

ALLOY EFFECTS IN NANOSTRUCTURES

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Abstract—*Thermal stability and microstructure of nanocrystalline alloys are determined by the interaction of the chemical components with the topological defects. An important aspect of this interaction is the reduction of the grain boundary specific energy by grain boundary segregation. Based on very general thermodynamic considerations, this work presents a concept for the stabilization of nanocrystalline solids against grain-growth by grain boundary segregation. It is predicted that, for alloy systems with a large heat of segregation, the poly- or nanocrystalline alloy is in a metastable state for a particular grain-size which decreases with increasing concentration of the solute element. In the metastable state, the specific grain boundary energy is zero. A narrowing of the glass-forming region in glass-forming alloy systems is predicted when the metastable polycrystal can form.*

1. INTRODUCTION

The growing interest in nanostructured solids has mostly been focused on pure metals and on ceramic systems (for a recent review see (1)). Pure metals are suited as simple model systems for studying the physical properties related to the high density of interfaces in nanostructured solids in terms of interface atomic structure and basic thermodynamics of metastable systems. Ceramics offer good perspectives for applications where net-shape forming or ductility is required.

Nanocrystalline alloys represent an additional group of nanostructured solids. Because in these solids the density of topological defects is comparable to the density of alloy atoms, they promise to exhibit exciting new physical effects. The interaction between topological defects and alloy atoms should profoundly affect the relative stability of the various alloy phases. In addition, by going from a pure element or a stoichiometric compound to an alloy, an additional degree of freedom for the nanometer scale spacial structuring of the solid is introduced. The characteristic atomic structures involved when alloy atoms interact with grain boundaries emerge as essential structural elements when the grain size is reduced to the nanometer scale.

Figure 1 is a schematic representation of several different microstructures of nanostructured alloys. The alloys may be mixtures of crystals of different phases, which alloy at the grain boundaries (left). Nanocrystalline Fe-Ag alloys have been observed to consist of a fine dispersion of pure elemental crystals of Fe and Ag (2). Fe and Ag are not miscible in either the solid or the liquid state. Alternatively, the microstructure of nanostructured alloys may be dominated by

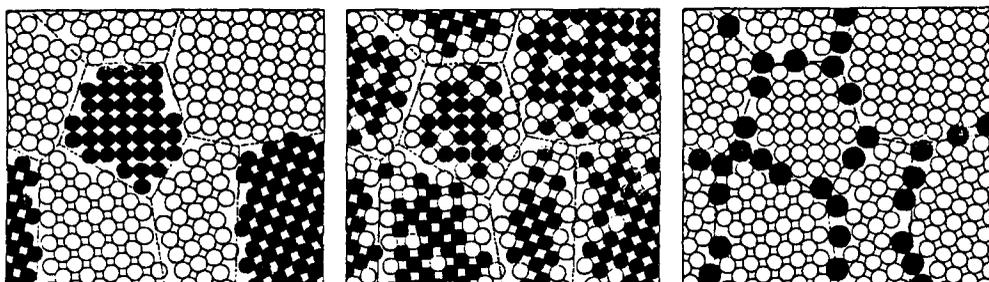


Figure 1. Schematic representation of different nanostructured alloy microstructures. The open and full circles represent two alloy components. Left: mixture of two phases. Center: extended gradients of density or composition. Right: grain-boundary segregation.

extended gradients of atomic density or composition perpendicular to each grain boundary (center). This has been observed in nanostructured amorphous Ti-Pd alloys (3). A particularly interesting type of nanostructured alloys is characterized by a strong tendency for grain boundary segregation, i.e. for an enrichment of the solute at the grain boundaries. In these alloys, the microstructure is such that one component is preferentially located in a segregation layer at the grain boundaries between crystals of the other component (right). A recent structural investigation of nanostructured Y-Fe alloys (4) demonstrates that the majority of Fe is segregated to the grain boundaries between nearly pure Y nanometer crystals.

There are two essential points of interest in nanocrystalline alloys involving grain boundary segregation. First, since the density of grain boundaries is high, these solids provide novel opportunities for experimental studies of grain boundary segregation. Such studies are difficult in conventional coarse-grained polycrystals because of the low concentration of segregation sites. Second, segregation may be a means of stabilizing the grain size in nanocrystalline solids. According to the Gibbs adsorption equation (5, 6), the specific grain boundary energy σ is reduced by segregation. If it was possible to reduce σ to a zero or negative value, then there would be no driving force for grain growth in such a solid. This would be an important step both towards application of nanostructured materials and towards fundamental studies of their properties at elevated temperatures. In fact, the stabilizing influence of grain boundary segregation has been speculated upon by several authors in the discussion of experimental results on nanostructured alloys (21, 4). Chapters 2-4 of the present work summarize results of a recent theoretical treatment of this question (7).

2. THERMODYNAMICS OF ALLOY POLYCRYSTALS

The general thermodynamic treatment of multicomponent systems containing an interface has been developed by Gibbs (5). In the present work, we shall follow Cahn (6) in applying Gibbs results, in a more modern notation, to grain boundaries. We neglect the dependence of grain boundary properties on crystal orientation and on curvature. Cahn defines layers surrounding each grain boundary, which are thick enough so that their outer bounds are everywhere located in regions where the crystal lattice is homogeneous and unaffected by the presence of the grain

boundary. The matter outside the layers is termed the matrix phase. The specific layer content of any extensive thermodynamic quantity, $[Y]$, can then be expressed as a function of the overall value of the quantity in the polycrystal, Y , and the respective overall value in the matrix phase outside the layer bounds, Y^M :

$$[Y] := \frac{Y - Y^M}{A} \quad ; \quad Y = Y^M + A[Y] \quad [1]$$

The thermodynamic properties Y^M of the matrix phase are those of an interface-free crystal with the same P , T , and number of atoms of component i , N_i^M , as in the matrix phase.

The layer concept, dividing the polycrystal into physically existing subsystems, is useful when discussing microscopic models (see chapter 4). In contrast, most experimental and certain theoretical (see e.g. (8)) results are given in terms of excess quantities. To determine the specific excess at the grain boundary, $\{Y\}$, of quantity Y , we compare the polycrystal to a homogeneous single crystal (the reference phase) with the same intensive properties (P, T, μ_i , concentrations) as the matrix phase, and with the same molar quantity of element '1' as the polycrystal. Hence, excess properties are defined, and can be determined from layer and matrix properties, by

$$\{Y\} := \frac{Y - Y^{REF}}{A} = [Y] - \frac{Y^M}{N_1^M} [N_1] \quad [2]$$

The total energy of a polycrystal is (6)

$$E = TS - PV + \sum \mu_i N_i + \sigma A \quad [3]$$

where σ is the specific grain boundary energy and A is the total interface area. All other symbols have their usual meanings. Gibbs shows that, in thermodynamic equilibrium, temperature and the chemical potentials of all components are constant everywhere within the system.

Equation [3], together with the definition of the Gibbs free energy, G , yields a total polycrystal value for G

$$G = \sum \mu_i N_i + \sigma A \quad [4]$$

with matrix and specific layer Gibbs free energies

$$G^M = \sum \mu_i N_i^M \quad ; \quad [G] = \sum \mu_i [N_i] + \sigma \quad [5]$$

The total differential of the Gibbs free energy G of a polycrystal is

$$dG = -SdT + VdP + \sum_i \mu_i dN_i + \sigma dA \quad [6]$$

A polycrystal which undergoes grain-growth at elevated temperature is considered here as a closed system ($dN_i = 0$, $dQ \neq 0$) where crystal lattice and grain boundaries are in thermodynamic equilibrium with respect to concentration of the solute atoms. The driving force for grain growth is the variation of Gibbs free energy of the polycrystalline closed system when the total grain

boundary area is reversibly varied at constant temperature and pressure. From equation [6], it is seen that this variation is $dG = \sigma dA$, and that the specific grain boundary energy σ is therefore governing the thermal stability of a polycrystal with respect to grain growth.

We shall now derive an expression which allows a direct evaluation of σ in an alloy polycrystal. To do so, we consider the change of G when solute is alloyed, at constant P, T , and A , into a pure component '1' polycrystal. From equation [4], the Gibbs free energy G^0 of the pure component '1' polycrystal is

$$G^0 = \mu_1^0 N_1 + \sigma^0 A \quad [7]$$

where μ_1^0 and σ^0 are the chemical potential of component 1 in its reference state and the specific grain boundary energy in pure component '1', respectively, at pressure P and temperature T .

The change in Gibbs free energy upon alloying, at constant P, T, A is of the form

$$\Delta G = \sum \mu_i^0 \Delta N_i + \Delta H^{\text{mix}} - T \Delta S^{\text{mix}} \quad [8]$$

which yields for polycrystal and matrix phase

$$G = \sum \mu_i^0 N_i + \Delta H^{\text{mix}} - T \Delta S^{\text{mix}} + \sigma^0 A \quad [9]$$

and

$$G^M = \sum \mu_i^0 N_i^M + \Delta H^{\text{mix},M} - T \Delta S^{\text{mix},M} \quad [10]$$

The polycrystal quantities ΔG^{mix} , ΔH^{mix} and ΔS^{mix} account for a combination of crystal lattice and layer properties; their values will in general be different from the corresponding single crystal values. Applying the definition of layer quantities [1] to determine $[G]$ from [9] and [10], and comparing to [5], we obtain an equation for the specific grain boundary energy in an alloy:

$$\sigma = \sigma^0 + [\Delta H^{\text{mix}}] - T [\Delta S^{\text{mix}}] - \sum (\mu_i - \mu_i^0) [N_i] \quad [11]$$

A useful form of this expression is obtained for the special case of a binary alloy where the matrix is a dilute solid solution of solute β in solvent α . In this case, integral molar heats of solution in matrix and grain boundary layer can be defined by

$$\Delta H_{\beta \text{ in } M}^{\text{sol}} := \frac{\Delta H^{\text{mix},M}}{N_{\beta}^M} \quad ; \quad \Delta H_{\beta \text{ in } \text{GB}}^{\text{sol}} := \frac{[\Delta H^{\text{mix}}]}{[N_{\beta}]} \quad [12]$$

and the chemical potentials are determined by the matrix composition:

$$\mu_{\alpha} = \mu_{\alpha}^0 + RT \ln \left(\frac{N_{\alpha}^M}{N^M} \right) \quad ; \quad \mu_{\beta} = \mu_{\beta}^0 + \Delta H_{\beta \text{ in } M}^{\text{sol}} + RT \ln \left(\frac{N_{\beta}^M}{N^M} \right) \quad [13]$$

Inserting [12] and [13] into [11] yields an expression for σ in the binary alloy with a dilute matrix:

$$\begin{aligned} \sigma_{(P,T)}^{\text{dilute M}} = & \sigma_{(P,T)}^0 - [N_\beta] \left(\Delta H_{\beta \text{ in M}}^{\text{sol}} - \Delta H_{\beta \text{ in GB}}^{\text{sol}} \right) \\ & - T \left(\left[\Delta S^{\text{mix}} \right] + [N_\alpha] R \ln \left(\frac{N_\alpha^M}{N^M} \right) + [N_\beta] R \ln \left(\frac{N_\beta^M}{N^M} \right) \right) \end{aligned} \quad [14]$$

Applying [2], we obtain the corresponding result in terms of excess quantities:

$$\begin{aligned} \sigma_{(P,T)}^{\text{dilute M}} = & \sigma_{(P,T)}^0 - \{N_\beta\} \left(\Delta H_{\beta \text{ in M}}^{\text{sol}} - \overline{\Delta H_{\beta \text{ in GB}}^{\text{sol}}} \right) \\ & - T \left(\left\{ \Delta S^{\text{mix}} \right\} + \{N_\beta\} R \ln \left(\frac{N_\beta^M}{N^M} \right) \right) \end{aligned} \quad [15]$$

where

$$\overline{\Delta H_{\beta \text{ in GB}}^{\text{sol}}} := \frac{\{ \Delta H^{\text{mix}} \}}{\{N_\beta\}} \quad [16]$$

In thermodynamic equilibrium, solute concentrations in matrix and layer or excess sites are related by an adsorption isotherm, the form of which depends on the microscopic details of the segregation process (see (9)). In the majority of those alloys which have a strong tendency for segregation, the excess of solute is experimentally observed to tend asymptotically towards a constant upper limit, the saturation coverage $\{N_\beta\}^{\text{sat}}$, as the solute concentration in the crystal lattice is increased at constant temperature and pressure, or as the temperature is decreased at constant solute concentration in the crystal lattice and constant pressure. Consequently, in a coarse-grained polycrystalline closed system, where the amount of solute exceeds the amount of segregation sites ($A\{N_\beta\}^{\text{sat}} \ll N_\beta$), the solute concentrations in lattice and grain boundaries are independent of the temperature in the low T limit. Hence, the entropy of mixing contribution to σ , represented by the last term on the right hand side of [15], vanishes with a linear temperature dependence at low T ($RT \ll \Delta H^{\text{seg}}$). As solute enrichment at grain boundaries is generally restricted to a layer with a width of the order of one atomic diameter, the absolute value of the excess entropy of mixing can be estimated (7) as $|\{ \Delta S^{\text{mix}} \}| \ll \{N_\beta\}^{\text{sat}} R \ln 2$. Hence, $\{ \Delta S^{\text{mix}} \}$ will contribute significantly to σ only at elevated temperatures. The specific grain boundary energy in the coarse-grained, low temperature limit then takes the simple form

$$\sigma = \sigma^0 - \{N_\beta\}^{\text{sat}} \left(\Delta H^{\text{seg}} + RT \ln \left(\frac{N_\beta^M}{N^M} \right) \right) \quad [17]$$

with the heat of segregation

$$\Delta H^{\text{seg}} := \Delta H_{\beta \text{ in } \alpha}^{\text{sol}} - \overline{\Delta H_{\beta \text{ in GB}}^{\text{sol}}}$$

It is seen that, if the atomic interactions in an alloy are such that the second term on the right hand side of [17] is larger than the first, then the very general thermodynamic considerations of

the present chapter indicate that the specific grain boundary energy of the coarse-grained alloy polycrystal must be negative, at least for not too high temperatures. In this case, according to [6], a polycrystalline closed system will tend to reduce its Gibbs free energy by spontaneously increasing A. If solute is enriched at the grain boundary, and if the lattice is stable with respect to spinodal decomposition ($d\mu_\beta/dx_\beta > 0$), then μ_β will decrease as the lattice concentration diminishes with increasing A, and, according to the Gibbs adsorption equation, σ will increase. If A is sufficiently large, there will be considerably more segregation sites than there are solute atoms, so that boundary and lattice are dilute solutions. For this case, σ has been shown (10) to vary as

$$\sigma = \sigma^0 - RT\{N_\beta\} \quad [18]$$

i.e. in the limit of large A, σ tends towards the positive value σ^0 . For positive σ , the polycrystal tends to spontaneously diminish A by grain-growth. At an intermediate value of A, σ equals zero, and, according to [6], the polycrystal is stable with respect to variation of A.

Hence, classical thermodynamics predict that, if the heat of segregation of an alloy system is sufficiently large, and if the overall solute concentration is not too small, then there exists a state for which the polycrystal is stable with respect to variations of its grain boundary area and of its grain-size. In general, this state will not correspond to the absolute minimum in G for the system; instead, the polycrystal is in a metastable state.

The critical assumptions used in the derivation of this result are first that segregation is of the saturation type, with a finite number density of segregation sites, and second that the number of solute and solvent atoms is conserved, i.e. the formation of phases with a lower μ_β than the lattice solid solution (pure crystalline β , an intermetallic phase or the alloy glass) must be suppressed, e.g. through a nucleation barrier.

3. INTERACTIONS BETWEEN ALLOY ATOMS AND GRAIN BOUNDARIES

The heat of solution in the crystal lattice can essentially be expressed as the sum of an electronic contribution and an elastic contribution (see e.g. (11)). The elastic contribution, due to the size-mismatch of the solute in the solvent lattice, is always positive and ranges, for metallic elements, to approximately 200kJ/mol (11). The electronic contribution, due to charge exchange between solute and solvent, may be of either positive or negative sign, and may reach absolute values up to 300kJ/mol for transition metal alloys (11).

The heat of solution in the grain boundary segregation sites may also be expressed as the sum of separate contributions (12). In addition to the elastic and electronic terms, the sum includes a 'defect energy' term, which accounts for the fact that the element with the lower defect energy tends to be enriched at the grain boundary. This term has been stated to be proportional to the difference in the specific grain boundary energies in the pure solvent and solute polycrystals (12,13). In a treatment of surface-segregation, Miedema (14) proposes a defect term which depends on the difference of the pure solute and solvent specific surface energies, but which also accounts for the different area fractions of the interface occupied by solvent and solute atoms with a large size difference. Since there seems to be no generally applicable topological model of grain boundary segregation, it is difficult to transfer such considerations to grain boundary segregation. A similar problem arises when treating electronic interaction energies in the grain boundary. Qualitatively, the electronic contributions to the integral heats of solution differ because the total

coordination number is reduced in the grain boundary, and because, if $\{N_\beta\} > 0$, then the number of solvent nearest neighbors to a solute atom in the grain boundary is reduced as compared to the lattice value (15). Hence, defect and electronic contributions to the heat of segregation—i.e. to the difference between the integral heats of solution in crystal lattice and grain boundary—are of either positive or negative sign, depending on the alloy system.

On the other hand, because at least part of the elastic strain is released when solute is transferred from lattice to boundary sites, the elastic contribution to the heat of solution in the grain boundary is generally considerably smaller than the corresponding lattice term, and elastic interactions therefore contribute a positive term to the heat of segregation. It has been stated that for incoherent grain boundaries, in particular, it is a good approximation to set the elastic strain energy due to segregated solute equal to zero (16). A high density of such incoherent high angle grain boundaries is present in nanocrystalline solids prepared by consolidating nm-sized crystals in random orientations (1). Hence, we may expect that heats of segregation in nanocrystalline solids may range up to a considerable fraction of the elastic energy of interaction in the crystal lattice, that is up to about 100 kJ/mol. Indeed, a value of $\Delta H^{\text{seg}} = 100$ kJ/mol is experimentally found for Bi-segregation in Cu polycrystals (12).

The molar number of atomic sites per unit area in a layer of thickness $\Omega^{1/3}$ (Ω is the average atomic volume, $\Omega^{1/3}$ is a measure of the distance between dense-packed atomic planes) is $1/(\Omega^{2/3}N_A)$, so the specific excess of solute in the saturated grain boundary, $\{N_\beta\}^{\text{sat}}$, can be correlated to Ω and to the number of monolayers of solute in the saturated grain boundary, Z , by the relation

$$Z := \{N_\beta\}^{\text{sat}} \Omega^{2/3} N_A \quad [19]$$

(N_A is Avogadro's number). For a typical atomic volume of a transition metal atom, $\Omega = 1.2 \cdot 10^{-29} \text{m}^3$, and for saturation at $Z = 1$ monolayer, equation [19] gives $\{N_\beta\}^{\text{sat}} = 3.2 \cdot 10^{-5} \text{mol/m}^2$. With $\Delta H^{\text{seg}} = 100$ kJ/mol, the reduction in σ predicted by equation [17] is 3J/m². Since σ^0 in pure metals is of the order of 1J/m² or less (17), it is seen that equation [17] predicts large negative values of σ for suitable alloy systems, e.g. those with a large atomic size mismatch.

4. MICROSCOPIC MODEL

An explicit expression for G is obtained when the formalism presented in chapter 2 is applied to McLean's microscopic model for grain boundary segregation (18,7). The model considers grain boundary and crystal lattice as random substitutional solid solutions with fixed numbers of sites, which are in thermodynamic equilibrium with each other. Concentration-independent interaction energies are attributed to solute atoms on lattice and grain boundary sites. In the present formalism, the total Gibbs free energy of the polycrystal, G^{PX} , is then:

$$\begin{aligned} G^{\text{PX}} = & N_\alpha \mu_\alpha^0 + N_\beta \mu_\beta^0 + \sigma^0 A + N_\beta^{\text{M}} \Delta H_{\beta \text{in } \alpha}^{\text{sol}} + N_\beta^{\text{GB}} \Delta H_{\beta \text{in GB}}^{\text{sol}} \\ & + RT \left(N_\beta^{\text{M}} \ln \left(\frac{N_\beta^{\text{M}}}{N^{\text{M}}} \right) + N_\alpha^{\text{M}} \ln \left(\frac{N_\alpha^{\text{M}}}{N^{\text{M}}} \right) + N_\beta^{\text{GB}} \ln \left(\frac{N_\beta^{\text{GB}}}{N^{\text{GB}}} \right) + N_\alpha^{\text{GB}} \ln \left(\frac{N_\alpha^{\text{GB}}}{N^{\text{GB}}} \right) \right) \quad [20] \end{aligned}$$

where N , N^M , N^{GB} are the overall number of atoms in the polycrystal, in the crystal lattice, and in the grain boundary, respectively, and N^M_i , N^{GB}_i denote the amount of component i in lattice and grain boundary, respectively. The concentrations in crystal lattice and grain boundary are governed by the Langmuir-McLean adsorption isotherm (18), which reads

$$\frac{N^{GB}_\beta}{N^{GB} - N^{GB}_\beta} = \frac{N^M_\beta}{N^M} \exp\left(\frac{\Delta H^{seg}}{RT}\right) \quad [21]$$

for a dilute solution in the crystal lattice.

Solving equation [21] for N^{GB}_β , and inserting in equation [20], an analytical expression for G as a function of $P, T, N_\alpha, N_\beta, A$ is obtained. We shall discuss the results here as an exemplary illustration of the thermodynamic properties of nanostructured alloys. For the rest of the discussion, we shall express A in terms of a more illustrative parameter, the grain size D , related to A by $A \approx 3V/D$ (however, since grain boundaries need not be planar, D is only a 'good' thermodynamic parameter in an idealized polycrystal with equiaxed grains and planar grain boundaries). The results given below were computed for the following parameters: $\{N\}^{sat}$ as above; ΔH^{sol}_β in $GB = 0$; ΔH^{sol}_β in $\alpha = \Delta H^{seg} = 100$ kJ/mol; $\sigma^0 = 1$ J/m²; $\mu^0_i = 0$. This model solid corresponds to the case of vanishing electronic contributions to the heats of solution in lattice and grain boundary, and to a vanishing 'defect contribution' to ΔH^{seg} .

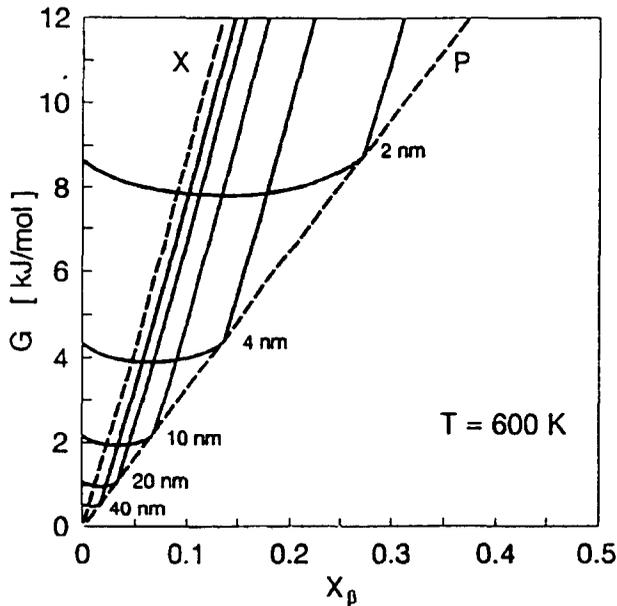


Figure 2. Variation of molar Gibbs free energy G with overall solute molar fraction x_β for a binary solid solution single crystal (dotted line marked 'X') and for alloy polycrystals with grain-sizes 2, 4, 10, 20, and 40 nm (full lines) at fixed P and T . The dotted line marked 'P' represents the Gibbs free energy of the metastable polycrystal, equation [22]. See text for parameters of the alloy system.

The variation of G^{PX} with D and x_β is illustrated in Figure 2. It is seen that G^{PX} assumes the value $\sigma^0 A$ for $x_\beta = 0$ and varies slowly with x_β as long as $x_\beta < N_{GB}/N$. In this regime, all solute is located in the grain boundary segregation sites. When $x_\beta > N_{GB}/N$, G^{PX} increases in parallel with the Gibbs free energy of the solid solution single crystal, G^X . In this regime, the segregation sites are occupied and additional solute is located in the energetically unfavorable lattice sites. For each grain size, there is a particular solute concentration above which the polycrystal has a lower Gibbs free energy than the single crystal. Furthermore, the individual G^{PX} curves are seen to intersect each other. The result is that, for each solute concentration, there exists a particular grain size for which G^{PX} is minimized. This grain size corresponds to the metastable state of the polycrystal. For large ΔH^{seg} , the Gibbs free energy G^P of the metastable polycrystal G^P increases linearly with x_β (7):

$$G^P = N_\alpha \mu_\alpha^0 + N_\beta \mu_\beta^0 + N_\beta \frac{\sigma^0}{\{N_\beta\}^{sat}} \quad [22]$$

This equation is represented by the dashed line marked 'P' in Figure 2; it is seen to form the envelope of all the G^{PX} curves which are generated when all possible values of D (or A) are considered.

Figures 3 and 4 display the variation of G^{PX} and σ with D (or A) for the same parameters as in Figure 2. The value of G^{PX} approaches the single crystal value for large D ; it reaches a minimum where $N_{GB} = N_\beta$. At this grain-size, the polycrystal is stable with respect to variation of D . σ (Figure 4) is negative for larger D , and positive for smaller D .

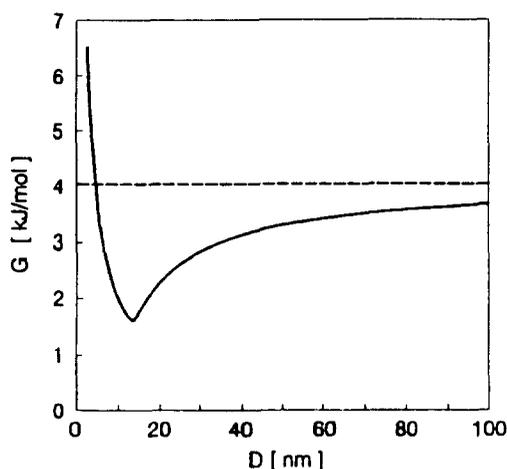


Figure 3. Variation of molar Gibbs free energy G of the polycrystal with grain size D for an overall solute molar fraction of $x_\beta = 0.05$ at fixed P and T . Dotted line: G of the solid solution single crystal with the same x_β .

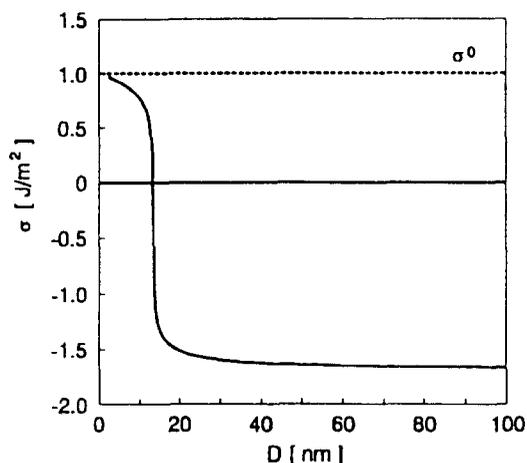


Figure 4. Variation of specific grain boundary energy σ with grain size D for an overall solute molar fraction of $x_\beta = 0.05$ at fixed P and T . Dotted line: specific grain boundary energy in the pure solvent polycrystal, σ^0 .

5. COMPARISON TO THE ALLOY GLASS

When experimental methods capable of achieving a high excess Gibbs free energy (such as rapid solidification, high-energy ball milling, or in situ consolidation of inert gas condensed nm particles) are applied to glass forming alloy systems, the glass is generally observed to form inside a certain interval of compositions, while poly- or nanocrystalline phases are formed for compositions outside this interval. When comparing the Gibbs free energy of the metastable polycrystal to that of the undercooled liquid alloy, or the glass, one is interested in the relative magnitudes of the quantity $\sigma^0/\{N\}^{\text{sat}} = \sigma^0\Omega^{2/3}N_A/Z$ in equation [22] on the one hand, and of the corresponding excess quantities in the undercooled melt on the other hand.

Empirically, σ^0 is found to scale with the solid-liquid interfacial energy γ^{SL} as $\gamma^{\text{SL}}/\sigma^0 \approx 0.3$ (17), and γ^{SL} scales with the heat of fusion ΔH^f as $\gamma^{\text{SL}}\Omega^{2/3}N_A \approx 0.5\Delta H^f$ (19), hence $\sigma^0\Omega^{2/3}N_A = a\Delta H^f$, with $a \approx 1.7$. In fact, a determination of the parameters a for metals from data for σ^0 in (17) yields an average value of $a = 1.3$. Hence, the excess Gibbs free energies of solid solution single crystal, ΔG^X , alloy glass, ΔG^L , and metastable polycrystal, ΔG^P , for a vanishing electronic contribution to the enthalpies of solution, can be summarized by the following equations:

$$\begin{aligned}
 \text{(a)} \quad \Delta G^X &= N_\beta \Delta H_{\beta \text{ in } \alpha}^{\text{sol,elastic}} - T\Delta S^{\text{mix}} \\
 \text{(b)} \quad \Delta G^L &= N(\Delta H^f - T\Delta S^f) - T\Delta S^{\text{mix}} \\
 \text{(c)} \quad \Delta G^P &= N_\beta \frac{\sigma^0}{\{N_\beta\}^{\text{sat}}} = N_\beta \frac{\alpha}{Z} \Delta H_\alpha^f; \alpha \approx 1.3
 \end{aligned}
 \tag{23}$$

Here ΔG^Y denotes the excess in Gibbs free energy of the matter in the system in state 'Y' as compared to the same amount of matter in its reference state, i.e. in the form of pure stable crystalline phases at T and P. ΔH^f and ΔS^f are weighted sums over the molar enthalpies and entropies of fusion, respectively, of the pure alloy components.

The Gibbs free energies given by equations [23] are graphically illustrated for two different temperatures in Figure 5. The parameters for G^X and G^P at $T = 600\text{K}$ are the same as for Figure 1. For consistency of the parameters, $a = 1.3$, and ΔS^m at T^m equals the gas constant R. ΔH^f and ΔS^f for temperatures below T^m are obtained according to (20). σ^0 is 1J/m^2 at $T = 600\text{K}$, with a realistic (17) temperature coefficient of $-0.2\text{mJ}/(\text{m}^2\text{K})$. The metastable polycrystal is seen to be thermodynamically more stable than the undercooled melt up to considerably higher solute concentrations than the solid solution single crystal. Hence, the glass forming region is expected to be narrowed when the metastable polycrystal can form.

In an attempt to check the predictions of the theory, a structural analysis of Y-Fe alloys with various compositions, prepared by in situ consolidation of inert gas condensed, nm sized particles, is presently performed (4). The alloy system features a large elastic and a small electronic contribution to the enthalpy of solution in the lattice. The grain size of these alloys is found to decrease with increasing solute content; the alloys are amorphous at high solute concentrations only. Hence, it seems not too unrealistic to anticipate that the metastable polycrystal and the glass may turn out to be competing states in certain experimental situations.

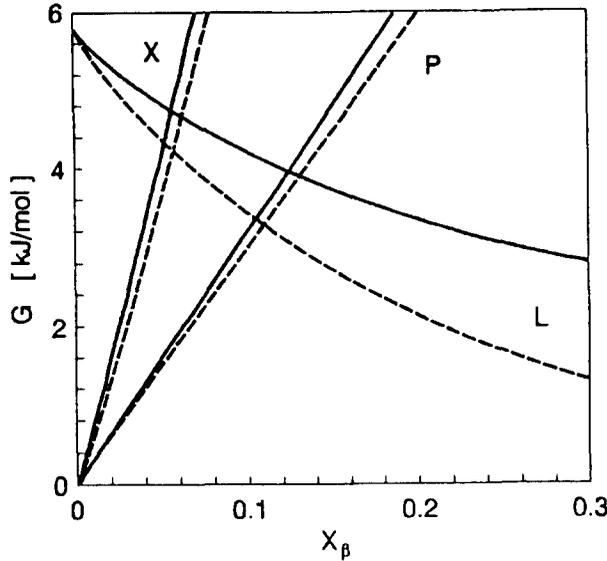


Figure 5. Variation of the excess Gibbs free energy G with overall solute molar fraction x_β for the solid solution single crystal (X), the metastable polycrystal (P), and the undercooled melt (L) at $T = 600\text{K}$ (solid lines) and at $T = 900$ (dotted lines). See text for parameters of the alloy system.

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