Undercooling studies on dispersed bismuth droplets

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Abstract. In the zinc-bismuth system, a monotectic reaction occurs at 689 K and 0·6 at.% Bi composition. Rapid solidification of the as-cast monotectic alloy led to a micromorphology in which bismuth was uniformly and bimodally distributed as small droplets in the zinc matrix. Statistical analysis of the electron micrographs obtained from different transparent regions of the foils revealed that the size of most of the droplets was about 6 nm. These droplets undercooled by 132 K. An analysis of the nucleation rate measurements shows that the activation energy barrier to nucleation is of the order of 39·8 kcal/mol at the maximum undercooling.

Keywords. Undercooling; nucleation; bismuth.

1. Introduction

The phenomenon of undercooling exhibited by liquid metals and alloys below their thermodynamic freezing temperature has been given due importance by materials scientists. Heterogeneities present within the bulk melt usually initiate crystal nucleation at low undercooling. However, various experimental techniques for extending the limit of undercooling are now available (Vonnegut 1948; Turnbull 1950; Duwez et al 1960; Southin and Chadwick 1978; Lacy et al 1981). The droplet dispersal technique proposed by Vonnegut (1948) and later employed by Turnbull (1950, 1952) and coworkers (Turnbull and Cech 1950) is an effective technique for extending the range of observable undercooling. One of the useful techniques for inducing large undercooling in bulk melts is the glass slag technique in which the melt is under the cover of a fluid glass slag in a crucible (Fehling and Scheil 1962). By repeated melting and freezing under the glass flux, drastic undercooling is achieved in the melt. An emulsification technique in which the droplets are supported in aromatic oils and stabilized by reaction with organic peroxides and organic acid modifiers was developed by Rasmussen and Loper (1975). Such an emulsification procedure segregates heterogeneities present in the bulk melt into a small fraction of the droplet population and permits measurement of the undercooling in the presence of different types of surface layers. Southin and Chadwick (1978) employed the so-called liquid-entrapment technique, described previously by Wang and Smith (1950), for the enhancement of the degree of undercooling. Binary eutectic or monotectic alloy systems are best suited for this technique. The composition of the alloy is adjusted such that the equilibrium structure contains a small fraction of either one of the monotectic phases or the eutectic mixture. Subsequent annealing, at temperatures between the solidus and liquidus of the alloy, for sufficient time leads to the formation of droplets within the solid matrix grains. Such isolated droplets, free from heterogeneities, undercool enormously and can even produce metastable phases (Ramachandrarao et al 1979). In monotectic alloy systems isolated droplets of the

second phase can also be produced through the process of rapid solidification (Chattopadhyay and Ramachandrarao 1980).

In the present study, the conventional gun-technique of rapid solidification is employed for the formation of isolated bismuth droplets in zinc matrix. The under-cooling behaviour of such entrapped droplets has been characterized and discussed in the light of earlier work and the available models for heterogeneous nucleation of melts.

2. Experimental

Zn-0·6 at.% Bi monotectic alloy and Zn-9·69 at.% Bi hypermonotectic alloy were prepared by melting the accurately weighed components together in a graphite crucible under an argon atmosphere. The alloys were made from 5 N purity metals. The alloy melt was vigorously shaken and then it was allowed to solidify in the crucible under an argon gas cover.

Small alloy pieces weighing approximately 20 mg were cut from the bulk alloy and were rapidly solidified using the gun-technique in order to disperse Bi in the Zn-matrix in the form of small droplets. The resultant product was in the form of irregular foils, which were transparent in many places to the electron beam. Electron microscopy of the foils was carried out and the micrographs were analyzed to arrive at the statistical size distribution of Bi droplets.

Using a differential scanning calorimeter (Perkin Elmer DSC II) and about 10 mg of the rapidly solidified foils, thermograms were recorded at heating and cooling rates of 2·5 K/min to study the undercooling behaviour and nucleation kinetics of Bi droplets. The lower and upper temperature limits of the DSC II were set at 323 K and 570 K respectively. In every run empty Al sample pan with cover served as a reference. Argon gas was used for purging throughout the experiment.

3. Results

Statistical analysis of electron micrographs obtained from different transparent regions of the foils reveals that the size of most of the Bi droplets is of the order of 6 nm (figure 1). However, in thicker sections some bigger droplets were also seen in the micrographs but they were few in number. The size of the bigger droplets was not less than 25 nm. In thin sections of the rapidly solidified product fine scale distribution was observed, whereas in thicker sections a bimodal distribution consisting of coarse as well as fine particles was observed. A typical micrograph is shown in figure 2(a, b). Several of the big Bi particles show faceting (figure 2b).

Undercooling behaviour restricted to well-defined exothermic crystallization events is illustrated in figures 3–6. Figures 3 and 4 present DSC thermograms for rapidly solidified Zn-0·6 at.% Bi and Zn-9·69 at.% Bi respectively. Figures 5 and 6 present DSC thermograms for as-cast Zn-0·6 at.% Bi and Zn-9·69 at.% Bi respectively. The melting temperature, T_L, recorded in the thermograms of figures 3–6 is 528 ± 1 K which simply represents the melting of Bi-rich droplets entrapped in Zn-matrix. Apart from this melting transition at 528 K one more small endothermic transition appears at ~ 440 K. By successive heating and cooling of the sample the area under the peak appearing at 440 K increases slightly. After the third cycle there
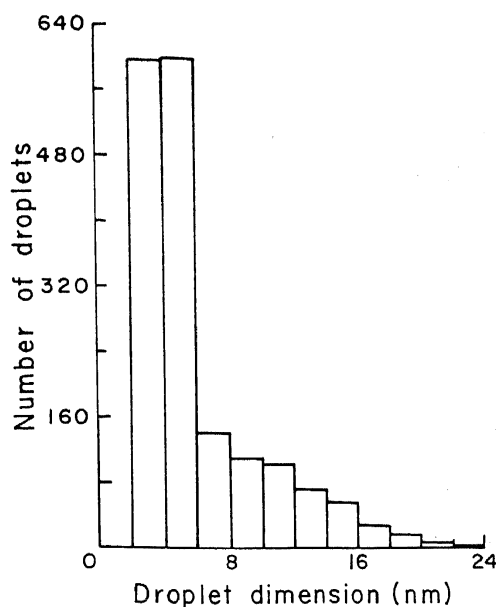
Figure 1. Histogram showing the droplet size distribution.

is an almost negligible increase in the area. Cooling thermograms in figures 3 and 4 show a number of exothermic peaks, the last one appearing at 397–396 K. The largest undercooling achieved is 132 K which is equivalent to about $0.25\ T_L$, where T_L is the liquidus temperature. Several experiments have shown that the number and position of exothermic peaks change. However, the position of last exothermic peak appearing at 397 K remains unchanged. Thermograms of figures 5 and 6 have been recorded for comparing the behaviour of rapidly solidified foils with the as-cast ones. As in figures 3 and 4, thermograms of figures 5 and 6 also show a number of exothermic peaks, the last one appearing at 398–397 K. As far as the highest degree of undercooling is concerned it is of the same order of magnitude as in the case of its rapidly solidified counterpart. Except for the last peak occurring at 397 K, the number and the position of other exothermic peaks change from sample to sample.

4. Discussion

The experimental results obtained in this work clearly show that crystallization of Bi-rich droplets entrapped in Zn-matrix occurs through several nucleation events. It is worthwhile to note that there is a close resemblance between the observations on slowly cooled samples of as-cast and rapidly solidified Zn-Bi alloys. Rapid solidification possibly restricts the layering mechanism in liquid monotectic alloys and results in granulation of Bi (Chattopadhyay and Ramachandrarao 1980). These granules or droplets are distributed on a coarse scale in thicker portion whereas fine scale distribution is observed in thin portion of the rapidly solidified product. Most of the active nucleants which are responsible for lesser undercoolings are restricted to within bigger and coarser droplets leaving the finer ones relatively free. A number of exothermic peaks at different temperatures indicate the presence of different types of heterogeneities, each becoming effective at different undercoolings.

Bulk samples of Bi were undercooled more than 60° when melted in a flux of
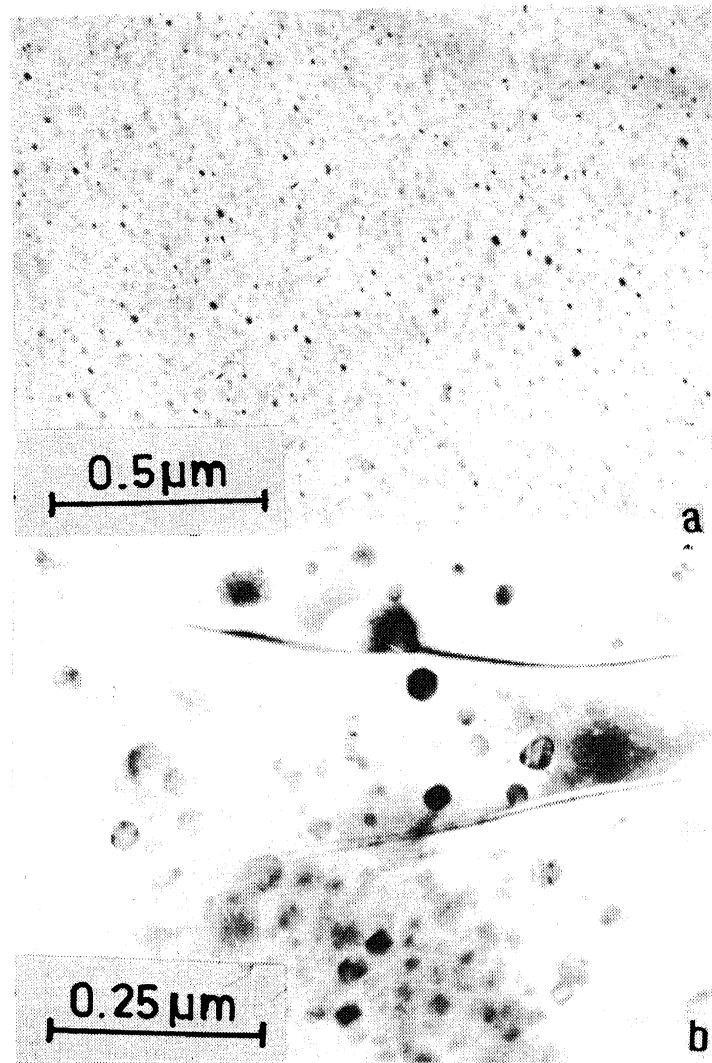
Figure 2. Electron micrographs showing dispersion of Bi particles. **a.** fine scale distribution and **b.** bimodal distribution.

$SnCl_2 + ZnCl_2$ (Bosio *et al* 1961). The maximum recorded undercooling, $\Delta T = 132$, is greater than the value reported by Turnbull and Cech (1950) which is 90°, but is less than the value reported by Perepezko (1984) which is 227°. According to Turnbull and Cech (1950) homogeneous nucleation for any metal was said to occur at approximately $0.2\ T_L$, T_L being the melting temperature. However, this limit does not seem to be appropriate. The substantial undercooling recorded in the present investigation may be understood as a consequence of surface catalytic effect and implies that the Zn-matrix containing Bi dispersion provides a suitable surface for catalyzing the nucleation of fine Bi droplets which are supposed to be relatively free from heterogeneities. The nucleation events occurring at lesser undercoolings are also heterogeneous in nature but impurity-aided. Fine Bi droplets exhibiting larger undercooling are clean and are in contact with only solid Zn surface. Therefore, it is appropriate to call the responsible nucleation process as clean heterogeneous nucleation (Southin and Chadwick 1978). The unspecified surface layer formed during emulsification in the experiments of Perepezko (1984) is less catalytic than the
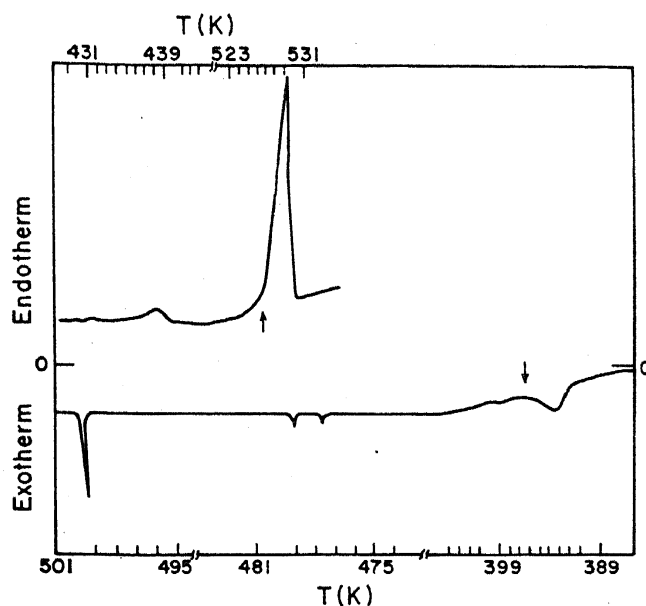
Figure 3. Thermogram for rapidly solidified Zn-0·6 at.% Bi recorded at the heating and cooling rates of 2·5 K min^{-1}. The transformation temperatures are marked by an arrow.

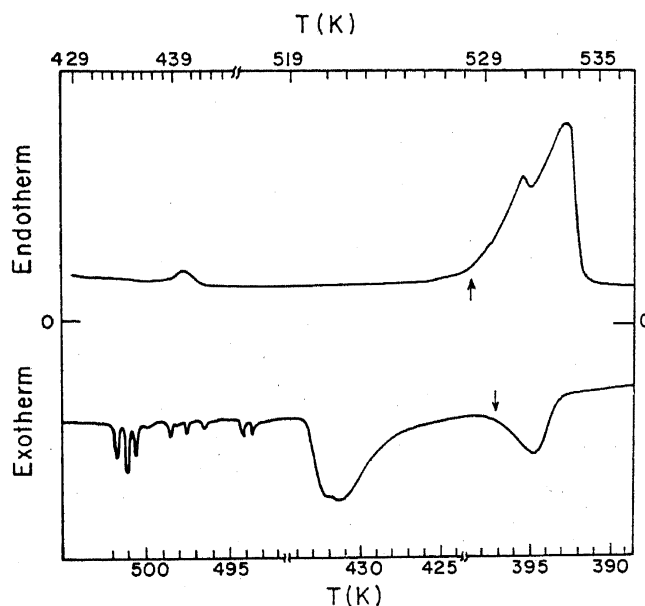**Figure 4.** Thermogram for rapidly solidified Zn-9·69 at.% Bi recorded at the heating and cooling rates of 2·5 K min^{-1}. The transformation temperatures are marked by an arrow.

solid Zn surface of the present case and hence results in the highest level of under-cooling for Bi reported till date.

The observation of the endothermic transition at 528 ± 1 K in the case of as-cast as well as rapidly solidified product of the Zn-Bi alloy is in accord with the phase diagram of Zn-Bi system (Hansen 1958). A notable feature observed in the thermo-grams of figures 3–6 is the appearance of one more endothermic transition at 440 K. This temperature did not correspond to the melting points of oxides of bismuth
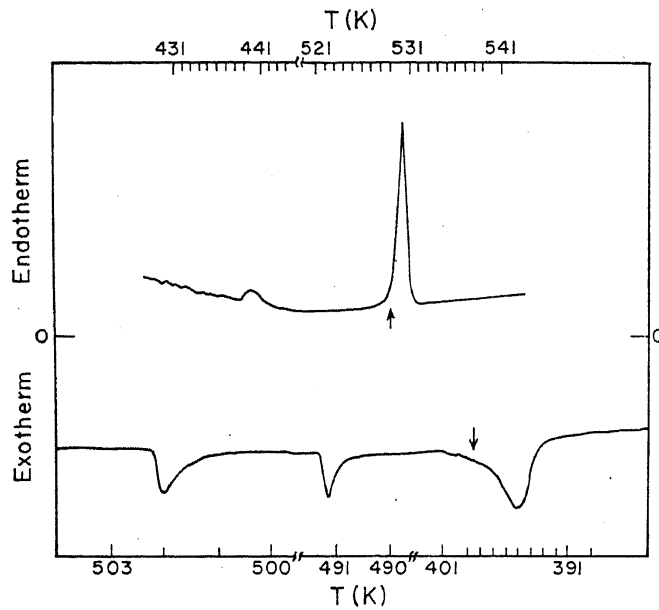
Figure 5. Thermogram for the as-cast Zn-0·6 at.% Bi recorded at the heating and cooling rates of 2·5 K min⁻¹. The transformation temperatures are marked by an arrow.

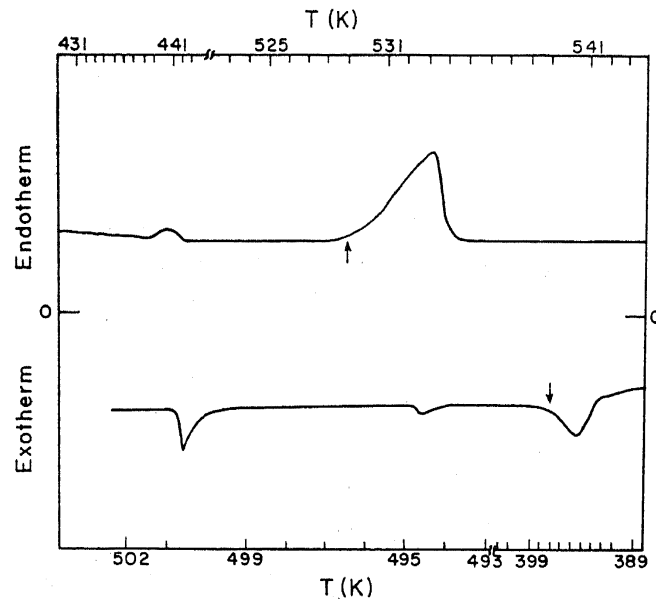**Figure 6.** Thermogram for the as-cast Zn-9·69 at.% Bi recorded at the heating and cooling rates of 2·5 K min⁻¹. The transformation temperatures are marked by an arrow.

(Weast 1977) and so the presence of any oxide of bismuth was ruled out. However, Bi is reported to undergo several polymorphic transformations (Perepezko 1980). A clear inspection of the areas under the two melting transitions indicates that the volume fraction of the phase appearing at 440 K is less than 5% of the total. X-ray diffraction studies did not give a clear evidence for the presence of a polymorph of Bi. However, it may not be possible to detect any polymorph by X-ray diffraction since the volume fraction of the phase is too small. Perepezko (1980) has already suggested

that at high undercooling solidification is initiated by the nucleation of Bi with different crystal structures. For the additional endotherm observed at 447 K he argued that the structural modification may be the Bi (II) phase.

If it is assumed that only one nucleation event per droplet is enough for solidification of each fine droplet, the heat released for a droplet solidification in a DSC will be the same as for any other droplet and hence the amount of heat released is a direct measure of the number of droplets to solidify. Following the base line correction employed by earlier workers (Scott and Ramachandrarao 1977) the total area under the cooling thermogram from any time t_1, A_{t_1} gives a measure of the number of droplets unsolidified at time t_1, N_{t_1}. After a short interval of time Δt, the area left, $A_{t_1 + \Delta t}$, is a measure of the number of droplets still unsolidified, $N_{t_1 + \Delta t}$. In a constant cooling experiment it has been shown that the nucleation rate per droplet during a small time interval Δt is (Wood and Walton 1970; Rasmussen and Loper 1976)

$$J_s = -\frac{1}{\Delta t} \ln \left(\frac{A_{t_1 + \Delta t}}{A_{t_1}} \right). \tag{1}$$

The nucleation rate thus calculated corresponds to some average temperature of the sample during the time interval Δt. Because of slow cooling rate, sample temperature does not change appreciably over the time interval Δt. The nucleation rate per droplet, J_s, where s is the average droplet surface area, has been calculated for thermograms recorded at a cooling rate of 2·5 K/min.

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

$$J = A \exp(-\Delta G^*/kT), \tag{2}$$

where ΔG^* is the thermodynamic barrier to nucleation and A is a factor which is practically insensitive to small changes of temperature. For heterogeneous nucleation process A is of the order of $10^{25 \pm 1} \sec^{-1} cm^{-2}$, whereas for homogeneous nucleation it is of the order of $10^{33 \pm 1} \sec^{-1} cm^{-3}$ (Turnbull 1950). For the homogeneous nucleation process

$$\Delta G^* = 16\pi\sigma^3/3\Delta G_v^2. \tag{3}$$

For the heterogeneous nucleation process

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2} f(\theta), \tag{4}$$

where $f(\theta) = \frac{1}{4}(2 - 3\cos\theta + \cos^3\theta)$, θ being the contact angle. σ and ΔG_v in (3) and (4) are solid-liquid interfacial tension and volume free energy change during crystallization respectively.

Recently Lele *et al* (1985) developed the following novel expression for ΔG accompanying crystallization of an undercooled melt

$$\Delta G = \Delta S_f \Delta T - [\Delta C_{pf} \Delta T^2/(T_f + T)]. \tag{5}$$

Table 1. Comparison between the observed and calculated ΔG values for undercooled liquid bismuth.

T	ΔT (K)	ΔG(Bi) (Olesinski and Abbaschian) (cal/mol)	ΔG(Bi) (Lele *et al* 1985) (cal/mol)
514	30	148	148
499	45	222	223
484	60	295	297
469	75	367	371
454	90	441	445
439	105	513	518
424	120	585	592
409	135	656	666
394	150	726	739

$$c^{-1} = \frac{1}{T\,\Delta T^2 \left(1 - \dfrac{\Delta C_{Pf}}{\Delta S_f}\dfrac{\Delta T}{T_f + T}\right)^2}$$
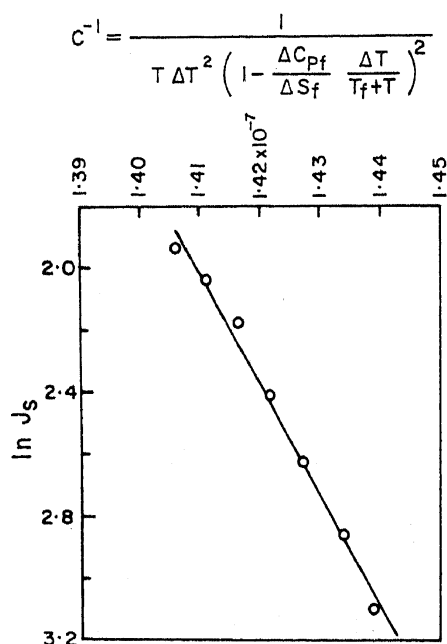
Figure 7. Temperature dependence of the nucleation rate.

ΔS_f and ΔC_{pf} in the above equation are entropy and heat capacity differences between the liquid and solid at the melting point. Suitability of the above equation has been checked with the help of an analytical equation for the Gibbs-free energy change for Bi which is written as (Olesinski and Abbaschian 1986)

$$\Delta G(\text{Bi}) = 4198 + 108\cdot96T + 15\cdot234 \times 10^{-3}T^2$$
$$- 19\cdot9493\,T\ln T + 2\cdot05 \times 10^5 T^{-1} \text{J/mol.} \tag{6}$$

Table 1 shows the comparison between the ΔG values calculated using (5) and (6) separately. From table 1 it is clear that even at higher undercoolings the agreement between both the values is quite satisfactory.

Combining (2), (4) and (5) we have the following expression for the heterogeneous

nucleation process

$$J = A \exp\left[-\frac{16\pi\sigma^3 f(\theta)}{3k\Delta S_f^2 C} \right],$$ (7)

where $\quad C = T\Delta T^2 \left[\dfrac{\Delta C_{pf}}{\Delta S_f} \cdot \dfrac{\Delta T}{(T_f + T)} \right]^2.$

From (7) it is clear that there must be a linear relationship between $\ln J$ and C^{-1}. Values of $\ln J_s$ calculated using (1) have been plotted against the temperature function, C^{-1}, in figure (7). As expected, a linear behaviour is observed over a range of the long tail on the thermogram which enabled us to arrive at the value of 39·8 kcal/mol for ΔG^*.

The present study shows that a reduction in the size of the droplets alone is not a sufficient requirement for enhancing the degree of undercooling in the present technique. The undercooling achieved is strongly dependent on the surface activity of the matrix entrapping the droplet. Experiments on Bi suspended in other matrices by a similar technique will throw further light on the inherent undercooling tendency of Bi.

Acknowledgements

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