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The effect of pressure on metastable phase formation in the undercooled Bi–Sn system

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A metastable phase was produced by the solidification of highly undercooled Bi–48.6 at% Sn alloy droplet samples. During heating the metastable phase was observed to melt at 116° C at ambient pressure. The onset of the metastable endotherm was found to increase with increasing pressure, while the liquidus and eutectic temperature for the structure stable at ambient pressure decreased with increasing pressure. Based on the pressure dependence of the melting trend, the metastable phase will be stable at the expense of the stable ambient pressure structure under high hydrostatic pressure conditions (above ~1 GPa). Both microstructural observations and X-ray examinations at ambient pressure revealed that the metastable phase was present in droplet samples and that the X-ray diffraction pattern was close to that of the high-pressure stable phase previously reported as a rhombic cell. High-pressure thermal analysis has also allowed for identification of the effect of pressure in promoting favourable formation kinetics and the kinetic transition from the equilibrium phases to the metastable phase at high undercooling.

1. Introduction

The Bi–Sn system has attracted the attention of many investigators because it provides a good model for studying the structure and properties of metallic materials under high pressure. The alloys in this system melt easily, the components have melting point/pressure relationships of different signs, and bismuth undergoes several polymorphic transformations in the pressure range up to 10 GPa. These component properties may lead to a marked change in the form of the *T–C* (temperature–composition) phase diagram and to the appearance of a number of new intermediate phases as a result of the application of elevated pressure. The equilibrium phase diagram for the Bi–Sn system shown in Fig. 1 is of the eutectic type at atmospheric pressure [1].

Bridgman [2] and Ponyatovskiy [3, 4] have reported the formation of a high-pressure phase in Bi–Sn alloys and have interpreted this phase as an intermetallic compound of equiatomic composition. A detailed investigation of the superconductive properties [5, 6], however, has shown that the high-pressure phase is of variable composition with quite a wide range of homogeneity including the concentration interval from 40 to 60 at % Bi at 2 GPa and 350 K. A thermodynamic interpretation of the Bi–Sn equilibrium diagram [7] has also shown that an intermediate phase of variable composition should be formed under pressure.

In a structural study of the phase transitions occurring under pressure, it is convenient to use the "quenching" method, in which a sample of an alloy of a given composition is subjected to a certain pressure, *P*, and temperature, *T*. It is then cooled under pressure to liquid-nitrogen temperature, and the pressure is lowered to the atmospheric value [8, 9]. Based on this method, in which it is assumed that no structural transformations occur during cooling or pressure relaxation, the high-pressure phase observed in the Bi–Sn system was suggested to be a body centred tetragonal, b c t, structure [9].

The Bi–Sn system has also been investigated at ambient pressure following rapid solidification processing (RSP). Kane *et al.* [10] obtained a metastable phase in a Bi–50 at % Sn alloy using the splat-quenching RSP method, and examined it by X-ray diffraction techniques at low temperature. The metastable phase observed was suggested to be a supersaturated tin solid solution with a b c t structure.

The relation between a metastable phase obtained by RSP and a high-pressure phase in the same alloy system has been considered by several investigators. Comparison of the structures of "quenched" samples, analysed by X-ray diffraction, with the results of X-ray [11, 12] and neutron [13] diffraction studies of alloys of the same compositions under pressure has shown that the high-pressure phases of the Pb–Bi and In–Bi systems were retained after "quenching" under pressure. However, in the case of the Bi–Sn system, the structure of the "quenched" alloys [9] differed from the structure observed directly under pressure [11, 13]. The structure of the "quenched" alloys which was claimed to be that of the high-pressure phase retained after "quenching" under pressure [5, 6, 14] was suggested to be a b c t structure [9], which was the

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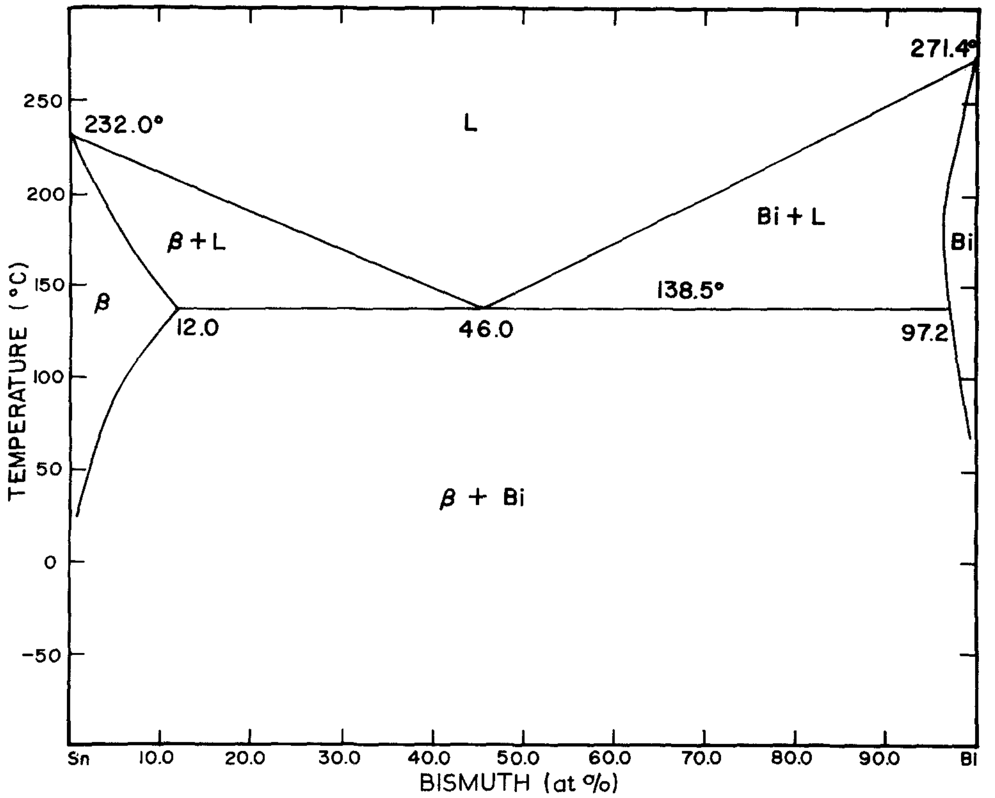

Figure 1 The bismuth–tin phase diagram [1].

same structure of the metastable phase reported in RSP [10]. However, *in situ* X-ray examination [11] and the neutron diffraction study [13] under pressure indicated that the high-pressure phase was not a bct structure. Instead, the structure of the high-pressure phase was suggested to be a rhombic or a monoclinic type [11, 13].

The conflict between the data obtained under high pressure and that from RSP work in terms of phase formation is still unsettled in the Bi–Sn system. As a slow cooling technique, the droplet emulsion method yields a high level of undercooling before the onset of solidification in a liquid sample (0.3 to 0.4 T_m) [15] and permits an evaluation of the kinetic competition between metastable and equilibrium phase formation. Therefore, a study was undertaken of the phase formation during rapid solidification of undercooled droplets at ambient pressure and of the thermal behaviour of droplet samples under hydrostatic pressure conditions in an attempt to identify the structure and the operative solidification kinetics.

2. Experimental procedure

To obtain a substantial level of undercooling at 1 atm, the droplet emulsion technique was used. This method is based on the idea that by subdividing a bulk sample, the impurity catalytic motes will be isolated into a small fraction of the total number of discrete particles so that the majority of the droplets can solidify without the influence of the motes. With this technique, a large amount of undercooling can be achieved [16, 17].

The alloy selected for the examination of undercooled samples under pressure has a composition of Bi–48.6 at % Sn which is near the equiatomic value which is usually used for pressure and RSP experiments. The bismuth and tin metals used in this investigation were of at least 99.999% purity and were encapsulated in a quartz tube to make a homogenized alloy. A mixture of an organic carrier fluid and molten Bi–48.6 at % Sn alloy was sheared at 30 000 r.p.m. to produce an emulsion. The final droplet size was in the range 1 to 20 μm. With differential thermal analysis (DTA), the melting and crystallization behaviours of a droplet sample were studied at 1 atm as well as at high pressure. X-ray diffraction (XRD) and microstructure examinations were conducted following DTA analyses. Pressures up to 400 MPa were amplified through an intensifier driven by an air pump, which was initiated by a hand pump. Further details of experimental apparatus and procedures have been presented elsewhere [18].

3. Results and discussion

Several sets of alloy emulsions were prepared for the study of the thermal behaviour at high pressure as well as at 1 atm from the Bi–48.6 at % Sn alloy. The thermal behaviour of the emulsion samples was monitored by DTA and the same samples were then used for microscopic and X-ray examinations.

3.1. Thermal behaviour

The sample sets underwent an equilibrium melting onset at the eutectic (T_e = 138.5° C) and a completion of melting at the liquidus (T_L = 168° C) at ambient pressure as shown in the heating cycles of Fig. 2. On the other hand, the nucleation temperature, T_n, varied from sample to sample. It should be noted that a typical DTA sample contains on the order of about 10^6 separate droplets. Owing to the surface coating on the droplets, each droplet is independent in its solidification behaviour. The thermal signals recorded during DTA, therefore, represent the summation of events in

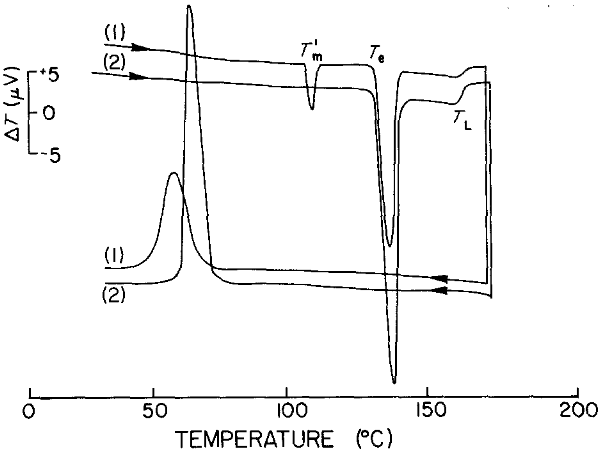

Figure 2 Thermal cycling behaviour of a Bi–48.6 at % Sn emulsion at 1 atm. Metastable endothermic behaviour appears in a droplet sample with relatively large undercooling.

a statistically significant number of droplets. At the same time, due to variations in droplet coating, different droplets may display different kinetic behaviour. As a result, during the main crystallization exotherm in Fig. 2 (thermogram 1) at 60° C, one droplet fraction can solidify as the equilibrium phase and melt at the eutectic and liquidus temperature while another fraction can solidify as a metastable phase, retain the metastable structure and melt during the metastable endotherm at 116° C. As seen in Fig. 2, only when high undercooling was achieved before the onset of crystallization during cooling, did the metastable phase melting endotherm appear at 116° C and 1 atm during a heating cycle (thermogram 1). Further investigation on alloys with other compositions is necessary to resolve the nature of the melting reaction involved in the metastable endotherm and to determine the complete details of the operative metastable phase equilibrium developed in droplet samples.

Both of the samples shown in Fig. 2 were pressurized up to 400 MPa. Even though the sample of thermogram 2 in Fig. 2 did not show a metastable phase melting at ambient pressure, it developed a metastable phase melting behaviour under an elevated pressure condition. The thermograms for the sample, which showed equilibrium crystallization at 1 atm, but showed a metastable structure under elevated pressure, are shown in Fig. 3. In addition, the pressure–thermograms for the sample which had exhibited a metastable phase melting at ambient pressure, thermogram 1 in Fig. 2, are shown in Fig. 4.

Two notable thermal behaviours of the metastable endotherm under pressure were observed. First, the onset temperature of the metastable endotherm increased, while those for the equilibrium melting (T_e and T_L) decreased with increasing pressure. Also, comparing the magnitude of the metastable peak with that for the equilibrium phase endotherm, by which the relative amount of a certain phase in the sample could be estimated, the amount of metastable phase increased at the expense of the equilibrium phase with increasing pressure.

The results of metastable and equilibrium endothermic and exothermic behaviours under hydrostatic pressure for the droplet sample are shown in Fig. 5. The endothermic temperatures for the equilibrium melting (T_e and T_L) decreased by 8.4 and 36.5 K GPa^{-1}, respectively and that for the metastable phase melting increased by 12 K GPa^{-1} steadily through the experimental pressure range (up to about 400 MPa). By linear extrapolation for both metastable and equilibrium endotherms to the high-pressure range, an intersection is estimated at about 1 GPa; above this point (~ 1 GPa), the metastable phase would be stable. If the compressibility difference between liquids and solids was considered, the melting trend slope could be steeper in the high-pressure range. Therefore, it is possible that the high-pressure phase

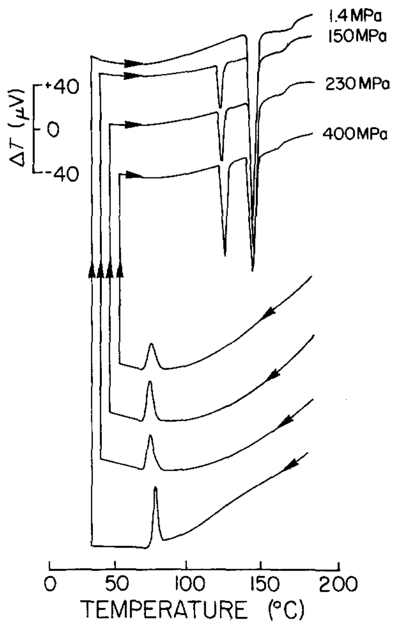

Figure 3 Thermal cycling behaviour of a Bi–48.6 at % Sn droplet sample under various pressures, where no metastable endothermic behaviour appears at ambient pressure.

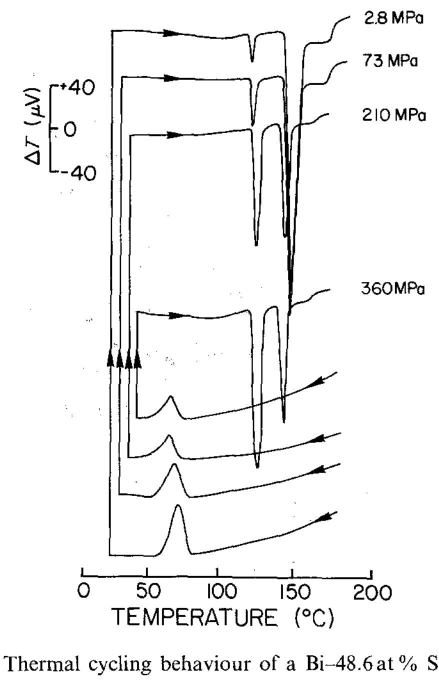

Figure 4 Thermal cycling behaviour of a Bi–48.6 at % Sn droplet sample under various pressures, where metastable endothermic behaviour already appears at ambient pressure.

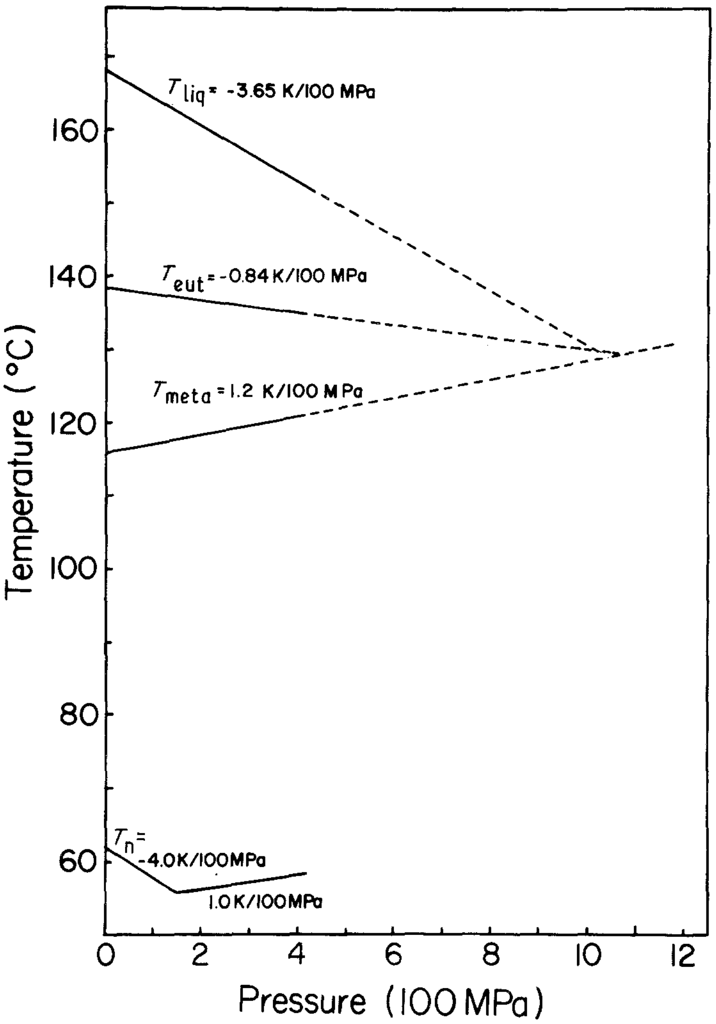

Figure 5 The experimentally observed P–T diagram for a Bi–48.6 at % Sn emulsion sample. Note that the melting temperature of the metastable phase will be higher than that of eutectic above ~ 1 GPa; i.e. the metastable phase will be stable above ~ 1 GPa.

might become a stable phase at a pressure somewhat below 1 GPa.

Unlike the endotherm trends, the nucleation temperature initially decreased and then increased with increasing pressure. The initial slope (i.e. dT_n/dP) was similar to that of the liquidus temperature (about $-40\,\mathrm{K\,GPa^{-1}}$) until the turning point at about 150 MPa. The slope of the second high-pressure part of the trend was about $10\,\mathrm{K\,GPa^{-1}}$, which in turn was similar to the value of the slope of the metastable phase melting under elevated pressure.

The trend of T_n which follows the trend of T_m on the P–T diagram has been observed previously [19, 20]. On the basis of classical nucleation theory [21] and a structural model for the liquid–solid interface [22], the trend of nucleation temperature of the sample to follow that of melting temperature of the sample on the P–T diagram can be rationalized [23]. For the present case, the behaviour of the nucleation temperature, therefore, can be analysed in the following manner: in the low-pressure range, the majority of the droplets may solidify as the equilibrium phase so that the nucleation trend may follow the equilibrium melting trend, but in the high-pressure range, the majority of droplets may solidify to a high-pressure phase due to the influence of pressure on the phase selection, so that T_n may change its pressure trend. In this study, the fact that the slope of the first part of the nucleation trend was roughly equal to that of liquidus and the value of the second part was about the same as that of high-pressure melting provides support for this explanation.

Another interesting thermal behaviour is shown in Fig. 6. The first thermal cycle shows a complete heating and cooling trace; however, the second cycle was stopped just after the metastable endotherm, T'_m, and then the sample was cooled. In the first cycle, two distinct exothermic peaks (T_{n1}, T_{n2}) appeared during cooling, but in the second cycle, only the T_{n2} nucleation peak at the highest undercooling was present. Based on this thermal behaviour, it is believed that the metastable endotherm was mainly associated with the most highly undercooled droplets even in the same sample; i.e. the largest undercooling is required for the metastable phase formation.

3.2. Conclusions from thermal behaviour

From consideration of the thermal behaviour of the

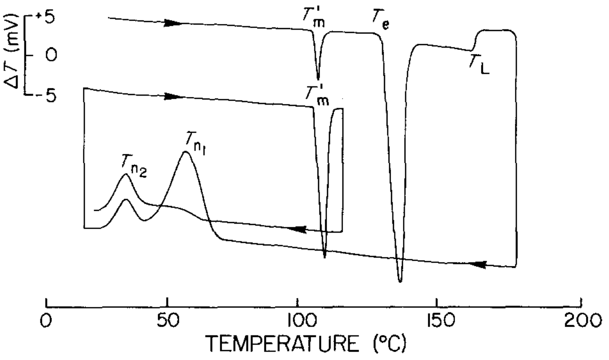

Figure 6 Thermal cycling behaviour of a Bi–48.6 at % Sn emulsion. The metastable endothermic behaviour is associated with droplets exhibiting the largest undercooling.

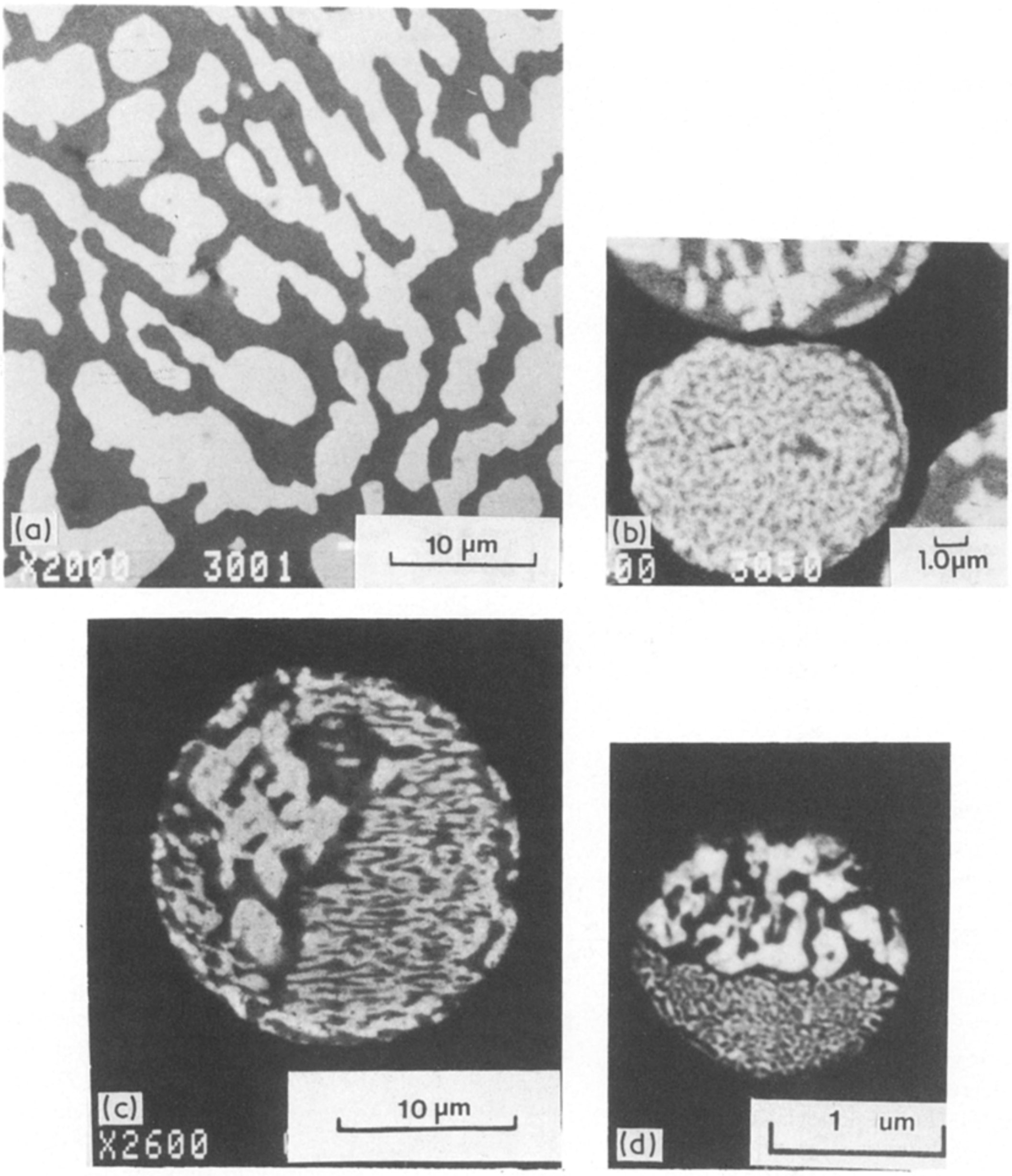

Figure 7 SEM microstructures of a Bi–48.6 at % Sn sample (back-scattered electron imaging). (a) Bulk (no significant undercooling); (b), (c), and (d) droplet samples.

Bi–48.6 at % Sn droplet samples at 1 atm and at high pressure, the metastable phase can be favoured kinetically either by large amounts of undercooling or by elevated pressure. Therefore, the present phase is not only a metastable phase, for which the formation can be enhanced by the large amount of undercooling, but also a high-pressure phase, which becomes stable as the pressure increases. Similar observations of polymorphic phase formation during rapid solidification of undercooled liquids of bismuth and antimony have been reported [19, 24]. In these cases, the metastable structural modifications are known to correspond to those determined to be equilibrium structures at high pressure.

3.3. Microscopic examination

The microstructure of the bulk sample, which exhibited no significant undercooling, is shown in Fig. 7a, and consisted of an irregular eutectic. The microstructure of the undercooled Bi–48.6 at % Sn emulsion sample (Fig. 7) has two regions; one bismuth-rich (light) and one tin-rich (dark). However, the morphology of the microstructures in the droplets is not uniform; i.e. some droplets shown an "irregular" eutectic-type morphology, where the bismuth-rich phase is randomly distributed with the tin-rich phase, while other droplets show a fine two-phase mixture (Fig. 7b). Among them, some are composed of irregular shape and a fine two-phase mixture shape (Figs 7c, d). If the microstructural morphology of the bulk sample (Fig. 7a) and previous work on undercooled structures [25] are considered, the "irregular" shape is usually the observed morphology in droplet samples having the eutectic composition. On the other hand, though the fine two-phase mixture (Fig. 7b) was sometimes observed in highly undercooled droplet samples, it was not a common morphology for the stable bulk eutectic samples. The morphology of the fine two-phase mixture may be the result of prior metastable phase formation in the droplets. According to the DTA and XRD results, the metastable phase may be a single phase. It was also observed that the number of droplets exhibiting the "irregular" eutectic morphology depended on the sample annealing time. That is, with increased annealing time at room temperature, the number of droplets having the completely decomposed (i.e. equilibrium "irregular") morphology was increased. Therefore, it seems likely that the single metastable phase decomposed to the fine two-phase mixture in the solid state.

Figs 7c and d show a droplet containing two different morphologies; one is the usual "irregular" structure and the other is a fine two-phase morphology. In this case, although two different morphologies are present in the droplet, it does not seem to be the result of the nucleation of the two different phases (e.g. one side metastable and one side equilibrium). Because of the fine droplet size ($< 20\,\mu$m), the nucleation time is far longer than the growth time, so that two different nuclei could not exist statistically at the nucleation period. This argument supports the conclusion that the two morphologies did not nucleate from the melt simultaneously. Therefore, it is more plausible that a solid state decomposition followed by a discontinuous coarsening may be a major mechanism to alter the morphological configuration in the droplet. According to observations [26], the conditions of low temperature and fine initial two-phase spacing may promote the discontinuous coarsening mode. Furthermore, discontinuous coarsening has been reported to start at a grain boundary or a sample surface. Thus, in the case of the droplets in Fig. 7c and d, the metastable phase was formed from the undercooled liquid, but during the preparation period for a microscopic examination, the metastable phase decomposed to a fine two-phase mixture. Further coarsening resulted in the formation of the irregular morphology by the discontinuous mode. Therefore, the unique mixed morphology (irregular plus fine two-phase) can be developed in some droplets as a result of incomplete solid state reaction.

3.4. X-ray diffraction examination

Deeply undercooled emulsion samples which solidified into the metastable phase at 1 atm were examined by powder X-ray diffraction. Owing to the relatively fast decomposition of the metastable phase at room temperature, XRD was conducted within about 2 h after solidification. A portion of the X-ray diffraction chart, in which Cu$K\alpha$ radiation was used, is shown in Fig. 8. The new peaks representing the metastable phase are evident. Because the sample was composed of a mixture of both the metastable phase and the stable phases, X-ray peaks for the equilibrium phases are also present.

Structural data on the high-pressure phase in this system examined by neutron diffraction [13] and X-ray diffraction [11] directly under high pressure, and the present X-ray diffraction results obtained at 1 atm, are compared in Table I. Two points should be noted before the structural data are compared. (1) Each data set was not observed at identical conditions; i.e. different pressure, temperature, sample type (thin foil in [11], small bulk in [13], and powder in the present case) and diffraction method were employed. (2) Because there were three phases in the present sample (bismuth, tin and metastable phase), some peaks were very close to each other or even overlapped, (e.g. the peaks of the Sn(0 2 0), Bi(1 1 3), and Bi(0 2 2), reflections were close to a metastable phase peak, and the Bi(1 0 5) overlapped with the Sn(1 2 1) peak). Furthermore, it is also possible that some metastable phase peaks are superimposed on strong stable peaks so that they cannot be detected reliably. In spite of the differences, the comparison between the X-ray diffraction pattern of the present metastable phase and that reported in previous high-pressure studies suggests that the crystal structure of the present metastable phase may be closer to the high-pressure phase reported in [11] and [13] than the bct structure reported in other RSP work [10]. The crystal structure of the high-pressure phase has not yet been identified, but it was suggested to be a rhombic cell based on high-pressure neutron and X-ray diffraction investigations [11, 13].

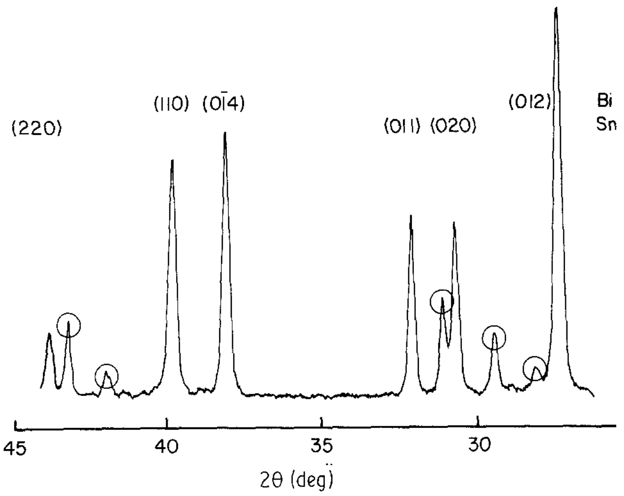

Figure 8 X-ray scan of a Bi–48.6 at % Sn emulsion sample. The circled peaks represent the peaks for the present metastable phase.

4. Conclusion

The droplet emulsion technique revealed that a metastable phase with a melting temperature of 116° C at 1 atm was observed in the Bi–48.6 at % Sn alloy system. The pressure–temperature behaviour of the same sample was monitored by DTA. The formation of the metastable phase was favoured under hydrostatic pressure. The amount of metastable phase in the sample increased at the expense of the equilibrium phase with increasing pressure level. Also, the melting temperature of the metastable phase increased by 12 K GPa^{-1} with pressure, while the liquidus and the eutectic of the low-pressure stable structure decreased by 37 and 8.4 K GPa^{-1}, respectively.

Microscopic examination of the undercooled droplets showed a non-equilibrium morphology which may be the result of prior metastable phase formation in the droplets. Furthermore, an X-ray diffraction study conducted at room temperature and pressure showed evidence that the metastable phase is not a bct structure, but may be isostructural with the high-pressure phase reported by X-ray diffraction [11] and neutron diffraction [13] examinations at high pressure and high temperature.

TABLE I Structural data on the high-pressure Bi–Sn phase*

Neutron diffraction (at 1.2 GPa, 100° C) [13]		X-ray diffraction (at 2 GPa, 23° C) [11]		X-ray diffraction (at 1 atm, 20° C) [present work]	
d_{hkl} (nm)	Intensity	d_{hkl} (nm)	Intensity	d_{hkl} (nm)	Intensity
0.403	2				
0.324	8	0.322	VW	0.318	28
0.290	20	0.277	S	0.304	60
0.279	100	0.268	VS	0.288	100
0.256	12	0.254	MW		
0.2288	34	0.225	M	0.215	25
0.2111	10	0.212	MW	0.209	75
0.1996	45	0.199	M	0.198	45
		0.191	MW		
0.1785	10	0.172	VW	0.172	15
0.1554	12	0.160	MS	0.153	20
0.1499	25	0.153	W	0.150	20
0.1485	9				
0.1448	10				
0.1412	10				
0.1370	2				

*Note that the above examinations were not conducted under identical conditions (different temperature and pressure). Also the specimen of each test was a small bulk ($V = 0.63\,\mathrm{cm}^3$), thin foil, and powder, respectively. Therefore, direct comparison between data sets in intensity values may not be valid.

According to the pressure, microscopic and X-ray results, the phase under study has a dual characteristic: (1) a metastable phase, which can form by the aid of the large amount of undercooling in RSP; and (2) a high-pressure phase, which can become stable at high pressure. Therefore, even though the metastable phase which is observed in the splat quenching [10] or in a "pressure quenched" sample [9] is not isostructural with the metastable phase obtained in the present investigation, the high-pressure phase of the Bi–Sn system can be formed as a metastable phase at ambient pressure by the droplet emulsion method.

As with the present case, the study of metallic systems under pressure reveals not only an understanding of the characteristics of high-pressure phases themselves, but also an interpretation of RSP product structures. Therefore, the combined effects of pressure plus undercooling on phase selection are useful in investigating the kinetic factors that promote formation of metastable product structures.

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