Modification in tin–antimony alloys

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Sn–10.4% Sb alloys containing 0 or 1% of only one of silver, copper or zinc were cooled from the liquid state rapidly and slowly. Then the alloys were examined by metallographic and electron (transmission and scanning) microscopy. Microhardness measurements were also carried out. The results obtained show that rapid cooling, compared with the slow cooling, greatly affects the structure and properties of Sn–Sb alloys. It leads to a much finer-grained structure and, therefore, gives rather better mechanical strength. It also leads to the formation of new phases, not found under equilibrium conditions, including a quasi-amorphous phase in the case of addition of silver.

1. Introduction

Tin–antimony alloys are widely used in type metals, in which the antimony content is usually kept below 20% to avoid brittleness. Tin–antimony alloys may be alloyed, to a certain degree, by other elements such as lead, silver, zinc, copper and alkalis, for certain industrial applications. All of these alloys have high specific gravity and low melting point (seldom over 450° C). The following applications of these alloys can be noted: automobile bearings, lead cable sheathing for telephone wires, plumber's solders, and for special anticorrosion purposes.

Tin–antimony alloys have been studied by many investigators [1–9], who are all in full agreement that the intermetallic compound SnSb is a very stable one. The density of this compound is less than that of the matrix (solid solution based on β-tin) from which it separates; therefore, the compound tends to float. Its rapid growth means that the latent heat of solidification is given up very quickly; this may increase the temperature of the melt above the β-tin phase solidification.

A recent investigation carried out by Kamal *et al.* [10], using ultra-pure materials and very sophisticated equipment, states that the composition of the intermetallic phase does not depend on the presence of certain elements (lead, zinc, copper and silver) in microadditions; this composition (SnSb) is also independent of cooling rate in their view. In special cases certain microadditions may lead to the formation of non-equilibrium phases, depending on the actual solidification conditions [11].

The aim of this work is to study the effects of the solidification rate and the microadditions (of silver, copper and zinc) on the mechanical properties and micromorphology of the Sn–10.4% Sb alloy.

2. Experimental procedure

Twelve alloys were prepared from tin-base alloys containing 10.4% antimony and 0 to 1% of only one of silver, copper or zinc from metal containing not more than 5 ppm impurities by vacuum melting in a graphite crucible. Melting was repeated several times at a temperature of 1073 K. The duration of each melting was 1 h. Rapid cooling was achieved by the technique reported by Kamal and Pieri [11]. Specimens were also frozen by

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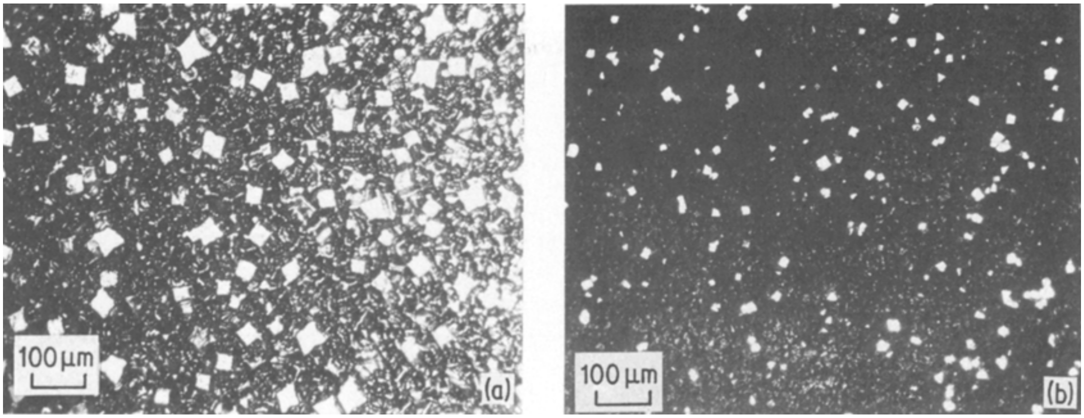

Figure 1 Optical micrographs of Sn–10 wt % Sb, illustrating the variation of SnSb size after (a) slow cooling and (b) fast quenching. Slow cooling was carried out from the liquid state at a rate of $1\,K\,min^{-1}$. Fast quenching was achieved by dropping the melt into a copper substrate at 273 K.

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3. Results and discussions

3.1. Metallographic study

The micrographs of optical microscopy (Figs. 1 to 4) show the difference in SnSb size of alloys after slow cooling and fast quenching. The microstructure of unmodified alloys (Fig. 1) indicates the intermediate phase as white areas, whereas the matrix (a tin-base solid solution) appears as black background.

The addition of 1% silver to this alloy leads to grain-refining (Fig. 2); more grain-refining is achieved by rapid cooling with some accumulation of SnSb compound in cuboidal and star forms.

When 1% copper was added to the alloy the microstructure after slow cooling (Fig. 3) shows the compound to be coarse cuboidal and needle shaped; fast quenching leads to a very strong grain-refining of the compound particles, which have the cuboidal shape only, but with very small dimensions.

The addition of 1% zinc to the alloy did not affect the compound's grain-size after slow cooling (Fig. 4), but the presence of some grey areas (one area is shown by an arrow) indicates the formation of a new ternary phase SnSbZn reported previously by Kamal *et al.* [10], who used electron-microprobe analysis in their study; fast quenching, in this case, also leads to a remarkable grain refining.

A quantitative metallographic study was carried out to determine the average dimensions of the SnSb phase and the average distribution density (Table I).

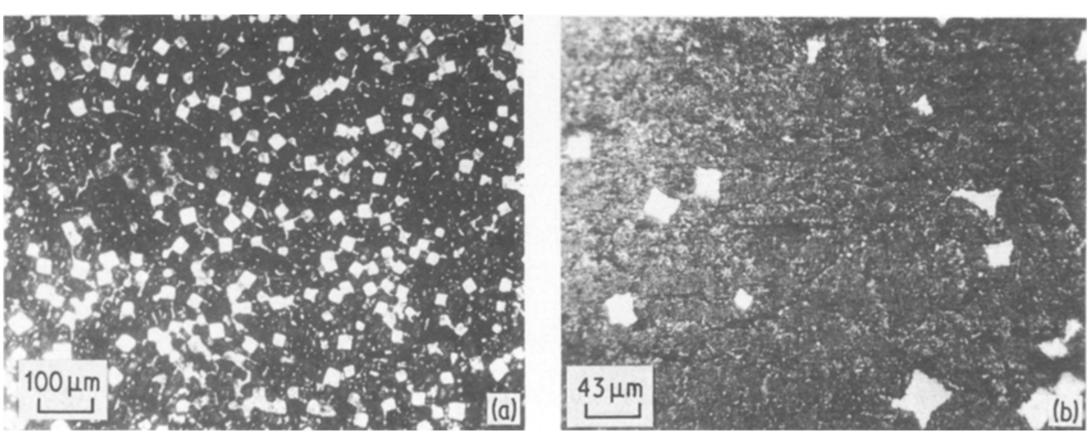


Figure 2 As Fig. 1, for Sn–10.4 wt % Sb–1 wt % Ag.

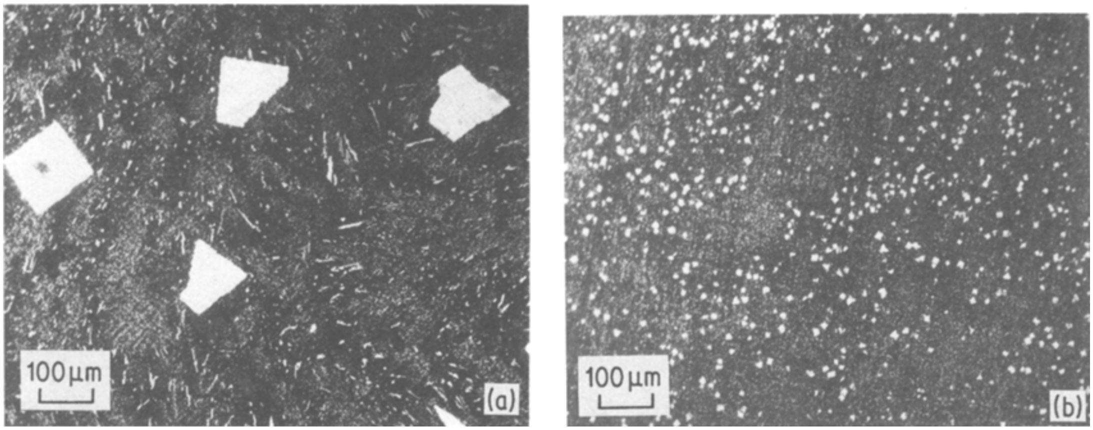


Figure 3 As Fig. 1, for Sn–10.4 wt % Sb–1 wt % Cu.

3.2. Transmission electron microscopy of the rapidly cooled specimens

These specimens, prepared by the technique reported by Kamal and Pieri [11], have thin edges which allow direct examination by the transmission electron microscope without previous polishing. A Jeol (80 kV) electron microscope was used to examine the specimens. Each micrograph obtained is associated with a diffraction pattern which allows identification of the crystal structure according to Jouffrey [12].

The specimen containing 1% silver (Fig. 5) is in the first precipitation stage of the intermetallic compound. Two crystal structures are revealed: a solid solution on the base of the tin and the SnSb intermetallic compound (Table II). Diffraction shows that the applied cooling is sufficient to obtain a quasi-amorphous state. (Previously noted by Kamal and Pieri [11].)

In the alloy containing 1% copper, the intermetallic compound can nucleate in spite of the rapid cooling. Fig. 6 also shows the first precipitation stage corresponding to the formation of a compound coherent with the matrix (Table III). It is remarked that the precipitation takes place inside each grain.

In the case of the addition of 1% zinc (Fig. 7) the intermetallic compound was revealed as in the previous case (Table IV).

The results obtained from the analysis of diffraction patterns clearly indicate that rapidly quenched Sn–10.4% Sb (with or without micro-additions) contain the SnSb compound. This disagrees with the results of Salli and Zamoilenko [8].

3.3. Scanning electron microscopy

This study was carried out using a Jeol JSM-U3 microscope. Qualitative analysis of the antimony

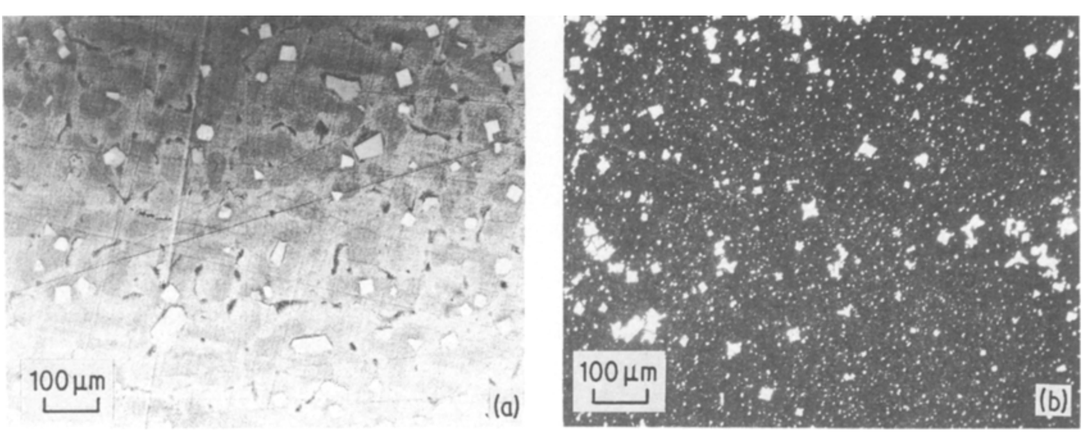


Figure 4 As Fig. 1, for Sn–10.4 wt % Sb–1 wt % Zn.

TABLE I Average dimensions and densities of the SnSb phase in the specimens

Alloy	Average dimensions (μm)		Average density $(10\,\mu m)^{-2}$	
	Slow cooling	Rapid cooling	Slow cooling	Rapid cooling
(a) Sn–10.4% Sb	30	10	1	4
(b) Sn–10.4% Sb–1% Ag	30	8	5	1
(c) Sn–10.4% Sb–1% Cu	50	10	1	10
(d) Sn–10.4% Sb–1% Zn	20	10	2	15

TABLE II

d (nm)	hkl	Type of crystals
0.3478	2 1 1	SnSb
0.1415	6 1 0	SnSb
0.1193	2 4 1 / 6 4 1	β-Sn or SnSb
0.0795	3 4 3	β-Sn

TABLE III

d (nm)	hkl	Crystal type
0.417 4	2 0 0	SnSb
0.238 5	3 2 0	SnSb
0.208 7	4 1 0	SnSb
0.139 1	3 3 0	β-Sn
0.128 4	6 3 1	SnSb
0.111 31	3 2 2	β-Sn
0.105 67	5 4 5	SnSb
0.104 35	4 1 0	β-Sn
0.098 2	6 0 0	β-Sn
0.090 3	3 1 3	β-Sn
0.081 44	4 2 3	β-Sn
0.075 9	2 0 4	β-Sn
0.074 04	5 3 0	SnSb
0.057 57	2 3 2	β-Sn

TABLE IV

d (nm)	hkl	Crystal type
0.2783	3 1 0	SnSb
0.2385	3 2 0	SnSb
0.1621	5 2 0	β-Sn
0.144	4 4 2	SnSb
0.139	3 3 0	β-Sn
0.134	2 2 2	β-Sn
0.093	6 2 0	β-Sn
0.088	5 6 2	β-Sn
0.076	2 0 4	β-Sn

content (and the content of other elements such as silver, copper and zinc) was carried out. The results of this study are shown in Figs. 8 to 10. These figures show the direct structure as well as the antimony content as found by Sb$L\alpha$ radiation. It is obvious that that the good adhesion and coherency with the matrix of the compound are responsible for the strength of this type of alloy.

It must be noted that the sensitivity of this method to determine the copper and zinc content is not good, but it is possible to determine the silver content by Ag$L\alpha$ radiation (Fig. 8c), in spite of the variation in silver concentration from one point to another.

3.4. Mechanical properties

Microhardness measurements were carried out using a "Shimadzu" hardness tester. The yield strength was determined using a non-standard tensile test.

The mechanical properties of the alloys investigated are given in Table V.

These results indicate that the microadditions to Sn–10.4% Sb alloy increase its mechanical strength after slow solidification. In the case of zinc addition, a slight decrease in microhardness is noted, due to the appearance of the ternary SnSbZn phase which weakens the matrix (β-Sn solid solution).

Rapid solidification remarkably increases both hardness and strength of all alloys. In this case the addition of 1% silver leads to the maximum mechanical strength. This is attributed to the formation of a quasi-amorphous metallic phase.

TABLE V Microhardness H_V and yield strength $(\text{kg mm}^{-2})\,\sigma_y$

Alloy	Slow cooling			Rapid cooling		
	H_V	σ_y	H_V/σ_y	H_V	σ_y	H_V/σ_y
(a) Sn–10.4% Sb	36	8.33	4.32	64.8	13.44	4.82
(b) Sn–10.4% Sb–1% Ag	39.2	12.26	3.19	83.6	20.64	4.05
(c) Sn–10.4% Sb–1% Cu	45.3	14.93	3.04	75.8	18.93	4
(d) Sn–10.4% Sb–1% Zn	33.9	10.5	3.23	75.2	13.87	5.42

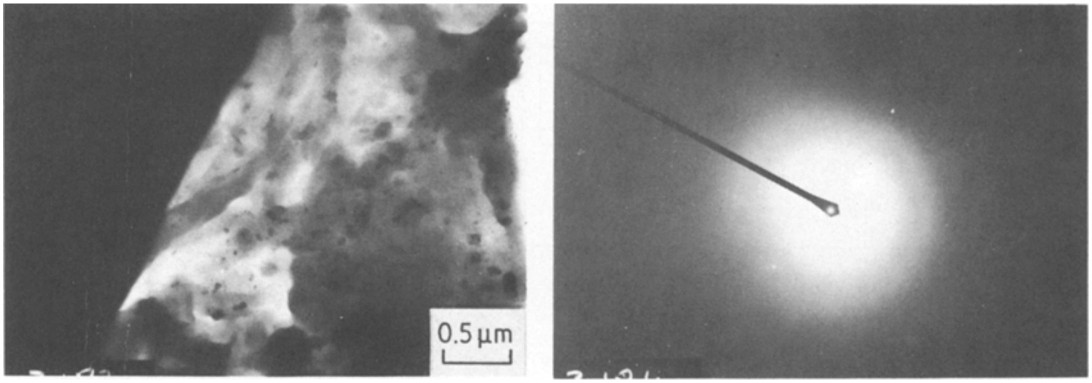


Figure 5 Electron micrograph and corresponding diffraction pattern taken from splat-cooled Sn–10.4 wt% Sb–1 wt% Ag showing a quasi-amorphous structure and precipitation within grains.

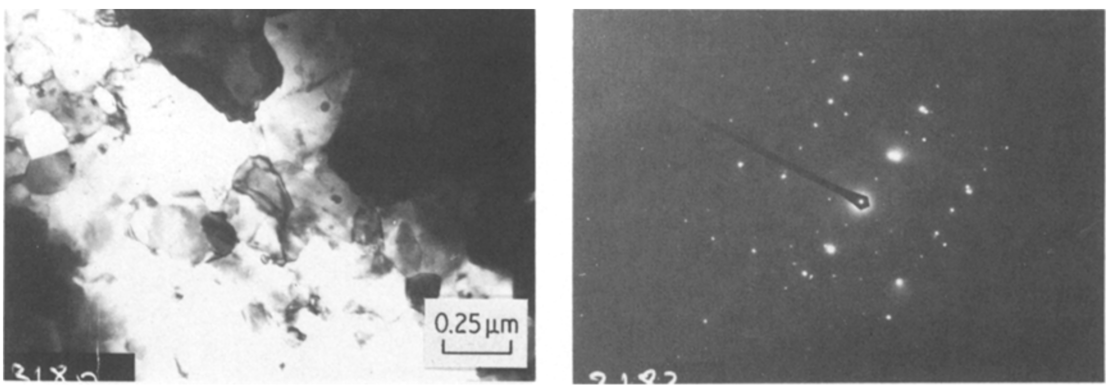


Figure 6 As Fig. 5, for Sn–10.4 wt% Sb–1 wt% Cu.

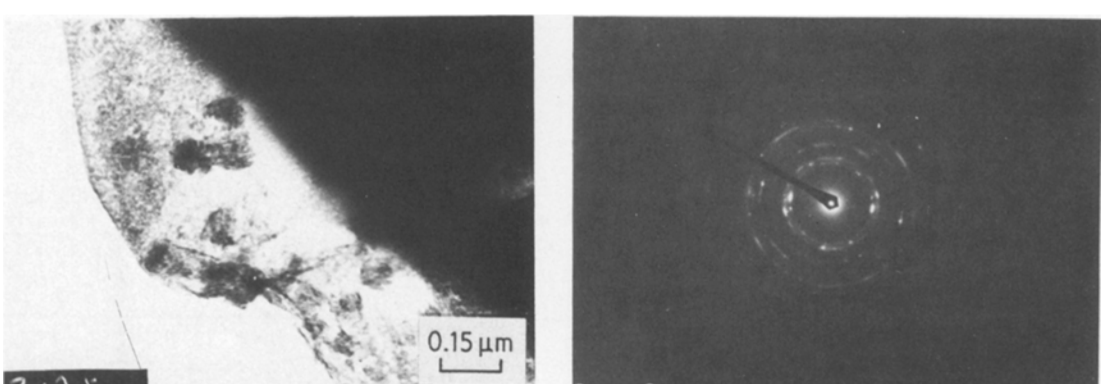
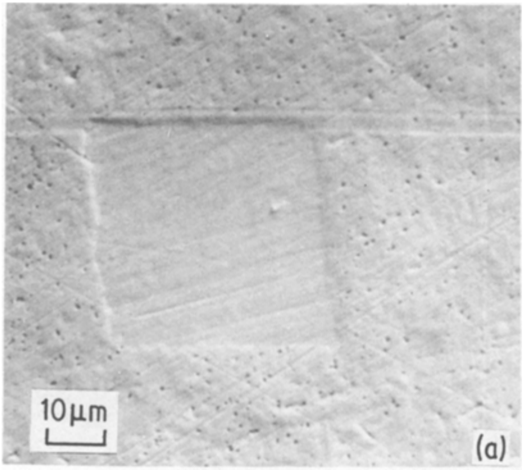


Figure 7 As Fig. 5, for Sn–10.4 wt% Sb–1 wt% Zn.



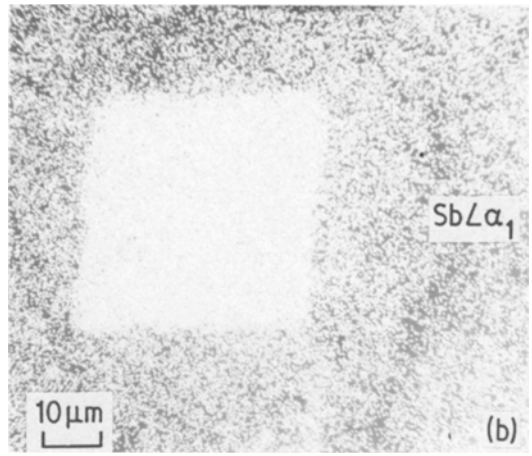
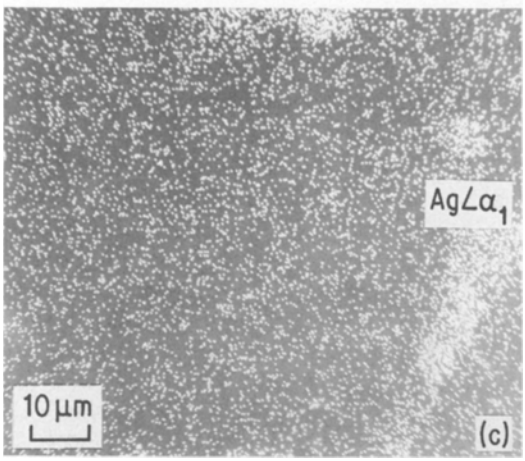


Figure 8 Scanning electron micrographs of Sn–10.4 wt % Sb–1 wt % Ag after slow cooling, illustrating analysis of the antimony content and other elements such as silver, copper and zinc.



4. Conclusions

1. The microadditions of silver, copper or zinc to the Sn–10.4% Sb, and fast quenching from the liquid state, cause a marked change in the growth morphology of SnSb cuboidal particles. This is associated with an increase in the mechanical properties due to the adsorption of the micro-addition into the heterogeneous nucleation centres of the SnSb compound; the additions affect its shape, dimensions and distribution density.

2. It is probable that when particles of the SnSb compound reach a certain size, further growth of the β-tin is inhibited because of its inability to deform SnSb to create more growth space for itself.

3. Rapid quenching from the melt leads to the formation of a metastable intermediate phase, particularly on addition of 1% silver to Sn–10.4% Sb alloy which favours the formation of a quasi-amorphous phase.

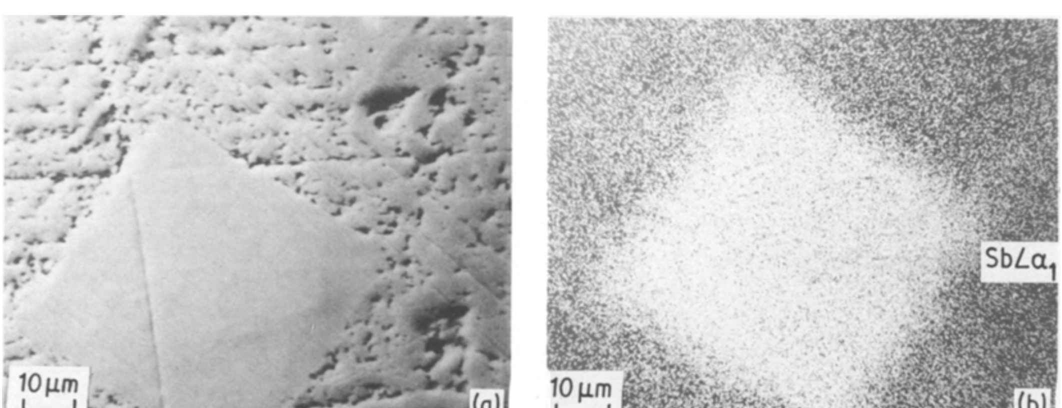


Figure 9 As Fig. 8, for Sn–10.4 wt % Sb–1 wt % Cu.

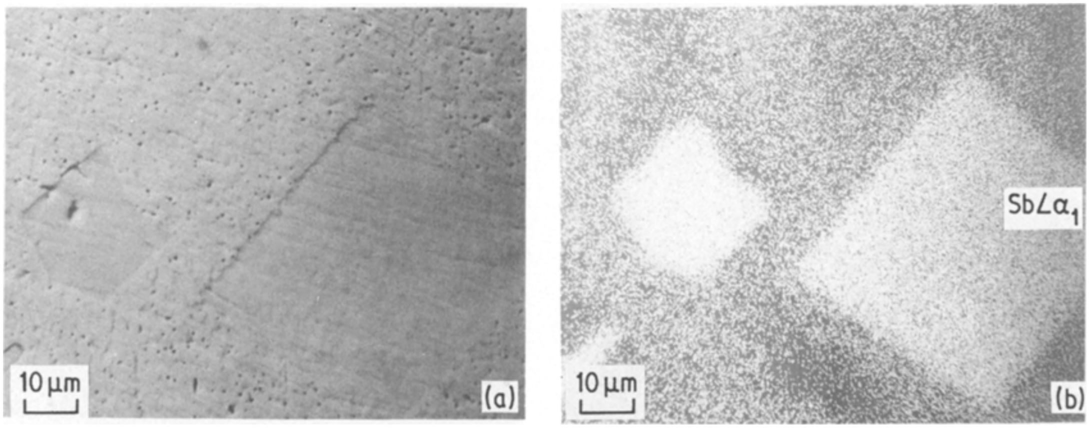


Figure 10 As Fig. 8, for Sn–10.4 wt% Sb–1 wt% Zn.

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