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Thermodynamic analysis of concentration fluctuations and homogeneous nucleation of crystal in undercooled liquid binary alloys: application to glass forming ability

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Thermodynamic analysis of the concentration fluctuations for large changes of composition, in undercooled liquid binary alloys is presented; a comparison between the Gibbs energy associated with their formation and the energy barrier for homogeneous nucleation is made. An extension of the Massalski T_0 concept for glass forming ability is proposed. Two systems are examined: Au–Si and Bi–Sn.

1. Introduction

Since the development of rapid quenching techniques of liquid alloys in the laboratory, many attempts have been made to establish criteria allowing one to foresee the possibilities of obtaining metastable crystalline phases or amorphous metals. The glass forming ability (GFA) has been discussed on the basis of the competition for stability between the undercooled liquid and the potential crystal forms that could crystallize from it [1]. A relatively high viscosity of the melt, whose composition is around the eutectic zone, with a predominance of heteroatomic bonding, reflected by a negative enthalpy [2] and volume of mixing [3, 4], are the main features of GFA. The crystalline phases which can nucleate from the liquid of a given concentration constitute a guide for GFA when one looks at their structure and their stability concentration range. The phase diagram, which in a manner synthesizes the above-mentioned characteristics, can yield a great deal of information about GFA [5].

The possibility of a composition-invariant single-phase nucleation in the form of a metastable crystalline phase remains an important feature for the competition for GFA in the rapid quenching of liquid binary alloys (A, B). This idea led Massalski [6] to introduce the "T_0 temperature concept" which is the temperature under which the crystallization from the liquid of composition x_A^L (x_A is the atomic fraction of A) to a crystal of the same composition ($x_A^S = x_A^L$) becomes thermodynamically possible, independent of the kinetics aspects, which have been discussed elsewhere [7]. This isoconcentration transformation is of interest because it can take place without prior fluctuation of concentration in the liquid.

This contribution presents a thermodynamic analysis of the concentration fluctuations, for large changes in composition, in an undercooled binary liquid alloy. A comparison between the Gibbs energy associated with these fluctuations and the energy barrier corresponding to the formation of a critical crystalline nucleus, is made. An extension of the T_0 concept, which takes into account the intrinsic fluctuations of concentration within the undercooled liquid, is proposed.

2. Gibbs energy associated with concentration fluctuations of large amplitude

Following Callen [8], the probability of fluctuations in the extensive variables X_0, X_1, X_i, X_n in a small portion of a system (the subsystem) the volume of which defines the size of the fluctuation, in contact with its surroundings, is given by:

$$\begin{aligned}\omega &= C \exp \frac{1}{k}\left(\hat{S} - \sum_0^n F_i\hat{X}_i - S[F_0, \ldots, F_n]\right)\\ &= C \exp\,(\sigma/k) \qquad (1)\end{aligned}$$

$\hat{S}$, $\hat{X}_i$ are, respectively, the "instantaneous" entropy and any extensive parameter, k is the Boltzmann's constant. F_i are the intensive variables of the "reservoir", $S[F_0, \ldots F_n]$ is the maximum of $(\hat{S} - \Sigma_0^n F_i\hat{X}_i)$ and is identical to the Legendre transform of the equilibrium entropy. C is a constant.

For the present case when studying concentration fluctuations in a liquid binary alloy (A, B) the subsystem including $n = \hat{n}_A + \hat{n}_B$ atoms is a small macroscopic part of the liquid sample which plays the role of the "reservoir". When concentration fluctuations proceed it can be considered that temperature, pressure and chemical potentials in the reservoirs remain constant. Let us first define the exponential term of Equation 1 for a binary alloy (A, B)

$$\begin{aligned}\sigma = \hat{S} - \sum_0^n F_i\hat{X}_i - S[F_0, \ldots, F_n] &= \hat{S} - \frac{\hat{U}}{T}\\ &- \frac{P\hat{V}}{T} + \frac{\mu_A\hat{n}_A}{T} + \frac{\mu_B\hat{n}_B}{T} - S + \frac{\langle U\rangle}{T} + \frac{P\langle V\rangle}{T}\\ &- \frac{\mu_A\langle n_A\rangle}{T} - \frac{\mu_B\langle n_B\rangle}{T}\end{aligned}$$

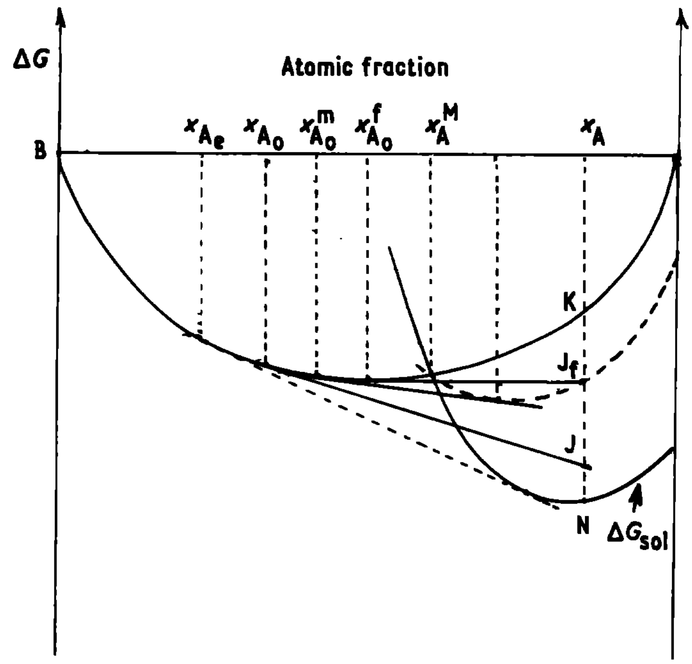

Figure 1 Molar Gibbs energy of formation of the liquid (A, B) (solid line) and of the solid solution rich in A (ΔG_{sol}) at T (referred to pure liquid elements).

where the symbol $\langle\ \rangle$ means the ensemble average. U and V are, respectively, the internal energy and the volume of the subsystem. μ_A and μ_B are the atomic chemical potentials of A and B in the reservoir. As temperature T and pressure P can be supposed to be homogeneous in the whole system when concentration fluctuations proceed (low atomic diffusion process compared to thermal diffusion and kinetics of reaching local mechanical equilibrium) the exponential term becomes:

$$\sigma = -\frac{\Delta\hat{G}}{T} + \frac{\mu_A}{T}\Delta n_A + \frac{\mu_B}{T}\Delta n_B$$

where $\Delta\hat{G}$ is the variation of the Gibbs energy of the *subsystem* corresponding to the fluctuation. $\Delta n_A = \hat{n}_A - n_A$; $\Delta n_B = \hat{n}_B - n_B$ are the fluctuations of the number of atoms in the subsystem. An equivalent expression for σ has been given by Landau [9] for dilute solutions. $\langle n_A\rangle/n = x_{A_0}$ is the average atomic fraction in the liquid and $\hat{n}_A/n = x_A$ the atomic fraction within the fluctuation, including $n = \hat{n}_A + \hat{n}_B$ atoms. Thus it follows that:

$$T\sigma = \frac{n}{N_a}\{x_A[\Delta\mu_A(x_{A_0}) - \Delta\mu_A(x_A)] + x_B[\Delta\mu_B(x_{A_0}) - \Delta\mu_B(x_A)]\}$$

where N_a is the Avogadro number. $\Delta\mu_A(x_A)$ is the difference of the classical molar chemical potential of A in the fluctuation and in the pure liquid A. $\Delta\mu_A(x_{A_0})$ is the difference between the molar chemical potential of A corresponding to the average concentration and its value in the pure liquid A. Thus the minimum work required or the Gibbs energy associated with the formation from the bulk of a fluctuation of n atoms and of concentration x_A is:

$$\begin{aligned} R_{\min} &= -T\sigma \\ &= \frac{n}{N_a}[\Delta G(x_A) - x_A\Delta\mu_A(x_{A_0}) - x_B\Delta\mu_B(x_{A_0})] \\ &= \frac{n}{N_a}\Delta G_f \end{aligned} \qquad (2)$$

where $\Delta G(x_A)$ is the molar Gibbs energy of formation of the liquid for the concentration x_A and temperature T, and ΔG_f represents the concentration-dependent term for the fluctuation. (Note that Equation 2 for the Gibbs energy of formation of a fluctuation is quite different from the classical quadratic form obtained for small fluctuation amplitudes [10].) A very simple representation of ΔG_f can be given on an isothermal Gibbs energy diagram (Fig. 1) representing the molar Gibbs energy of formation of the liquid (A, B) from the pure liquid elements as a function of atomic fraction x_A. It results from trivial geometric relationships that the positive quantity ΔG_f for a fluctuation of concentration x_A in a liquid, whose average concentration is x_{A_0}, is represented by the segment JK on Fig. 1 where the point J is at the intersection of the tangent to the Gibbs energy curve for x_{A_0} with the vertical line at x_A.

As we are studying fluctuations in concentration of great amplitude we are concerned with a non-uniform system and, in the frame of Cahn's formulation [11], we should have considered a gradient-dependent term in the previous Gibbs energy calculation. However, in the following discussion we are mostly concerned with melts which do not exhibit a miscibility gap, and we can take into account the non-uniformity by an interfacial energy term corresponding to a sharp compositional transition at the interface [12].

Applying the zero layer model or Becker's model [13] to the liquid–liquid interface, the excess energy per unit area, e^{xs}, corresponding to the fluctuation x_A in the liquid of concentration x_{A_0} is given by:

$$e^{xs} = \frac{m\lambda}{\Omega}(x_A - x_{A_0})^2 \qquad (3)$$

where m is a structural parameter, Ω is the mean molar interfacial area and λ is the classical molar exchange energy of the liquid for a regular solution. Positive values of λ lead to a miscibility gap in the liquid either in the stable or metastable temperature range of the liquid state. Far below the critical temperature [12] Equation 3 is a good approximation for the interfacial tension between the two unmixed liquids.

For systems exhibiting a predominance of heteroatomic bonding, λ and, consequently, e^{xs} are negative. The negative value for e^{xs} can be easily understood by the excess number of heteroatomic pairs appearing at the edge of the fluctuation when referring to the average number of heteroatomic pairs formed between two atomic layers within the bulk.

Considering that fluctuation is of spherical symmetry, the total work required for its formation is

$$W_f = \tfrac{4}{3}\pi\varrho\Delta G_f r^3 + \frac{4\pi m}{\lambda}(x_A - x_{A_0})^2 r^2 \qquad (4)$$

where r is the radius of the fluctuation and ϱ is the number of moles per unit volume in the fluctuation. (Formally, the negative value of the r^2 term of W_f could give a negative minimum in W_f for smaller r, which could mean a stabilization of the fluctuation. For a high negative value of λ the value of r which gives a negative minimum for W_f is of the order of 0.1 nm. This makes no sense, as Equation 4 is only valid for a macroscopic fluctuation.)

For typical values of critical radius for crystalline nucleation $r \geqslant 1$ nm, which we will consider in the following; the second term of Equation 4 is only a few per cent of the first one. Thus an overestimated value for the minimum work required to form a spherical fluctuation in a binary liquid alloy with $\lambda < 0$ is given by:

$$W_f = \tfrac{4}{3}\pi\varrho\Delta G_f r^3 = \frac{n}{N_a}\Delta G_f \qquad (5)$$

This approximated expression for W_f will be used in the following treatment.

3. Relation between the minimum work required for the formation of a fluctuation of concentration and minimum work required to form a critical crystalline nucleus in an undercooled binary liquid

The classical theory of homogeneous nucleation [14] in undercooled binary metallic melts (A, B) leads to the following expression for the Gibbs energy barrier, ΔG_n^*, for the formation of a spherical critical nucleus whose concentration is x_A and containing n^* atoms:

$$\Delta G_n^* = \frac{16}{3}\pi\frac{\sigma^3}{\varrho_s^2\Delta G_v^2}$$

where ϱ_s is the number of moles per unit volume of the solid, σ is the crystal–melt interfacial energy. ΔG_v, which is the molar Gibbs energy change when forming a small amount of solid of composition x_A from the liquid, is given by:

$$\Delta G_v = \Delta G_{sol} - x_A\Delta\mu_A(x_{A_0}) - x_B\Delta\mu_B(x_{A_0}) \qquad (7)$$

with

$$\Delta G_{sol} = x_A[\mu_{A_s}(x_A) - \mu^0_{A_L}] + x_B[\mu_{B_s}(x_A) - \mu^0_{B_L}] \qquad (8)$$

where μ_{A_s} and μ_{B_s} are the chemical potentials of A and B in the solid solution, $\mu^0_{A_L}$ and $\mu^0_{B_L}$ are the corresponding chemical potentials of the pure liquid elements. (ΔG_{sol} is represented in Fig. 1.) It is well known from the classical tangent rule that ΔG_v, which is necessarily negative, can be represented by the segment JN on the Gibbs energy–composition diagram of Fig. 1. ΔG_n^* is related to ΔG_v by using the following classical relations.

The number of atoms in the critical nucleus of radius

$$r_c = -\frac{2\sigma}{\varrho_s\Delta G_v} \qquad (9)$$

is

$$n^* = \tfrac{4}{3}\pi r_c^3\varrho_s N_a = -\tfrac{32}{3}\pi\frac{N_a\sigma^3}{\varrho_s^2\Delta G_v^3} = -\frac{2N_a\Delta G_n^*}{\Delta G_v}$$

Thus

$$\Delta G_n^* = \frac{1}{2}\frac{n^*}{N_a}(-\Delta G_v) \qquad (10)$$

Combining Equations 5 and 10 yields

$$W_f/\Delta G_n^* = 2n\Delta G_f/n^*(-\Delta G_v)$$

Let us consider a fluctuation of concentration with the same composition and the same size as the critical nucleus $n = n^*$; it follows that:

$$W_f/\Delta G_n^* = -2\Delta G_f/\Delta G_v$$

a relation giving the relative value of the energy barrier for the fluctuation to the critical nucleus one, without any information on the interfacial energy σ.

Going back to the graphical representation of Fig. 1, to compare W_f with ΔG_n^* is equivalent to comparing the segments 2 JK with NJ.

An interesting case which will be discussed later in more detail is obtained $W_f = \Delta G_n^*$, which is equivalent to the condition:

$$2\Delta G_f = -\Delta G_v; \; (2\,\mathrm{JK} = \mathrm{NJ} \text{ or } \mathrm{JK} = \tfrac{1}{3}\mathrm{NK}) \qquad (11)$$

The corresponding point J_f is one-third of the way along KN starting from K. Drawing the tangent from J_f to the Gibbs energy curve of the liquid we get the composition $x^f_{A_0}$ of the oversaturated liquid, for this temperature, which can give a critical nucleus of composition x_A for the same amount of energy as that for the corresponding fluctuation. In other words, as W_f and ΔG_n^* both appear in exponentials in the expressions of the probability of a fluctuation and the frequency of nucleation [14], it follows that Equation 11 corresponds to a rapid change in the frequency of appearance within the liquid of critical nuclei and fluctuations for the same size and composition. Typically a difference of 1% in the energy barrier for nucleation to the condition $\Delta G_n^* = W_f$ gives a ratio:

$$\exp -\frac{N^*}{N_a}\frac{W_f}{kT}\bigg/\exp -\frac{n^*}{N_a}\frac{\Delta G_n^*}{kT}$$

of the order of 10^6, for a nucleus of 2 nm radius. Thus, whatever the preexponential factors are, there is a drastic variation in the relative frequency of appearance of critical nucleus and fluctuation around the condition $\Delta G_n^* = W_f$. Considering now the whole range of possible composition for a critical nucleus $x_A^M < x_A \leqslant 1$ (x_A^M is the composition at the intersection

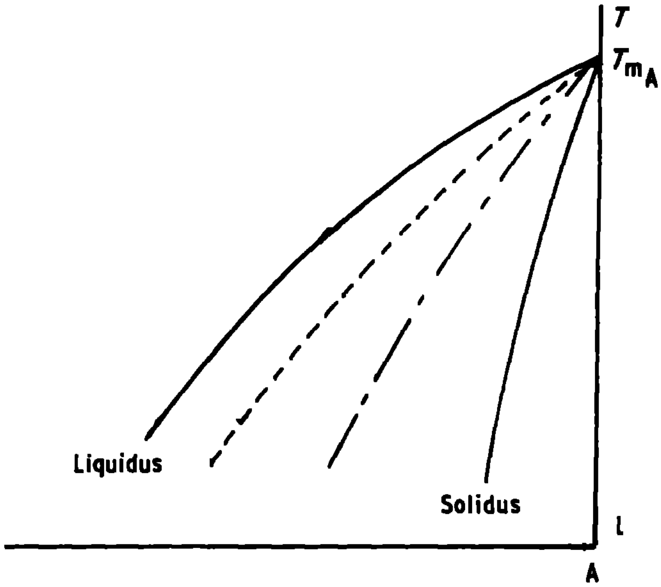

Figure 2 Relative positions of (---) T_F and (-----) T_0 curves between the liquidus and the solidus of the phase diagram.

of the Gibbs energy of formation curves for the liquid and solid alloys; this concentration is at the basis of the Massalski T_0 curves defining the limit of the possible partitionless crystallization from the liquid). The locus of the points J_f, for which $W_f(x_A) = \Delta G_n^*(x_A)$, is represented by the dashed curve in Fig. 1.

Within the oversaturated range of composition for the liquid at T, what is the maximum value of the oversaturation $x_{A_0}^m$ under which the Gibbs energy of formation of the concentration fluctuation in the range $x_A^M < x_A \leqslant 1$ is larger than the energy of formation for the critical nucleus? This $x_{A_0}^m$ value is thus given in Fig. 1 by drawing the common tangent to the locus curve of J_f and to the Gibbs energy curve for the liquid. The contact point with the liquid curve gives $x_{A_0}^m$. It must be noticed that the other contact point defines a concentration which does not correspond exactly to the solid composition which is more likely to nucleate in the liquid of concentration $x_{A_0}^m$. This concentration is given by the maximum value of $|\Delta G_V|$. A simple graphical method to evaluate this last composition has been given by Thompson and Spaepen [15].

By varying the temperature, the locus of the $x_{A_0}^m(T)$ can be represented on the phase diagram. Under this T_F curve, fluctuations of concentrations are comparatively energetically favorable. The general aspect of a T_F curve is given in Fig. 2 which also shows a T_0 curve. Of course the undercooling allowed to avoid fluctuations of critical size is much less than that to prevent partitionless transformation.

Massalski's approach represents a preliminary attempt to extrapolate arguments used to interpret massive phase transformations to the problem of GFA. If one considers that the fluctuations of concentrations which appear with a higher frequency than the critical nucleii below the T_F curves could play the role of privileged sites for crystalline nucleation, the T_F curves will reduce considerably the total range of composition for GFA allowed from the T_0 curves and will make this range closer to the eutectic region. The T_F curves have been calculated for the two systems Au–Si and Bi–Sn. The two following circumstances have been chosen for the Au–Si system.

First, solid solubilities are neglected (Fig. 3). The two T_F curves intercept in the negative temperature range. The highest undercooling to reach the T_F curves is around the eutectic composition which corresponds to the classical region for GFA by rapid quenching from the liquid. Note that in this case the T_0 curves coincide with the vertical axes on both composition limits of the phase diagram which would yield, according to Massakski's criteria, the whole range of composition as apt for GFA.

Second, the Au–Si T_F curves were evaluated considering very small reciprocal solubilities in the solid state (these solubilities cannot be shown on the scale chosen to represent the phase diagram in Fig. 4).

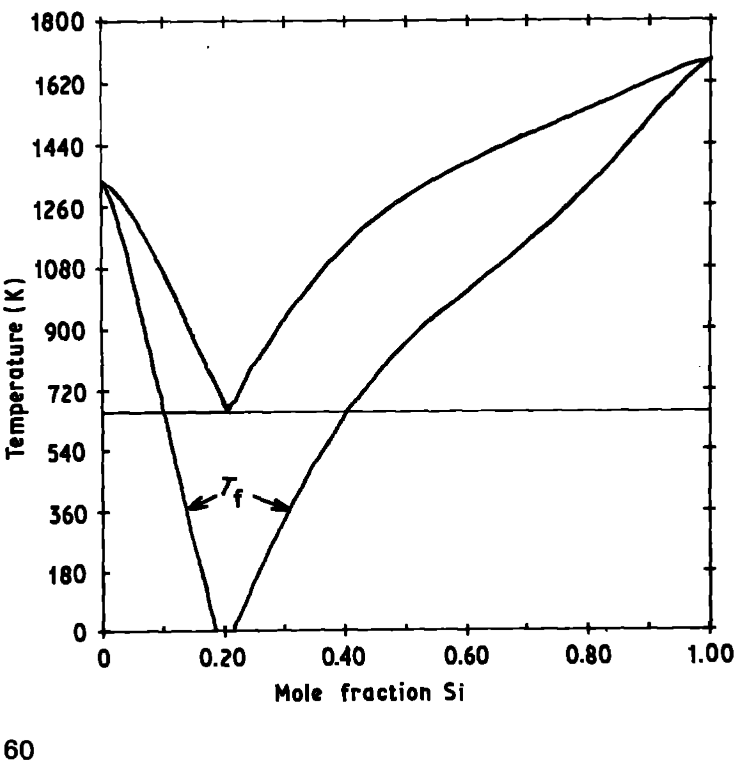

Figure 3 Calculated T_F curves for the system Au–Si, assuming no solid solutions.

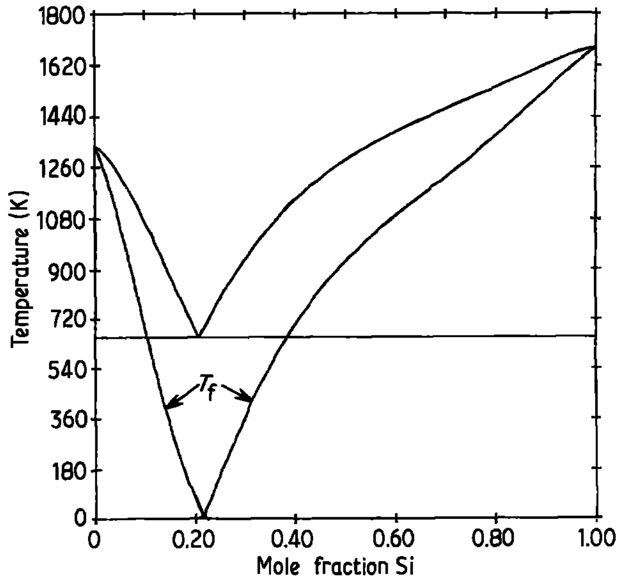

Figure 4 Calculated T_F curves for the system Au–Si, assuming small solid solubilities.

There is a sensitivity in the T_F curves to the extent of solid solutions which brings the T_F curves closer to the liquidus and, consequently, narrows the GFA composition range.

Obviously, for the small concentration range in the liquid (gold, silicon) phase the difference $T_L - T_F$ between the liquidus temperature and the T_F curve is surely smaller than the maximum undercooling which is, to our knowledge, unknown experimentally for this system. In fact, one has to keep in mind that even though the condition $W_f = \Delta G_n^*$ is fulfilled in this region, the great number of atoms in the critical nucleus n^* makes the probability infinitely small for the formation of either the fluctuations or the critical nucleus.

T_F curves for the system Bi–Sn are presented in Fig. 5 with the maximum undercooling temperatures determined experimentally by Perepezko *et al.* [16] for the whole range of composition. First, the T_F curves intercept for a positive temperature (T_i = 350 K) and delineate a domain for privileged fluctuations in the whole range of composition. The maximum undercooling temperatures lie entirely in this domain, which means that when homogeneous nucleation proceeds with the highest frequency in the melt the fluctuations of concentration might play the role of privileged sites for nucleation. Moreover, it can be emphasized that amorphous alloys Bi–Sn have not been obtained so far, from rapid quenching of the liquid.

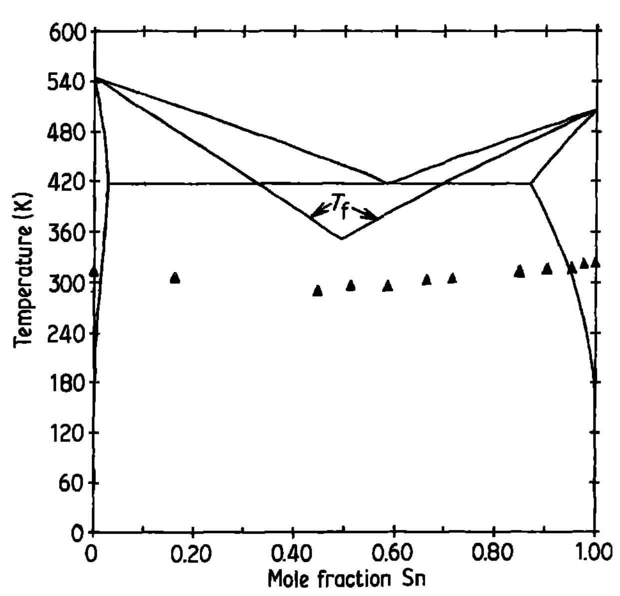

Figure 5 Calculated T_F curves for the system Bi–Sn. The black triangles represent the maximum undercooling temperatures measured by Perepezko *et al.* [16].

The present criterion is coherent with Sommer's [17] and Giessen's [18] approach to GFA based on a small Gibbs energy change on crystallization as a consequence of the relatively high stability of the liquid. In fact, a smaller Gibbs energy change on crystallization gives a common tangent to the J_F locus curve and the ΔG_{liquid} with a lower slope, in absolute value, and leads to higher values for $x_{A_0}^m$ which lowers the T_F curves and, consequently, increases the composition range for GFA.

4. Discussion and conclusions

Let us discuss more deeply the condition $W_f = \Delta G_n^*$. First, let us draw the whole Gibbs energy balance for the formation of a classical nucleus of radius r_c and composition x_A via fluctuations of concentration to be compared with the classical barrier ΔG_n^*.

As we have considered the case for which the minimum work required to create the fluctuation is equal to the energy barrier for the classical critical nucleus of the same concentration and size ($W_f = \Delta G_n^*$), the path via fluctuations will be energetically equivalent as a whole to the classical one only if the total Gibbs energy variation Δg_{LS} when forming the critical nucleus of radius r_c inside the prior fluctuation is found to be equal to zero. Of course, this condition has to be verified by virtue of the first principle.

We start with the infinitesimal expression for the Gibbs energy variation inside the fluctuation where the solid–liquid interface has to be built:

$$dg_{LS} = 8\pi\sigma_{iso} r\,dr - 4\pi\varrho_s[\Delta G_f - \Delta G_v]r^2\,dr \qquad (12)$$

where $(\Delta G_f - \Delta G_v)$ represents the new driving force for nucleation inside the fluctuation (segment NK in Fig. 1). σ_{iso} is the solid–liquid interfacial energy for isoconcentration of the solid and liquid. The integration of Equation 12 between $r = 0$ and $r = r_c$ and the use of Equation 9 leads to:

$$\Delta g_{LS} = \Delta G_n^* \left[3\frac{\sigma_{iso}}{\sigma} + 2\frac{\Delta G_f - \Delta G_v}{\Delta G_v}\right] \qquad (13)$$

Applying the zero layer model, already used before, one can find

$$\sigma_{iso} - \sigma = -\frac{m\lambda}{\Omega}(\Delta x)^2 \qquad (14)$$

which we can notice is equal to the excess interfacial energy associated with the formation of the fluctuation given by Equation 3. ($(\Delta x)^2$ is substituted for $(x_A - x_{A_0})^2$ which appears in Equation 3). Thus Equation 13 becomes:

$$\frac{\Delta g_{LS}}{\Delta G_n^*} = 1 + 2\frac{\Delta G_f}{\Delta G_v} - \frac{3m\lambda}{\Omega\sigma}(\Delta x)^2 \qquad (15)$$

Let us now again write the condition $W_f = \Delta G_n^*$ without neglecting the e^{xs} term in Equation 4 as we are doing an energy balance:

$$\frac{n^*}{N_a}\Delta G_f + \frac{4\pi m}{\Omega}\lambda(\Delta x)^2 r_c^2 = -\frac{1}{2}\frac{n^*}{N_a}\Delta G_v$$

as $n^*/N_a = \frac{4}{3}\pi r_c^3 \varrho_s$, the condition $W_f = \Delta G_n^*$ is equivalent to:

$$1 + 2\frac{\Delta G_f}{\Delta G_v} - \frac{3m\lambda}{\Omega\sigma}(\Delta x)^2 = 0 \qquad (16)$$

Consequently, if Equation 11 is satisfied, the right-hand term of Equation 15 is equal to zero and we find $\Delta g_{LS} = 0$. Thus we have checked that in the framework of the model used for calculation of interfacial energies, the path via fluctuations is energetically equivalent to the classical one. As a matter of fact, the condition $W_f = \Delta G_n^*$ appears to be a particular case of the more general relation expressing the first principle through the two thermodynamic paths:

$$(W_f)_{r=r_c} + (\Delta g_{LS})_{r=r_c} = (\Delta G_n^*)_{r=r_c}$$

an equation which can also be easily checked from the previous relations.

let us now pay attention to the values of Δg_{LS} inside the fluctuation for $r < r_c$. Integration of Equation 12 between 0 and r for $0 < r < r_c$ leads to:

$$\Delta g_{LS} = 4\pi r^2 \sigma_{iso} - \frac{4}{3}\pi\varrho_s[\Delta G_f - \Delta G_v]r^3$$

Δg_{LS} presents a maximum value between 0 and $r = r_c$ for:

$$r^* = \frac{2\sigma_{iso}}{\varrho_s(\Delta G_f - \Delta G_v)}$$

The corresponding value for the maximum of Δg_{LS} inside the fluctuation is:

$$\Delta g_{LS}^* = \frac{16}{3}\pi\frac{\sigma_{iso}^3}{\varrho_s^2[\Delta G_f - \Delta G_v]^2}$$

Dividing by the classical energy barrier for $r = r_c$ we get:

$$\frac{\Delta g_{LS}^*}{\Delta G_n^*} = \frac{\sigma_{iso}^3}{\sigma^3}\left(\frac{\Delta G_v}{\Delta G_f - \Delta G_v}\right)^2$$

which gives, when Equation 11 is satisfied and using Equations 14 and 16:

$$\frac{\Delta g_{LS}^*}{\Delta G_n^*} = \frac{4}{9}\left[1 - \frac{m\lambda}{\Omega\sigma}(\Delta x)^2\right]$$

For typical values of λ, Ω, σ the term in $(\Delta x)^2$ stays lower than unity, and consequently the energy barrier inside the fluctuation is smaller than that necessary to form the critical nucleus of radius r_c.

In this paper we have defined a significant particular thermodynamic state in the undercooled binary liquid for which the Gibbs energy variation leading to the classical critical nucleus is equivalent to the Gibbs energy of formation of the fluctuation of concentration of same size and concentration. For higher undercooling, the number of fluctuations per unit time is expected to become much greater than that of classical nucleus and the fluctuations might play the role of privileged sites for nucleation. The nucleation inside these fluctuations involves a Gibbs energy barrier lower than the classical one and inside the fluctuation critical nuclei could be formed; they are, of course, of smaller size when compared to the classical critical one. However, when the total energy balance is drawn for a given temperature we have to include the minimum work required to form the preexisting fluctuation (of n^* size) and the total energy found is higher than the classical energy barrier. The case of pre-existing fluctuations at higher temperature and as-quenched in the undercooled liquid would be interesting to study from both the energetic and kinetic points of view.

We have proposed an extension of Massalski's T_0 concept which is consistent with the general criterion due to Sommer and Giessen and gives a significant concentration region for GFA even though the extent in concentration of the solid phases which are supposed to crystallize is very small; this is specifically the case for systems exhibiting an easy GFA. This criterion can be extended to systems including more than two elements.

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References

1. R. W. CAHN, *J. Phys. Coll.* **43** (1982) C9-55.
2. P. G. ZIELINSKI and .H MATYJA, Proceedings RQ2 Sec. I edited by N. J. Grant and B. C. Giessen (Massachusetts Institute of Technology, Cambridge, Massachusetts, 1976) p. 237.
3. A. R. YAVARI, P. HICTER and P. DESRE, *J. Chim. Phys.* **79** (1982) 579.
4. P. RAMACHANDRARAO, *Z. Metallkde* **71** (1980) 172.
5. I. W. DONALD and H. A. DAVIES, *J. Non-Cryst. Solids* **30** (1973) 77.
6. T. B. MASSALSKI, Proceedings RQ4 1, (Japan Insitute of Metals, Sendai, 1982) p. 203.
7. P. GRESSIN, N. EUSTATHOPOULOS and P. DESRE, *Scripta Metall.* **17** (1983) 711.
8. H. B. CALLEN, "Thermodynamics" (Wiley, New York, 1960).
9. L. D. LANDAU and E. M. LIFSHITZ, "Statistical Physics", (Pergamon, London, Paris, 1959) p. 362.
10. P. GLANSDORFF and I. PRIGOGINE, "Structure-Stabilité-Fluctuations" (Masson, Paris, 1971) p. 102.
11. J. W. CAHN and J. E. HILLIARD, *J. Chem. Phys.* **28** (1958) 2.
12. L. COUDURIER, N. EUSTATHOPOULOS and P. DESRE, *Fluid Phase Equilibria* **4** (1980) 71.
13. R. BECKER, *Ann. Phys.* **32** (1938) 128.
14. I. S. KAMENETSKAYA, "Growth of Crystals", Vol. 8, edited by N. N. Sheftal (Consultants Bureau, New York, 1969) p. 271.
15. E. V. THOMPSON and F. SPAEPEN, *Acta Metall.* **31** (1983) 2021.
16. J. H. PEREPEZKO, D. H. RASANNUSSEN, I.-E. ANDERSON and C. R. LOPER Jr, International Conference on Solidification and Casting, Sheffield (1977) 2, p. 21.
17. F. SOMMER, *Z. Metallkde* **73** (1982) 77.
18. B. C. GIESSEN, Proceedings RQ4 Vol. 1, edited by T. Masumoto and K. Susaki (Japanese Institute of Metals, Sendai, 1982) p. 213.

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