.V. Rogozhkin. Phys. solid state **37**, *12*, 3565 (1995). (in Russian).

[18] P.C. Millett, R.P. Selvam, A. Saxena. Acta Mater. **55**, 2329 (2007).

[19] I.K. Razumov. FTT **56**, *4*, 749 (2014). (in Russian).

[20] I.K. Razumov. ZhFKh **88**, *3*, 485 (2014). (in Russian).

[21] G. Kaptay. J. Mater. Science **51**, *I.4*, 1738 (2016).

[22] J.A.V. Butler. Proc. Royal Soc. London A **135**, *I.827*, 348 (1932).

[23] A.G. Bembel. Fiziko-khimicheskiye aspekty izucheniya klasterov, nanostruktur i nanomaterialov. Tver. gos. un-t, Tver (2017). Vyp. 9. pp. 81–88. (in Russian).

[24] J. Weissmuller. Nanostruct. Mater. **3**, *1−6*, 261 (1993).

[25] K.A. Darling, R.N. Chan, P.Z. Wong, J.E. Semones, R.O. Scattergood, C.C. Koch. Scripta Mater. **59**, *5*, 530 (2008).

[26] E. Botcharova, J. Freudenberg, L. Schulz. Acta Mater. **54**, *12*, 3333 (2006).

[27] K. Ishida. J. Alloys Comp. **235**, *2*, 244 (1996).

[28] J.W. Christian. The theory of transformations in metals and alloys. Part I. Equilibrium and general kinetic theory. Pergamon Press, Oxford (1975).

[29] Cs. Cserhati, I.A. Szabo, D.L. Beke. J. Appl. Phys. **83**, *6*, 3021 (1998).

[30] P.S. Popel, V.E. Sidorova, M. Calvo-Dalborg, U. Dalborg, V.V. Molokanov. Rasplavy **3**, 223 (2020). (in Russian).

[31] G.E. Abrosimova, A.S. Aronin, S.V. Dobatkin, I.I. Zverkova, D.V. Matveev, O.G. Rybchenko, E.V. Tatyanin. Phys. solid state **49**, *6*, 983 (2007). (in Russian).

[32] D. Kondepudi, I. Prigogine. Modern thermodynamics. From heat engines to dissipative structures. John Wiley & Sons, Chichester (1998).

[33] S. Stølen, T. Grande. Chemical thermodynamics of materials: macroscopic and microscopic aspects. John Wiley & Sons Ltd, The Atrium, Chichester (2004).

[34] W. Ebeling. Eine einführung in die theorie dissipativer strukturen. BSB B.G. Teubner Verlagsgleseilschaft, Leipzig (1976).

[33] V.I. Fistul, V.I. Petrovsky, N.S. Rytova, P.M. Grinstein. Fizika i tekhnika poluprovodnikov **13**, *7*, 1402 (1979). (in Russian).

[34] S.V. Terekhov, A.I. Limanovsky. Fizika i tekhnika vysokikh davleniy, **28**, *3*, 65 (2018). (in Russian).

[35] S.V. Terekhov. Fizika i tekhnika vysokikh davleniy **22**, *2*, 22 (2012). (in Russian).

[36] E.S. Ventsel. Probability theory. Academia, M. (2005). (in Russian).

[37] A.A. Smirnov. Molekulyarno-kineticheskaya teoriya metallov. Nauka, M. (1966). (in Russian).

[38] Ya.I. Gerasimov, V.A. Geyderikh. Termodinamika rastvorov. MGU, M. (1980). (in Russian).

[39] S.V. Terekhov. Modelirovanie teplovykh i kineticheskikh svojstv real'nykh sistem. Veber, Donetsk (2007). (in Russian).

[40] S.V. Terekhov, V.D. Zaporozhets. Fizika i tekhnika vysokikh davleniy **29**, *3*, 65 (2019). (in Russian).

[41] A.W. Adamson. Physical chemistry of surfaces. John Wiley & Sons, N.Y. (1976).

[42] V.N. Zakharchenko. Kolloidnaya khimiya. Vysshaya shkola, M. (1989). (in Russian).

[43] M.V. Mamonova, V.V. Prudnikov, I.A. Prudnikova. Fizika poverkhnosti. Teoreticheskie modeli i eksperimental'nye metody. Fizmalit, M. (2011). (in Russian).

Translated by A.Akhtyamov