

Alloy thermodynamics in nanostructures

Jörg Weissmüller

Universität des Saarlandes and Institut für Neue Materialien, Gebäude 43,
D-66041 Saarbrücken, Germany

(Received 12 January 1993; accepted 24 August 1993)

The importance of the interactions between alloy atoms and topological defects for the thermodynamic properties of nanostructured alloys is pointed out. The McLean model for grain boundary segregation is extended to yield an expression for the total Gibbs free energy of an alloy polycrystal. This provides a simple conceptual basis for a qualitative discussion of the thermodynamic properties of nanocrystalline alloys. It is demonstrated that certain alloy poly- or nanocrystals may reach a metastable state, where the alloy is stable with respect to variation of its total grain boundary area.

A growing number of investigations on thermodynamic and structural properties of nanostructured alloys is lately being reported. A characteristic attribute of these systems is their high density of interfaces. For example, in a 3 nm grain size polycrystal, roughly half of the atoms are located on sites immediately adjacent to a grain boundary.¹ Hence, the concentrations of topological defects and alloy atoms are comparable in nanostructured alloys. When discussing the properties of these solids, it is therefore of central importance to consider the interaction between alloy atoms and topological defects. While these interactions *per se* have been investigated for a long time, the resulting knowledge is often neglected in studies of nanostructures. The present paper aims at pointing out the importance of this issue for the thermodynamic properties of nanostructured alloys.

Alloy atoms interact with grain boundaries via essentially three mechanisms²⁻⁴: first, part or all of the elastic strain energy due to atomic size mismatch is released when solute segregates to the grain boundaries; second, because the like and unlike atom coordination numbers in the grain boundary segregation sites differ from the lattice site coordination numbers, the electronic energies of interaction in the grain boundary sites are different from those in the lattice sites; third, the total "defect energy" of the grain boundaries is reduced when solute with a lower grain boundary energy segregates. As a result, the enthalpy of solution in the grain boundary segregation sites, $\Delta H_{\beta \text{ in } GB}^{\text{sol}}$, differs from the one in the crystal lattice, $\Delta H_{\beta \text{ in } \alpha}^{\text{sol}}$. The difference between both quantities, the enthalpy of segregation, is known to reach values of up to 100 kJ/mol.² Consequently, in thermodynamic equilibrium, the solute concentrations in lattice and grain boundary may differ by several orders of magnitude. This implies that the composition of nanostructured alloys may vary on a nanometer scale; hence, the alloys must not generally be considered to be homogeneous solid solutions or compounds.

We now give an exemplary illustration of how the thermodynamic properties of a solid solution are affected when the concentration of topological defects is comparable to the concentration of solute atoms, and when there is a strong interaction between those components. For this purpose, the McLean model for grain boundary segregation^{2,5} is extended to yield the total Gibbs free energy of an alloy polycrystal, G^{PX} , as a function of P , T , of the overall molar quantities of solvent " α " and solute " β ," N_{α} and N_{β} , and of the total grain boundary area, A . The model considers grain boundary and crystal lattice as random substitutional solid solutions with fixed molar quantities of sites, N^{GB} and N^M , respectively, which are in thermodynamic equilibrium with each other. We shall assume that N^{GB} , as well as the amounts of solvent and solute in the grain boundary layer, N_{α}^{GB} and N_{β}^{GB} , are proportional to the extensive thermodynamic variable A : e.g., $N^{GB} = A[N]$, where the bracket denotes the specific layer content of the respective quantity.⁶⁻⁸ The remaining quantities of solvent and solute, N_{α}^M and N_{β}^M , are situated in the crystal lattice (the "matrix phase" containing the grain boundary).

McLean attributes concentration-independent interaction energies to solute atoms on lattice and grain boundary sites. The expression given by McLean, which in its original form accounts only for the Gibbs free energy due to the solute atoms, implies that the total Gibbs free energy is

$$\begin{aligned} G^{PX} = & N_{\alpha} \mu_{\alpha}^0 + N_{\beta} \mu_{\beta}^0 + \sigma^0 A \\ & + N_{\beta}^M \Delta H_{\beta \text{ in } \alpha}^{\text{sol}} + N_{\beta}^{GB} \Delta H_{\beta \text{ in } GB}^{\text{sol}} \\ & + RT \left\{ N_{\beta}^M \ln \left(\frac{N_{\beta}^M}{N^M} \right) + N_{\alpha}^M \ln \left(\frac{N_{\alpha}^M}{N^M} \right) \right. \\ & \left. + N_{\beta}^{GB} \ln \left(\frac{N_{\beta}^{GB}}{N^{GB}} \right) + N_{\alpha}^{GB} \ln \left(\frac{N_{\alpha}^{GB}}{N^{GB}} \right) \right\} \quad (1) \end{aligned}$$

where μ_α^0 and μ_β^0 are the chemical potentials of the pure components in their reference state at P and T , and σ^0 is the specific grain boundary energy in the pure solvent at P and T . R is the gas constant. Besides a change in notation, the Stirling approximation has been applied to the original equation, and the first three terms on the right-hand side of the equation have been added. They are required for the expression to yield the correct result in the limiting cases of a solid solution single crystal ($A = 0$) and of a pure α polycrystal ($N_\beta = 0$).

Alternatively, Eq. (1) can be rationalized in another way: The first three terms on the right-hand side represent the Gibbs free energy of the components before mixing: pure α polycrystal and pure β single crystal. The remaining terms describe the variations of enthalpy and entropy when the components are mixed at constant P , T , and A . Both variations are separated into contributions from the crystal lattice on the one hand and from the grain boundary layer on the other hand. The description of systems containing an interface by a combination of crystal lattice and layer properties is discussed in more detail in Refs. 6–8. The specific grain boundary energy σ varies upon alloying; the variation is implicitly accounted for by the enthalpy and entropy terms in Eq. (1) [see also Eq. (3) below].

The concentrations in crystal lattice and grain boundary are governed by the Langmuir–McLean adsorption isotherm,^{2,5} which reads

$$\frac{N_\beta^{GB}}{N_\beta^{GB} - N_\beta^{GB}} = \frac{N_\beta^M}{N^M} \exp\left(\frac{\Delta H_{\beta \text{ in } \alpha}^{\text{sol}} - \Delta H_{\beta \text{ in } GB}^{\text{sol}}}{RT}\right) \quad (2)$$

for a dilute solution in the crystal lattice. Solving Eq. (2) or N_β^{GB} , and inserting in Eq. (1), an analytical expression for G^{PX} as a function of P , T , N_i , and A is obtained.

The McLean model has the drawback of neglecting solute-solute interactions in the grain boundary. On the other hand, these interactions may be small in alloys with a small electronic contribution to the heat of solution. For the purpose of the present work, the use of the simple model is motivated by the perception that it accounts for the most basic features of grain boundary segregation, namely: first, the existence of a number of sites with specific grain boundary properties, available to solute atoms; second, the fact that the number of sites is proportional to the total grain boundary area; third, the existence of a positive contribution, $\sigma^0 A$, to the solids' total energy, which is also proportional to the total grain boundary area; fourth, the distribution of solute and solvent atoms on lattice and segregation sites, governed by the thermodynamic equilibrium between lattice and grain boundary. Hence, the McLean model can provide an instructive qualitative picture of the thermodynamic properties of alloy poly- and nanocrystals.

The results given below were computed from the combined Eqs. (1) and (2) for the following parameters: $[N] = Z/(\Omega^{2/3} N_A)$, with an atomic volume $\Omega = 1.2 \times 10^{-29} \text{ m}^3$ for a typical transition metal and $Z = 1$ mono-layer of segregation sites (N_A is Avogadro's number); $\Delta H_{\beta \text{ in } GB}^{\text{sol}} = 0$; $\Delta H_{\beta \text{ in } \alpha}^{\text{sol}} = 100 \text{ kJ/mol}$; $\sigma^0 = 1 \text{ J/m}^2$; $\mu_i^0 = 0$; $T = 600 \text{ K}$. With these parameters, the model solid corresponds to an idealized alloy where the interactions between solute and solvent are of purely elastic origin, and where the corresponding strain energy is totally released upon segregation to the grain boundary.

For an idealized polycrystal with spherical grains, the total grain boundary area A can be related to a more illustrative parameter, the grain size D , and to the sample volume V , by $A \approx 3V/D$. The variation of G^{PX} with the overall solute molar fraction x_β is illustrated for different grain sizes D in Fig. 1. For large grain size, G^{PX} (solid lines) approaches the Gibbs free energy of the solid solution single crystal, G^X (dotted line marked "X"), whereas for grain sizes of a few nanometers, the variation of G^{PX} with x_β is fundamentally different. G^{PX} assumes the value $\sigma^0 A$ for the nanocrystalline pure solvent ($x_\beta = 0$) and varies slowly with increasing x_β as long as $x_\beta < N_\beta^{GB}/N$. In this regime, all solute is located in the grain boundary segregation sites. When $x_\beta > N_\beta^{GB}/N$, G^{PX} increases in parallel with G^X . In this regime, the segregation sites are occupied and additional

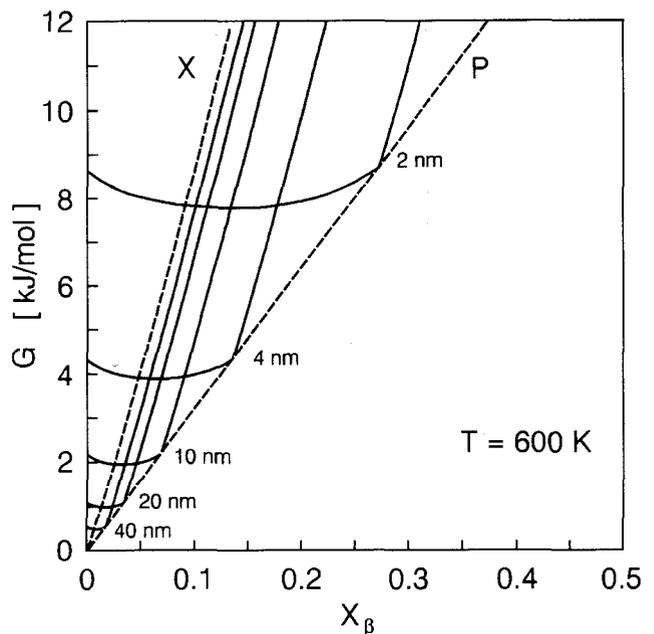


FIG. 1. Variation of molar Gibbs free energy G with overall solute molar fraction x_β for a binary solid solution single crystal (dotted line marked "X") and for binary alloy polycrystals with grain sizes 2, 4, 10, 20, and 40 nm (full lines) for fixed P and T . The dotted line marked "P" represents the Gibbs free energy of the metastable polycrystal with x_β , Eq. (4). See text for parameters of the alloy system.

solute is located in the energetically unfavorable lattice sites. For each grain size, there is a particular solute concentration above which the poly- or nanocrystalline alloy 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. Evidently, this grain size corresponds to a metastable state of the polycrystal.

The minimum in G^{PX} is further illustrated in Fig. 2, which displays the variation of G^{PX} with grain size for an overall solute molar fraction $x_\beta = 0.05$ at $T = 600$ K. For a large grain size, G^{PX} tends asymptotically to the Gibbs free energy of the single crystalline alloy of same overall solute content, represented by the dotted line in the figure. As the grain size diminishes, G^{PX} is reduced because the gain in internal energy from transferring solute from the lattice to the segregation sites exceeds the expense of energy needed to increase the grain boundary area. When the grain size is reduced below about 14 nm, G^{PX} increases because most of the solute atoms are now withdrawn from the crystal lattice, and a further increase in A will not gain significant segregation enthalpy, while energy is needed to increase A . The grain size of about 14 nm at the minimum in G^{PX} corresponds to the metastable state of the polycrystal.

A recent work establishes the theoretical foundation for metastability in polycrystalline alloys, based on rigorous phenomenological thermodynamic arguments⁷ (see also Ref. 8 for a short discussion of the issue). As

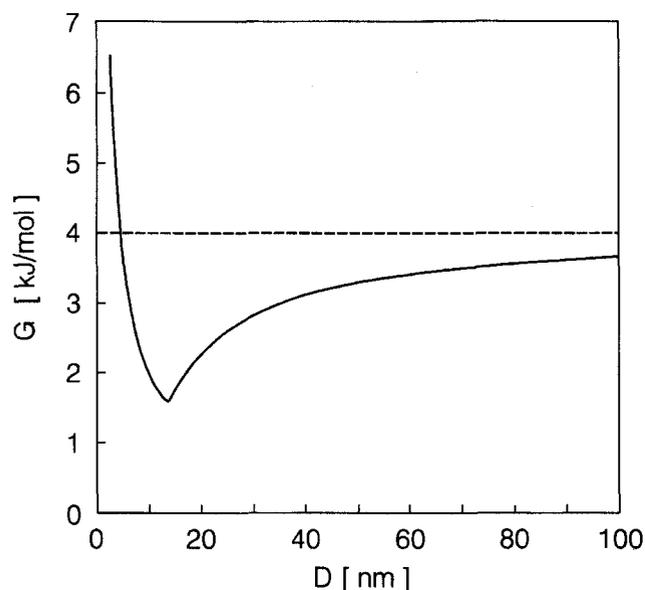


FIG. 2. Variation of the molar Gibbs free energy G of a binary alloy polycrystal with grain size D at fixed P , T , and fixed overall solute concentration $x_\beta = 0.05$. The dotted line denotes the Gibbs free energy of the solid solution single crystal with the same x_β . See text for parameters of the alloy system.

compared to the case of a single crystal, the expression for the Gibbs free energy of the polycrystal contains an additional set of conjugate variables, one extensive, the total grain boundary area A , and one intensive, the specific grain boundary energy σ .^{6,9} For a binary alloy polycrystal, and a dilute solution in the crystal lattice, σ is shown in Refs. 7 and 8 to be given by

$$\sigma_{(P,T)} = \sigma_{(P,T)}^0 - [N_\beta] \left(\Delta H_{\beta \text{ in } M}^{\text{sol}} - \Delta H_{\beta \text{ in } GB}^{\text{sol}} \right) - T \left([\Delta S^{\text{mix}}] + [N_\alpha] R \ln \left(\frac{N_\alpha^M}{N^M} \right) + [N_\beta] R \ln \left(\frac{N_\beta^M}{N^M} \right) \right) \quad (3)$$

where $[\Delta S^{\text{mix}}]$ is the grain boundary layer content in entropy of mixing. For a given alloy composition, a metastable state is shown to exist if σ in the coarse-grained alloy polycrystal ($N^{GB} \ll N_\beta$) assumes a negative value. For the McLean model with the parameters considered above, Eq. (3) yields negative values for σ in the coarse-grained limit at overall solute concentrations $x_\beta > 1.2 \times 10^{-6}$; for $x_\beta = 0.05$ (Fig. 2), a value of $\sigma = -1.7 \text{ J/m}^2$ is obtained for the coarse-grained polycrystal. Crucial requirements for metastability are (1) there is an upper limit to the specific excess¹⁰ of solute at the grain boundary, (2) lattice and grain boundary are in thermodynamic equilibrium with respect to solute concentration, and (3) the nucleation of second phases, as e.g., intermetallic compounds, is suppressed.⁷

If curvature effects on σ are neglected, then lattice and grain boundary composition in the metastable polycrystal are shown in Ref. 7 to be independent of the overall solute concentration; when x_β is increased, the grain size decreases to accommodate the additional solute. As a result, for alloys with a large heat of segregation, the Gibbs free energy of the metastable polycrystal, G^P , increases linearly with x_β (Ref. 7):

$$G^P = N_\alpha \mu_\alpha^0 + N_\beta \mu_\beta^0 + N_\beta \frac{\sigma^0}{\{N_\beta\}^{\text{sat}}} \quad (4)$$

where $\{N_\beta\}^{\text{sat}}$ is the specific excess of solute in the saturated grain boundary. Equation (4) is represented by the dotted line marked "P" in Fig. 1, which 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. For overall solute concentrations of a few atomic percent or more, the grain size of the metastable polycrystal is in the nanometer range.

From the data in Figs. 1 and 2, it is evident that the variation of Gibbs free energy with composition is both quantitatively and qualitatively changed when the grain size of an alloy polycrystal is decreased to the nanometer range. This demonstrates that the properties of nanostructured alloys can be understood only if the total concentration of topological defects and their interactions with the alloy components is accounted for.

The importance of the issue is further underlined by results of a recent structural analysis of nanostructured Y–Fe alloys prepared by *in situ* consolidation of inert gas condensed, mm-sized particles.¹¹ The grain size of the alloys is found to decrease with increasing solute content, with up to an overall of 30 at. % of Fe soluble in the grain boundary segregation sites between Y crystallites. In accordance with the considerations of the present work, the variation of grain size with solute content in the as-prepared state and upon annealing seems to imply a thermodynamic rather than kinetic stabilizing factor opposing grain growth in those nanostructured alloys.

LIST OF SYMBOLS

A	total grain boundary area
D	grain-size
$G^P(P, T, N_\alpha, N_\beta)$	Gibbs free energy of the metastable polycrystal
$G^X(P, T, N_\alpha, N_\beta)$	Gibbs free energy of the single-crystal
$G^{PX}(P, T, N_\alpha, N_\beta, A)$	Gibbs free energy of the poly- or nanocrystal
$\Delta H_{\beta \text{ in } \alpha}^{\text{sol}}(P, T)$	(integral) molar heat of solution in the crystal lattice
$\Delta H_{\beta \text{ in } GB}^{\text{sol}}(P, T)$	(integral) molar heat of solution in the grain boundary layer
N	total molar amount of matter
N^{GB}	molar amount of matter in the grain boundary layer
N^M	molar amount of matter in the crystal lattice outside the grain boundary layer
N_A	Avogadro's number
N_α	total molar amount of solvent
N_α^{GB}	molar amount of solvent in the grain boundary layer
N_α^M	molar amount of solvent in the crystal lattice outside the grain boundary layer
N_β	total molar amount of solute
N_β^{GB}	molar amount of solute in the grain boundary layer
N_β^M	molar amount of solute in the crystal lattice outside the grain boundary layer
P	Pressure
R	gas constant
$\Delta S^{\text{mix}}(P, T)$	entropy of mixing
T	temperature
V	volume

Z	number of atomic monolayers of solute in the saturated grain boundary
$\mu_\alpha^0(P, T)$	pure solvent chemical potential
$\mu_\beta^0(P, T)$	pure solute chemical potential
$\sigma(P, T, N_\alpha, N_\beta, A)$	specific grain boundary energy in the alloy
$\sigma^0(P, T)$	specific grain boundary energy in the pure solvent
Ω	atomic volume (assumed identical for solvent and solute)

Brackets

[]	specific grain boundary layer content of an extensive thermodynamic quantity; see definition in Refs. 6–8
{ }	specific excess of an extensive thermodynamic quantity at the grain boundary; see definition in Ref. 10

ACKNOWLEDGMENTS

When the present work was in preparation, R. Birringer and W. L. Johnson were independently investigating a similar concept. The author acknowledges intense and stimulating discussions with R. Birringer and a fruitful dialogue with H. Gleiter. This work was supported by Deutsche Forschungsgemeinschaft through the G. W. Leibniz program (H. Gleiter).

REFERENCES

1. H. Gleiter, *Prog. Mater. Sci.* **33**, 223–315 (1991).
2. E. Hondros and M. Seah, in *Physical Metallurgy*, edited by R. W. Cahn and P. Haasen (North Holland, Amsterdam, 1983), pp. 855–931.
3. P. Guyot and J. P. Simon, *J. de Physique C4*, **36**, 141–149 (1975).
4. M. Guttman and D. McLean, in *Surface Segregation in Metals and Alloys*, edited by W. C. Johnson and J. M. Blakely (ASM, Metals Park, OH, 1979).
5. D. McLean, *Grain Boundaries in Metals* (Oxford University Press, Oxford, 1957), pp. 116–150.
6. J. W. Cahn, in *Surface Segregation in Metals and Alloys*, edited by W. C. Johnson and J. M. Blakely (ASM, Metals Park, OH, 1979).
7. J. Weissmüller, *Phys. Rev. B* (unpublished research).
8. J. Weissmüller, *NanoStructured Materials* **3** (1993, in press).
9. J. W. Gibbs, *Trans. Conn. Acad.* **III**, 108–248 (1876); 343–524 (1878).
10. R. Fowler and E. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1952).
11. J. Weissmüller, W. Krauss, T. Haubold, R. Birringer, and H. Gleiter, *NanoStructured Materials* **1**, 439–447 (1992).