

THE INDIUM-ANTIMONY SYSTEM

BY T. S. LIU AND E. A. PERETTI

Abstract

The binary system indium-antimony has been investigated by thermal, X-ray, and metallographic methods of analysis. The existence of an intermediate phase corresponding closely to the composition InSb was confirmed. It melts at 525 °C and forms a eutectic with both indium and antimony. The In-InSb eutectic contains 0.7% antimony and melts at 154.8 °C, and the InSb-Sb eutectic occurs at 69.5% antimony and melts at 494 °C. The single-phase regions in the solid state are quite restricted.

A SURVEY of the literature reveals the existence of very few published reports of experimental work on indium-antimony alloys. Goldschmidt (1)¹ and Iandelli (2) prepared the intermediate phase InSb and concluded that the crystal structure is face-centered cubic, zinc blende type. Goldschmidt's value for the lattice parameter is 6.452Å. Iandelli's measurements resulted in an a_0 of 6.461Å. The latter, in preparing his alloys, used indium containing 2% germanium; the purity of the antimony is not stated.

It was the purpose of the present investigation to study thoroughly the entire phase diagram, using thermal analysis, X-ray diffraction, and microscopic examinations.

EXPERIMENTAL PROCEDURE

The indium used was obtained from the Indium Corporation of America and had a guaranteed purity of 99.97%, with the following chemical analysis: copper 0.002%, lead 0.006%, tin 0.01%, and zinc 0.01%. The antimony came from two sources: Johnson Mathey and Company of London and the J. T. Baker Chemical Company. The metal from the first source was spectrographically standardized and analyzed as follows: arsenic 0.031%, copper 0.001%, iron 0.015%, nickel 0.001%, sulphur 0.012%, lead 0.017%, bismuth 0.00005%, aluminum 0.005%, and silicon 0.006%. The label on Baker's antimony listed the following amounts of impurities: iron 0.007%, sulphur 0.03%, arsenic 0.005%, lead 0.02%, and copper 0.002%.

¹The figures appearing in parentheses pertain to the references appended to this paper.

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Forty-eight alloys were prepared; of these, twenty-three were made by accurately weighing the pure constituents on an analytical balance, and the remainder were produced by diluting with either antimony or indium. Melting was carried out with constant stirring in either Pyrex or Vycor tubes in an argon atmosphere and at a temperature above the melting point of the highest-melting ingredient. As melting losses were negligible, the intended composition could be safely used without chemical analysis. No one alloy was used more than two times to make subsequent alloys.

Cooling and heating curves were obtained with uncontrolled and controlled heating rates that ranged from $\frac{1}{2}$ to 4 °C per minute. For controlled rates the apparatus previously described (3) was employed. For the high-indium alloys Pyrex or Vycor crucibles could be used for cooling curve experiments, but at higher antimony contents the alloys would expand so much upon freezing that the crucibles cracked. Therefore, for these alloys there was used a crucible machined from graphite rod, which was provided with a lid through which was inserted a thermocouple, stirring rod and argon inlet tube. Seventy-five grams of metal were used for each determination. Temperatures were measured with calibrated iron-constantan and chromel-alumel thermocouples.

For microscopic examination of the alloys the technique described by Carapella and Peretti (4) was used with slight modification. Flat surfaces were prepared from specimens containing less than 20% antimony by cutting with a razor blade, but when the antimony content exceeded 20%, sections were prepared by slicing with an abrasive wheel. Vilella's reagent was used as the etchant over the entire compositional range.

To check the results of thermal and microscopic studies, X-ray diffraction patterns were taken of many of the alloys, using characteristic cobalt K-alpha radiation at 30 KVP and 10 ma at exposure times of $1\frac{1}{2}$ to 3 hours. Debye and symmetrical back-reflection focusing cameras were used.

RESULTS

In Table I are listed the arrest points obtained by thermal analysis. Since supercooling occurred with most of the alloys, particularly with those containing the higher percentages of antimony, it is believed that the liquidus temperatures are probably not more accurate than ± 2 °C. Due to the consistency of the temperature values obtained for the eutectic reactions, these results are probably accurate to ± 0.5 °C.

The phase diagram of the system indium-antimony is shown in Fig. 1, and Figs. 2 to 14 are photomicrographs of alloys ranging in composition from that of high-purity indium to high-purity antimony.

Table I
Thermal Data of the System Indium-Antimony

Weight % Sb	Atomic % Sb	Liquidus, °C	Solidus, °C
0	0	156.4	156.4
5.00	4.73	282.7	155.0
10.00	9.48	329.1	155.0
20.00	19.07	420.0	154.8
25.00	23.91	451.8	154.8
30.00	28.77	479.4	154.6
35.00	33.67	496.7	154.8
40.00	38.59	511.8	154.3
45.71	44.24	522.5	153.6
51.48	50.00	525.0	525.0
55.09	53.62	524.0	492.6
60.01	58.58	517.5	493.6
65.00	63.64	510.0	493.6
70.00	68.74	495.2	494.1
72.50	71.30	507.3	494.2
75.00	73.87	527.4	494.3
80.00	79.04	547.2	494.1
82.52	81.65	560.2	493.6
85.00	84.23	572.0	492.1
87.50	86.84	582.8	492.2
90.00	89.45	592.7	492.8
92.00	91.55	599.6	491.9
94.00	93.66	609.8	492.3
96.00	95.77	615.9	492.3
98.00	97.88	624.1	492.5
99.00	98.94	625.4	...
100.00	100.00	630.5	630.5

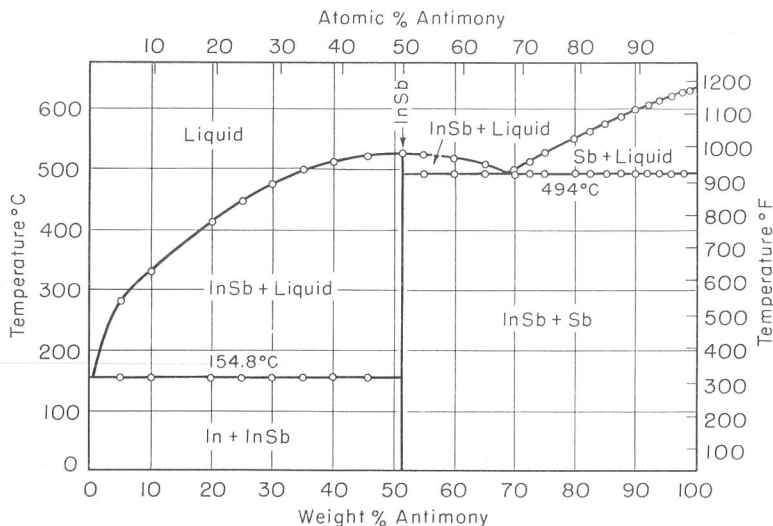


Fig. 1—The Indium-Antimony Phase Diagram.

An intermediate phase, InSb, melts congruently at 525 °C and is shown in Fig. 9. As alloys within 0.5% on either side of this composition exhibited a two-phase structure, and X-ray photographs showed no discernible change in lattice spacing, it was concluded that this one-phase region must be very small. Precision

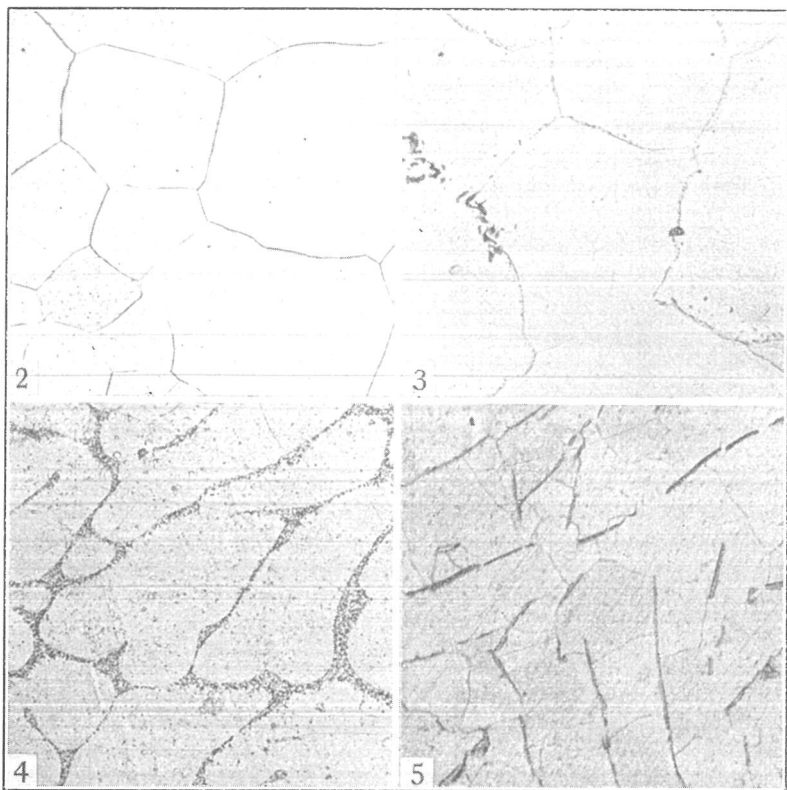


Fig. 2—High-Purity Indium, As-Cast. $\times 115$.

Fig. 3—0.05% Antimony, 99.95% Indium, As-Cast. Primary indium plus eutectic. $\times 300$.

Fig. 4—0.4% Antimony, 99.6% Indium, As-Cast. Primary indium plus eutectic. $\times 300$.

Fig. 5—0.7% Antimony, 99.3% Indium, As-Cast. Eutectic composition. $\times 300$.

lattice constant determinations of this phase gave a value of 6.4760\AA at 25°C .

The InSb phase forms a eutectic with indium at 0.7% antimony (Fig. 5), which melts at 154.8°C . The composition of this eutectic was determined wholly by metallographic examination of specimens whose antimony content varied from 0.05 to 5%. When the specimen contained primary InSb, it could be clearly differentiated from the eutectic, as can be seen in Figs. 6, 7, and 8. However, due to supercooling and eutectic divorcement, it was difficult to determine when primary indium existed in the alloys if the composition was close to that of the eutectic (see Figs. 3 and 4). Therefore, the eutectic point was obtained by preparing alloys containing a diminishing percentage of antimony and noting the point of disappearance of the primary InSb phase.

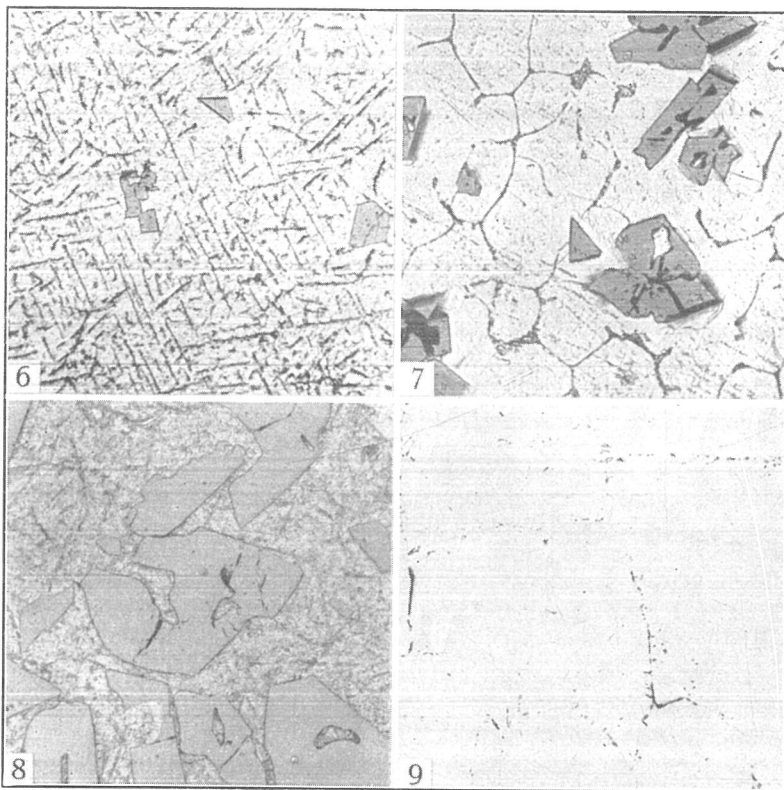


Fig. 6—2% Antimony, 98% Indium, As-Cast. Primary InSb plus eutectic. $\times 300$.
 Fig. 7—5% Antimony, 95% Indium, As-Cast. Primary InSb plus eutectic. $\times 400$.
 Fig. 8—30% Antimony, 70% Indium, As-Cast. Primary InSb plus eutectic. $\times 300$.
 Fig. 9—51.48% Antimony, 48.52% Indium, Annealed 10 Days at 150°C. Almost wholly InSb. $\times 50$.

The liquidus for indium alloys bearing less than 0.7% antimony could not be determined, due either to an insufficient heat evolution or to supercooling to the eutectic temperature. As can be seen from Fig. 3, the solid solubility of antimony in indium must be less than 0.05%. X-ray photograms showed no measurable difference in the lattice spacings of pure indium and indium in two-phase alloys.

The InSb also forms a eutectic with antimony. It contains 69.5% antimony and has a melting point of 494°C. Figs. 9 to 14 depict typical microstructures encountered in this portion of the binary system. The composition of this second eutectic could be bracketed more closely than the one occurring at the high-indium end of the diagram because the primary phases on either side of the eutectic can be easily differentiated from each other and from the eutectic, as can be clearly seen in Figs. 10, 11, 12 and 13.

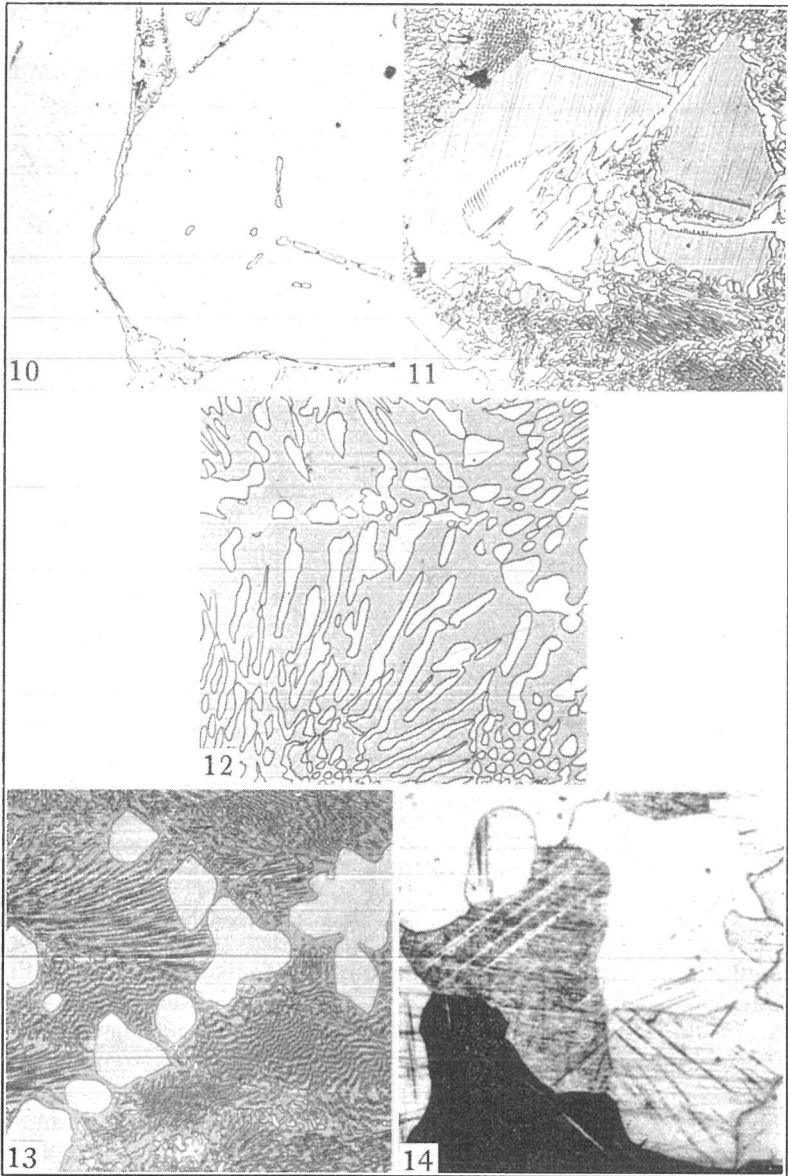


Fig. 10—52% Antimony, 48% Indium, Furnace-Cooled. Primary InSb plus eutectic of InSb-Sb. $\times 100$.

Fig. 11—60% Antimony, 40% Indium, As-Cast. Primary InSb plus eutectic. $\times 400$.

Fig. 12—69.5% Antimony, 30.5% Indium, As-Cast. Eutectic of InSb and Sb. $\times 400$.

Fig. 13—72.5% Antimony, 27.5% Indium, As-Cast, Unetched. Primary antimony plus eutectic. $\times 400$.

Fig. 14—High-Purity Antimony, As-Cast. $\times 75$.

The solid solubility of indium in antimony was concluded to be small for the same reasons advanced for the low solubility of antimony in indium.

The addition of antimony to indium increases the hardness of "as-cast" specimens from 1 Brinell to a maximum of about 165 Brinell for the InSb phase. With further antimony additions the hardness decreases to that of antimony, about 47 Brinell.

Alloys in the InSb-Sb portion of the system are very brittle. Those containing InSb and In are somewhat stronger, but most of these crack after a reduction in area of only a few per cent.

SUMMARY

1. The phase diagram of the system indium-antimony has been determined by means of thermal analysis and X-ray and metallographic techniques.

2. Two eutectic reactions occur: one at 154.8 ± 0.2 °C, containing 0.7% antimony, and the second one at 494 ± 0.5 °C with 69.5% antimony.

3. An intermediate phase exists, corresponding closely to the composition InSb. This phase melts congruently at 525 ± 0.5 °C. It has a face-centered cubic, zinc blende-type, structure with a lattice parameter of 6.4760\AA at 25 °C.

4. The single-phase regions in the solid state were found to be quite small.

ACKNOWLEDGMENT

The authors wish to express their indebtedness to the Indium Corporation of America for the generous loan of indium used in the investigation.

References

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2. Aldo Iandelli, "Sulla Struttura Dei Composti InP, InAs e InSb", *Gazzetta Chimica Italiana*, Vol. 71, No. 1, 1941, p. 58.
3. E. A. Peretti and S. C. Carapella, Jr., "The Indium-Bismuth Phase Diagram", *TRANSACTIONS*, American Society for Metals, Vol. 41, 1949, p. 947.
4. S. C. Carapella, Jr., and E. A. Peretti, "Metallography of Indium and Indium-Rich Alloys", *METAL PROGRESS*, Vol. 56, No. 5, November 1949, p. 666.

DISCUSSION

Written Discussion: By Max F. W. Heberlein, director of research, United States Metals Refining Co., Carteret, N. J.

The authors should be congratulated for their fine work in developing the phase diagram of the system indium-antimony. This is only one part

in a larger program which apparently Professor Peretti and associates are following to investigate the alloying characteristics of indium.

Up until a little more than a decade ago this metal was known only as one of many in the Periodic Chart, but otherwise it did not attract any interest. Consequently, very little effort had been spent prior to World War II to investigate and utilize the physical metallurgical properties of indium. The published information was unreliable, incomplete and contradictory and it is for this reason that the present paper describing the thorough methods to determine the phase diagram of the system indium-antimony must be considered a very valuable contribution to the physical metallurgical literature.

The diagram shown in Fig. 1 indicates that indium apparently forms, very readily, intermetallic compounds with the alloying metal in preference to the formation of eutectic alloys. This confirms observations which the writer made a number of years ago.

When reducing In_2O_3 with metallic sodium by fusion electrolysis as described in U. S. Patent No. 2,521,217, temperatures which were considerably higher than the melting point of indium were required to keep the reduced metal in the molten condition. A preliminary investigation indicated the formation of peritectic alloys with small additions of sodium to indium.

A more thorough metallographic investigation of indium-sodium alloys with sodium contents of up to 10% proved the absence of any eutectic, but rather the formation of intermetallic compounds of indium with sodium.

Because sodium oxidizes very readily at elevated temperatures, it was necessary to alloy the sodium with the indium in a neutral atmosphere of dried nitrogen. The time-temperature curves for the various indium-sodium alloys were determined under this neutral atmosphere, while allowing the respective alloys to cool from approximately 900 °F to room temperature. The observed breaks in the cooling curves were noted and are shown in the following tabulation:

Sample No.	% Na	Liquidus, °F	Solidus, °F	Remarks
1	0.76	325	...	
2	1.57	324	...	
3	2.08	329	320	
4	2.25	345	320	
5	3.90	624	320	
6	5.07	695	320	
7	6.38	675	320	In_3Na — 6.27% Na
8	7.71	635	320	
9	8.86	791	324	In_2Na — 9.10% Na
10	15.15	791	...	
11	17.13	787	...	InNa —16.70% Na

These results were used to plot the accompanying diagram.

They show that the first addition of sodium raised the melting point from 311 °F for pure indium to 325 °F. While raising the sodium content to 1.57% did not change this new melting point, a sodium content of 2.08% in the alloy showed a slight increase of the liquidus temperature to 329 °F and a distinct solidus temperature of 320 °F.

The curve indicates a high point in the liquidus curve with a sodium content between those of Samples 6 and 7, which corresponds to the intermetallic compound In_3Na with a theoretical sodium content of 6.27%.

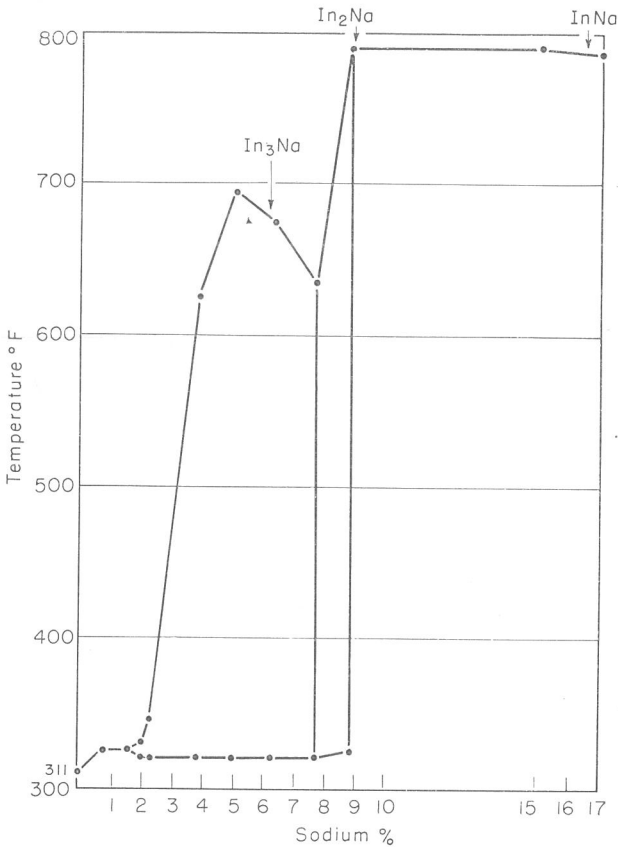


Fig. 15—Indium-Sodium System.

Sample 9 indicates a second maximum temperature at 791 °F, corresponding to the intermetallic compound In_2Na with a theoretical sodium content of 9.10%.

A eutectic reaction point for the two phases of In_3Na and In_2Na has been considered to be at or near the 7.7% sodium content of the alloy. This point is represented by Sample 8, which not only showed a low point in the liquidus curve but also a break in the straight-line solidus temperatures.

No indications of solidus temperatures were found in Samples 10 and 11, which were composed to show the properties of the intermetallic compound InNa .

All investigated alloys were liquid at temperatures above 800 °F.

It is necessary to point out that this investigation was conducted for the sole purpose of explaining the reason for the high temperatures required in the reduction of In_2O_3 by metallic sodium with the aid of NaOH-fusion electrolysis.

These results are presented with the object of throwing additional light on the peculiar alloying properties of indium. They should not be considered to be authentic, because the performed investigation was not sufficiently thorough for any such claim.

On the other hand, the curve in Fig. 15 shows sharp changes at or near the sodium contents of intermetallic compounds. For this reason it is felt that the presented curve may be considered as being reasonably accurate.

This discussion is presented as an encouragement for continued investigation of the metallurgical properties of indium alloys.

Written Discussion: By S. C. Carapella, Jr., research metallurgist, American Smelting and Refining Co., Barber, N. J.

The excellent work of the authors in evaluating the system indium-antimony is gratifying to us, since it was found to be in complete correlation with the unpublished phase diagram developed several years ago at the Central Research Laboratories of the American Smelting and Refining Company by the late Dr. Fraenkel.

During the investigation of this system, it was experienced that alloys prepared in the vicinity of the compound composition InSb would upon solidification exude the low melting constituent present and form beads on the top surface of the alloy. The exudation was found to be most pronounced in alloys containing an excess of indium. The appearance of these beads was attributed to the restricted expansion of the primary InSb in the crucible forcing the low melting constituent to the top surface of the alloy. The authors report no observation concerning the expansion of the compound InSb on solidification other than the statement "but at higher antimony contents the alloys would expand so much on freezing that the crucibles cracked".

Authors' Reply

We wish to thank Mr. Heberlein and Dr. Carapella for their kind comments.

The exudation described by Dr. Carapella was also noticed by us. In the parlance of the copper smelter, the alloys would "throw a worm" when the last bit of liquid to freeze was forced out of the center portion of the solidifying ingot. This commonly happens when freezing is accompanied by an increase in volume. This phenomenon was observed in this system to occur with alloys containing more than .30% antimony.