Nucleation kinetics studies on embedded nanosized indium (In) particles

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Indium exhibits a monotectic reaction with Al at an invariant temperature (910 K) and composition (4.7 at.% In). Ultra rapid cooling, using gun technique, of monotectic compositioned alloy led to a microstructure in which In was distributed uniformly with a bimodal size distribution. Quantitative metallographic analysis revealed size of small sized In particles to be in the range of 10-20 nm whereas bigger particles were found to be even greater than 200 nm in size. These particles of In undercooled by 19 K in the rapidly solidified product of Al-In system. In the as-cast condition the degree of undercooling was only 9 K. Analyses of the nucleation rate measurements showed that the activation energy barrier to nucleation is 2.666 kcal/mol at undercoolings approaching 19 K. The nucleus-substrate contact angle was found to be 20°, which signifies that Al provides a potent catalytic surface for the nucleation of In.

Solidification behaviour of liquid metals and alloys below their thermodynamic freezing temperature has been the area of interest to materials scientists. In ordinary castings undercooling of only a few degrees usually takes place as heterogeneities present within the melt initiate crystal nucleation at temperatures close to the melting point. However, several experimental techniques for extending the range of observable undercooling are now available. Microstructural developments in the solid state, which are dependent on the degree of undercooling, are of great significance to metallurgists. The droplet dispersal technique proposed by Vonnegut and later on employed by Turnbull and his coworkers, is a powerful technique for enhancing the limit of undercooling as it restricts the heterogeneities in a small fraction of the droplet population, leaving the majority free from active sites. Such impurity free droplets undercool enormously. Uniform droplet configuration can be easily achieved through rapid solidification processing (RSP) in binary monotectics as mutual solubility of the components in one another below monotectic horizontal is very small. As a result of this the equilibrium phases at normal temperature and pressure consist of pure Al and In and hence melting and crystallization processes of pure In can individually be observed during thermal analysis.

The present study is aimed at establishing the inherent undercooling tendency of nanosized In particles entrapped within the Al matrix and respective calculation of activation energy barrier to nucleation by means of differential scanning calorimetry.

Experimental Procedure

Al-In alloy of monotectic composition (Al-4.7 at% In) was prepared by melting weighed constituents of 5 N purity elements in a graphite crucible under argon atmosphere. Gun technique of rapid solidification was employed to disperse In particles in the Al matrix. As-quenched foils were examined in JEOL 200CX electron microscope operating at an accelerating potential of 200 kV. Thermal analysis of In dispersions embedded in Al matrix was carried out in a Perkin Elmer Differential Scanning Calorimeter (DSC II).

Results and Discussion

Figure 1a is a typical electron micrograph of the rapidly solidified Al-4.7 at% In alloy. As is be seen in the micrograph, In particles are distributed uniformly and bimodally. Almost all the particles, including fine ones also, show faceting (Fig.1b), characteristic of the crystalline particles. The bigger In particles are of the order of 200 nm in size but the fine ones fall in the size range of 10-20 nm. The representative histogram is shown in Fig. 2.
During the investigation it was also observed that ultra thin foils of rapidly solidified Al-In alloy disintegrate to fine blackish powder. The process of disintegration completes in about an hour from the time of quenching. Relatively thicker portions remained unchanged even after a period of one year.

Thermograms representing melting and freezing of In particles entrapped in Al matrix are shown in Figs 3 and 4. Figure 3 is a representative thermogram of In dispersed in Al matrix through rapid solidification, whereas Fig. 4 is for In in the as-cast Al-In monotectic samples. A remarkable feature in the heating thermogram of Fig. 3 is the presence of a humped portion apart from the main melting transition at $T_m = 429$ K. It appears as if a second melting transition starts at around 435 K, giving a peak at $\approx 440$ K. Except for this no other peak appears in the whole scan range of 323-460 K. Successive heating and cooling of the sample did not affect the shape of the melting curve. Initiation of melting at 429 K belongs to coarse In particles. The second one corresponds to melting of fine In particles. Repeated attempts with different samples gave consistent results. Cooling thermogram of Fig. 3 shows the presence of three exothermic events starting at 428, 418 and 410 K respectively. With reference to starting temperatures in melting and freezing cycles, the

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Fig. 1a— Bright field image of the electron transparent region in a rapidly solidified Al-4.7at.% In sample showing uniform and bimodal distribution of In.

![Fig. 1a](image)

Fig. 1b— Same region (as shown in Fig. 1a) at higher magnification showing faceting.

![Fig. 1b](image)

Fig. 2— Histogram showing the particle size distribution of In in Al matrix through rapid solidification.

![Fig. 2](image)

Fig. 3— DSC trace recorded at heating and cooling rates of 2.5 K/min for rapidly solidified Al-4.7at.% In sample (transformation temperatures are indicated by arrows) showing the beginning of a humped portion at around 435 K towards the endotherm.
maximum degree of undercooling, $\Delta T$, for In is only 19 K, which is equivalent to 0.04$T_m$. Initiation of melting at $\approx 429$ K in the heating thermogram of Fig. 4 obtained from the as-cast Al-In samples represents melting of pure In. Apart from this an indication of the slope change at 435 K is also observable. As is clear from the cooling thermogram of Fig. 4, freezing of In starts at 429 K. A faint peak at around 420 K was also observed. This indicates that a minor fraction of In in the as-cast alloy also undercooled by 9 K. Some of the rapidly solidified samples, however, gave only one broad exothermic peak extending from 429 K to 410 K (over a range of 19 K) as shown in Fig. 5, and beyond this the curve followed the usual base line trend.

Using the expression of Lele et al.\textsuperscript{29} for the volume free energy change during crystallization in the undercooled temperature regime ($\Delta G_v$), the temperature dependence of the nucleation rate for In particles entrapped in Al has also been established from the cooling thermogram of Fig. 5, which is shown in Fig. 6. Thermodynamic barrier to nucleation, $\Delta G^*$, calculated from the slope of Fig. 6 is found to be 2.666 kcal/mol.

Process of disintegration of rapidly solidified Al-In product has been explained in terms of the surface activity of the foil due to quenching strains\textsuperscript{30}. In thicker sections of the foil quenching strains are insufficient to cause crumbling because of relatively low cooling rates. X-ray analysis of the crumbled black powder did not confirm any structure.

Particulate structure of the second phase In particles in the rapidly solidified Al-In alloy samples is a result of granulation\textsuperscript{25-27}. Depending on the cooling rate during rapid solidification, particles attain dimensions varying from very fine to coarse ones and because of the rapidity of the process their distribution is homogeneous. Initial melting of In particles in both rapidly solidified as well as the as-cast material starting at 429 K, the eutectic temperature of the Al-In system, can be considered as the true melting of In because it is very close to the equilibrium melting temperature of In (429.6 K). In the case of rapidly solidified Al-In samples the melting curve (Fig. 3) showing an inflection in the endothermic direction at 435 K and finally taking the form of a peak at around 440 K, indicates the possibility of superheating. For the as-cast samples also a slope change (indicating the presence of a very small peak) at around 435 K indicates the same phenomenon as above (Fig. 4). Repeated attempts with used as well as fresh samples gave the same result.

Present experimental findings through differential scanning calorimeter throw some light on the size dependence of melting and crystallization...
temperatures of In particles. Earlier experimental results on In particles with free surfaces show a diminishing trend in melting temperature with a reduction in size of the particles (Fig. 7). Such a depression in melting point is not observed in the present study. In contrast rather a reverse trend in the melting temperature appears. Small increase in melting temperature in the present study has been attributed to a stressed state of the particle as observed in the case of Sn micro crystals. For smaller In particles (radius 4 nm on average) embedded in Al matrix a superheating of 23 K has been observed by Dybkjaer et al. The degree of superheating, however, was found to decrease for large inclusions (radius 40 nm on average). Such an elevation of melting point for embedded In particles within the Al matrix grains (in the range 0-40 K above the bulk equilibrium In melting point) has also been observed by Zhang and Cantor.

Larger degree of undercooling in the rapidly solidified condition (Fig. 3) is attributed to potent isolation of many of the effective nucleation sites in a small fraction of the droplet population through granulation, leaving the majority free from heterogeneities. Intermediate exothermic peaks before the last one are due to the presence of different kinds of nucleants, each becoming effective at its characteristic temperature. In the as-cast condition (Fig. 4), since the layering is more pronounced, denucleation or removal of the active sites is not possible in a major fraction, thus giving rise to a massive start of nucleation just below the equilibrium melting point. Only a minor fraction, which possibly has formed due to monotectic reaction, nucleates by a characteristic catalyst at an undercooling of only 9 K. Maximum degree of undercooling observed in the rapidly solidified Al-In samples, which is \( \approx 0.04T_m \), far less than the value suggested for homogeneous nucleation by Turnbull and Cech, is because of the fact that solid Al offers very strong catalytic surface for the nucleation of In. During in-situ cooling in the electron microscope Saka et al. observed an undercooling of 53 K for In embedded in Al through rapid quenching process. Such a large difference between the present value and that of Saka et al. can only be interpreted in terms of the sensitiveness of the two methods, viz., differential scanning calorimetry and electron microscopy.

Through an unknown emulsifying reagent Perepezko observed an undercooling of 110 K for In emulsions. The unspecified thin surface coating on In
emulsions seems to be much less catalytic as compared to the solid Al surface of the present case. Undercooling of 106 K for In droplets (5-100 nm in diameter) obtained by condensation of vapour on amorphous substrate in high vacuum, as reported by Pocza\textsuperscript{29}, however, is in agreement with general expectation as any glassy or amorphous substrate is assumed to be less catalytic as compared to the solid substrate. Present low undercooling limit is mainly due to a heterogeneous nucleation process characterized by an interfacial energy barrier to nucleation. Theory of Tiller and Takahashi\textsuperscript{40}, however, gains support from the result of the present finding as the difference in electron work function however, gains support from the result of the present nucleation. Theory of Tiller and Takahashi\textsuperscript{40} due to a heterogeneous nucleation process between the substrate and nucleus, obtained from the finding as the difference in electron work function in Al expression for the Gibbs free energy change of Lele et al.\textsuperscript{29} accompanying crystallization of an undercooled melt due to Lele et al.\textsuperscript{29} has been used, suitability of which has been already checked by Chaubey et al.\textsuperscript{26}. Combining Eqs. (1), (2) and expression of Lele et al.\textsuperscript{29} for $\Delta G_r$, expression for the heterogeneous nucleation process is written as

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

... (3)

where

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

$\Delta S_f$ and $\Delta C_p$ are entropy and heat capacity differences between liquid and solid at the melting point and are easily accessible quantities. As expected, Eq. (3) gave a linear relationship between $\ln J$ and $C_f$ over a range of 3 K of the long tail on the thermogram, as shown in Fig. 6, which finally gave the value of $\Delta G_r$ as 2.666 kcal/mol. The contact angle, $\theta$, between the nucleated In and Al substrate can be determined from the gradient value, $m = 16\pi\sigma^3 f(\theta)/3k\Delta S_f^r$, provided correct value of the interfacial tension, $\sigma$, is known. In the thermodynamic modeling of the freezing of In particles Saka et al.\textsuperscript{28} used the value of $\sigma$ as 30 ergs/cm\textsuperscript{2}. Though the temperature coefficient of solid-liquid tension of pure metals is not known but its value is expected to be low\textsuperscript{44}. For Al-In system\textsuperscript{35} its value has been found to be -0.18 erg/K. cm\textsuperscript{2}. In view of this $\sigma = 30$ ergs/cm\textsuperscript{2} seems to be an appropriate choice for calculation purposes. This finally yields a value of $2.46 \times 10^3$ for $f(\theta)$ which gave $\theta = 20^\circ$. Such a low value of $\theta$ suggests a strong catalytic power of Al for the nucleation of In.

**Conclusions**

Thermal studies reveal that reduction in size of the particles alone is not the sufficient requirement for increasing the undercooling values. Surface effects provided by the matrix entrapping the particles, play dominant role in respect of undercooling as well as superheating of embedded particles. Currently observed low value of undercooling is in conformity with the low value of contact angle between the nucleated In and entrapping Al and suggests heterogeneous process as the operative mechanism for nucleation of In in the present study.
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References