On the Operative Mechanisms in the Solidification of Undercooled Melts*

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Abstract

The role of undercooling in controlling the operative mechanisms of solidification and in promoting the formation of extended solid solutions in the Ag–Cu and Cd–Zn systems is discussed. Use is made of a novel expression for the free energy of an undercooled liquid in arriving at several characteristic temperatures controlling the mechanism of solidification. The temperature T_0, of equal free energy of solid and liquid phases, the temperature T_f at which fluctuations in the liquid state can become potent nucleants and the temperature T_a at which the driving forces for the processes of solute redistribution and of diffusionless solidification become equal are determined for the two systems. The prominent role of the entropy of fusion in determining the mixing parameters from phase diagram data is highlighted.

1. Introduction

For pure metallic melts, it is customary to evaluate a critical nucleus size r^* by imposing the extremum condition with respect to size on the total free-energy change ΔG_t accompanying nucleation. A critical nucleus is one whose growth or dissolution reduces the free energy. The critical size is inversely proportional to ΔG_V, the free-energy change in transformation per unit volume. A critical nucleus will have a size ranging from a minimum value at the given temperature to infinity at the equilibrium melting temperature. Use of a similar procedure for a binary melt requires that the two cases when $\{\partial(\Delta G_t)/\partial r\}_{x_B}$ and $\{\partial(\Delta G_t)/\partial x_B\}_r$ are zero be considered separately for the evaluation of the critical size r^* and critical solute concentration x_B^*. The concentration at which the critical nucleus has the smaller size $x_B(r_m)$ need not necessarily coincide with the concentration x_B^* at which the work of formation of a critical nucleus is the smallest. We thus have to distinguish between a critical nucleus, a minimum critical nucleus and a nucleus with the smallest energy of formation [1].

Aptekar and Kamenetskaya [2] considered solidification to be composed of a process of redistribution of elements at the interface and another process of transformation at constant concentration of the solid phase. The former has a driving force ΔG_a given by

$$\Delta G_a = a(\Delta\mu_A - \Delta\mu_B) \tag{1}$$

while the latter is driven by the free-energy difference

$$\Delta G_c = (1 - x_{Bs})\,\Delta\mu_A + x_{Bs}\,\Delta\mu_B \tag{2}$$

where a is the fraction of solid formed, and $\Delta\mu_A$ and $\Delta\mu_B$ represent the difference between the chemical potentials of the components A and B in the liquid and solid phases with solute concentrations x_{Bl} and x_{Bs} respectively. In the particular case when $x_{Bl} = x_{Bs} = x_{B0}$, $\Delta G_c = 0$ at a characteristic temperature T_0 and corresponds to $G_l(x_{B0}) = G_s(x_{B0})$.

The rates of the exchange and rearrangement processes depend on the temperature. Above T_0 where $\Delta G_c > 0$, only the redistribution process is favoured while, below T_0, both processes are possible. At a characteristic temperature T_d, both rates will become equal. Considering only the energy factors governing the rates, Aptekar and Kamenetskaya [2] evaluated a temperature T_a where the equality $(1 - x_B)x_B|\Delta G_a| = \Delta G_c$ is satisfied for the case where a liquid transforms to a solid of the same concentration. T_a is an approximate measure of the ΔT necessary to drive a diffusionless transformation.

Recently, Desre [3] has considered the possibility of a large concentration fluctuation in the liquid, leading to nucleation. The special case of when the total work required for the formation of a spherical fluctuation of the same size and concentration as a critical nucleus is equal to the activation energy for the formation of a critical nucleus was considered. For this case the condition $2\Delta G_f = -\Delta G_V$ is satisfied. ΔG_f is the free energy of formation of a fluctuation in concentration x_B in liquid of average concentration x_{B0}. Solution of the above equation for a given value of x_{B0} will yield a temperature T_f. Since the fluctuations with the critical size and concentration considered are capable of nucleating the solid phase, Desre concluded that, at temperatures below T_f, fluctuations act as privileged sites for nucleation.

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The thermodynamic information needed for the estimation of ΔG_a, ΔG_c, ΔG_f, ΔG_v (and consequently T_0, T_f and T_a) are available in the phase diagram. Since we are likely to deal with the liquid phase at large undercoolings, a correct formulation of $G_l - G_s$ at such temperatures will aid in a correct evaluation of T_0, T_a and T_f and throw light on the possible route to the production of the metastable states.

We chose two eutectic systems Ag–Cu and Cd–Zn for the present analysis. The constituent elements of both systems satisfy the Hume-Rothery conditions for the formation of extended solid solutions but do not form these under equilibrium conditions [4]. On rapid solidification, solid solutions are formed over the entire composition range in the Ag–Cu system [5] while a limited extension of solubility is noticed in the Cd–Zn system [6, 7].

2. The free energies of the solid and liquid phases

Since the constituent elements have the same crystal structure, for both the systems the free energy of the nucleating solid phase can be represented by a single expression as a function of both temperature and concentration. For both solid and liquid phases, we used the subregular solution approximation including a temperature dependence as recently employed by Murray [8].

Accordingly, the free energy of any solution at a temperature T is given by

$$G_i = G_{Ai}{}^0 x_{Ai} + G_{Bi}{}^0 x_{Bi} + RT(x_{Ai} \ln x_{Ai} + x_{Bi} \ln x_{Bi})$$
$$+ (h_{1i} + s_{1i}T)x_{Ai}x_{Bi} + (h_{2i} + s_{2i}T)x_{Ai}x_{Bi}(x_{Ai} - x_{Bi}) \quad (3)$$

where the subscript i stands for either the liquid or the solid phases with x_A and x_B denoting the concentrations of A and B respectively. $G_{Ai}{}^0$ and $G_{Bi}{}^0$ are the free energies of the pure constituent elements in the same state as the solution; h_1, h_2 and s_1, s_2 are the parameters which yield the excess free energy in the solution model used. One of the parameters required for the evaluation of G_i is the free-energy difference between the liquid and solid states of any component j. Lele et al, [9] have recently shown that

$$\Delta G_j = -(G_{jl}{}^0 - G_{js}{}^0)$$
$$= \Delta S_{mj} \, \Delta T_s \left(1 - \frac{\Delta C_{pmj}}{\Delta S_{mj}} \frac{\Delta T_j}{T_{mj} + T}\right) \quad (4)$$

where ΔT_j is the undercooling $T_{mj} - T$ and ΔC_{pmj} is the value of the heat capacity difference between the two states at T_{mj}. The above expression can be visualized as a modification of the standard Turnbull ex-

pression [10] and faithfully reproduces $\Delta G_j{}^0$ up to $T_{mj}/2$. We have employed this expression to arrive at G_i with the aid of eqn. (3). In order to arrive at the values of h_{ji} and s_{ji} for the specific cases of the Ag–Cu and Cd–Zn systems, we have used eqns. (3) and (4) in conjunction with the phase diagram data. The magnitudes of T_{mj}, ΔS_{mj} and ΔC_{pmj} were taken from standard sources [11, 12].

3. Results and discussion

The values of the constants used are given in Table 1, and the magnitudes of solution parameters obtained, together with the earlier results of Murray [8], on these two systems are given in Table 2. The concentrations calculated by us to represent solvus, solidus and liquidus lines in these systems match those reported by Murray to within $\pm$ 0.005 in the solute mole fraction. Attention is drawn to the differences between the s_1 and s_2 reported by us and those by Murray for the solid and liquid phases. The differences are a direct consequence of the use of eqn. (4) for $G_{As}{}^0$ and $G_{Bs}{}^0$ and are attributable to the influence of the correction term to the standard Turnbull [10] expression for the free-energy difference between solid and liquid phases. Murray used the Turnbull expression only.

The mixing parameters evaluated from our solution model parameters are in very good agreement with the experimental data [11, 13, 14]. Further, the mixing parameters have been found to be dependent on the ΔC_{pmj} and ΔS_{mj} values used. Small variations in ΔS_{mj} confined to within the experimental errors can cause significant changes. When ΔS_{mAg} was changed from 9.67 to 9.96 J mol^{-1} K^{-1}, the mixing enthalpy changed from 3580 to 3800 J mol^{-1} at $x_{Cu} = 0.5$ and shifted from being in agreement with the data of Choudary and Gosh [13] to being in agreement with the data of Kleppa and Watanabe [14]. This has to be contrasted with the work of Ishihara and Shingu [15] who had almost to halve the actual values of ΔS_{mAg} to achieve agreement with the phase diagram data.

The concentration dependence of T_f, T_0 and T_a ($a = 0.5$ and 1.0) in the Ag–Cu and Cd–Zn systems is shown in Figs. 1(a) and 1(b) respectively. The T_a plots

TABLE 1 Thermodynamic data for Ag–Cu and Cd–Zn systems

Element	ΔS_m (J mol^{-1} K^{-1})	ΔC_{pm} (J mol^{-1} K^{-1})	T_m (K)
Ag	9.67	1.5488	1234
Cu	9.62	1.4651	1357
Cd	10.286	0.1800	594
Zn	10.668	1.8042	693

TABLE 2 Solution parameters evaluated for the Ag–Cu and Cd–Zn systems

System	Reference	h_{1s} (J mol^{-1})	h_{2s} (J mol^{-1})	h_{11} (J mol^{-1})	h_{21} (J mol^{-1})	s_{1s} (J mol^{-1})	s_{2s} (J mol^{-1})	s_{11} (J mol^{-1})	s_{21} (J mol^{-1})
Ag–Cu	Present analysis	32656	−6599	14316	−2531	−7.3989	2.2997	−1.5554	1.0946
Cd–Zn	Present analysis	21631	−6998	8919	−14.73	−8.0736	7.0311	−1.6766	−0.7104
Ag–Cu	Murray [8]	34532	−5996	15171	−2425	−9.178	1.725	−2.537	0.946
Cd–Zn	Murray [8]	21665	−7062	8625	−78	−8.139	7.145	−1.235	−0.564

show the existence of two cusps at all values of $a \neq 0$. An interesting observation can immediately be made with respect to the relative differences between T_f and T_0 for the two systems. For the Ag–Cu system the maximum difference is only 55 K while in the Cd–Zn system its value is as much as 125 K. Similar behaviour is observed with respect to T_f and T_a also. As discussed earlier, at any temperature below T_f a liquid

Fig. 1. Phase diagrams and plots of concentration dependence of characteristic temperatures T_0, T_a and T_f for the systems (a) Ag–Cu and (b) Cd–Zn.

is unstable with respect to fluctuations and can nucleate via such local changes in concentration. T_0 defines the minimum thermodynamic undercooling required for a diffusionless transformation. T_a ($a = 1$) defines the temperature at which such a transformation becomes kinetically competitive. The faster the interval $T_f - T_a$ ($a = 1$) is traversed, the greater are the chances of obtaining a homogeneous solid solution phase. For similar rates of cooling, a system with a smaller interval will be more prone to yield extended solid solutions. This conclusion is in agreement with the experimentally observed behaviour of these two systems when subjected to rapid solidification [5–7].

The results on the undercooling behaviour of the eutectic Cd–Zn alloy reported earlier by Ojha et al. [16] are also in good agreement with the present analysis. A maximum undercooling of 34 K was reported and the observed temperature of nucleation corresponds to the T_f calculated by us. The proportions of the primary phase observed in the undercooled alloy microstructure and the subsequent decomposition of this phase indicated that the concentration of the nucleating solid is close to the eutectic concentration (26.5 at.% Zn) [17]. The solid likely to form as a result of a fluctuation in the eutectic liquid is estimated by us to contain 25 at.% Zn. The agreement in this respect is also fairly good.

When a liquid is undercooled, the likely processes of nucleation and transformation will be a function of the degree of undercooling achieved. At temperatures between the liquidus and T_0, two processes are possible, i.e. redistribution of solute and nucleation of an appropriate solid. At temperatures below T_f and above T_0, even a liquid devoid of heterogeneous nucleants can nucleate by fluctuations. Diffusionless solidification of a liquid becomes thermodynamically possible only below T_0 but will not actually take place because of kinetic factors. It becomes competitive to the process of redistribution only at T_a and will actually occur at temperatures below T_d.

$\Delta G_c = 0$ defines the possible range of concentration for a nucleus and the range is dependent on T and x_B. In Fig. 2, we plot this range for a Cd–10at.%Zn liquid alloy as a function of temperature. It may be noted that this range extends from near zero to about
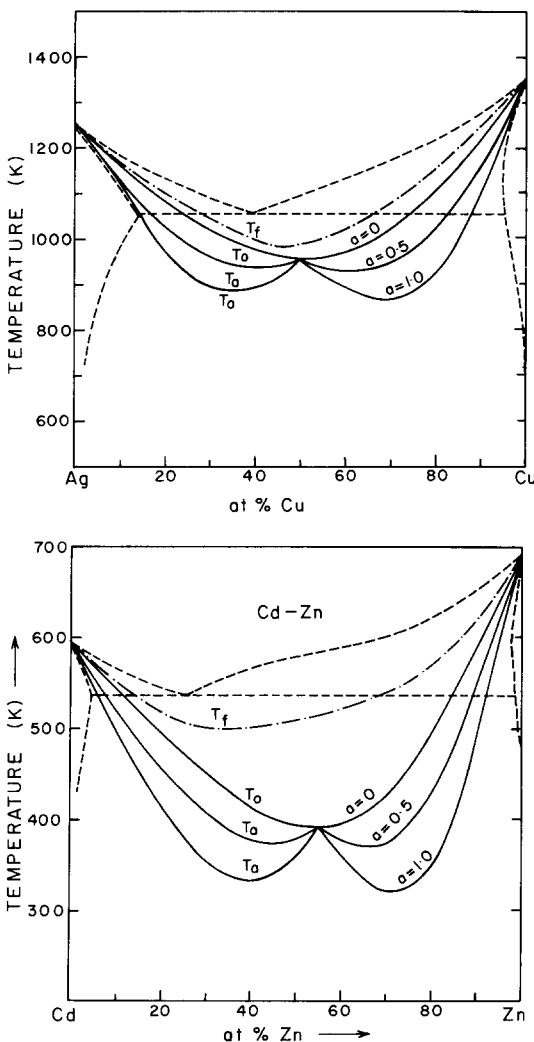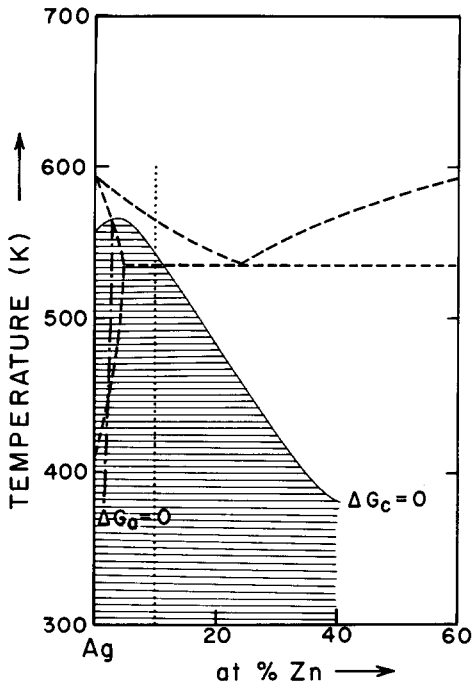
Fig. 2. Range of possible nucleus concentrations ($\Delta G_c = 0$) (▭) and the locus of the concentration of the minimal nucleus ($\Delta G_a = 0$) for liquid Cd–10at.%Zn in the Cd–Zn system.

40 at.% Zn at 380 K. Also shown on the graph are the values of the concentration of the minimal nucleus solid whose nucleation is most favoured with the maximum driving force.

The occurrence of extended solid solutions on undercooling [16, 17] or on rapid solidification [6, 7] clearly demonstrates that the redistribution process (controlled by ΔG_a) is suppressed to a large extent at the undercooling achieved. The present analysis is based on thermodynamic and kinetic arguments and differs from that of Aziz [18] which is a crystal-growth-based model. Conditions imposed by both analyses may have to be satisfied for metastable extension of solid solubility.

4. Conclusions

We have evaluated several characteristic temperatures T_0, T_a and T_f on the basis of phase diagram data for the binary systems Ag–Cu and Cd–Zn using a subregular solution model with due consideration of the temperature dependence of the interaction parameters. The relative magnitudes of T_0 and T_f play a significant role in determining the ease of formation of metastable solid solutions. The mixing parameters derived for the liquid are strongly dependent on the entropy of fusion of the constituent elements.

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