Studies on relative catalytic efficiencies of zinc and aluminium on nucleation of dispersed bismuth droplets

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Abstract. In Zn–Bi and Al–Bi systems, both of which belong to monotectic class, dispersion of second phase particles within the matrix have been produced through rapid solidification processing (RSP) route. In order to understand relative catalytic efficiencies of Zn and Al matrices in catalyzing nucleation of Bi particles entrapped in the respective metal matrices, thermal analysis in constant program mode was performed. Thermal analyses revealed that Bi undercools by 132° in Zn matrix and by 157° in Al matrix. Thermodynamic barrier to nucleation (ΔG^*) for Bi has also been calculated, which is 39·8 kcal/mole and 47·085 kcal/mole, in Zn and Al matrices, respectively at the maximum recorded undercoolings.

Keywords. Monotectic; nucleation; undercooling; bismuth.

1. Introduction

The phenomenon of undercooling exhibited by liquid metals and alloys below their thermodynamic freezing temperature has been given due importance in the field of materials research because of its invaluable use in understanding the fundamentals of nucleation behaviour (Turnbull 1952, 1969). Of the two, viz. homogeneous and heterogeneous nucleation, the former is considered as an unlikely event while the latter is more physically probable and mostly encountered in practical situations. The degree of undercooling is of immense importance in determining many microstructural developments in the solid state and thus it has a marked influence on the properties of the final product (Perepezko *et al* 1979; Perepezko 1980, 1984; Mueller *et al* 1985; Graves and Perepezko 1986; Devaud and Turnbull 1987; Ojha 2001; Aoyama *et al* 2004; Fecht and Johnson 2004). Several experimental techniques for extending the range of observable undercooling are available (Turnbull 1950a; Turnbull and Cech 1950; Wang and Smith 1950; Duwez *et al* 1960; Fehling and Scheil 1962; Shiraishi and Wood 1964; Rasmussen and Loper Jr. 1975; Southin and Chadwick 1978; Lacy *et al* 1981). One of the most attractive and powerful methods amongst them for extending the undercooling limit is the droplet technique (Vonnegut 1948), because of its efficient isolation capability, which was later on employed successfully by Turnbull (1950b, 1952) and his coworkers (Turnbull and Cech 1950). Droplet configuration has also been frequently observed in monotectic systems (Dobatkin *et al* 1979). When such an alloy melt is subjected to

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ultra rapid cooling, the process restricts layering phenomena, which is common in liquid monotectic alloys, leading to granulation of the second phase particles (Chattopadhyay and Ramachandrarao 1980; Chaubey *et al* 1987, 1988). As solidification process of liquid droplets is profoundly influenced by the surrounding matrix (Chattopadhyay 1992), Zn–Bi and Al–Bi systems have been presently chosen to study the nucleation behaviour of entrapped Bi particles in respective metal matrices and also to assess the catalytic power of substrate materials.

2. Experimental

Alloys of monotectic and hypermonotectic (equivalent to 20 volume % Bi) compositions of Zn–Bi and Al–Bi systems were made from high purity metals, by melting the accurately weighed components together in a graphite crucible under an argon atmosphere. The alloy melt was vigorously shaken and then it was allowed to solidify in the crucible under an argon gas cover.

In order to get dispersion of Bi in the respective metal matrices, gun technique of rapid solidification was employed.

Differential scanning calorimetric analyses were performed using Perkin Elmer DSC II in the constant program mode in order to study the nucleation behaviour of Bi in the two matrices. Argon gas had been used for purging throughout the experiment.

3. Results

Earlier results of Chaubey *et al* (1987) on rapidly solidified Zn–Bi system revealed that size of most of the Bi

droplets was ≈ 6 nm and the value of undercooling, ΔT, for Bi in Zn matrix was 132°. Nucleation rate measurements yielded the activation energy barrier to nucleation as 39·8 kcal/mole at maximum undercooling.

Rapidly solidified Al–Bi products were found to be highly unstable. Within 5 min of quenching, thin foils of the product disintegrated into fine brownish powder. Thicker portions, however, remained stable for nearly 1 h.

Constant heating and cooling thermograms for monotectic (Al–0·45 at.% Bi) and hypermonotectic (Al–10·48 at.% Bi), equivalent to 20 volume % Bi, compositions of Al–Bi system in the rapidly solidified as well as as-cast condition are shown in figures 1–4. Figures 1 and 2 are the differential scanning calorimetric (DSC) traces for the rapidly solidified Al–Bi system. In the DSC runs, thick portions of the foil, which do not disintegrate for atleast 1 h, were used. Figures 3 and 4 represent thermograms for the as-cast Al–Bi system.

Melting temperature, T_m (≈ 540 K), recorded in the thermograms of figures 1 and 2 represents melting of fine Bi particles entrapped in the Al matrix as a result of rapid solidification. Apart from this a very small endothermic transition is also seen at ≈ 440 K. Successive heating and cooling of the samples did not affect the shape and hence area under the peak appearing at ≈ 440 K. Cooling thermogram of figure 1 shows only one crystallization exotherm appearing at 386 K whereas the thermogram of figure 2 indicates the occurrence of two exothermic events at 446 K and 386 K, respectively. The maximum undercooling, ΔT (difference of melting temperature and the temperature at which last exothermic event occurred), attained by Bi particles, is thus 154°, equivalent to

$0·285 T_m$, in the Al matrix. Melting transition observed at 544 K in the thermograms of figures 3 and 4, for the as-cast Al–Bi samples, corresponds to melting of pure Bi. There is minute trace of an endothermic event at ≈ 440 K in figure 4, which corresponds to hypermonotectic Al–Bi sample, however, there is no indication of any such transition in figure 3, which corresponds to as-cast Al–Bi monotectic samples. During cooling, several of the as-cast Al–Bi monotectic samples showed intermediate exothermic events at different temperatures but the last one appeared at 433 K in all the samples. Thus the maximum undercooling recorded for Bi in the as-cast condition of the monotectic compositioned alloy is $\approx 111°$ as shown in figure 3. In case of hypermonotectic Al–Bi as-cast samples, the last exothermic peak during cooling was found to appear at ≈ 387 K, i.e. at an undercooling of $\approx 157°$ (equivalent to $0·288 T_m$) in all the samples as shown in figure 4. The maximum value of ΔT for Bi in as-cast condition of the hypermonotectic alloy is thus almost of the same order of magnitude as for its rapidly solidified counterpart. With the help of cooling thermograms, recorded at a rate of 2·5 K/min, temperature dependence of nucleation rate for Bi particles entrapped in Al matrix has been determined at the maximum undercooling and is shown in figure 5. The thermodynamic barrier to nucleation (ΔG^*), for Bi has been calculated as 47·085 kcal/mole in Al matrix from figure 5 by using the expression of Lele *et al* (1985) for Gibbs free energy change (ΔG_v) in the undercooled temperature regime.

4. Discussion

It is interesting to note that disintegration of the rapidly solidified product is restricted only to Al–Bi system and not for the Zn–Bi system (Chaubey *et al* 1987). As-cast Al–Bi alloys, however, did not show any such tendency for decomposition. In fact, with increase in cooling rates more quenching strains are developed in the final product and these possibly change the surface free energy in a way by which surface becomes highly reactive to oxygen. When such a thin surface is exposed to atmosphere, oxidation is very pronounced and leads to crumbling of the foil immediately. The tendency of disintegration decreases with increase in thickness of the rapidly solidified foils of Al–Bi system due to lower cooling rates and hence they are less prone to oxidation at ambient conditions. In fact, cooling rate decreases by two orders of magnitude for an order of increase in the thickness of the foil. Thus, it may be derived that the rapidity of oxidation is inversely proportional to thickness of the foil.

Though direct observation of droplet structure has not been possible for the rapidly solidified foils of Al–Bi system owing to its unstable nature, it is believed that Bi exists as droplets in the Al matrix because of granulation occurring through rapid quenching (Chattopadhyay
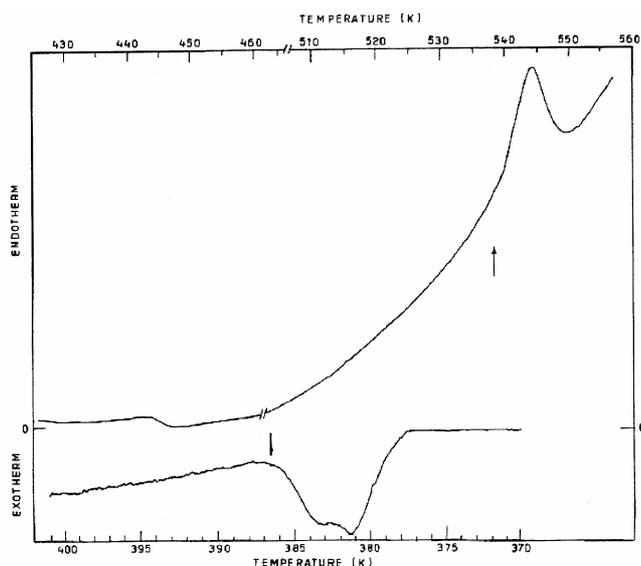
Figure 1. DSC thermogram recorded at heating and cooling rates of 2·5 K/min for rapidly solidified Al–0·45 at.% Bi. The transformation temperatures are marked by an arrow.
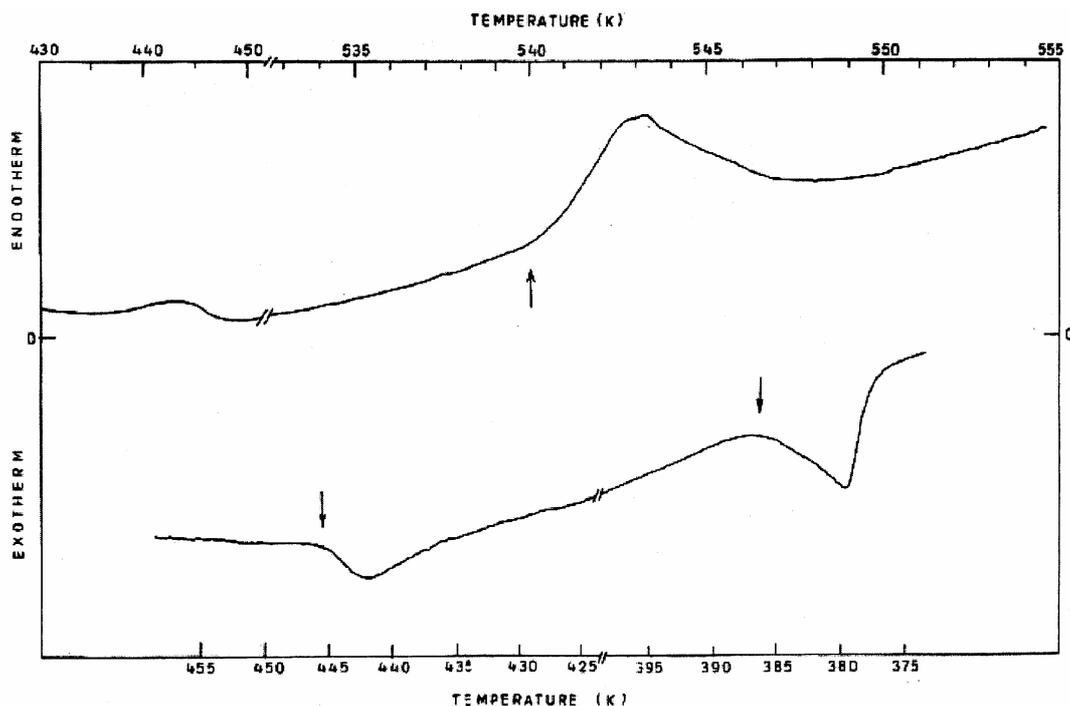
Figure 2. DSC thermogram recorded at heating and cooling rates of 2·5 K/min for rapidly solidified Al–10·48 at.% Bi. The transformation temperatures are marked by an arrow.
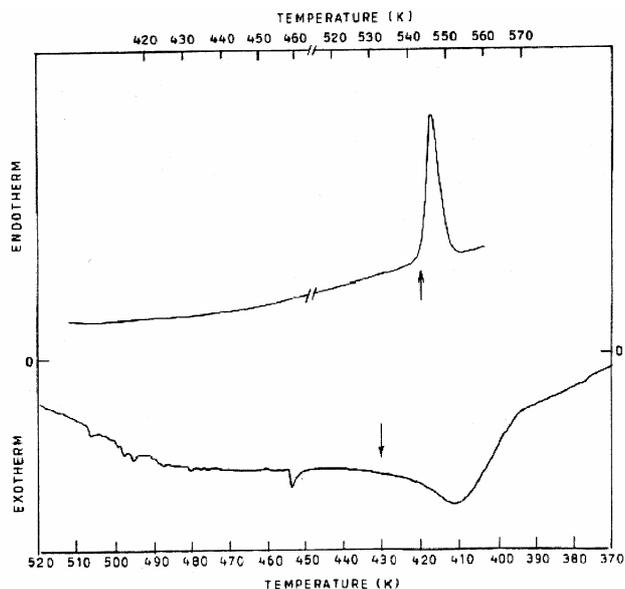
Figure 3. DSC thermogram for the as-cast Al–0·45 at.% Bi recorded at heating and cooling rates of 2·5 K/min. The transformation temperatures are marked by an arrow.

and Ramachandrarao 1980; Chaubey *et al* 1987, 1988).

The onset of melting at 540 K (figures 1 and 2) for dispersed Bi particles obtained through rapid quenching is slightly lower than the melting point of pure Bi in the as-cast alloys of Al–Bi system (figures 3 and 4). The first experimental observation of depression of melting temperature of small particles (<50 nm) was demonstrated by Takagi (1954). Coombes (1972) had shown a substantial decrease of the melting temperature of Pb particles with a radius of 3 nm. Goswami and Chattopadhyay (1996, 1999) have observed an unusual trend in the solidification behaviour of Bi. They showed lowering of melting temperature of Bi particles embedded in an amorphous Al–Fe–Si alloy, which was explained by formation of domain structures in the particles. The formation of domain structures was attributed to the crystallographic constraint of the spherical shape due to amorphous nature of the matrix. Such a depression in melting temperature of Pb and Bi particles in quasicrystalline matrix was explained by Singh and Tsai (2003) in terms of the difference of interface energies between liquid particle and matrix and solid particle and matrix. Bi inclusions in Al matrix were observed to melt at temperatures at or below the Bi bulk melting point by Thoft *et al* (1995) also. Average inclusion size ranged from a few nm to some tens of nm. Bi is known to be the only metallic particle which shows a lowering in melting temperature in the Al matrix (Andersen and Johnson 1995). A notable feature observed in the heating thermograms of figures 1, 2 and 4 is the appearance of one more endothermic transition at ≈440 K. This temperature did not correspond to the melting points of oxides of Bi (Weast 1977) and so the presence of any oxide of Bi was ruled out. Inspection of areas under two
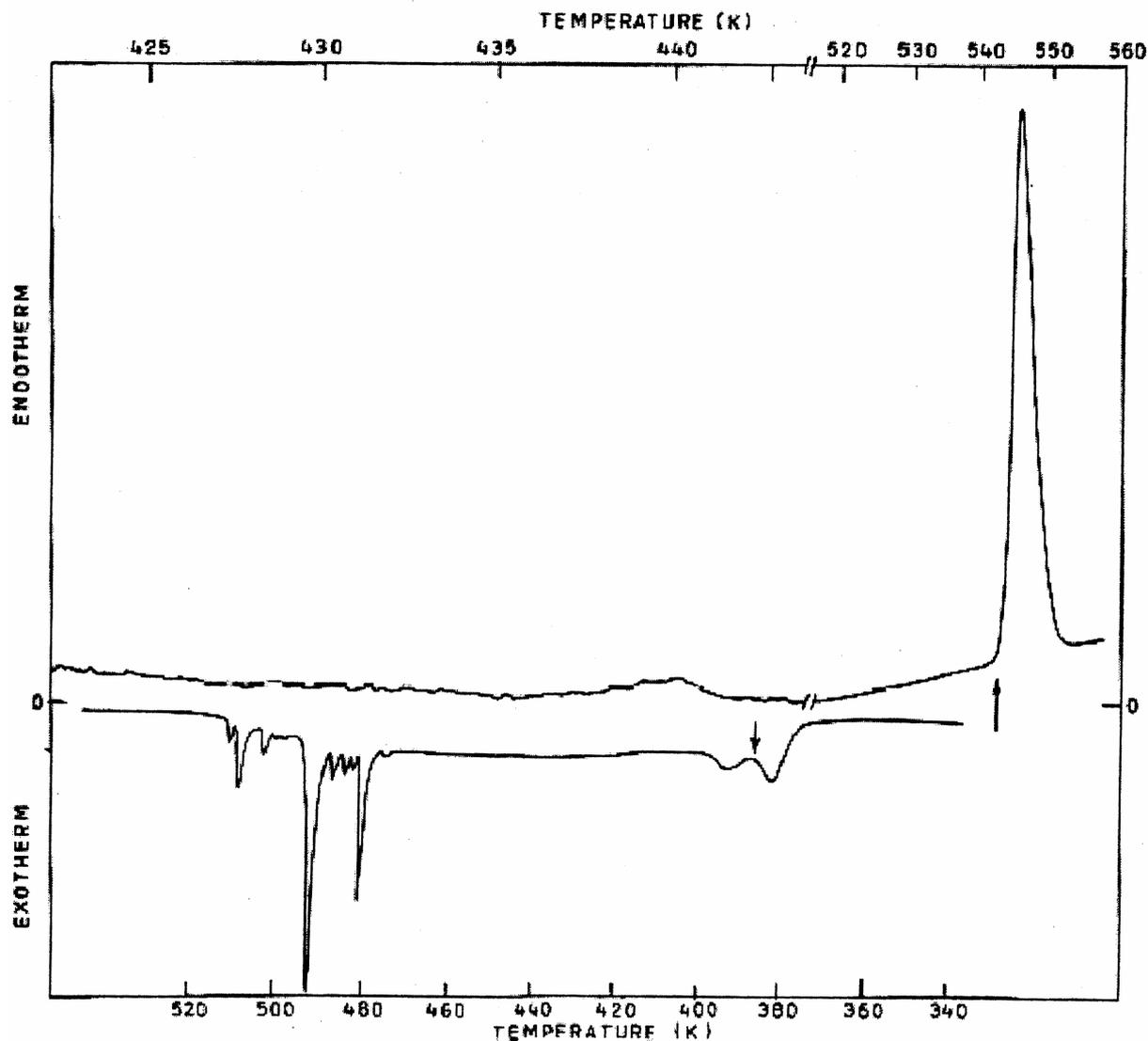
Figure 4. DSC thermogram for the as-cast Al–10·48 at.% Bi recorded at heating and cooling rates of 2·5 K/min. The transformation temperatures are marked by an arrow.

melting transitions indicates that volume fraction of the phase appearing at ≈440 K is < 5% of the total. X-ray diffraction studies did not give clear evidence for the presence of any polymorph of Bi, although Bi is reported to undergo several polymorphic transformations (Klement *et al* 1963). However, it may not be possible to detect any polymorph by X-ray diffraction since the volume fraction of the phase is too small. It has already been suggested by Perepezko (1980) that at high undercooling, solidification is initiated by the nucleation of Bi with different crystal structures. For the additional endotherm observed at approximately same temperature as in the present communication, Perepezko (1980) argued that the structural modification may be the metastable Bi (II) phase. The degree of undercooling obtained by him was of course much higher and this could be the reason for

higher volume fraction of Bi (II) phase observed by him. It is evident from the experiments that crystallization of Bi, entrapped in either Zn or Al matrix, occurs through several nucleation events. Number of exothermic peaks, at different temperatures, indicates the presence of different types of heterogeneities, each becoming effective at different levels of undercooling.

It is worth noting that with regard to the degree of undercooling, ΔT, there is a close resemblance between the observations on slowly cooled samples of the as-cast and rapidly solidified Al–Bi as well as as-cast and rapidly solidified Zn–Bi (Chaubey *et al* 1987) alloys. The maximum level to which Bi undercools in Al matrix, whether in the droplet configuration obtained through rapid quenching or in the as-cast condition (except for the as-cast samples of Al–0·45 at. % Bi), is ≈0·28T_m. This limit is reduced to

$0.25T_m$ in the case of Bi-rich droplets in the Zn matrix (Chaubey *et al* 1987). An undercooling of 65° for Bi in Zn matrix had been reported by Sundquist and Mondolfo (1961). Turnbull and Cech (1950) reported the value of ΔT for Bi as 90°, whereas the value reported by Perepezko (1984) was 227°. Substantial undercooling of Bi in rapidly solidified products of both the systems have been attributed to effective isolation of nucleation catalysts. Out of the total droplet population, a fraction remains free from nucleation catalysts owing to granulation. Such impurity free Bi particles, apart from the lumps of Bi resulting due to layering and segregation, which is very common and frequently observed in monotectic alloys, also form by a monotectic reaction in the as-cast samples (Dobatkin *et al* 1979). Hence, these droplets attain the same level of undercooling even in the as-cast condition. Especially in the Al–0·45 at.% Bi as-cast monotectic samples it seems layering effect was more pronounced and even if some droplets had formed as a result of monotectic reaction, they were not completely impurity free. This is the cause of lesser undercooling in those samples (figure 3). Undercooling results recorded in the present communication is understood in terms of surface catalytic effect. It implies that the matrix, whether Zn or Al, containing Bi dispersion, provides a suitable surface

for catalyzing the nucleation of Bi droplets which are supposed to be relatively free from heterogeneities. Thus the mechanism of heterogeneous nucleation, based on interfacial energy barrier to nucleation becomes operative (Volmer 1929; Fisher 1948; Turnbull 1950a). Accordingly the large undercooling for Bi is attributed to large σ_{SL} (solid liquid interfacial tension) value for Bi (Mondolfo *et al* 1984–85). The nucleation events occurring at lesser undercoolings are also heterogeneous in nature but impurity aided. Majority of Bi particles exhibiting large undercooling are definitely clean because they are only in contact with solid matrix surface. It would be appropriate to call the responsible nucleation process as clean and contamination free heterogeneous nucleation (Southin and Chadwick 1978). Using droplet technique, Southin and Chadwick (1978) were able to undercool Bi in Zn matrix by a comparable amount ($\approx 122°$). Rasmussen and Loper Jr. (1975) observed a maximum undercooling of 160° for Bi emulsions prepared by both air and ditertiary butyl peroxidation. The unspecified surface layer formed during emulsification in the experiments of Perepezko (1984) is supposed to be less catalytic than the solid Zn or Al surfaces of the present case and hence resulted in highest level of undercooling for Bi reported till date.

The ΔT values of $0.25T_m$ and $0.28T_m$ for Bi in Zn and Al matrices, respectively reflect significant difference in the relative nucleation efficiencies of the two matrices. Similar result had also been observed for entrapped Sn droplets (Southin and Chadwick 1978).

The present findings, however, do not seem to fully support the conclusions of Sundquist and Mondolfo (1961), that metals with simple structures were poor heterogeneous nucleants and those with complex structures were good heterogeneous nucleants. The lattice misfit theory (Cibula 1949–1950; Reynolds and Tottle 1951; Turnbull and Vonnegut 1952), which states that nucleated solid and the nucleating catalyst should have similar crystal structures for good heterogeneous nucleation, i.e. for low undercooling, rather seems to be in little agreement with the present experimental results. As observed by Southin and Chadwick (1978), an increasing trend in the degree of undercooling for Bi with increase in melting point of the substrate is found in the present investigation.

On the basis of the observation of Takahashi and Tiller (1969) and Acrivos (1976), which gives linear relationship between liquid drop size and undercooling (increase in ΔT for smaller diameter particles and *vice versa*), it accordingly appears that only small droplets produced either through rapid quenching or monotectic reaction have undergone deep levels of undercooling. This in turn implies a greater chance only of smaller droplets to be impurity free.

The theory of Tiller and Takahashi (1969) predicts an electrostatic contribution to the total interfacial energy at the catalyst/nucleus interface in controlling heterogeneous nucleation behaviour. According to this theory if the

$$C^{-1} = \cfrac{1}{T\,\Delta T^2\left(1 - \cfrac{\Delta C_{p_f}}{\Delta S_f}\,\cfrac{\Delta T}{T_f + T}\right)^2}$$
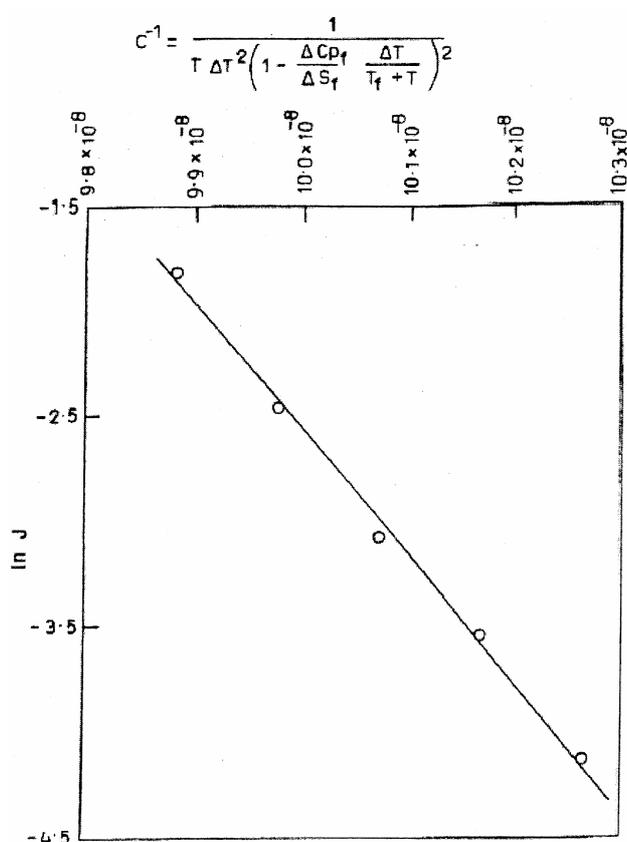
Figure 5. Temperature dependence of the nucleation rate for Bi in Al.

differences in electron work function ($\Delta\psi$) between the substrate and nucleus were positive, the analysis indicated the substrate material to be a good nucleant whereas for negative $\Delta\psi$ it suggested a rather poor nucleating effect of the substrate. Based on the available data of electron work function (Weast 1977), $\Delta\psi$ is 0·06 and 0·11, both positive, for Al–Bi and Zn–Bi systems, respectively. In view of the above, this model is not in agreement with the present findings. This rather suggests further examination of the theory of Tiller and Takahashi (1969).

At the highest level of undercooling, which is restricted to fine droplets only, it is assumed that a single nucleation event is sufficient for the solidification of each fine droplet. The nucleation rate thus calculated from the DSC thermogram recorded at 2·5 K/min, on the basis of the expression used by Rasmussen and Loper Jr. (1976) and Boswell and Chadwick (1980) corresponds to some average temperature of the sample during the time interval, Δt (very small). Because of the slow cooling rate (2·5 K/min), sample temperature does not change appreciably over the time interval, Δt.

In the approximation of a spherical nucleus the temperature dependence of nucleation rate for constant cooling experiment is given by the expression (Turnbull 1952)

$$J = A \exp\left(-\frac{\Delta G^*}{kT}\right), \tag{1}$$

where ΔG^* is the thermodynamic barrier to nucleation and A a factor which is practically insensitive to small changes of temperature. For heterogeneous nucleation process, A is of the order of $10^{25\pm1}$ s^{-1} cm^{-2} (Turnbull 1950a).

For heterogeneous nucleation process

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_V^2} f(\theta), \tag{2}$$

where $f(\theta) = 1/4(2 - 3\cos\theta + \cos^3\theta)$, θ being the contact angle. σ and ΔG_V in (2) are solid–liquid interfacial tension and volume free energy change during crystallization, respectively. For determining temperature dependence of nucleation rate for Bi in Al, like Bi in Zn (Chaubey *et al* 1987), expression for the Gibbs free energy change (ΔG_V) accompanying crystallization of an undercooled melt due to Lele *et al* (1985) has been used suitability of which has already been checked by Chaubey *et al* (1987). Combining (1) and (2) and using the expression of Lele *et al* (1985) for ΔG_V, expression for the heterogeneous nucleation process is written as

$$J = A \exp\left[-\frac{16\pi\sigma^3 f(\theta)}{3k\Delta S_f^2 C}\right], \tag{3}$$

where

$$C = T\Delta T^2 \left(1 - \frac{\Delta C_{Pf}}{\Delta S_f} \frac{\Delta T}{(T_f + T)}\right)^2 .$$

ΔS_f and ΔC_{Pf} are entropy and heat capacity differences between liquid and solid at the melting point and are easily accessible quantities. Equation (3) gives a linear relationship between $\ln J$ and C^{-1} as shown in figure 5, which finally gave the value of ΔG^* as 47·085 kcal/mole. Further, the gradient, $m = 16\pi\sigma^3 f(\theta)/3k\Delta S_f^2$, of (3) enables to calculate $\sigma^3 f(\theta)$, which in turn helps calculating the wettability factor, $f(\theta)$, provided reliable value of interfacial tension between the crystal and liquid, σ, is known. Published values of σ for metals are generally scanty because most of them have been estimated from Turnbull's classical homogeneous nucleation experiments on pure metals. With consistent refinements in the techniques, the undercooling limits have been continuously increasing, so uncertainty in the values is quite likely. Previously determined values of σ for Bi, based on undercooling measurements are 54·4 ergs/cm^2 (Turnbull 1950a) and 79·3 ergs/cm^2 (Perepezko *et al* 1979). Glicksman and Vold (1971) obtained a value of 82 ± 4 ergs/cm^2 at the melting point of Bi. Mondolfo *et al* (1984–85) have reported a value of 83 ergs/cm^2 at the melting point. A comparative study shows that the value of σ changes very little between nucleation temperature and equilibrium melting temperature and hence in the present communication its temperature dependence has been neglected. Substitution of the values of σ (Mondolfo *et al* 1984–85), k (Boltzmann's constant) and ΔS_f (for Bi) in the gradient value, obtained from the plot of figure 5, gave a value of 0·817 for the wettability factor, $f(\theta)$. This finally gives the value of contact angle, θ, as 117°, which nucleating Bi makes with the Al substrate, at the highest undercooling observed. Earlier calculations by Chaubey *et al* (1987) have given $f(\theta) = 0.486$ and $\theta = 89°$ for nucleating Bi on Zn substrate at the observed maximum undercooling. This simply indicates that Bi wets Zn more as compared to Al and that is the reason why higher ΔT for Bi is obtained in Al matrix rather than in the Zn matrix. ΔG^* values for Bi, which are 47·085 kcal/mole and 39·8 kcal/mole (Chaubey *et al* 1987) in Al and Zn matrices, respectively further confirm the above statement and conclude that Zn provides more efficient catalyst surface as compared to Al.

5. Conclusions

The present study reveals that undercooling achieved is strongly dependent on the catalytic activity of the surface of the matrix entrapping second phase particles. Reduction in size of the droplets, achieved through whatsoever means, is not the only requirement for increasing the undercooling limits.

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