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# Stabilization and transformation kinetics of the metastable phases of liquid-quenched antimony

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Electron diffraction and differential thermal analysis studies have shown that the formation of metastable phases in antimony on liquid-quenching bythe "gun" technique is dependent on the rupture pressure of the "gun". The transformation temperatures, associated heats of transformation, and transformation kinetics of these metastable phases are reported.

## 1. Introduction

Changes in the structure and consequently in properties that are brought about as a result of ultra-fast quenching of metals and alloys are being studied extensively at present. Discrepancies regarding the structural data exist in the literature between different rapid solidification studies, presumably due to different quenching parameters. However, very few investigations have been made to throw light on the effect of variables such as melt temperature and rate of cooling in the splat-quenching process on the stabilization of metastable phases. The role of the initial melt temperature has been investigated by Scott [1] who observed that the constitution of a splat-quenched gold–germanium eutectic alloy is dependent on the initial melt temperature. Similarly Ramachandrarao *et al.* [2] have claimed the formation of three new tetragonal metastable phases on quenching eutectic gold–germanium alloy onto a copper substrate from 480, 550 and 800° C respectively. Three distinct structures have been observed in a gold–cadmium–indium alloy on quenching at different cooling rates obtained by three different techniques, namely splat-quenching ("gun" technique), quenching of the molten droplets from the "gun" apparatus directly into water, and by casting of filaments [3].

The effect of the rupture pressure on the stabilization of metastable phases by the "gun" technique has not so far been investigated. Cooling rates in the "gun" technique should, in principle, depend on the rupture pressure when other quenching parameters are the same. Recently we have reported the formation of a number of metastable new crystalline phases in lead and antimony on splat-quenching at a typical "gun" rupture pressure of 80 kg cm$^{-2}$ [4, 5]. It is of much interest to establish that the stabilization of these phases is dependent on different rupture pressure conditions. The role of rupture pressure on metastable phase formation and the transformation characteristics of the various metastable phases in antimony are reported in this paper.

## 2. Experimental details

The "gun" apparatus used in the present investigations has been described in detail elsewhere [4]. Aluminium foils of thicknesses approximately 25, 50, 75 and 100 $\mu$m were used as diaphragms and ruptured at pressures of approximately 20, 40, 60 and 80 kg cm$^{-2}$ respectively. Since one of the objectives of the present investigations was to study the effect of "gun" rupture pressure, great care was taken to ensure that all other conditions were the same.

About 100 mg of pure antimony (99.999% pure) was quenched onto water-cooled copper substrate from 680° C (~ 50° C above the liquidus temperature) at rupture pressures of 20, 40, 60 and 80 kg cm$^{-2}$. The copper substrate was abraded with a fine SiC paper and cleaned prior to each quench to ensure that it was free of oxide. Antimony was melted in a graphite crucible having an orifice of ~ 1 mm in the bottom. Prior to quenching, the chamber containing the splat-

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quenching "gun" was evacuated to $\sim 10^{-1}$ Torr and continuously flushed with high purity argon so as to maintain an argon pressure of $\sim 5$ Torr inside the chamber. The resulting foils were irregular and could be easily stripped from the copper substrate.

Differential thermal analysis of the as-quenched specimens was carried out using a Stanton Redcroft DTA thermal analyser. About 20 to 30 mg of sample was accurately weighed and heated in a specimen can in the DTA at a rate of 10° C min$^{-1}$ in each case. Pure alumina powder was used as the reference sample. To ascertain the structural changes associated with each heat peak, the as-quenched specimens were annealed at suitable temperatures in vacuum. The as-quenched and annealed samples were examined in a transmission electron microscope operating at 80 kV.

## 3. Results and discussion

The metastable crystalline phases of antimony obtained on splat-quenching at different rupture pressures are summarized in Table I. Details of *d*-spacings and indices of reflection (*h k l*) for these phases have been reported in an earlier paper [5] for specimens prepared at a typical rupture pressure of 80 kg cm$^{-2}$. The lattice parameter values are, however, given on the flow chart showing the transformation behaviour of the metastable phases (Fig. 1). Note that no change in the lattice spacings has been observed with change in the rupture pressure.

Foils obtained at a rupture pressure of 20 kg cm$^{-2}$ produced equilibrium rhombohedral, h c p, f c c and simple cubic phases. The equilibrium phase was observed only in thicker portions of the foil. Thinner portions revealed the presence of the h c p phase which did not transform on *in situ* heating in the electron microscope. F c c and simple cubic phases were observed in very thin electron transparent regions. On electron beam heating, these phases transformed to the h c p phase.

TABLE I Metastable crystalline structures of liquid-quenched antimony at various "gun" rupture pressures

| Rupture pressure (kg cm$^{-2}$) | Structures | | | | |
|---|---|---|---|---|---|
| 20 | eq. rhomb. | h c p | f c c | | |
| 40 | | h c p | f c c | new rhomb. | |
| 60 | | | f c c | new rhomb. | tetrag. |
| 80 | | | f c c | new rhomb. | tetrag. |

Foils obtained at a rupture pressure of 40 kg cm$^{-2}$ consisted of h c p, f c c, simple cubic and new rhombohedral phases. The h c p, f c c and simple cubic phases showed the same transformation behaviour, as discussed above. However, the metastable rhombohedral phase transformed directly to the equilibrium rhombohedral phase in the heating stage of the electron microscope.

Foils obtained at rupture pressures of 60 and 80 kg cm$^{-2}$ did not exhibit any of the h c p and equilibrium rhombohedral phases but showed an additional metastable tetragonal phase. On electron beam heating, the f c c, simple cubic and tetragonal phases transformed to the h c p phase, and the new rhombohedral phase to the equilibrium rhombohedral phase. Though the metastable phases present in two kinds of specimens (60 and 80 kg cm$^{-2}$) are the same, it is noteworthy that their proportions in these specimens are not the same, as revealed by areas under first two DTA peaks corresponding to these specimens (Fig. 2).

DTA curves for all the specimens are shown in

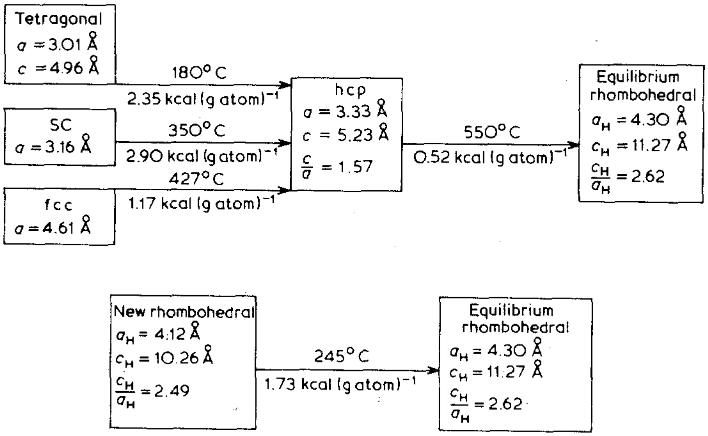

*Figure 1* Flow chart, showing transformation temperatures, phase obtained on transformation, and associated heats of transformation for various metastable phases of liquid-quenched antimony.

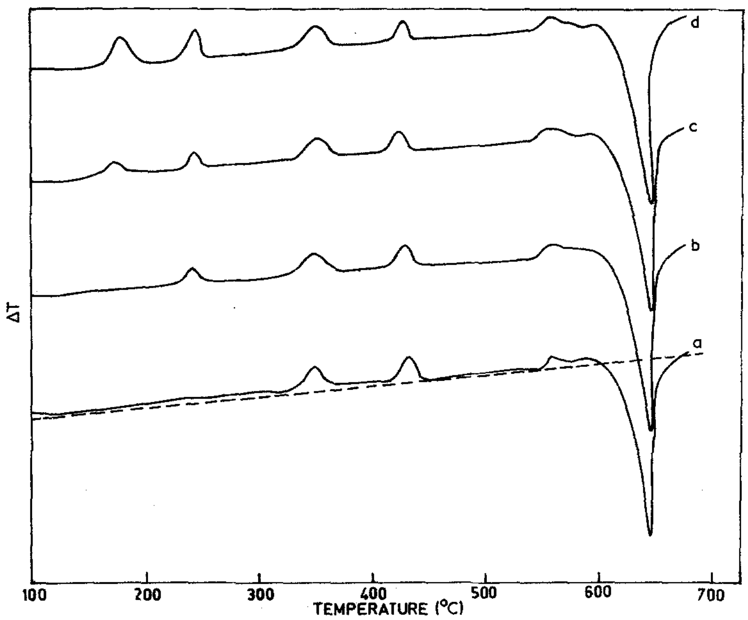

*Figure 2* DTA thermograms of antimony foils quenched at rupture pressures: (a) 20, (b) 40, (c) 60, and (d) 80 kg cm$^{-2}$. ——— heating cycle; — — — base line run.

Fig. 2. The peaks are exothermic in nature (except the endothermic melting peak) and correspond to transformation temperatures of ~180, 245, 350, 427 and 550° C. The specimens prepared at rupture pressures of 60 and 80 kg cm$^{-2}$ were annealed at 200° C in vacuum for thirty minutes and examined in an electron microscope. No tetragonal phase was observed in these specimens, though traces of h c p phase were observed along with the f c c, simple cubic and new rhombohedral phases. It is therefore evident that the tetragonal phase transforms to the h c p phase at this temperature, as confirmed by the absence of an exothermic peak at 180° C in DTA curves of these annealed samples. The DTA peaks indicate that the proportion of the tetragonal phase in 80 kg cm$^{-2}$ specimens is greater than in those prepared at rupture pressure of 60 kg cm$^{-2}$.

Foils prepared at rupture pressures of 40, 60 and 80 kg cm$^{-2}$ (showing an exothermic peak at 245° C) were annealed at 260° C in vacuum for thirty minutes. Examination of these foils in an electron microscope revealed the presence of simple cubic, f c c, h c p, and equilibrium rhombohedral phases. This indicates the transformation of new rhombohedral phase to the equilibrium rhombohedral phase. These annealed samples did not show any exothermic peak at 180 or 245° C, thus confirming the transformation of tetragonal and new rhombohedral phases. The presence of the h c p phase in annealed samples of 80 and 60 kg cm$^{-2}$ rupture pressure is due to the transformation of tetragonal phase at 180° C during heating. It is noteworthy that the proportion of the new rhombohedral phase in 80 kg cm$^{-2}$ samples is more than in 60 kg cm$^{-2}$ samples (as revealed by areas under the DTA peaks at 245° C for these two specimens).

All samples annealed at 360° C in vacuum for thirty minutes showed no traces of simple cubic phase. Samples annealed at 440° C did not exhibit the f c c phase either. These samples were heated in an electron microscope to confirm their transformation to the h c p phase. Further confirmation was obtained by DTA studies of these annealed samples.

The h c p phase obtained in as-quenched (at 20 and 40 kg cm$^{-2}$ rupture pressure) specimens and by transformation of metastable tetragonal, simple cubic and f c c phases (in all specimens) did not transform on heating in the electron beam as reported elsewhere [5]. The broad exothermic DTA peak observed at 550° C suggested transformation at this temperature. Therefore all the samples were annealed at 550° C in vacuum for thirty minutes. Electron microscopy examination of these specimens revealed that h c p phase was still present in some portions of the foil. However, on annealing for one hour, the whole of the h c p phase transformed to the equilibrium rhombohedral phase. These samples did not show any exothermic peak in the differential thermogram.

An accurate quantitative analysis of the associated heats of transformation is not possible because the proportions of different metastable phases in as-quenched specimens are not known. The areas under the DTA peaks at 180 and 245° C, corresponding to the transformation of tetragonal and new rhombohedral phases, are larger in samples prepared at rupture pressure of 80 kg $cm^{-2}$ than in samples prepared at rupture pressure of 60 kg $cm^{-2}$. However, a rough calculation can be made if we take a typical differential thermogram corresponding to 80 kg $cm^{-2}$ samples and assume equal proportions of tetragonal, new rhombohedral, simple cubic, and fcc phases in these samples. This yields values of heats of transformation for these phases to be 2.35, 1.73, 2.90 and 1.17 kcal (g $atom)^{-1}$ respectively. It should be noted that these values correspond to the transformation of tetragonal, simple cubic and fcc phases to the hcp phase and transformation of the new rhombohedral phase to the equilibrium rhombohedral phase. This gives a value of 0.52 kcal (g $atom)^{-1}$ for the heat of transformation of hcp phase to the equilibrium rhombohedral phase. It is emphasised here that the values given are only approximate because the proportion of a particular phase in the as-quenched sample is completely unknown. The transformation temperatures, phases obtained on transformation, and associated heats of transformation for all the metastable phases are summarized in the flow chart of Fig. 1.

Since foils obtained by "gun" splat-quenching are very irregular in thickness, a range of cooling rates may exist in any one foil so that many phases may be present in the foil. However, the presence of different phases and their different relative proportions in specimens quenched at different rupture pressures cannot be attributed to foil thickness only. The contact of the molten droplets with the substrate (determining the heat transfer coefficient) is an important parameter even for the same thicknesses of foil. Since other quenching parameters (the initial melt temperature, surface condition of the substrate, and quenching ambient) are approximately the same in all cases, the "gun" rupture pressure becomes an important parameter in stabilizing the metastable phases. Increasing rupture pressure increases the shock wave intensity resulting in (i) better atomization of the melt and (ii) enhanced contact of atomized droplets with the substrate, as the droplets impinge on the substrate at higher velocities. This high degree of atomization of the melt and its enhanced contact with the substrate increases the cooling rates appreciably. By examining a large number of micrographs, the average value of grain size at different rupture pressures was calculated. It was found that the average grain size decreases with increasing rupture pressure, thus implying that the cooling rate increases as the rupture pressure is increased.

From Table I we see that the metastable tetragonal phase is observed in samples prepared at rupture pressures of 60 and 80 kg $cm^{-2}$ only. Its proportion in as-quenched samples increases considerably with increase in rupture pressure, as revealed by areas under the DTA peaks at 180° C corresponding to these specimens (Fig. 2). This means that the tetragonal phase is stabilized at the highest rates of cooling and its transformation to the hcp phase at 180° C shows a higher degree of metastability of this phase with respect to other phases. The metastable new rhombohedral phase stabilizes at rupture pressures of 40, 60 and 80 kg $cm^{-2}$ and not at a rupture pressure of 20 kg $cm^{-2}$. Cooling rates required to stabilize this phase are, therefore, lower than those required to stabilize the tetragonal phase. It transforms at 245° C and is, therefore, more stable than the tetragonal phase but has a higher degree of metastability as compared to the simple cubic and fcc phases. The simple cubic and fcc phases are observed in samples prepared at all rupture pressures and transform to hcp phase at higher temperatures. It is, therefore, clear that these phases stabilize at comparatively low cooling rates and remain stable up to higher temperatures.

The hcp phase is observed in as-quenched samples prepared at low rupture pressures only, which means that the hcp phase stabilizes at low cooling rates (but higher than those obtained in bulk quenching). The metastable tetragonal, simple cubic, and fcc phases transform to the hcp phase on heating and the hcp phase transforms to the equilibrium rhombohedral phase at higher temperatures (only 80° C below the liquidus temperature). According to Ostwald's rule, a system undergoing reaction proceeds from a less stable through a series of increasingly more stable intermediate states to reach the final equilibrium state. Our observations, therefore, suggest a high degree of stability of the hcp phase. It should be pointed out that the equilibrium rhombohedral phase is observed in as-quenched samples prepared at rupture pressure of 20 kg $cm^{-2}$ only in thicker portions of the foil, implying that the quenching rates in these regions are of the same order as those obtained in bulk quenching. It is, therefore, concluded that the cooling rates required to stabilize the various phases increase in the order: hcp, fcc, simple cubic, new rhombohedral, and tetragonal metastable phases.

Metastable phases are generally the high temperature and/or high pressure polymorphs of a material (see, for example [6]). The hcp and simple cubic phases are the known high pressure (90 and 50 kbar) phases of antimony [7]. Ramachandrarao *et al.* [3] have shown that the sequence of transformations observed in high-pressure studies is correlated with that observed in splat-quenched foils of alloys in the gold–cadmium–indium system. The stabilization processes are complex and varied. Guided by these observations, we may predict the existence of tetragonal, new rhombohedral and fcc phases at high pressures. It would, therefore, be of considerable interest to study antimony at pressures exceeding 90 kbar.

## 4. Conclusions

(1) Shock wave intensity (determined by the rupture pressure of the gun diaphragm) is an important parameter in stabilizing metastable phases by splat-quenching. High rupture pressures lead to higher rates of cooling, owing to the higher degree of atomization of the melt and its enhanced contact with the substrate.

(2) Cooling rates required to stabilize the hcp, fcc, simple cubic, new rhombohedral and tetragonal metastable phases of antimony are in increasing order and the thermal stability is in decreasing order for the sequence of phases from hcp to tetragonal.

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