Regular article

Thermodynamic model of porosity stabilization in polycrystalline solids

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We demonstrate that a strong surface segregation of one of the components of the binary polycrystalline material can lead to barrier-less pore formation at the triple and quadruple junctions of the grain boundaries. These pores deplete the bulk of the polycrystal from the segregating component, which can lead to a local minimum in the dependence of the Gibbs free energy of the system on the pore size. We show that in some cases a porous polycrystal can be thermodynamically stabilized.

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Nanocrystalline materials exhibit a number of attractive properties, yet because of the high driving force for grain growth their thermal stability is rather poor [1]. The kinetic stabilization of the nanocrystalline microstructure (i.e. through the solute or Zener drag of grain boundary (GB) motion) can reduce the rate of grain growth, but cannot eliminate its thermodynamic cause, namely, the excess free energy of the GBs [2]. Weissmüller has demonstrated that the GB energy in the closed binary system with a strong tendency of the solute to segregate at the GBs can become negative, thus driving the process of grain refinement rather than growth [3]. Such a system eventually arrives at the metastable equilibrium corresponding to the local minimum of Gibbs energy of the entire system with respect to grain size (formally corresponding to zero GB energy). This thermodynamic stabilization of the nanocrystalline grain size is very attractive since it ensures the stability of the nanocrystalline state against local perturbations of microstructure. The original treatment [3] was refined and further developed in a series of subsequent studies [4–7]. In particular, it was shown that the models of regular solid solutions in the bulk and in the GBs provide a plausible explanation of the experimental data. However, it is often overlooked that in many cases the solutes strongly segregating to the GBs exhibit even stronger tendency to segregate on the free surfaces. This in turn leads to a steeper decrease in surface energy compared to GB energy with increasing solute concentration. For example, Schöllhammer et al. have observed that the ratio of γ_{gb}/γ_s (here γ_{gb} and γ_s are the energies of the GB and of the surface, respectively) increases from 0.44 in pure Cu bicrystal with the $\Sigma19a$ tilt GB (here Σ is a reciprocal density of coincidence lattice sites) to 0.68 in the same bicrystal doped with 50 ppm of Bi [8]. In this work we will show that the binary alloy, in

which the solute segregates stronger to the free surfaces than to the GBs, may exhibit a fundamental microstructural instability associated with barrier-less nucleation and growth of pores at the triple and quadruple GB junctions. Depending on the energy parameters of the system, this may lead either to a complete disintegration of the polycrystalline aggregate, or to a thermodynamic stabilization of the porosity at the GB junctions.

The most fundamental condition for the thermodynamic stability of polycrystalline solids is $\gamma_{gb} < 2\gamma_s$. If this inequality is violated, individual crystalline grains simply do not adhere to each other and could not form a polycrystalline aggregate. Moreover, considering the energy balance during formation of prismatic pores at the triple junctions (TJs) of GBs and tetrahedral pores at the grain edges yields the following, more restrictive stability criteria

$$\gamma_{gb} < \sqrt{3}\gamma_s$$

$$\gamma_{gb} < \sqrt{\frac{8}{3}}\gamma_s \qquad (1b)$$

for the prismatic (Eq. (1a)) and tetrahedral (Eq. (1b)) pores. Fortunately, in most cases the fundamental stability condition $\gamma_{gb} < 2\gamma_s$ and more restrictive conditions (Eqs. (1a) and (1b)) are satisfied, and the vast majority of polycrystalline solids are stable. For example, the typical range of energies of the random large angle non-special GBs in pure materials is $0.3–0.6$ γ_s and $0.8–1.5$ γ_s for metals and oxide ceramics, respectively [9,10], with the intermetallic compounds lying in-between [11]. Segregation of impurities to the GBs and free surfaces decreases their energies [8,12] and may change their ratio. As an illustration, let us consider the segregation of the solute (B) to the GBs or free surfaces of the binary solid A-B in the framework of regular solution models, similar to

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the approach of Abdeljawad et al. [13]. The detailed description of the model is given in Supplementary Material, while here we present the resulting dependencies of the GB/surface energy on the solute concentration in the bulk for different values of the interaction parameter of the regular solution in the GB/surface, ε_s (see Fig. 1). The bulk interaction parameter employed in calculations was $\frac{\varepsilon_{bulk}}{kT} = 3$, corresponding to the solubility limit and the spinodal point of 7 and 21.1 at.% of B, respectively (here kT has its usual thermodynamic meaning, and only the A-rich half of the system is considered). Other parameters employed in calculations corresponded to a typical metallic material: $n_s kT = 0.41$ J/m^2, where n_s is the number of atoms per unit area of the GB/surface, and $\gamma_A - \gamma_B = 0.5$ J/m^2, where γ_A and γ_B are the GB/surface energies of the pure A and B, respectively. One can see from Fig. 1 that when the surface interaction parameter ε_s is significantly lower than that of the GB, the surface energy decreases much faster than the GB energy with increasing c, and the stability conditions (Eqs. (1a) and (1b)) can be violated. In the case of coarse grained polycrystal this may lead to the unrestricted growth of pores at the GB junctions and disintegration of the polycrystal. Recently, Zhang and Luo observed this type of TJ instability in the Ni-Bi system contaminated with sulfur [14].

In the case of multiple nucleation of pores at the GB junctions the former will create a well-developed internal surface competing for the available solute atoms with the bulk and with the GBs. This may lead to thermodynamic stabilization of porosity. In what follow we will formulate a model of such stabilization based on the ideal solid solution model (the latter was selected for the sake of simplicity and extension to the regular solution model is straightforward).

Let us consider binary A-B polycrystalline material with pores and GBs. All N atoms of the crystal are distributed between three different regions: (i) the internal surfaces of the pores (here we neglect the segregation to the external surface of the specimen), $N^s = n_s A_s$, (ii) the GB region: $N^{gb} = n_{gb} A_{gb}$, and (iii) the bulk: $N^{bulk} = N - N^s - N^{gb}$. Here n_s and n_{gb} are numbers of atoms per unit area of the pore surface and of the GB, respectively, and A_s and A_{gb} are the total areas of the surfaces of the pores and of the GBs, respectively. We suppose that all three regions are in thermodynamic equilibrium. The Gibbs energy of the whole system is

$$G = N_1 \mu_1(c) + N_2 \mu_2(c) + A_s \gamma_s(c) + A_{gb} \gamma_{gb}(c) \tag{2}$$

Here μ_i ($i = 1,2$) is chemical potential of the component i ($i = 1$ and 2 correspond to the component A and B, respectively), N_i is the number

of atoms of the component i in the system (constant), and c is the bulk concentration of the component 2 (B).

The change of the Gibbs energy of the system caused by small variation of the surface and GB areas (for $N_i = $ constant) is

$$dG = \gamma_s(c) dA_s + \gamma_{gb}(c) dA_{gb} \tag{3}$$

Of course, the bulk concentration c in Eq. (3) also changes with the changing surface and GB areas. This concentration can be found from the mass balance condition. We suppose that the segregation of B on the surfaces of the pores and at the GBs follows Langmuir-McLean segregation equation [15], thus

$$Nc_0 = (N - n_s A_s - n_{gb} A_{gb})c + n_s A_s \frac{b_s c}{1 - c + b_s c} + n_{gb} A_{gb} \frac{b_{gb} c}{1 - c + b_{gb} c} \tag{4}$$

Here c_0 is average concentration of the component B in the system ($c_0 = N_2/N$), and b_s and b_{gb} are the segregations coefficients for surface and GB regions, i.e. $b_{s,gb} = \exp(-\frac{\Delta g_{s,gb}}{kT})$, Δg being the appropriate Gibbs energy of segregation [15]. The dependencies of the surface and GB energies on bulk composition follow Szyszkowski equations:

$$\gamma_s = \gamma_{sA} - n_s kT \ln(1 - c + b_s c)$$

$$\gamma_{gb} = \gamma_{gbA} - n_{gb} kT \ln(1 - c + b_{gb} c) \tag{5b}$$

where γ_{sA} and γ_{gbA} are the surface and the GB energies, respectively, of the pure component A. The relationship between A_s and A_{gb} depends on the geometrical arrangement of grains in the polycrystal. We assume that all grains are equally sized, space-filling tetrakaidecahedra (a body-centered-cubic array of polyhedral grains oriented so that the square and hexagonal facets correspond to (100) and (111) planes, respectively, see Fig. 2), and denote the distance between the square facets of an individual grain as D. Then the volume of one grain is $V_{grain} = 0.5D^3$, and the total GB area per grain A_{gb}, the total length of the TJs per grain, L_{tj}, and total number of the corners per grain, N_c are given by [16]

$$A_{gb} = 1.675D^2 \equiv \alpha_2 D^2,$$
$$L_{tj} = 4.25D \equiv \alpha_1 D, \tag{6}$$
$$N_c = 6.0 \equiv \alpha_0$$

While the numerical constants in Eq. (6) are approximate and depend on detailed geometry of the grains, the functional dependencies of A_{gb}, L_{tj} and N_c on D reflect a three-dimensional nature of our model and are assumed to be exact.

Fig. 1. The dependence of the change of the GB or the surface energy, γ-γ_A (γ_A being the energy of the GB or the surface in the pure component A), on the molar fraction of B, c, in the binary A-B alloy, for the different values of the regular solution model interaction parameter in the GB/surface, ε_s. The calculations were performed in the framework of regular solution models both in the bulk of the alloy, and on the surface/in the GB.
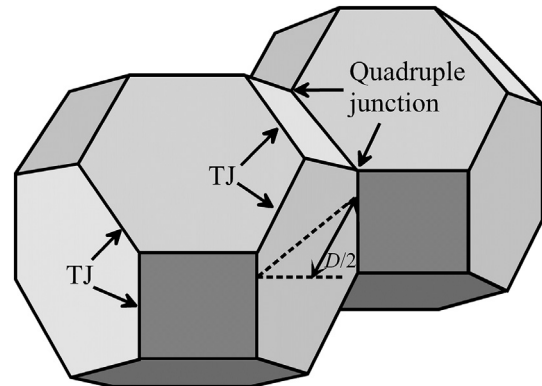

Fig. 2. Two tetrakaidecahedral grains of the dense polycrystal with the TJs and quadruple junctions serving as nucleation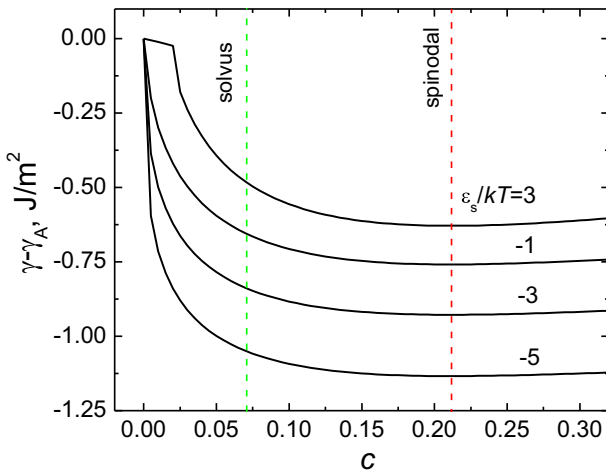 sites for prismatic and tetrahedral pores.