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Undercooling and crystallization behaviour of antimony droplets

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The level of liquid undercooling below the equilibrium melting point experienced typically in a bulk material is limited by the presence of potent heterogeneous nucleation sites. By subdividing the material into a collection of fine (10 to 150 μm) droplets the most potent nucleants are isolated into a small fraction of the droplet population, allowing the remainder to reach deep levels of undercooling prior to the onset of solidification. Droplet surface coating characteristics influence both the level and uniformity of the undercooling and, in addition, may alter the nucleation kinetics thereby encouraging the formation of a metastable crystalline phase from the undercooled liquid. An effective means of both creating a stable dispersion of fine droplets and influencing the surface coating is through the droplet emulsion technique. This approach has allowed the level of undercooling for pure antimony to be extended from 0.08 to $0.237T_m$ through proper control of droplet size, surface coating and applied cooling rate. The formation of a metastable simple cubic phase from the melt has been confirmed using both differential thermal analysis and X-ray diffraction techniques. The simple cubic phase is retained in droplets to temperatures approaching the melting point at a heating rate of 20° C min^{-1}. Drop tube treatment of emulsified samples has also been successful at producing the metastable simple cubic structure by containerless processing.

1. Introduction

Production of a metastable crystal structure from the melt requires both a certain level of liquid undercooling (below the equilibrium melting point) as well as favourable nucleation kinetics. An effective means of achieving large undercoolings in a controlled manner is based upon the droplet emulsion technique [1]. This method involves dispersing a molten sample into a large number of fine (10 to 150 μm) droplets in an appropriate carrier medium. In this manner, the most potent nucleation catalysts present in the bulk material are isolated into a small fraction of the droplet population, allowing the remainder to achieve high levels of undercooling prior to the onset of solidification. An additional advantage of the droplet technique is that, through proper selection of the emulsification carrier medium, a surface coating may be produced which not only allows for a large undercooling, but also allows for nucleation kinetics favourable to the formation of a nonequilibrium crystal structure [1].

While studies concerning metastable phase formation from undercooled liquids have primarily dealt with multicomponent systems, a number of observations have been reported for pure materials. In the case of pure gallium, droplet samples have yielded maximum undercoolings in excess of one-half the melting temperature of the stable α-phase [2]. Furthermore, the melting behaviour of the samples revealed the presence of a variety of crystal structures, some of which may be stabilized under high pressure [2]. In addition to gallium, studies have indicated that highly undercooled droplets of bismuth may crystallize into a metastable structure corresponding to the high pressure bismuth (II) phase [2].

In a manner similar to gallium and bismuth, antimony undergoes high-pressure polymorphic transformations, as illustrated in Fig. 1, from a rhombohedral structure at ambient pressure, to a simple cubic (sc) phase, and finally to the high-pressure antimony III phase whose crystal structure has not been well defined [3]. In previous studies concerning metastable phase formation in pure antimony, rapid cooling techniques have been employed [4–6]. Splat-quenched foils produced using the "gun" method revealed a variety of structural modifications including tetragonal, fcc, sc, hcp and a modified rhombohedral crystal structure, in addition to the equilibrium rhombohedral phase [5]. Examination of antimony films produced through vapour deposition yielded similar results. In addition, amorphous films could be produced by vapour deposition at liquid nitrogen temperatures [4].

Application of the droplet emulsion technique to antimony in the present work has produced a significant increase in the maximum undercooling of the liquid compared to bulk sample behaviour. In addition to allowing evaluation of parameters which influenced the undercooling behaviour, such as droplet size, surface coating and applied cooling rate, the emulsification technique proved successful at altering the nucleation kinetics such that formation of a metastable simple cubic phase was encouraged.

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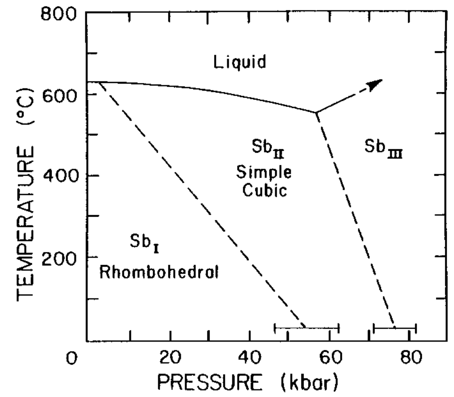

Figure 1 Temperature/pressure diagram for pure antimony [3] (1 kbar = 100 MPa).

2. Experimental procedure

Using an emulsification technique [1], antimony droplets were produced by shearing approximately 2 g liquid metal in a molten salt carrier medium. In order to evaluate the effect of initial purity on undercooling behaviour, both 99.8 and 99.999% pure antimony ingots were used. The carrier medium chosen was a K_2SO_4–$ZnSO_4$ salt of eutectic composition which produced a droplet surface coating stable to temperatures in excess of 800° C. Following emulsification, the antimony droplets were recovered by dissolution of the salt in distilled water and were subsequently classified according to size.

In order to evaluate the melting and solidification behaviour of the material, differential thermal analysis (DTA) techniques were employed using a Perkin-Elmer DTA 1700 system. For enhanced cooling rate studies a recently developed quenching apparatus [7] was used to obtain thermal information at cooling rates in excess of $500^\circ\,C\,sec^{-1}$. Following thermal processing, X-ray powder diffraction techniques (using a copper target and nickel filter) were effective in determining the phase(s) present in the droplet samples.

An alternative technique used to process droplet samples was a laboratory scale drop tube. As illustrated in Fig. 2, the drop tube is an environmentally isolated cylindrical quartz chamber approximately 3 m high through which powder specimens both melt and solidify in transit during free fall. For this study a resistance heated tantalum coil, located near the top of the chamber, was used to melt the droplets. All samples were processed under a purified helium gas environment at 1 atm pressure.

3. Results

3.1. Factors influencing undercooling behaviour

The presence of potent heterogeneous nucleation sites often limits the undercooling observed in bulk samples even of relatively high purity. Using powder produced by crushing which has an oxide coating similar to that of a bulk sample, the singular effect of nucleant isolation on the nucleation temperature, T_n, may be observed. As illustrated in the DTA thermogram of Fig. 3, the undercooling of the droplet sample produced by crushing ($T_n = 472^\circ$ C) exceeded that of the bulk ($T_n = 552^\circ$ C) by approximately 80° C. The difference in sharpness and intensity of the exotherms is due to the larger mass and continuous nature of the bulk sample compared to the droplet sample.

In order to evaluate systematically the influence of a variety of parameters on the undercooling behaviour of antimony, emulsified droplet samples with size ranges of 18 to 28, 28 to 38, 38 to 44, 63 to 88 and 88 to 150 μm were produced. Thermal analysis results, as summarized in Fig. 4, revealed that, as the droplet size was reduced, the level of maximum undercooling consistently increased (T_n = 499, 496, 489, 481 and 461° C, respectively). In each case the "nucleation temperature" (T_n) was taken to be the maximum in the exothermic peak, with this point being both reproducible and insensititve to external variables such as the amount of sample processed. The broadness of the crystallization peaks in Fig. 4 may be attributed to slight variations in the droplet surface coating characteristics which induce nucleation over a range of temperature even for a droplet sample having a narrow size distribution [8].

In order to reduce possible annealing effects during cooling from the nucleation to ambient temperature and to evaluate the effect of cooling rate on the

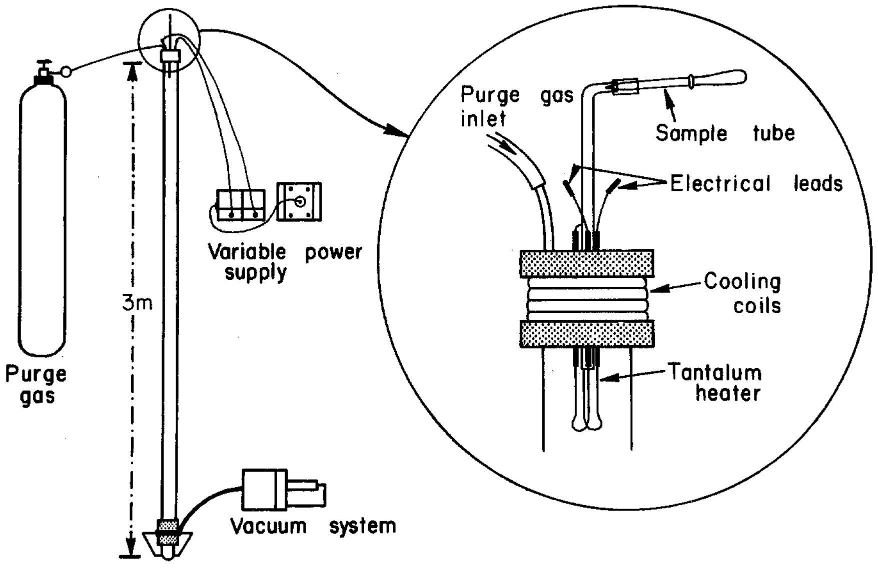

Figure 2 Schematic illustration of drop tube apparatus.

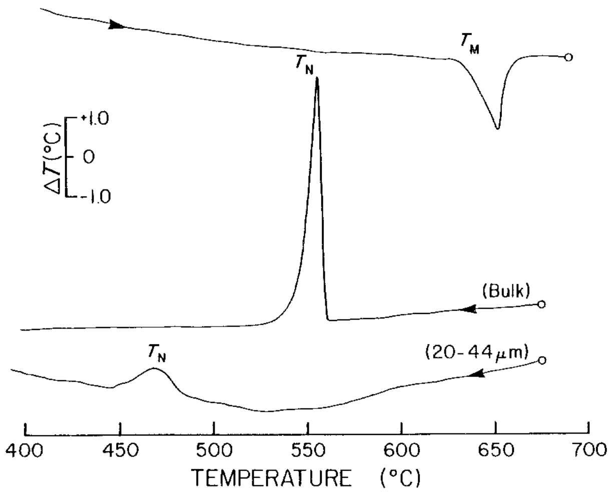

Figure 3 Comparison of undercooling response for both a bulk and crushed (20 to 44 μm) droplet sample.

undercooling behaviour of antimony, a rapid quench technique was employed using emulsified powder of size 38 to 44 μm. Increasing the cooling rate from 0.33° C sec^{-1} to approximately 500° C sec^{-1} produced an increase in undercooling from 142° C ($0.16T_m$) to 212° C ($0.23T_m$), respectively.

The effect of initial material purity on the undercooling behaviour was examined using both 28 to 38 μm and 44 to 63 μm droplet samples. In both instances, increasing the purity from 99.8% to 99.999% increased the maximum undercooling approximately 11% and created a more uniform crystallization behaviour (i.e. a narrower nucleation exotherm). Varying the applied superheat over the range 10° to 170° above the melting point altered the crystallization behaviour very little.

Based upon previous studies [9] the nature of the droplet surface coating may have a significant influence upon the level of undercooling obtained in a droplet sample. With pure antimony, a comparison may be made between droplets produced through crushing and those produced by emulsification. The coating on crushed droplets is that of a simple oxide, Sb_2O_3, while the emulsified droplets are encased within a more complex surface coating identified by X-ray diffraction analysis as $ZnSb_2O_4$ [10]. As illustrated in the thermogram of Fig. 5, for similar size droplet samples the alternative coating produced through emulsification increased the undercooling by approximately 26° C.

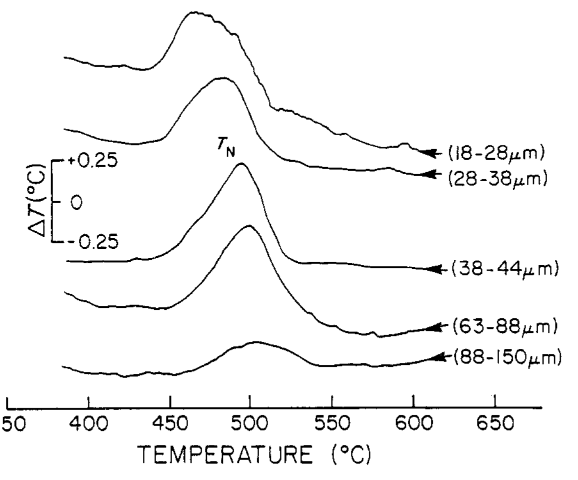

Figure 4 Effect of droplet size on the undercooling of emulsified antimony.

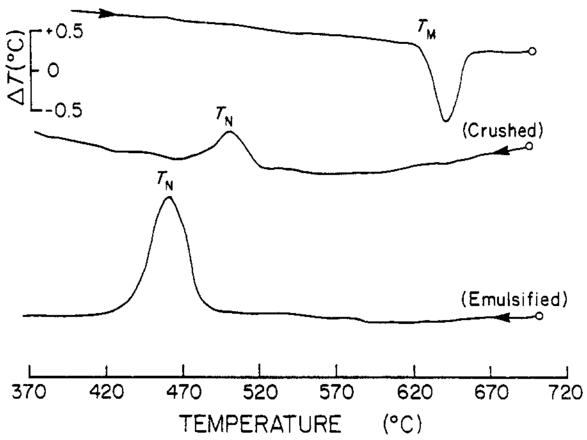

Figure 5 Comparison of the undercooling behaviour for similar size crushed and emulsified powders.

3.2. Melting behaviour

A common observation for emulsified antimony was that, upon reheating a droplet sample that had solidified at a deep level of undercooling, a broadened melting endotherm appeared over a temperature range which included the equilibrium melting point. One cause of this thermogram behaviour is the overlap of two or more transformations over a narrow temperature range. In order to evaluate this possibility for antimony, the thermal cycling treatment illustrated in Fig. 6 was applied. The powder sample was first carried through a complete melting/solidification cycle to establish the transformation temperatures. After cooling well below the nucleation peak (to 300° C) the sample was reheated to a temperature slightly beyond the initial deviation from the baseline (627° C), point "A", and held there for 6 min in order to equilibrate the sample. The sample was then cooled to approximately 560° C to establish a new baseline and reheated

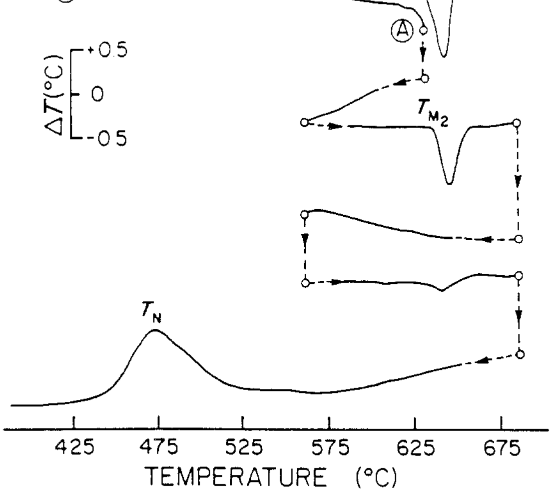

Figure 6 Illustration of the thermal cycling treatment applied to an emulsified droplet sample. Point A denotes the temperature at which the sample was isothermally held for 6 min.

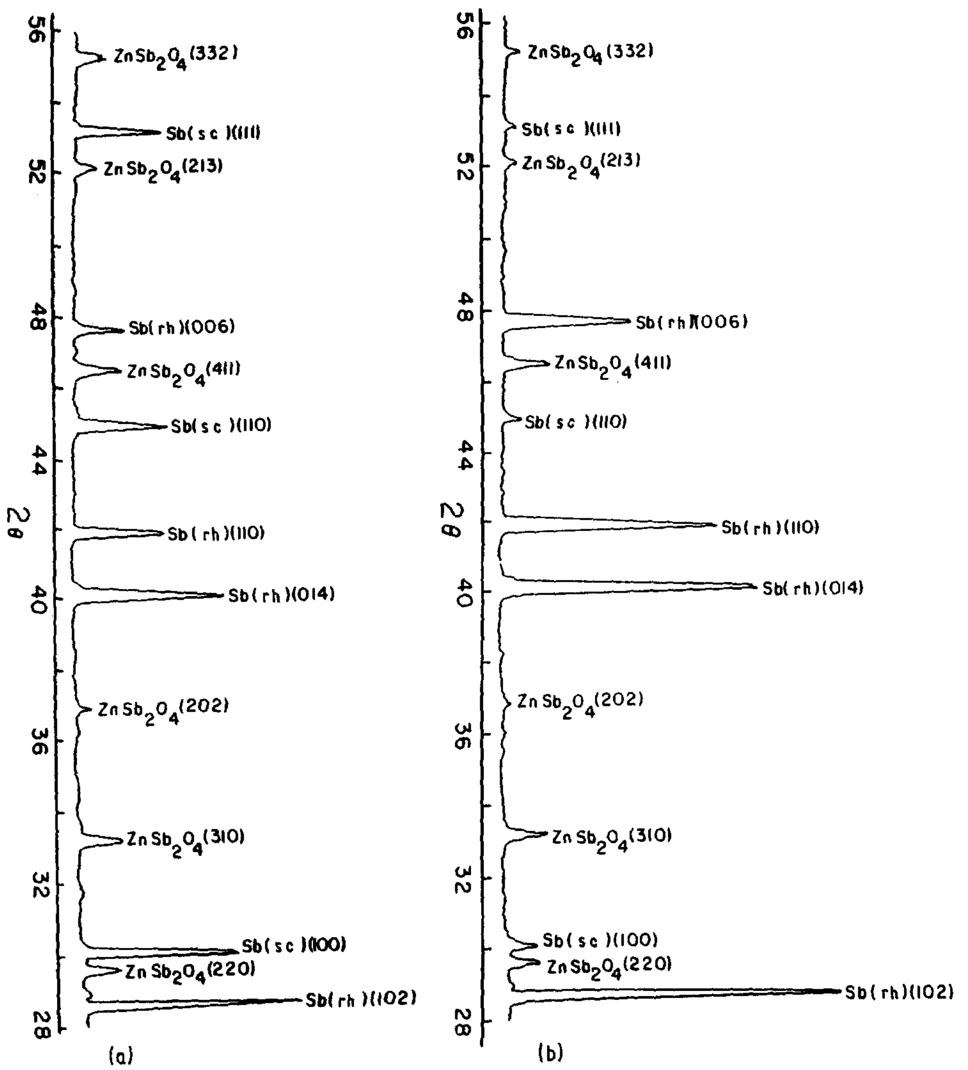

Figure 7 Representative X-ray diffraction charts for emulsified antimony samples both (a) immediately following thermal analysis (ΔT = 135° C) and (b) after an extended annealing treatment (4 h at 540° C). rh = rhombohedral; sc = simple cubic.

completely through the melting region. A distinct melting endotherm was once again observed; however, the onset temperature had increased slightly over the original onset (cycle 1). The entirely liquid sample was then cooled to 560° C and reheated again through the entire melting region. The occurrence of a relatively minor melting endotherm confirmed that no significant degree of crystallization had occurred during the previous cycle. Thus, thermal cycling suggests that the broadened endotherm may, in fact, be due to dual melting peaks separated by only a few degrees, with the initial melting (T_{m1}) occurring at 625° C and the second melting (T_{m2}) occurring at 630° C.

3.3. Drop tube studies

Droplet samples of size 38 to 44 μm, produced by both crushing and emulsification, were processed in the laboratory scale drop tube, with the solidification structures being compared to those processed by DTA and rapid quenching. While the level of applied superheat was minimized, it is probable that the Sb_2O_3 (T_m = 656° C) coating on the crushed powder melted upon heating. The crushed powder spherodized completely during the free fall period while the emulsified particles remained slightly irregular in shape due to the higher melting point of the surface coating produced during emulsification.

3.4. X-ray diffraction results

X-ray diffraction following thermal processing of each emulsified antimony sample (including that processed in the drop tube) revealed the presence of two crystalline phases of antimony, the equilibrium rhombohedral phase and a metastable sc phase. While the volume fraction of each phase varied slightly with droplet size, a significant amount ($>30\%$) of the metastable phase was found in each sample. Annealing the droplet samples for 4 h at 540° C greatly reduced the intensity of the sc diffraction peaks while increasing those of the equilibrium phase peaks, as illustrated in Fig. 7. Droplets produced by crushing, while experiencing relatively large undercoolings, showed no evidence of metastable phase formation in either the DTA or the drop tube processed samples.

4. Discussion

4.1. Undercooling characteristics

A number of processing parameters have been identified which influence the undercooling behaviour in pure antimony. Of primary importance is the degree of size refinement in the sample. The extension in undercooling from 0.08 to $0.18T_m$ by simple crushing implies that the bulk undercooling is limited by either the influence of internal catalysts or a catalyst/coating interaction effect. By dispersing these potent catalysts

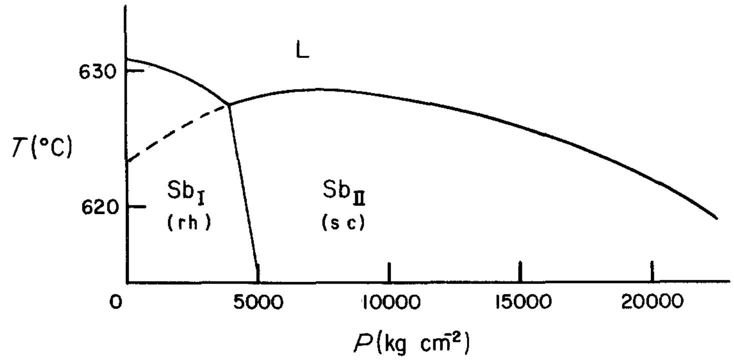

Figure 8 Enlarged view of the *T–P* diagram for pure antimony showing extrapolation of s c/liquid phase boundary to 1 atm pressure [14]. rh = rhombohedral; s c = simple cubic. (1 kg cm^{-2} = 98.067 kPa.)

into a small fraction of droplets, other less potent nucleants which may be distributed in either the volume or surface are allowed to operate at deeper levels of undercooling.

Application of the droplet emulsion technique retains this nucleant isolation advantage while providing a less catalytic surface coating. Nucleant isolation effects are once again identified by the increase in undercooling with reduction in droplet size. The less uniform crystallizatation behaviour of these droplets (compared to those produced by crushing) may be attributed to a variation in surface coating characteristics similar to that observed in pure indium droplet emulsions [8].

The significant increase in undercooling (0.16 to $0.23T_m$) with increase in cooling rate (10^{-1} to 10^2 °C sec^{-1}) for emulsified antimony droplets implies that the heterogeneous nucleation site operating at the slower rate was kinetically "bypassed" at the higher rate [11]. Thus a less potent nucleant was allowed to operate at a deeper level of undercooling. A more complete analysis of the nucleation kinetics for this system is currently underway [12].

4.2. Metastable phase formation

As a liquid is progressively cooled below its equilibrium melting point it may become metastable not only with respect to the equilibrium solid phase, but also to solids which are thermodynamically disallowed under normal solidification conditions [13]. As illustrated in Fig. 8 [14], extrapolation of the antimony II/liquid phase boundary to one atmosphere pressure on the equilibrium *T–P* diagram reveals that an undercooling of only a few degrees is required to create a thermodynamic driving force for the formation of the metastable s c phase. By this simple graphical extrapolation, the melting point of the s c phase is approximately 624° C at 1 atm pressure, in close agreement with the experimentally determined melting point (T_{ml} in Fig. 6) of 625° C. As the undercooling exceeds this value, the driving force for both the equilibrium and metastable phase continues to increase. The solid which initially forms is determined by nucleation kinetics, with the phase having the lowest barrier to nucleation at a given level of undercooling being favoured. The level of undercooling obtained in crushed antimony was well in excess of thermodynamic requirements for formation of the s c phase. The formation instead of the equilibrium phase is thus attributed to nucleation kinetics which favoured equilibrium phase formation.

Emulsified droplets experienced undercoolings slightly in excess of those produced in crushed powders thereby increasing the driving force for formation of both the equilibrium and metastable phases. The production of an alternative surface coating on these droplets created a condition in which the nucleation kinetics for a significant portion of the sample favoured the formation of s c antimony. The importance of the droplet coating in influencing the nucleation kinetics may be seen by comparing 88 to 150 μm emulsified powder to 20 to 44 μm crushed powder. Although the undercooling of the crushed powder exceeds that of the emulsified powder by 15° C, a significant portion of the emulsified sample yields the metastable phase while the crushed droplets produce an entirely equilibrium structure.

Structural information concerning the droplet surface coating can yield insight into phase selection during solidification in an undercooled melt. The $ZnSb_2O_4$ coating produced during emulsification typically occurs in tetragonal form ([15] p. 62), while the Sb_2O_3 coating present on crushed powder has either a cubic ("senarmontite") or orthorhombic ("valentinite") crystal structure ([15] p. 59). Certain orientations of $ZnSb_2O_4$ offer close lattice parameter matching with the s c phase of antimony, while select Sb_2O_3 parameters pair well with the rhombohedral crystal structure. These favourable orientation relationships may influence the nucleation kinetics, favouring formation of the metastable s c and equilibrium rhombohedral phase, respectively, in the undercooled droplets.

Formation of the metastable s c phase from the undercooled melt lowers the free energy of the system, however, there remains a driving force for the metastable to equilibrium solid state transformation. Retention of the metastable phase following the relatively slow cooling of DTA to ambient temperatures, as well as evidence of the melting of this phase upon reheating, testifies to the stability of the metastable product. One reason for this stability lies in the single crystal nature of the emulsified droplets. The lack of favourable grain-boundary sites for initiation of decomposition encourages retention of the metastable structure [1].

Based upon X-ray diffraction results, the mean value for the lattice parameter of the s c phase is 0.2935 nm with a corresponding 95% confidence interval being given by: $0.2880\,\text{nm} < a_0 > 0.2991\,\text{nm}$. Previous measurements taken at high pressure (5 GPa) provide a lattice parameter of 0.296 nm for the s c phase [16]. Assuming a compressibility factor of $20\,\mathrm{pPa}^{-1}$ [17] that is independent of crystal structure and that varies linearly with pressure, the lattice parameter of the sc phase at standard pressure would be estimated at 0.307 nm. This value is within 5% of the lattice parameter determined experimentally in the present study, which is a reasonable agreement considering the uncertainty in extrapolating high pressure lattice parameter values to ambient pressure.

5. Conclusions

The droplet emulsion technique has been successful in allowing examination of the undercooling and crystallization behaviour of pure antimony. Through proper control of the droplet size and applied cooling rate the maximum undercooling was extended from 0.08 to $0.23T_{\mathrm{m}}$. While simple crushing of the material was effective at increasing the undercooling through nucleant isolation, the oxide surface coating encouraged formation of the equilibrium rhombohedral structure. Using emulsification techniques an alternative droplet coating was produced which appears to provide a favourable crystallographic matching for an effective nucleation catalysis of a metastable simple cubic structure. Using thermal analysis, the melting temperature of the simple cubic phase was determined to be approximately 625° C. The single crystal nature of the droplets allowed retention of the metastable product to temperatures approaching the melting point. X-ray diffraction results provided a mean lattice parameter of 0.2935 nm for the simple cubic structure.

Drop tube processing of emulsified droplets under a helium gas atmosphere resulted in the formation of the metastable simple cubic phase of antimony, while processing of similar size crushed powder produced the equilibrium rhombohedral crystal structure.

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References

1. J. H. PEREPEZKO, in "Rapid Solidification Processing: Principles and Technologies II", edited by M. Cohen, B. H. Kear and R. Mehrabian (Claitor's, Baton Rouge, Los Angeles, 1980) p. 56.
2. J. H. PEREPEZKO and I. E. ANDERSON, in "Synthesis and Properties of Metastable Phases", edited by E. S. Machlin and T. J. Rowland (TMS-AIME, Warrendale, Pennyslvania, 1980) p. 31.
3. C. W. F. J. PISTORIUS, *Proc. Solid State Chem.* **11** (1976) 1.
4. D. AKHTAR, V. D. VANKAR, J. C. GOEL and K. L. CHOPRA, *J. Mater. Sci.* **14** (1979) 998.
5. *Idem, ibid.*, p. 2422.
6. D. AKHTAR, V. D. VANKAR, J. C. CHOPRA, *Thin Solid Films* **58** (1979) 327.
7. B. A. MUELLER, MS thesis, University of Wisconsin, Madison (1983).
8. J. H. PEREPEZKO and J. S. PAIK, in "Proceedings of the MRS Symposium: Rapidly Solidified Amorphous and Crystalline Alloys", edited by B. H. Kear and B. C. Giessen (North Holland, New York, 1982) p. 49.
9. J. J. RICHMOND, MS thesis, University of Wisconsin, Madison (1983).
10. J. A. GRAVES, National Aeronautics and Space Administration Contractor Report 175013 (NASA, Washington, DC, 1985).
11. J. H. PEREPEZKO, Y. SHIOHARA, J. S. PAIK and M. C. FLEMINGS, in "Rapid Solidification Processing: Principles and Technologies III", edited by R. Mehrabian (NBS, Washington DC, 1982) p. 28.
12. J. H. PEREPEZKO and J. A. GRAVES, to be published.
13. J. C. BAKER and J. W. CAHN, "Solidification" (ASTM, Metals Park, Ohio, 1971) p. 23.
14. S. M. STISHOV and N. A. TIKHOMIROVA, *J. Exp. Theoret. Phys. (USSR)* **48** (1965) 1215.
15. W. F. McCLUNE (ed.), "Powder Diffraction File" (JCPDS-International Centre for Diffraction Data, Swarthmore, Pennyslvania, 1984) p. 62.
16. S. S. KABALKINA and V. P. MYLOV, *Sov. Phys. Dolk.* **8** (1964) 917.
17. G. C. KENNEDY and R. N. KEELER, in "American Institute of Physics Handbook", edited by D. E. Gray (McGraw-Hill, New York, 1972) p. 4-38.

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