The composition and microstructure of electrodeposited solder on electroless nickel in the presence of gelatine

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The effect of gelatine addition to the electrodeposition bath on the tin content of the solder deposits was investigated. The results showed that as little as 0.5 g l^{-1} gelatine greatly enhanced the tin content of the deposits. The maximum tin content achievable for the deposit was approximately equal to the percentage of tin in the deposition bath. A lower current density and a greater metal content of the deposition bath tended to offset the effect of gelatine in promoting tin content of the deposit. Gelatine was found, with the aid of scanning electron microscopy and X-ray diffractometry, strongly to affect the morphology and facet orientation of the deposits.

1. Introduction

Tin–lead can be easily deposited from fluoroborate, sulphamate, chloride, fluorosilicate and pyrophosphate baths, of which the fluoroborate bath is probably the most commonly used. The composition of the deposit is affected by several factors. Increasing current density tends to enhance the tin content of the deposit [1–4], which is also enhanced by increasing the percentage of tin in the bath and the bath metal concentration [2]. However, agitation and higher temperature tend to lower the tin content of the deposit [2].

The electrodeposition of tin–lead alloy has been improved by incorporating with an addition agent in order to manipulate the properties of the deposit and the process performance. A small addition of copper, antimony or arsenic was able to improve the strength and fatigue resistance of the deposit [5]. Gelatine, glue [5], thiourea or cystine [6] have a grain-refining effect and resorcinol minimizes the composition variation of the deposit [5]. A bath incorporating peptone was reported to give a high throwing power of tin–lead deposition [3]. The adsorption behaviour of peptone on the electrode [7] and the effect of peptone on the electrodeposition rate [8] have also been investigated. In addition to the above-mentioned addition agents, hydroquinone [3, 9], a polyethoxyether [10], phenolphthalein, Triton X-100 [11, 12], a polymer TX, Triton X-100, an isobenzofuranone and lactone [12] have also been investigated to determine their effects on throwing power [9, 10], cathode efficiency [9, 10] and deposition speed [11].

The microstructure of the tin–lead alloy electrodeposit is also affected by various deposition parameters. The electrodeposited tin–lead alloy was reported to form a supersaturated solid solution of 10%–12% tin in lead [13]. This observation of the formation of a supersaturated solid solution was ascribed to fine-grained deposits, while a ⟨100⟩ orientation with a pyramidal morphology develops at higher applied potential.

The present work investigated the effect of gelatine on the composition, morphology and growth behaviour of the tin–lead deposits.

2. Experimental procedure

The 99.5% Al plate, $30 \times 40 \times 4$ mm, was ultrasonically cleaned in acetone followed by degreasing in a 5% NaOH solution for 30 s. The degreased aluminium plate was further acid cleaned in a 50% HNO$_3$ solution for 30 s prior to zincating for 30 s in a solution consisting of 120 g l^{-1} NaOH, 20 g l^{-1} ZnO, 1 g l^{-1} NaNO$_3$ and 50 g l^{-1} C$_4$H$_4$KNaO$_6\cdot$4H$_2$O. The zincated aluminium plate was deposited with electroless nickel in an acidic nickel sulphate solution at 80 °C. The phosphorus content, analysed with an energy dispersive spectroscope (EDS), of the 3 µm electroless nickel deposit was around 4.4 wt %. The solder was electrodeposited on the electroless nickel layer under a controlled temperature with graphite as the anode in a fluoroborate solution. The fluoroborate solution consisted of 100 g l^{-1} HBF$_4$, 25 g l^{-1} H$_3$BO$_3$ and varying Pb(BF$_4$)$_2$, Sn(BF$_4$)$_2$ to manipulate the Pb–Sn contents of the solution. Gelatine was added in the desired quantity. The relative composition of the solder electrodeposit was analysed with EDS. The phases of the solder were identified with X-ray diffractometry (XRD) while the surface morphology was investigated with scanning electron microscopy (SEM).

3. Results and discussion

The electrodeposition of Pb–Sn was said to be a diffusion-controlled process [8, 15]. The Pb^{2+} exhibits a greater diffusion coefficient than that of Sn^{2+} in the fluoroborate solution [16]. As such it is expected that lead will be deposited faster than tin. On the other hand, for a diffusion-controlled process, an increase in current density tends to enhance the polarization phenomenon [17] which results in amounts close to the relative elemental contents of the alloy deposit. On the basis of the above descriptions, it is expected, as seen in Fig. 1, that the electrodeposition of solder tends to produce deposits with greater lead content. It is also seen in Fig. 1 that the tin content of the tin–lead alloy deposit can be enhanced by increasing the current density. However, the increase in current density does not seem to change the deposition mechanism, as the deposition profile maintains the same shape regardless of the current density variation.

The addition of gelatine to the deposition bath, however, seems to induce tremendous polarization behaviour in the solution. The effect of gelatine on polarization was also reported in the deposition of copper [6]. It was further reported [8] that the additive effect on raising the activation enthalpy of the solder constituent elements is greater for lead than for tin in electrodeposition. Accordingly, the addition of gelatine to the solder deposition bath significantly increases the tin content of the deposits, as seen in Fig. 2. However, the effect of gelatine on the polarization behaviour will approach an optimum magnitude as the addition increases [3]. Thus the increase in tin content of the deposits approaches a maximum value soon after $0.5\,g\,l^{-1}$ additive was introduced, Fig. 3. This maximum value is approximately the relative concentration ratio of tin and lead in the deposition bath as seen in Figs 2 and 3.

The effect of gelatine on the polarization, and hence on increasing the tin content of the deposits is greatly offset by the total metal content of the deposition bath. It is seen in Figs 4 and 5 that higher total bath metal contents, 82 and $150\,g\,l^{-1}$, significantly lower
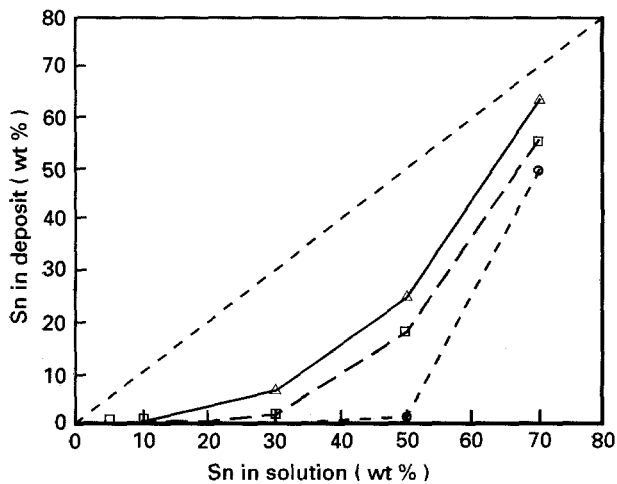

Figure 1 The effect of current density and tin concentration in the bath on the deposit composition, in the absence of gelatine. Total metal content $35.5\,g\,l^{-1}$. Current density: (O) 1, (□) 2, (△) 3 A dm⁻².
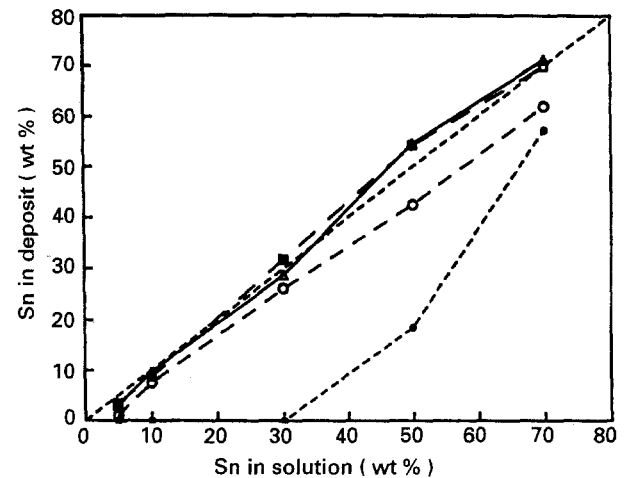

Figure 3 The effect of gelatine and tin concentration in the bath on the deposit composition, at 2 A dm⁻², with a total metal content of $35.5\,g\,l^{-1}$. Gelatine content: (●) 0, (O) 0.5, (□) 1.5, (△) 5 g l⁻¹.

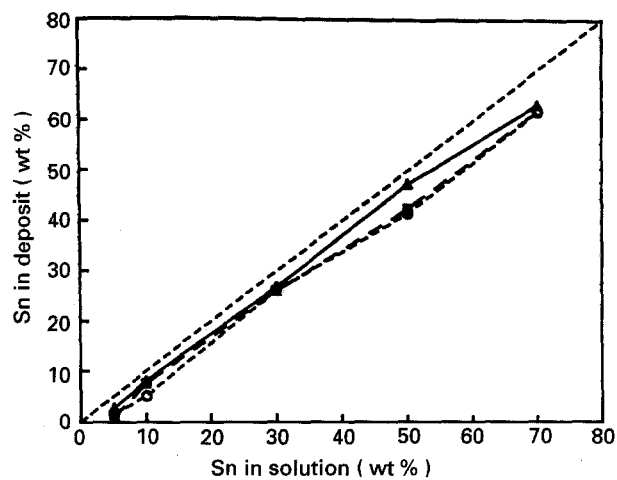*Figure 2* The effect of current density and tin concentration in the bath on the deposit composition, with $0.5\,g\,l^{-1}$ gelatine and $35.5\,g\,l^{-1}$ total metal concentration in the bath. Current density: (O) 1, (□) 2, (△) 3 A dm⁻².

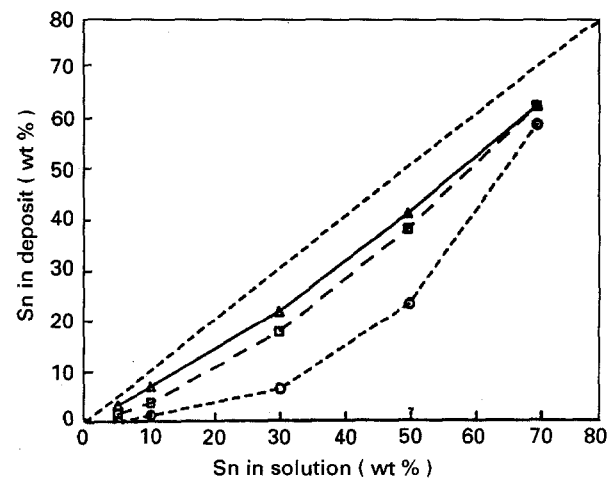*Figure 4* The effect of current density and tin concentration in the bath on the deposit composition, with $0.5\,g\,l^{-1}$ gelatine and $82\,g\,l^{-1}$ total metal concentration in the bath. Current density: (O) 1, (□) 2, (△) 3 A dm⁻².

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the tin content of the deposits. This behaviour is expected because the increasing surface concentration of metal ions tends to compete with the surface adsorption of gelatine. The lower surface adsorption of gelatine at higher metal ion concentrations greatly diminishes the effect of gelatine on the polarization behaviour and thus gradually brings the deposition behaviour back to that of deposition without additive.
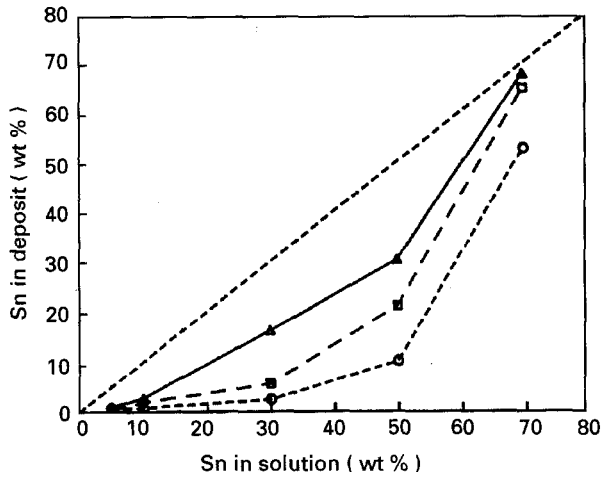
The backscattered electron image (BEI) of the 70Sn–30Pb deposit, Fig. 6, evidently indicates that the deposit consists of two phases. The light area is due to the tin-in-lead solid solution while the dark area is the lead-in-tin solution. The XRD results in Fig. 7 further confirm the existence of the two-phase

Figure 5 The effect of current density and tin concentration in the bath on the deposit composition, with $0.5\,gl^{-1}$ gelatine and $150\,gl^{-1}$ total metal concentration in the bath. Current density: (O) 1, (□) 2, (△) 3 A dm^{-2}.

Figure 7 The XRD of the deposits obtained from the bath containing (a) $5\,g\,l^{-1}$ gelatine (product 71Sn–29Pb), (b) $1.5\,gl^{-1}$ gelatine (70Sn–30Pb), (c) $0.5\,gl^{-1}$ gelatine (62Sn–38Pb), and (d) $0\,gl^{-1}$ gelatine (51Sn–49Pb). The total metal concentration of the bath is $35.5\,gl^{-1}$ with 70 wt % Sn.
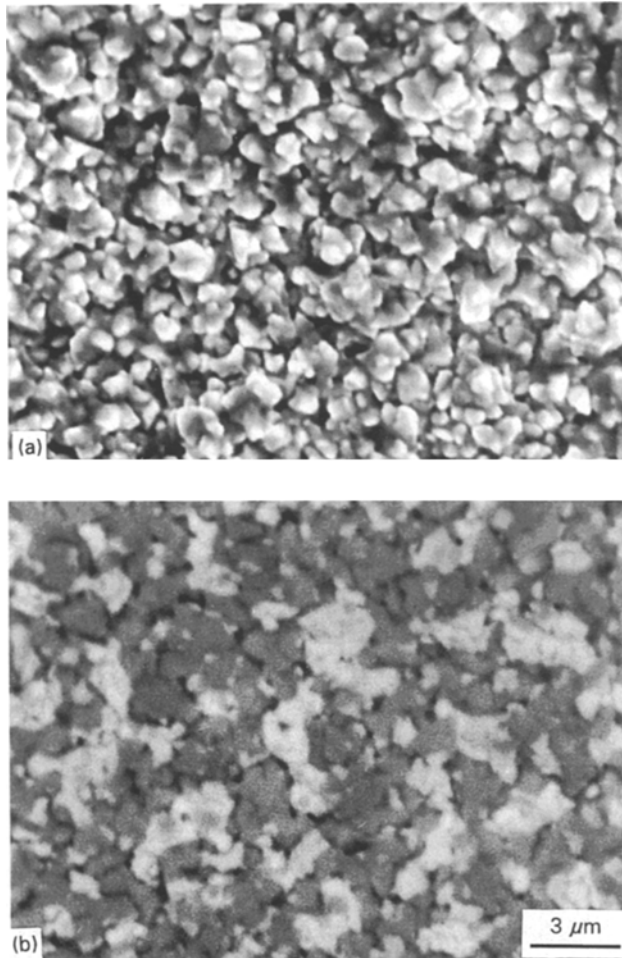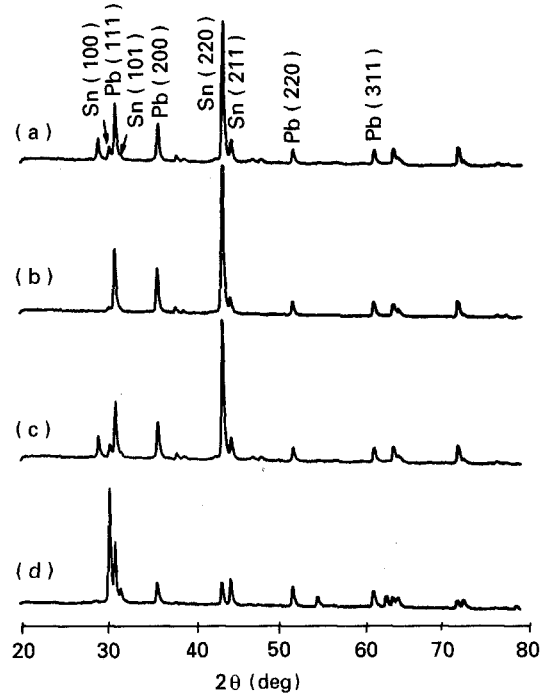

Figure 6 (a) The secondary electron image of 70Sn–30Pb deposit. (b) The backscattered electron image of 70Sn–30Pb deposit.
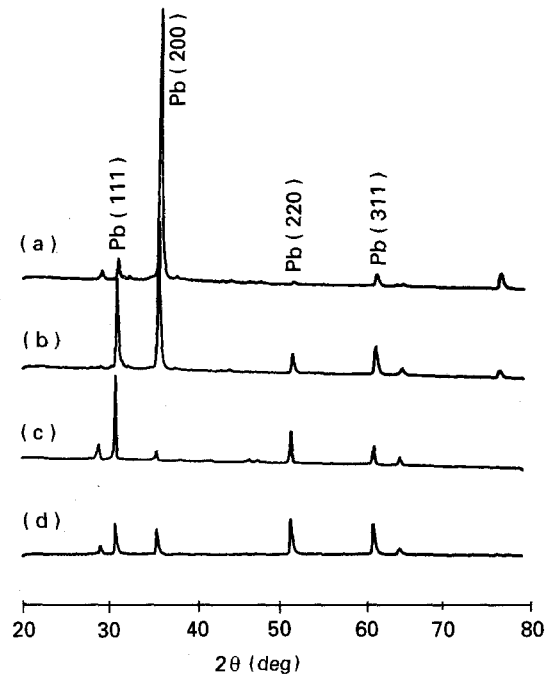
Figure 8 The XRD of the deposits obtained from the bath containing (a) $5\,gl^{-1}$ gelatine (product 9.7Sn–90.3Pb), (b) $1.5\,gl^{-1}$ gelatine (8.2Sn–91.8Pb), (c) 0.5 gl^{-1} gelatine (7.5Sn–92.5Pb), (d) $0\,gl^{-1}$ gelatine (pure lead). The total metal concentration of the bath is $35.5\,gl^{-1}$ with 10 wt % Sn.
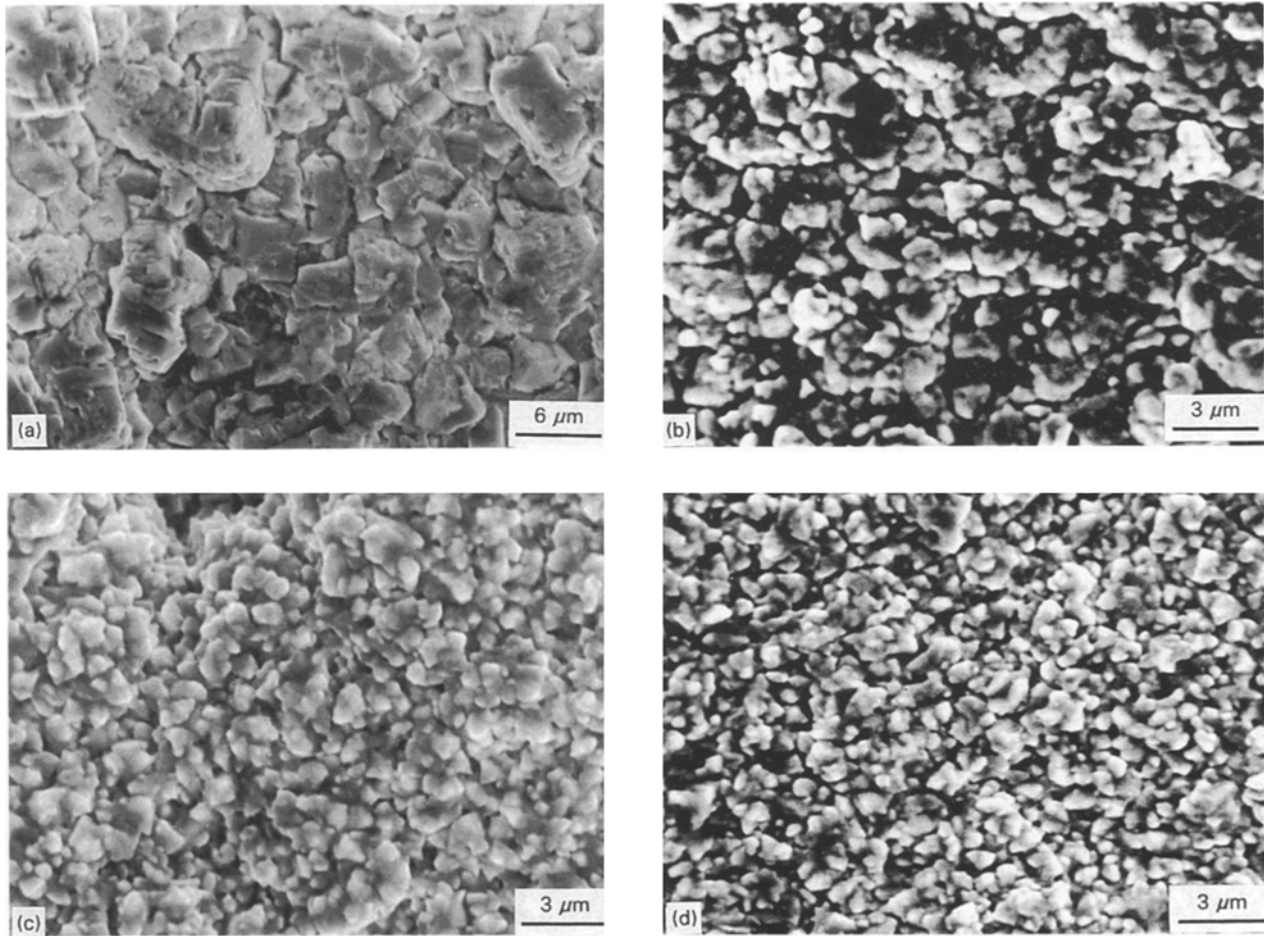
Figure 9 Effects of gelatine on the morphology of solder plating. Gelatine additions: (a) 0, (b) 0.5, (c) 1.5, (d) 5 g l^{-1}. The plating bath contained 70% Sn and platings contained 51%, 62%, 69.9% and 71.2% Sn (a–d) respectively.

structure for deposits of various tin contents, controlled by varying the gelatine addition as described in Fig. 3. A single-phase deposit was obtained in the present work only when the tin content of the deposit was less than 10%, Fig. 8, which approaches the single-phase region of the binary tin–lead eutectic system [19].

Brenner reported [17] that the tin–lead deposit exhibits the finest surface grain morphology when the Sn:Pb atomic ratio is 1:1. This phenomenon was ascribed to the interference between tin and lead [17]. Nevertheless, the deposit grain refining in the presence of gelatine does not seem to be restricted to the 1:1 atomic ratio. It is seen in Fig. 9 for 51%–71% Sn deposits that, by controlling the tin content with gelatine addition up to 5 g l^{-1}, all other deposition conditions being the same, the surface structure continues to be refined. The microstructural refining in the presence of gelatine in the bath was also observed for deposits of lower tin contents, as seen in Fig. 10. In addition to the microstructural refining behaviour, gelatine was further seen to change the morphology of the lower tin content deposits from polygonals (0% Sn content) to square pyramid (8.2%–9.7% Sn). The surface adsorption of gelatine on the deposit is believed to inhibit the primary growing position which allows the growth to occur on the secondary growing position [12]. The surface adsorption of organic additive also inhibits surface diffusion of adatoms [18]. The adsorp-

tion of additive thus exhibits a microstructural refining effect on the deposits.

The deposit facet orientation is also significantly influenced by the addition of gelatine. The XRD results of Figs 7 and 8 correspond to the deposits shown in Figs 9 and 10, respectively. It is seen from the XRD results of the higher tin content deposit, Fig. 7, that the major facet of the tin phase varied from (1 0 0) to (2 2 0) as the gelatine was added. In addition, the major facet of the lower tin deposits, Fig. 8, varies from Pb(1 1 1) to Pb(2 0 0) as the gelatine addition was increased. It is believed that in both lower and higher tin content deposits the gelatine was adsorbed on to, and suppressed the growth of, the closest packed facet, the above-mentioned Sn (1 0 0) and Pb (1 1 1), and thus allows the growth of the less-dense facets, as shown in the XRD results.

4. Conclusion

The addition of 0.5 g l^{-1} and above of gelatine to the fluoroborate solder electrodeposition bath greatly enhanced the tin content of the solder deposits. The increase in total metal contents of the deposit tended to offset the effect of gelatine. Gelatine also shows a microstructural refining effect on the deposit. The facet orientation of the lower tin contents (0–9.7 wt %) deposit varies from Pb (1 1 1) to Pb (2 0 0), while the higher tin contents (51–71.2 wt %)
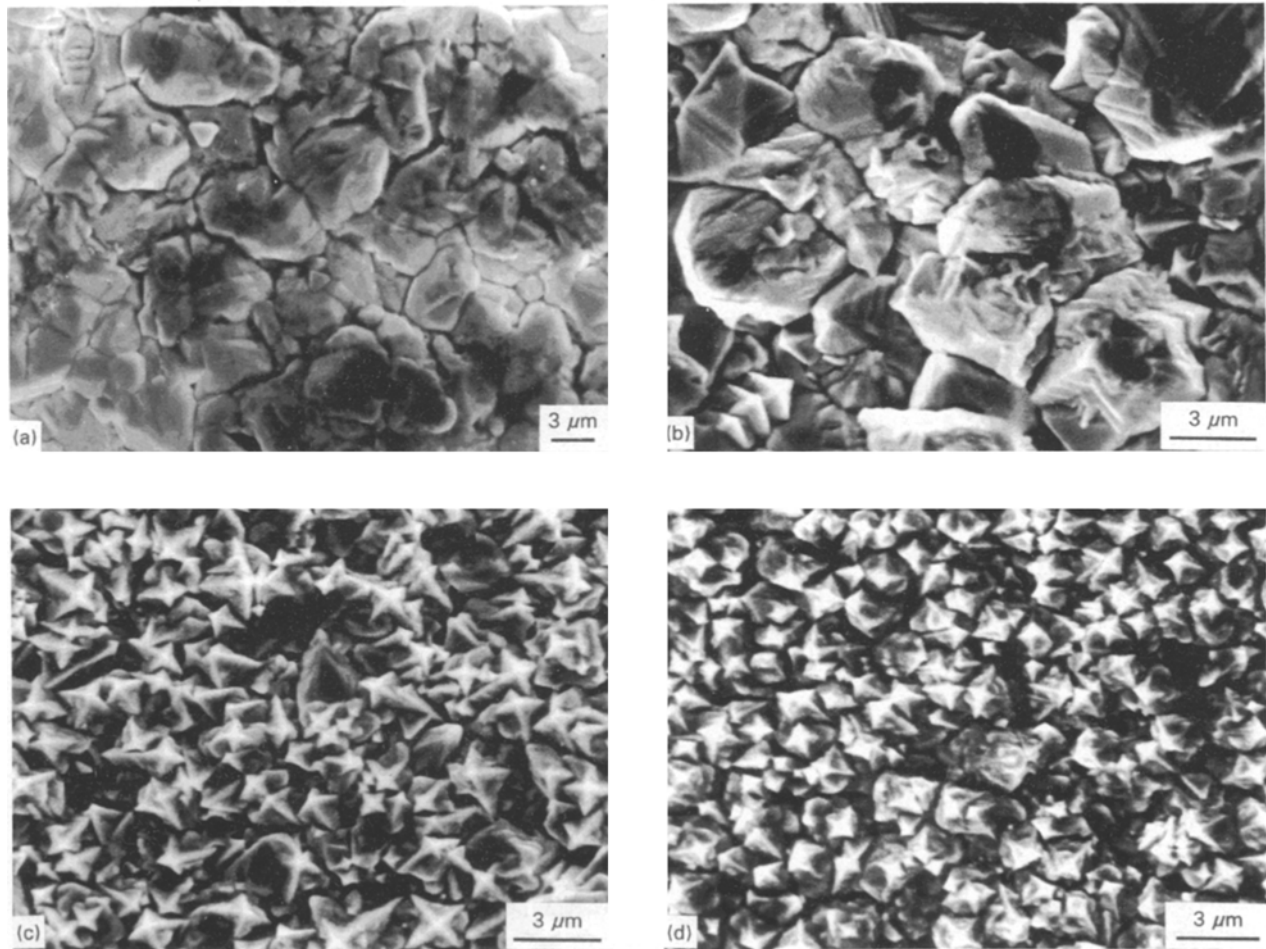
Figure 10 Effects of gelatine on solder plating morphology. Gelatine additions: (a) 0, (b) 0.5, (c) 1.5, (d) 5 g l^{-1}. The plating bath contained 10% Sn and the platings contained 0%, 7.5%, 8.2% and 10% Sn (a–d) respectively.

deposit changes from Sn (1 0 0) to Sn (2 2 0) with respect to an increase in tin content.

Acknowledgement

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