The solid solubility of silver, gold and zinc in metallic tin

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In other studies [1], it has been found that dilute tin alloys containing one of the fast-diffusing solutes Ag, Au and Zn display marked but transitory increases in hardness when quenched from near eutectic temperatures. In this paper, it is shown that an examination of such hardness increases as a function of solute concentration and the equilibrium temperature prior to quenching provides a means of determining the solvus boundaries for the system concerned. Solvus data is derived for Ag, Au and Zn in Sn.

1. Introduction

In other studies [1] experiments have been carried out in which dilute Sn–Ag, Sn–Au and Sn–Zn alloys were rapidly quenched from temperatures up to their respective eutectic temperatures. Those alloys quenched from the higher temperatures displayed a marked increase in hardness of 40 to 160%, as compared with those of well-annealed slowly-cooled samples. Subsequent 'ageing' at room temperature or above resulted in a gradual reduction in hardness, accompanied ultimately by the appearance of precipitates at grain boundaries and within grains.

We believe that this instantaneous increase in hardness on quenching was not the classic precipitation (age-)hardening found in Al–Cu alloys but, rather, that it occurred as a direct result of the ability of these solutes to diffuse interstitially over long distances ($\simeq 300$ atomic diameters) between successive substitutional-site rest positions. When such an alloy is rapidly quenched, it is presumed that solute in interstitial transit is 'trapped' giving rise to considerable strain-hardening. This solute would be expected to remain trapped until a migrating vacancy appears and provides a (near strain-free) substitutional site.

The instantaneous increase in hardness, H, could be observed in all alloys which existed as single phases at the elevated temperature, T_q, but became two-phase at the temperature of the quenching medium, T_0, (Fig. 1) and was found to be related to the quantity of alloying element present in the β-tin and to the quenching temperature.
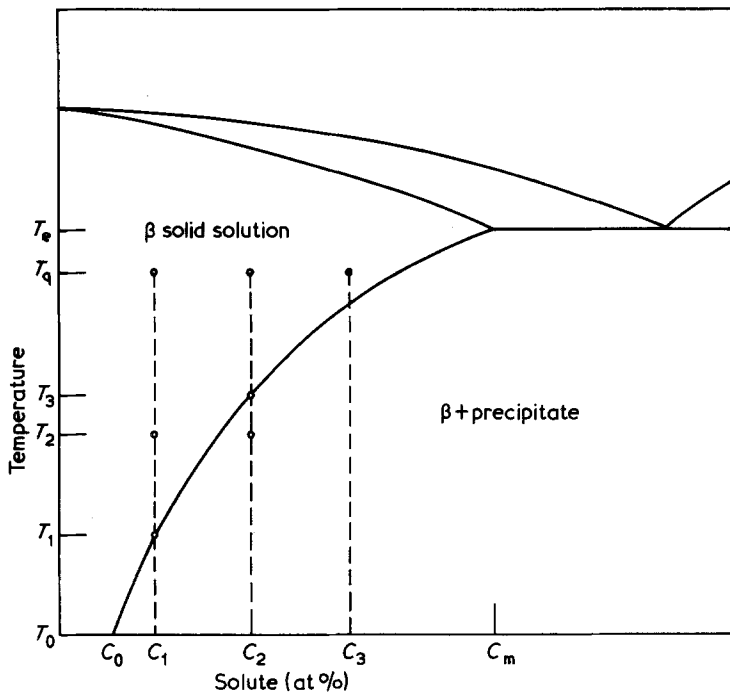
Thus the hardness increases appeared to be proportional to the number of solute atoms in excess of the equilibrium concentration and which became trapped in the interstitial spaces of the matrix. This number is likely to be dependent on the changing supersaturation of the matrix and the ability of the diffusion processes to respond to this as the temperature falls.

The situation may be illustrated with reference to the generalized phase diagram shown in Fig. 1. Here, three dilute alloys of compositions c_1, c_2 and c_3 are quenched from the temperature T_q to T_0. At the temperature T_1 the relevant supersaturations are 0, $(c_2 - c_1)$ and $(c_3 - c_1)$. Further, if it is assumed that similar heterogeneous nucleation sites would be available for all three alloys and that the precipitation processes occurring in each alloy are similar, then it might be expected that

$$H_{c_1} < H_{c_2} < H_{c_3}, \qquad (1)$$

where H_{c_1}, H_{c_2} and H_{c_3} are the quench-hardnesses of alloys c_1, c_2 and c_3, respectively, as is observed.

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In addition to the increase in hardness expected with increasing solute content, it is also to be expected, for a given composition, the supersaturation, and therefore the hardness, would also be dependent on the temperature from which the alloy was quenched, as long as this was in the precipitation range. Thus alloy c_2 would show the same quench hardness at T_0 irrespective of the particular temperature between T_3 and T_q from which it was quenched. This implies that any small increase in hardness due to quenched-in vacancies may be neglected. (In pure tin quenched from 200° C to 25° C and immediately tested, it was found that the hardness increase was less than the limits of experimental error.)

By contrast, if alloy c_2 is equilibrated below T_3, at, for example, T_2, it is found to consist of a fine precipitate lying in a solute-depleted matrix, which, upon quenching, will experience a correspondingly smaller increase in hardness. Some slight precipitation hardening might be expected to result from the presence of a relatively small amount of precipitate also in the matrix.

The above statement may be generalized: alloys of the same composition quenched from any temperature above the solvus line show the same instantaneous hardness. If, however, these alloys are quenched from temperatures below the solvus line, their hardnesses would decrease with the decrease in quench-temperature. Thus, for alloys

of composition $c_0 < c < c_m$, see Fig. 1, the plots of quench-hardness against quench-temperature should show sharp discontinuities at those temperatures where the limits of solid solubility for the given solute concentration have been reached.

This principle has been applied for the determination of solvus lines for the tin-rich alloys of Au, Ag and Zn.

2. Experimental results

Dilute alloys of Sn–Ag, Sn–Au and Sn–Zn were prepared by melting the components in pyrex in vacuum, chill-casting and then rolling into strips 1 mm thick. Specimens of each alloy were heated to their near-eutectic temperatures and then cooled down to a particular quench temperature to be "soaked" until equilibrium was established, i.e. when further soaking produced the same increase in hardness on subsequent quenching as the previous, shorter soaking. Finally, they were quenched in an ice-water bath and their hardness (VPN) was determined as soon as possible. A mean was taken of 15 readings measured for each specimen. The variations in quench-hardness with composition for various "soaking" temperatures are shown in Fig. 2. From this it is seen that, for each quench temperature, there is a concentration above which the quench-hardness remains virtually constant. This concentration is the solid solubility limit for the particular solute at that temperature.
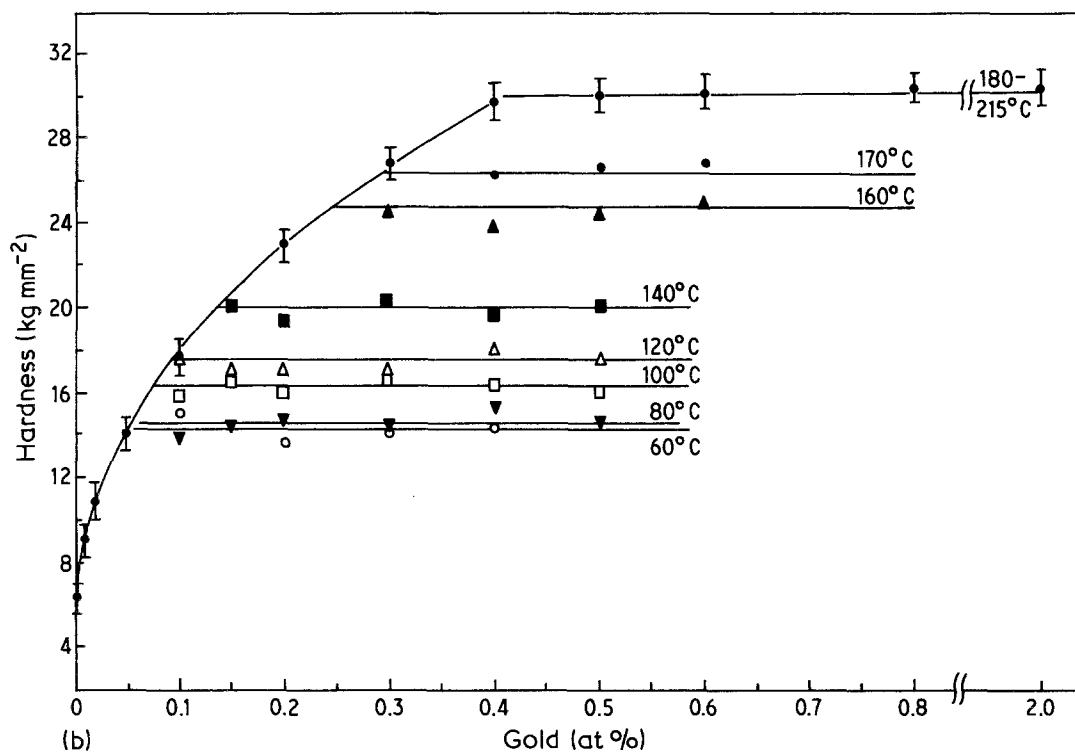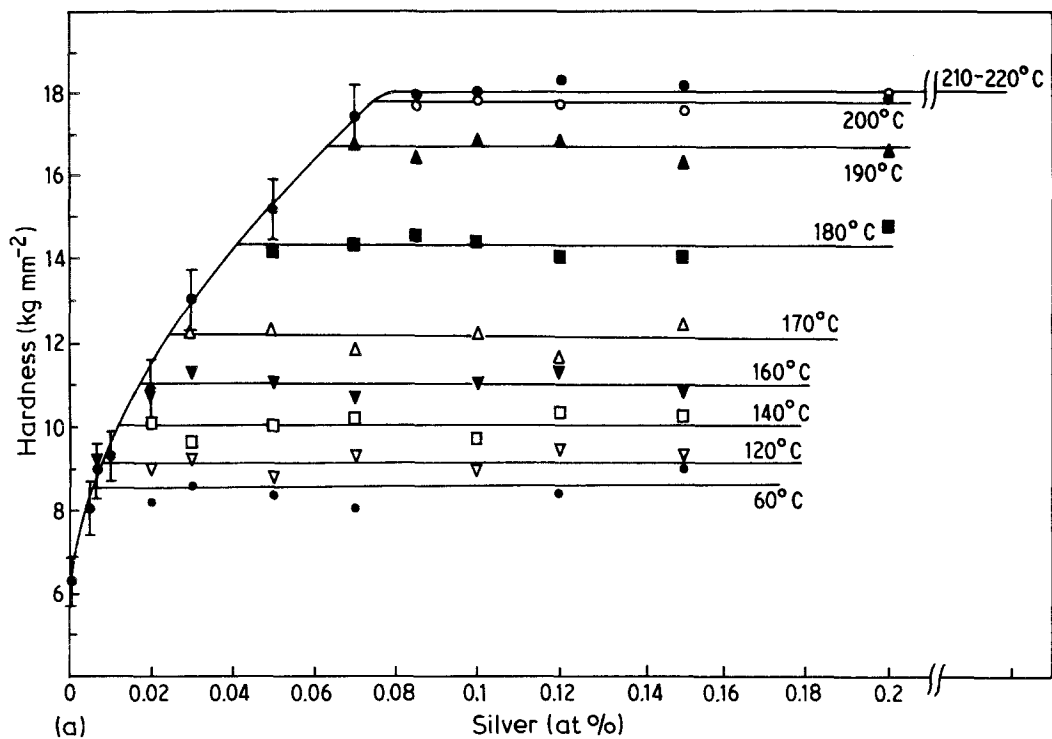
Figure 2 Quench-hardness against composition of dilute Sn alloys, annealed at various temperatures: (a) Sn—Ag; (b) Sn—Au; (c) Sn—Zn.
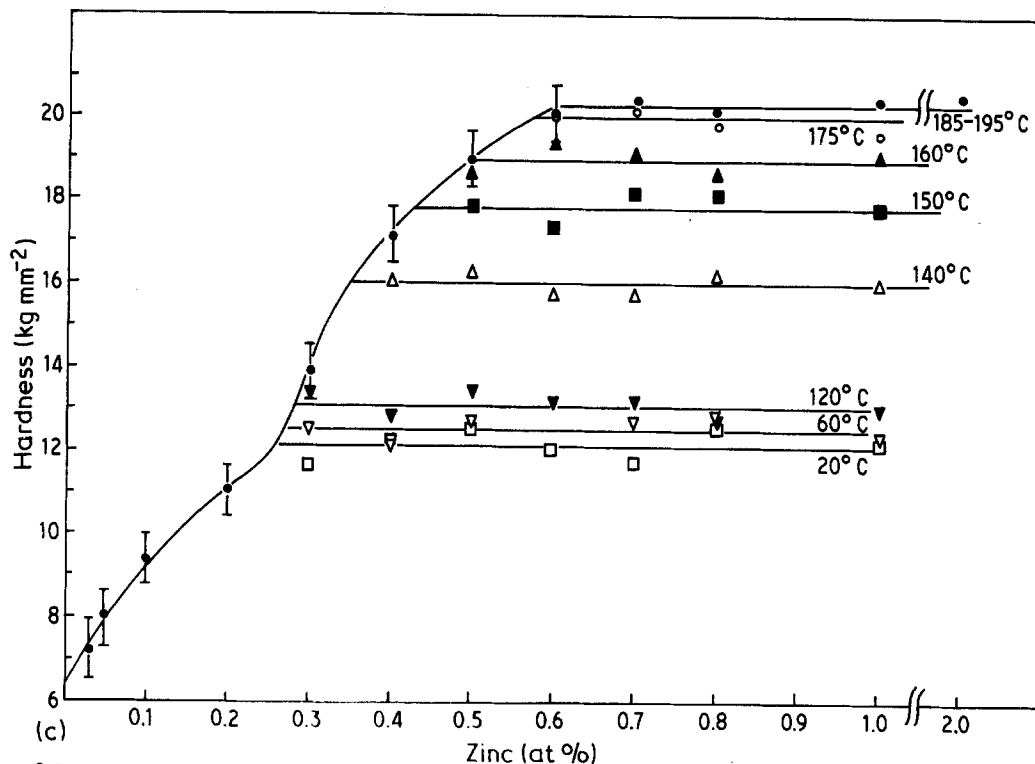
Figure 2 Continued.

If these values are plotted the solvus curves shown in Fig. 3 may be obtained. Thus it may be concluded that the respective solid solubility limits in Sn are:

(a) at 25° C: 0.004 at% Ag, 0.05 at% Au, 0.24 at% Zn;

(b) at eutectic temperature: 0.09 at% Ag, 0.4 at% Au, 0.6 at% Zn.

3. Discussion

The shape of phase boundaries shown in Fig. 3 is unusual but not unique. In fact, there are several binary systems which display solvus lines with inflexion points, e.g. Ag–Al [2], Be–Cu [3].

However, in general, it is difficult to obtain reliable values for solid solubility limits for temperatures close to room temperature since equilibrium tends only to be obtained after very extended annealing times. Even then, the solubility limits are generally small and so sensitive measurement techniques must be used. As a result, there is little reliable data to compare with the solvus lines reported here. Some of this has been collected in Table I. It is seen that, for fast-diffusing solute at least, quench hardness measurements provide a reliable estimate of solid-solubilities and their variation with temperature.

TABLE I Reported values of solid solubilities of the solutes Ag, Au and Zn in Sn

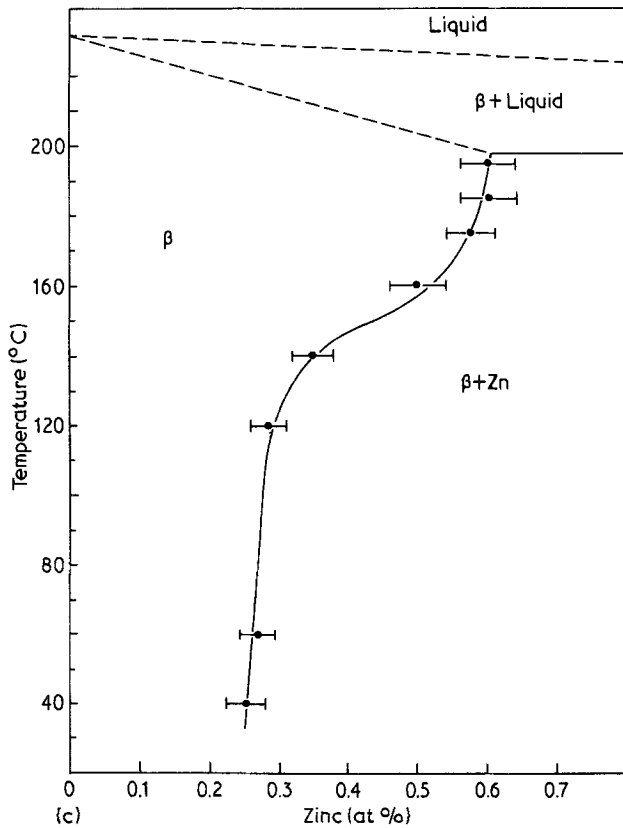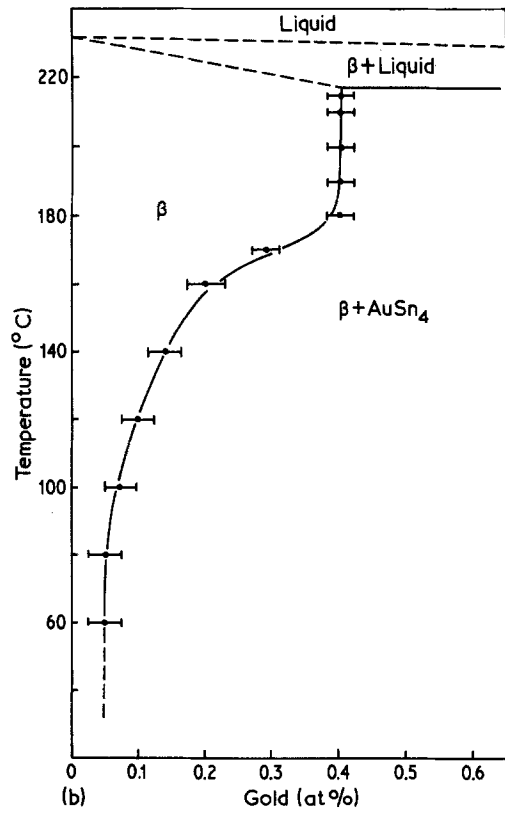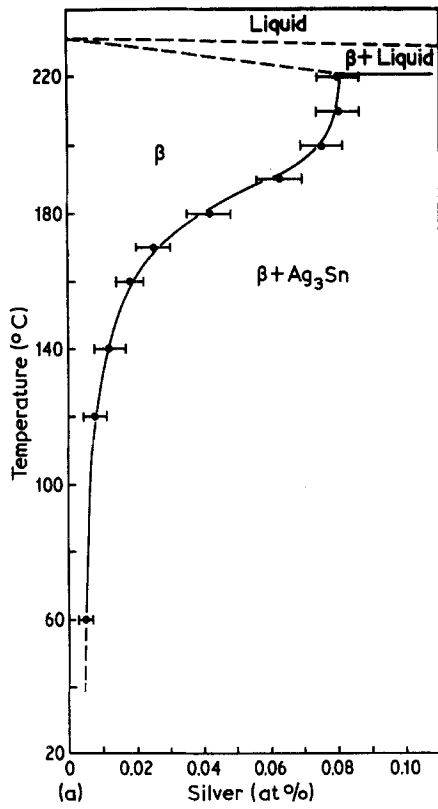| Alloy	Solid solubility limit in Sn (at%)			
	Method of measurement			
	Quench-hardness (this study)	Metallographic (from [3] and [4])	X-rays (from [5])	Resistivity (from [6])
Sn–Ag	25° C, 0.004 221° C, 0.09	25° C, 0.022 220° C, 0.036		20° C, ⩽ 1 × 10³% 175° C, 0.022
Sn–Au	25° C, 0.05 217° C, 0.4			20° C, ⩽ 1 × 10²% 175° C, 0.24
Sn–Zn	25°C, 0.24 198° C, 0.6	25° C, 0.36 185° C 1–3 199° C, 0.582	198° C, > 0.7	20° C, < 1 × 10⁻³% 175° C, ~ 0.72

Figure 3 Solvus lines for tin-rich alloys determined from the quench-hardness against quench-temperature curves shown in Fig. 2: (a) Sn—Ag; (b) Sn—Au; (c) Sn—Zn.

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