An X-ray study of splat-quenched Sn-Bi and Cu-Sb alloys by energy-dispersive diffraction

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A metastable shift of the solubility limit was produced by splat-quenching in Sn—Bi alloys containing 15, 20 and 25 at. % bismuth. Decomposition of the supersaturated α phase was investigated in the temperature range —40 to 0° C. An activation energy of $39.8 \pm 3.0 \, \text{kJ mol}^{-1}$ was obtained for the decomposition of Sn—25 at. % Bi. Splat-quenched Cu—Sb alloys with different compositions were also studied. The decomposition of the retained β high-temperature phase was followed at 200 and 330° C. Neither an increase of solubility of copper into antimony nor new phases at the eutectic composition were observed in quenched foils.

1. Introduction

The tin—bismuth equilibrium diagram features a simple eutectic at 43.0 at. % Bi and 139° C (Fig. 1). The maximum solubility of Bi in Sn is 13.1 at. % at the eutectic temperature. Kane *et al.* [2] have reported extensions of primary solid solubility of Bi in Sn. On rapid quenching from the melt below —100° C, solubility could be raised from 13.1 at. % Bi at the eutectic temperature to 50 at. % Bi, beyond the eutectic concentration.

The copper—antimony equilibrium phase diagram (Fig. 2) shows that this system has six intermediate phases which are stable at higher temperatures. The β phase has a f c c superstructure with the b c c substructure [4]. The phases η, ϵ, ϵ' and $\mathscr{H}$ belong to the same structure type A3. Earlier,

Giessen *et al.* [5] splat-quenched Cu—63 at. % Sb alloys and no new phases were found.

In the present study, splat-quenched foils of these two systems with various compositions have been investigated. The main purpose was to investigate the transformation processes of metastable solid solutions into equilibrium phases. The energy dispersive X-ray diffraction method was suitable for observing the structural changes during isothermal annealing treatments.
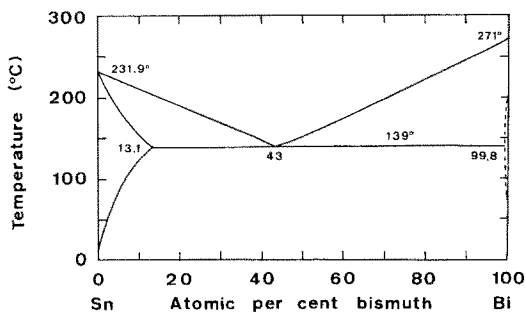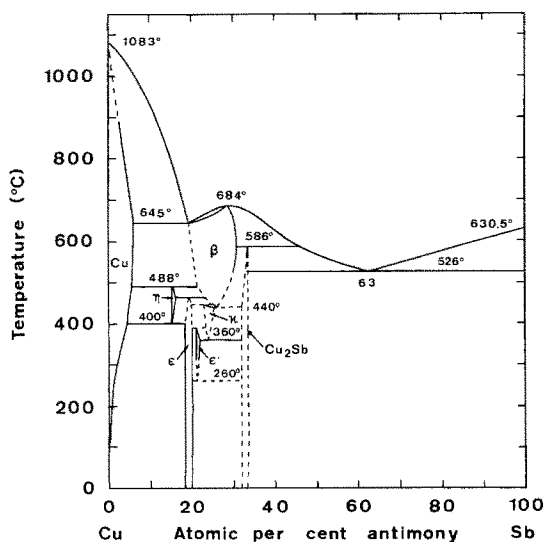

Figure 1 The Sn—Bi equilibrium diagram [1].

Figure 2 The Cu—Sb equilibrium diagram [1, 3].

2. Experimental

Alloys were made in 2 to 3 g quantities using tin and bismuth of purity better than 99.999% and copper and antimony of purity better than 99.99%. Components were weighed to an accuracy of ± 1 mg, and melted in a graphite crucible under an atmosphere of pure argon. Weight losses amounted to less than 0.02% in all cases. The samples were sealed in silica under vacuum and homogenized. 200 mg specimens of the alloys were splat-quenched by a piston-and-anvil technique, similar to that described in detail elsewhere [6]. For quenching Sn—Bi alloys, the anvil and the piston were cooled to about −100° C to prevent premature precipitation. In splat-quenched Cu—Sb alloys, precipitation was not observed at room temperature, so that it was not necessary to cool the piston and the anvil.

The X-ray diffraction measurements were carried out using the energy-dispersive diffraction method [7—9]. Isothermal heat treatments of the splat-quenched foils were carried out using a modified Anton Paar low- and high-temperature attachments for the diffractometer.

3. Results and discussion
3.1. Sn—Bi

Three alloys of tin containing 15.0, 20.0 and 25.0 at.% bismuth were investigated. Bismuth dissolved completely in the tin in all three alloys during splat-quenching, when both piston and anvil were cooled to cryogenic temperatures. Precipitation was found to occur to a detectable extent when the temperature was increased to −40° C. Above

0° C, the transformation rates became so high that the low-temperature attachment could not reach the desired temperature before changes began to occur in the foil. During measurement, the temperature of the foil was kept constant within ± 1.0° C.

In tentative measurements it was found that the reflection of pure bismuth was most valid for determining the transformation rates. These were determined by measuring the ratio of the intensity of the (1 1 0) reflection of Bi during ageing to its intensity in the stable specimen. Transformation curves for the alloys containing 15.0, 20.0 and 25.0 at.% Bi are shown in Fig. 3. The time required to measure the intensity was 20 sec and measurements were made every 30 sec during the isothermal annealing experiments.

The rate of a thermally activated rate process v is usually expressed by the equation
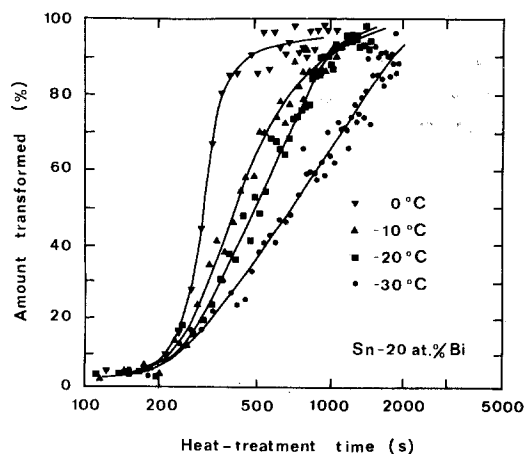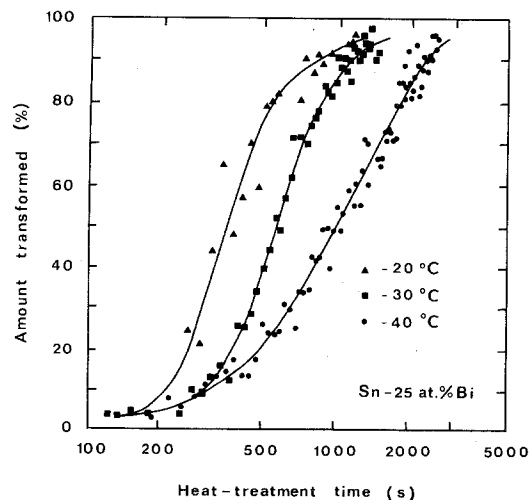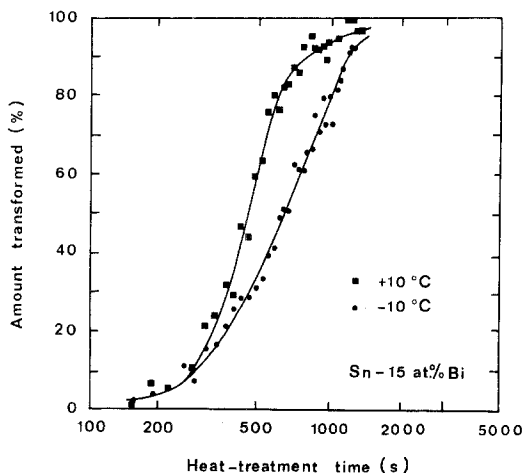
$$v = v_0 \exp(-Q/RT), \qquad (1)$$

Figure 3 Transformation curves for three Sn—Bi alloys as determined by X-ray energy dispersive diffraction.

where Q is the activation energy for the process, R is the gas constant, T is the absolute temperature and v_0 is a proportionality factor, usually called the frequency factor. If v_0 in Equation 1 can be considered as constant, and the rate v is measured at two different temperatures, the activation energy for the transformation can be calculated from the equation

$$Q = R \ln \frac{v_2}{v_1} \bigg/ \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \qquad (2)$$

or, because v is proportional to $1/t$,

$$Q = R \ln \frac{t_1}{t_2} \bigg/ \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (3)$$

At the point of inflection, the transformation rate is at its maximum (cf. Fig. 3). If t is taken as the time elapsed at the point of inflection (corresponding to a particular stage of a transformation), the activation energy can be calculated from Equation 3 [10]. With this method the activation energy for the transformation in the Sn—25.0 at.% Bi was calculated to be $39.8 \pm 3.0 \, \text{kJ mol}^{-1}$.

3.2. Cu—Sb

The preliminary investigations with angle-dispersive as well as energy-dispersive powder diffractometry showed that the X-ray reflections from the phases $\mathscr{X}$, ϵ and ϵ' overlap. For this reason phases $\mathscr{X}$ and ϵ cannot be detected separately, although they are the most important decomposition products of the β phase.

The precipitation studies were carried out with splat-quenched foils of the alloy Cu—21.6 at.% Sb. The measuring temperatures were 280 and 330° C. According to the equilibrium diagram, the precipitation reaction of the β phase produces first the η phase, then $\epsilon + \mathscr{X}$, and then the ϵ' phase. According to Günzel and Schubert [11] the eutectoid reaction

$$\mathscr{X} \rightarrow \epsilon' + \text{Cu}_2\text{Sb}$$
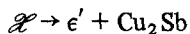
proceeds so slowly at 300° C, that during our precipitation measurements the ϵ' phase did not develop noticeably.

Some high-intensity X-ray reflection from the β phase would be most suitable for following the decomposition of the β phase. Such reflections however interfere with reflections from other phases. This fact led us to follow a strong 21.5 keV reflection at the detector position $2\theta = 21.0°$. This energy corresponds to the (2 1 2) and
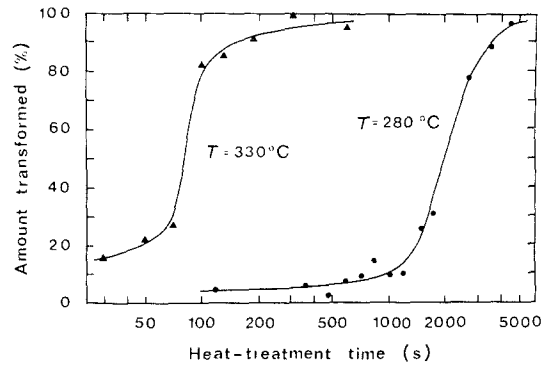
Figure 4 Decomposition of β phase of the alloy Cu—21.6 at.% Sb at temperatures 280 and 330° C.

(0 2 2) reflections from $\mathscr{X}$, (7 0 2) from ϵ and (1 0 2) from η. The intensities of the reflections in question from $\mathscr{X}$ and ϵ are identical. The possible effect of the (1 0 2) reflection from η phase is small, because the volume fraction of the η phase is very small, even in the most advantageous case.

The decomposition of the β phase at temperatures 280 and 330° C is shown in Fig. 4. The curves are obtained from the intensities observed by subtracting the background from the integrated intensities of the peaks. At 330° C, the transformation was very rapid, the annealing time was less than 100 sec. At 280° C, the transformation time was tens of minutes.

In Fig. 5 are shown fourteen energy spectra of a Cu—21.6 at.% Sb foil after different heat-treatment times at 280° C. The measuring time of every diffraction spectrum was 10 min to ensure a sufficient number of pulses. In every measurement, the sample was placed exactly at the same position in the goniometer in order to make the intensities comparable with each other. In this study an attempt was made to extend the solubility of copper in antimony by splat-quenching an alloy containing 95.3 at.% antimony. Peaks from the Cu_2Sb phase were clearly observed in the diffractometer traces of the quenched foils, and on the basis of this it can be said that the solubility of copper was not extended observably.

In the equilibrium state, lattice parameter measurements by other investigations have not revealed any solubility of copper in antimony. With other methods, a value of 0.95 at.% Cu has been obtained at high temperatures [1].

The quenched foils were strongly textured. The intensities of the reflections with the hexagonal indices (0 0 3) and (0 0 6) from antimony foils
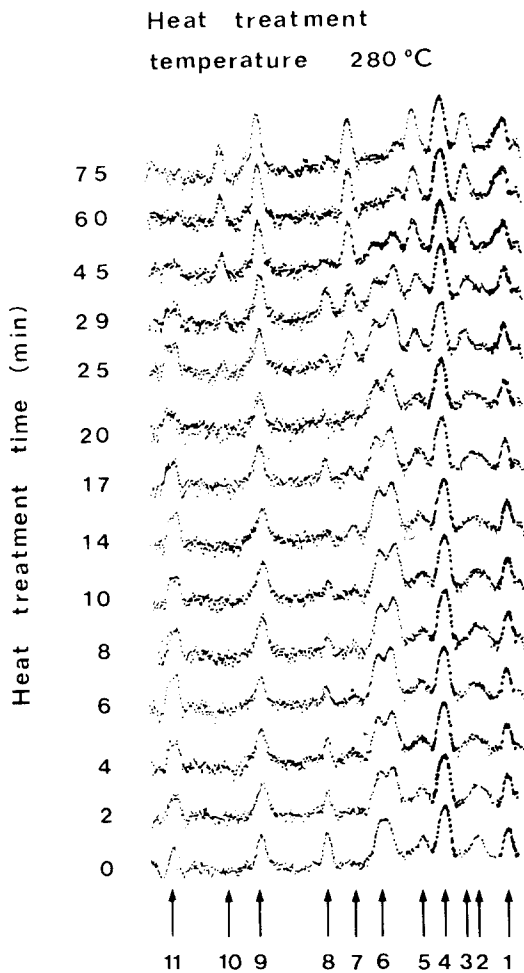
Heat treatment
temperature 280 °C

Figure 5 The energy dispersive X-ray diffraction chart of a splat-quenched Cu–21.6 at. % Sb foil after different heat-treatment times. The more detailed report on the charts is given in Table I.

were very strong compared with the intensities from a powder sample. Hence the close-packed layers of antimony in quenched foils were oriented parallel to the faces of the splatted foils.

The Cu–63.0 at. % Sb alloy was used to examine whether splat-quenching produces new metastable crystalline phase structures. This alloy concentration was selected because eutectic composition favours creation of new phases [12]. However, according to the empirical rules [12], this eutectic concentration has the disadvantage that the characteristics of the metallic component, here those of copper are not dominant.

The diffractometer examinations of the quenched eutectic alloys showed that no new structures were produced. Peaks from antimony and Cu_2Sb only were seen in the angle dispersive diffractometer trace. Cooling of the piston and anvil had no effect.

Acknowledgement

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TABLE I Indices of the reflections in Fig. 5.

Peak number	Fluorescence	Indices		
		β phase [4]	$\mathscr{X}$ phase [11]	ϵ phase [13]
1	SbKβ_1			
2		2 2 4*		
3			2 1 3*, 0 2 3*	7 0 3
4	SbK$\alpha_{1,2}$			
5		0 2 4	4 0 0*, 2 3 0*	7 7 0
6		0 0 4*	3 2 0	10 1 1
7			2 1 2*, 0 2 2*	7 0 2
8		2 2 2	3 1 0, 2 0 2	6 4 1
9		0 2 2*	2 1 1*, 0 2 1*	7 0 1
10		0 2 2	2 1 0*, 0 2 0*	7 0 0, 4 4 0
11		0 0 2	0 1 1	3 1 1, 3 3 0

*substructure reflection

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