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Effect of preheating on the mechanical properties of tough pitch copper made from copper scraps

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When hot rolled tough pitch copper is made from copper scraps, lead is intentionally or unintentionally added to the melt. The major role of this lead seems to be the removal of metallic tin by the formation of $PbO–SnO_2$. A continuously cast and hot rolled copper rod was preheated at temperatures between 673–1173 K for 1 h prior to cold drawing. The maximum diameter of the $PbO–SnO_2$, of 1–2 μm, was obtained by preheating at 873 K. This preheating temperature also produced the maximum decrease in the recrystallization temperature and the maximum electrical conductivity of the 89.4% cold drawn wire within the investigated experimental range. This can be attributed to a decrease in the dissolved impurity concentration due to the growth of $PbO–SnO_2$ particles at that temperature. The decrease in recrystallization temperature enhanced the room temperature multiple upset weldability. When preheated at 1173 K, Zn_2SnO_4 particles were formed, but the recrystallization temperature increased and the electrical conductivity decreased due to the dissolution of $PbO–SnO_2$.

1. Introduction

If tough pitch copper wires are produced by continuous casting and subsequent hot rolling then copper scraps may be used for economic reasons. When copper scraps are used, the tough pitch copper contains impurities such as lead, tin, iron and zinc that are mostly in the form of complex oxides, which deteriorate hot workability, for example, breakouts during continuous casting and surface cracking during hot rolling. After cold drawing, such impurities deteriorate the mechanical properties, the electrical conductivity and the room temperature multiple upset weldability of cold drawn wires. Such behaviours have been attributed to the dissolution of impurities in the copper matrix, which increases the recrystallization temperature of copper. Smart and Smith [1–3] have studied the effect of impurity elements such as iron, nickel and cobalt on the recrystallization behaviour of commercially produced high purity copper. In addition many investigators have studied the effects of small amounts of impurities on the mechanical properties of cold drawn copper wires [4–7]. Pitt *et al.* [8] have studied the effect of small amounts of silver, selenium and tin on the recrystallization temperature of copper. They reported that preheating had no effect on the recrystallization temperature in the solid solution range of alloying and that the greatest increase in the recrystallization temperature was obtained by the addition of tin. This is due to the solubility limit of tin in the copper matrix being considerably larger than that of other elements such as silver and selenium. A tin oxide was believed to be formed in the molten copper [9]. Later a thorough study of the effect of lead concentration on the annealing properties of cold drawn copper wires was carried out by Aoyama *et al.* [10–13] and Urao *et al.* [14]. When the cold drawn copper wires containing lead as a major impurity were preheated before cold drawing, the softening of the cold drawn copper wires was accelerated compared to that of the cold drawn copper wires without preheating. However, the preheating of a cold drawn wire containing no lead showed no change in the recrystallization temperature. It is thought that these phenomena are due to a decrease in the lead dissolved in the copper matrix and the formation of oxides containing lead. However, no detailed understanding of the microstructural behaviour of the lead oxides in the copper matrix currently exists.

The room temperature joining of copper wires is achieved using the multiple upset or cold welding process. This is a solid-state process in which pressure is applied at room temperature [15]. A characteristic of the process is the absence of heat, which is applied externally. Generally cold drawn pure copper wires are easily joined by multiple upset welding, however cold drawn tough pitch copper wires are difficult to join using this technique. This problem appears to be related to the increase in the recrystallization temperature of cold drawn copper wires containing impurities.

The purpose of this article is to investigate the effect of preheating on the formation of lead oxide and thus

TABLE I Chemical composition of the hot rolled copper rod made from copper scraps (ppm)

Cu	Pb	Sn	Zn	Fe	Sb	Bi	As	Ni	Ag	Se	O
Bal.	482	39	95	23	9.3	6.4	11	104	47	1.3	295

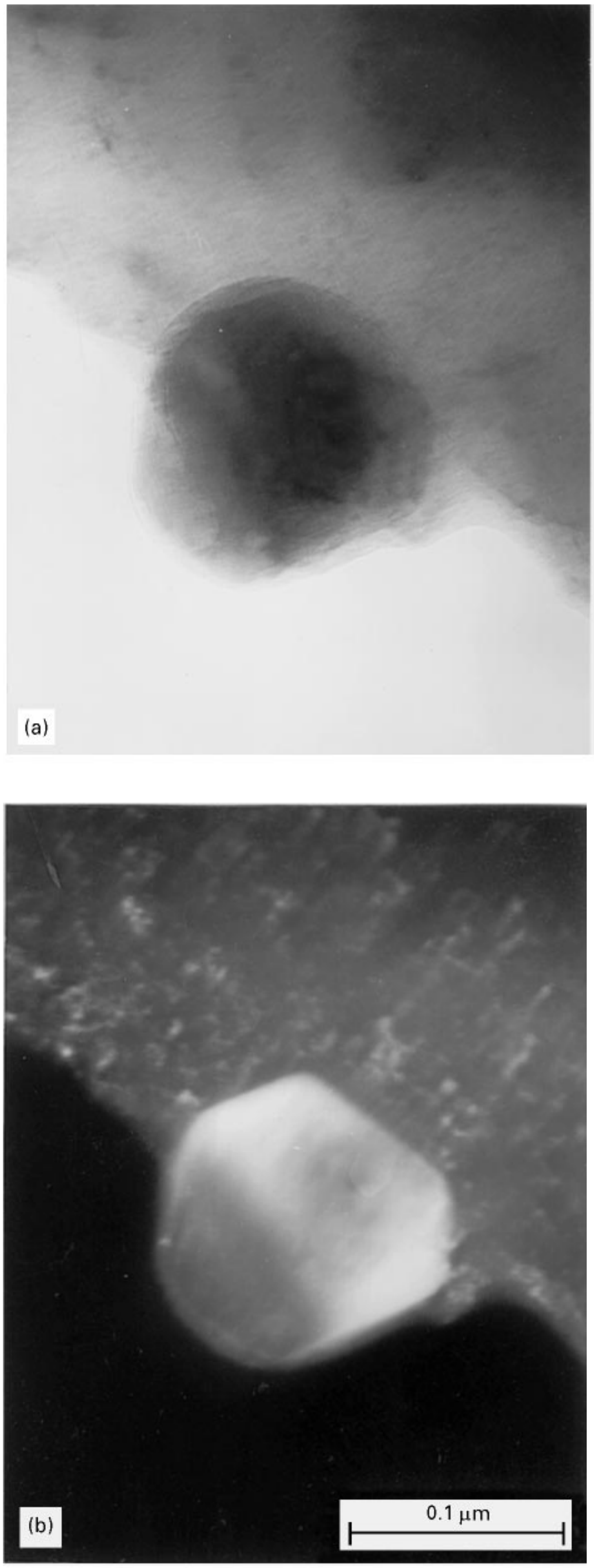

Figure 1 Transmission electron micrographs of a lead containing particle in the continuously cast bar made from copper scraps. (a) Bright field image, (b) dark field image, (c) diffraction pattern and (d) indexed pattern.

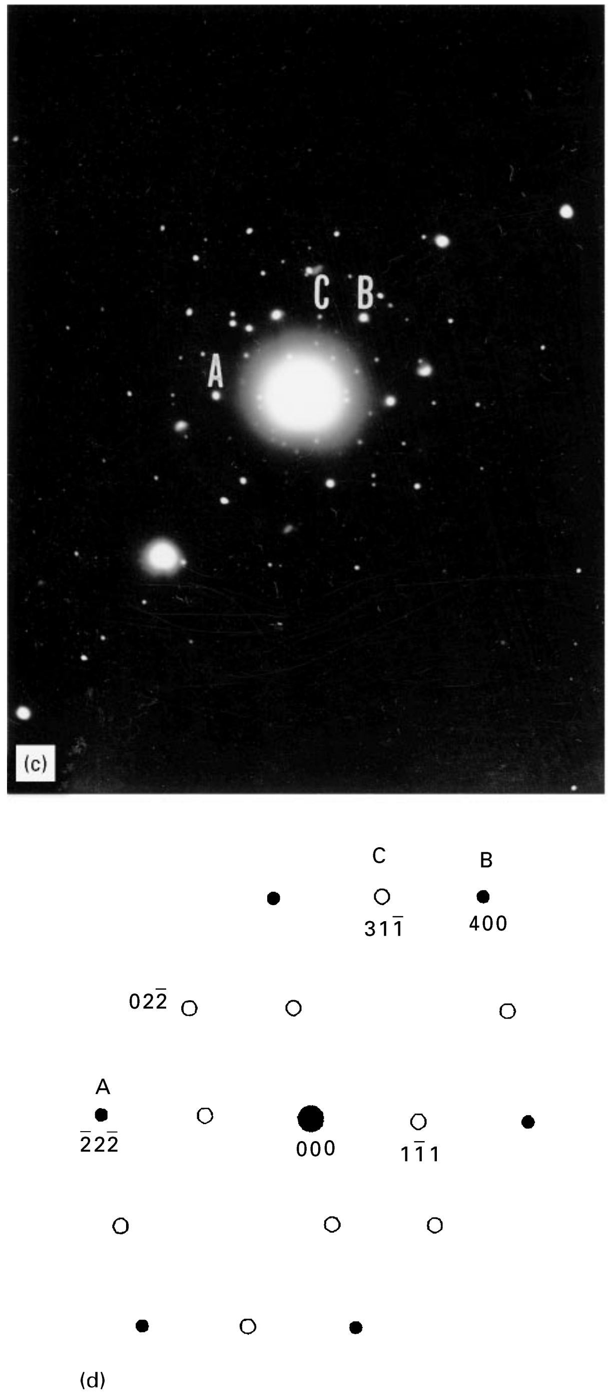

Figure 1 Continued.

the mechanical properties, the electrical conductivity and multiple upset welding of cold drawn copper wire made from copper scraps.

2. Experimental procedure

A tough pitch copper rod of 8 mm diameter was made from the melting of copper scraps, followed by continuous casting and hot rolling. The chemical composition of the hot rolled tough pitch copper rod is presented in Table I.

The hot rolled copper rods were preheated at temperatures from 673–1173 K for 1 h in air prior to cold drawing, and were pickled in dilute H_2SO_4 solution to remove any surface oxide layer. The preheated copper rods were cold drawn to a diameter of 2.6 mm at a drawing speed of 10 m per min. The cold drawn copper wires were annealed at temperatures between 413–873 K for 1 h. The Vickers hardness of the preheated copper rods was measured under a load of 5 kg. In addition the micro Vickers hardness of the upset welded interface between cold drawn copper wires that had been preheated at temperatures between 673–1173 K was measured under a load of 100 g. Also annealed copper wires of a gauge length of 25 mm were tensile tested at room temperature at a crosshead speed of 10 mm per min. The recrystallization temperature was determined by measuring the tensile strength and elongation as a function of the annealing temperature. The electrical conductivity of the cold drawn copper wires was measured at room temperature with a Double Bridge Type 2752. The microstructures of the cast bar and the preheated

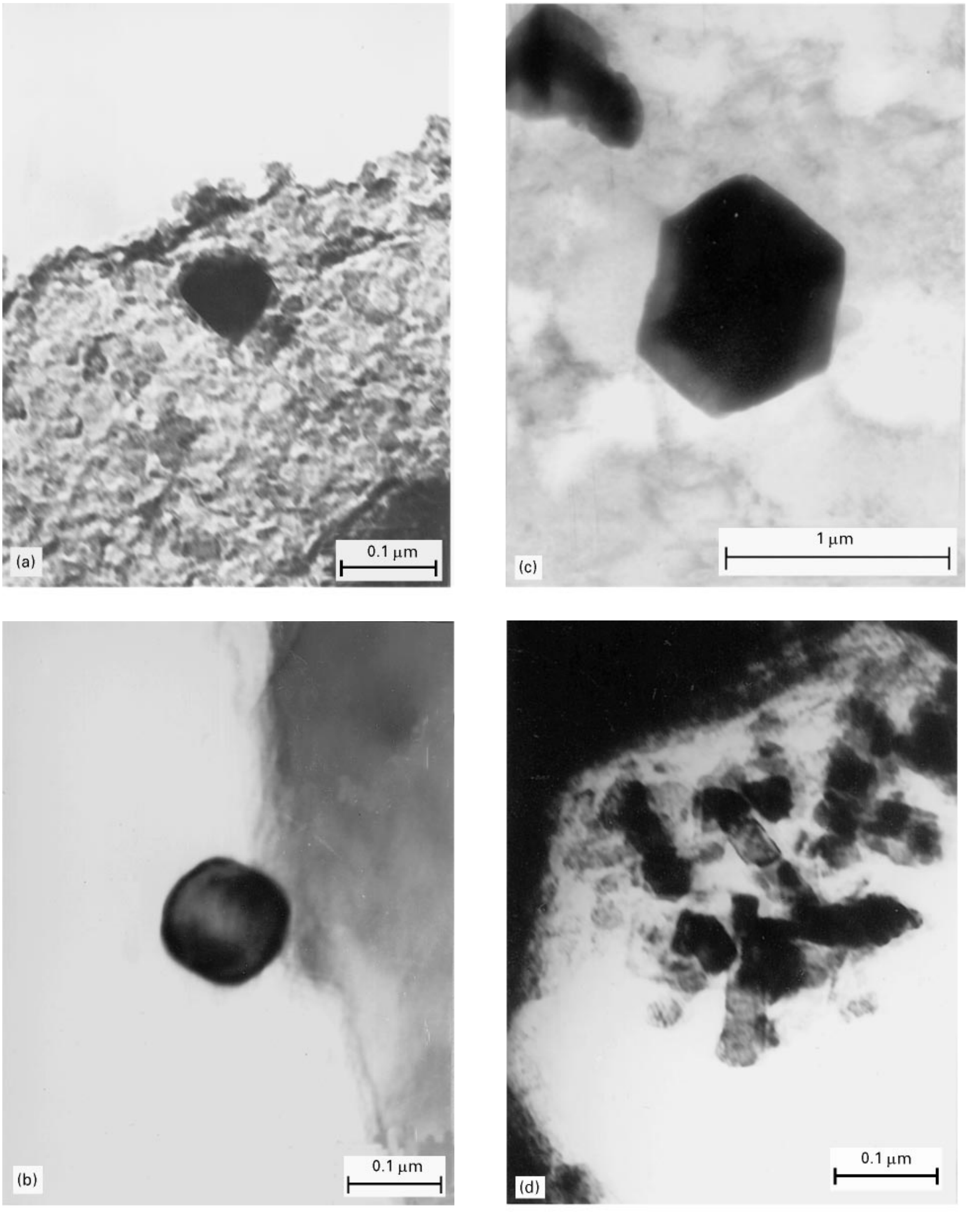

Figure 2 Transmission electron micrographs of $PbO–SnO_2$ particles at various preheating temperatures. (a) As hot rolled, (b) 773 K, (c) 873 K, (d) 973 K, (e) 1073 K and (f) 1173 K.

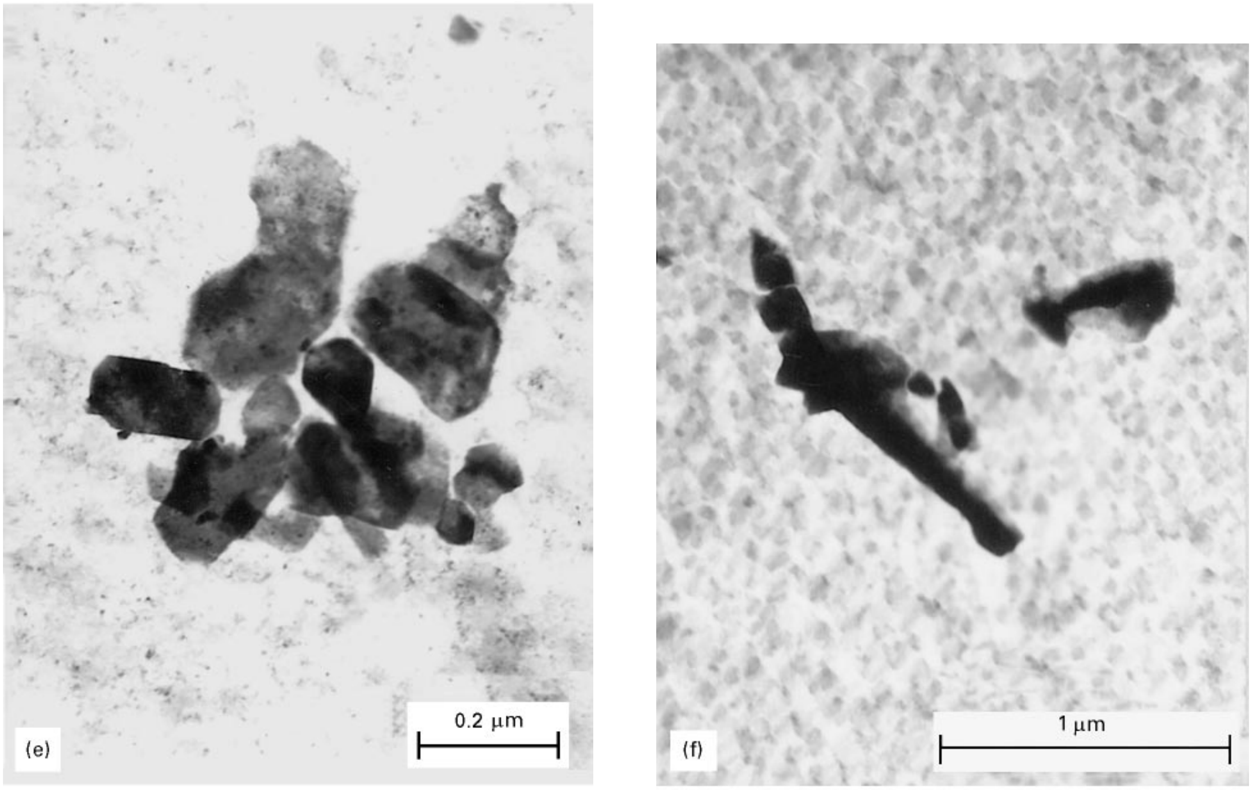

Figure 2 Continued.

copper rods were observed in a Philips CM20 transmission electron microscope (TEM) equipped with an energy dispersive spectroscopy (EDX). The TEM specimens were jet-electropolished in a mixture of 33 vol% nitric acid and 67 vol% methanol at -30–$40\,^{\circ}$C, 50–60 V. The microstructure of the welded interfaces of the 89.4% cold drawn copper wires were observed after etching with a solution of 20 g $FeCl_3$, 5 ml HCl and 100 ml H_2O.

3. Results and discussion
3.1. Microstructures
Fig. 1(a and b) shows typical bright and dark field transmission electron micrographs of a lead containing particle in the continuously cast bar made from copper scraps. The particle size was 0.05–0.1 μm in diameter and the typical shape was mainly observed to be hexagonal. The majority of the particles in the matrix were copper oxide (CuO_2) and the shape was

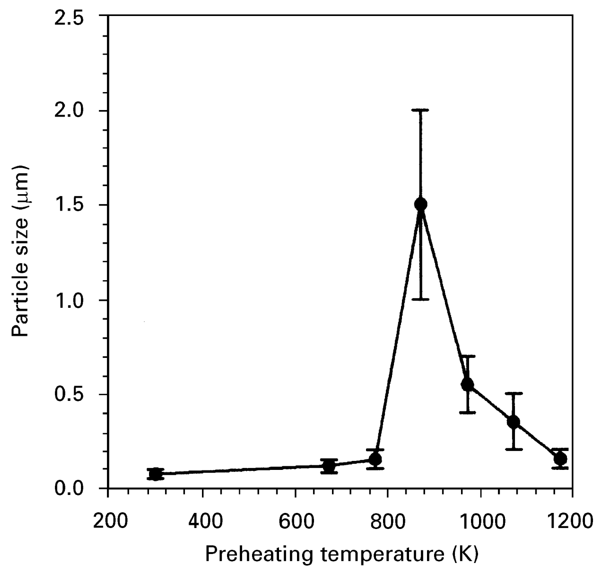

Figure 3 The size of PbO–SnO_2 particles measured using the TEM as a function of preheating temperature.

TABLE II Composition and crystal structure of lead containing particles in the hot rolled copper rod preheated for 1 h

Preheating temperature (K)	Particle composition (wt %)						Structure
	Pb	Sn	Zn	Fe	Ni	Sb	
As hot rolled	35.89	16.78	34.98	5.79	6.56		PbO–SnO_2
673	38.59	18.76	30.14	5.96	6.55		PbO–SnO_2
773	38.53	22.96	26.43	5.81	6.27		PbO–SnO_2
873	10.17	16.48	36.23	37.12			PbO–SnO_2
973	61.01	14.69	4.05			20.25	PbO–SnO_2
1073	74.59	9.83				15.58	PbO–SnO_2
1173	64.58					35.42	PbO–SnO_2
		36.51	48.36	6.05	9.08		Zn_2SnO_4

round. An EDX examination of the lead containing particle indicated that the particle contained lead, tin, iron, nickel and zinc. Fig. 1(c and d) shows an electron diffraction pattern taken from a particle and its schematic indexing diagram, respectively. The particle has

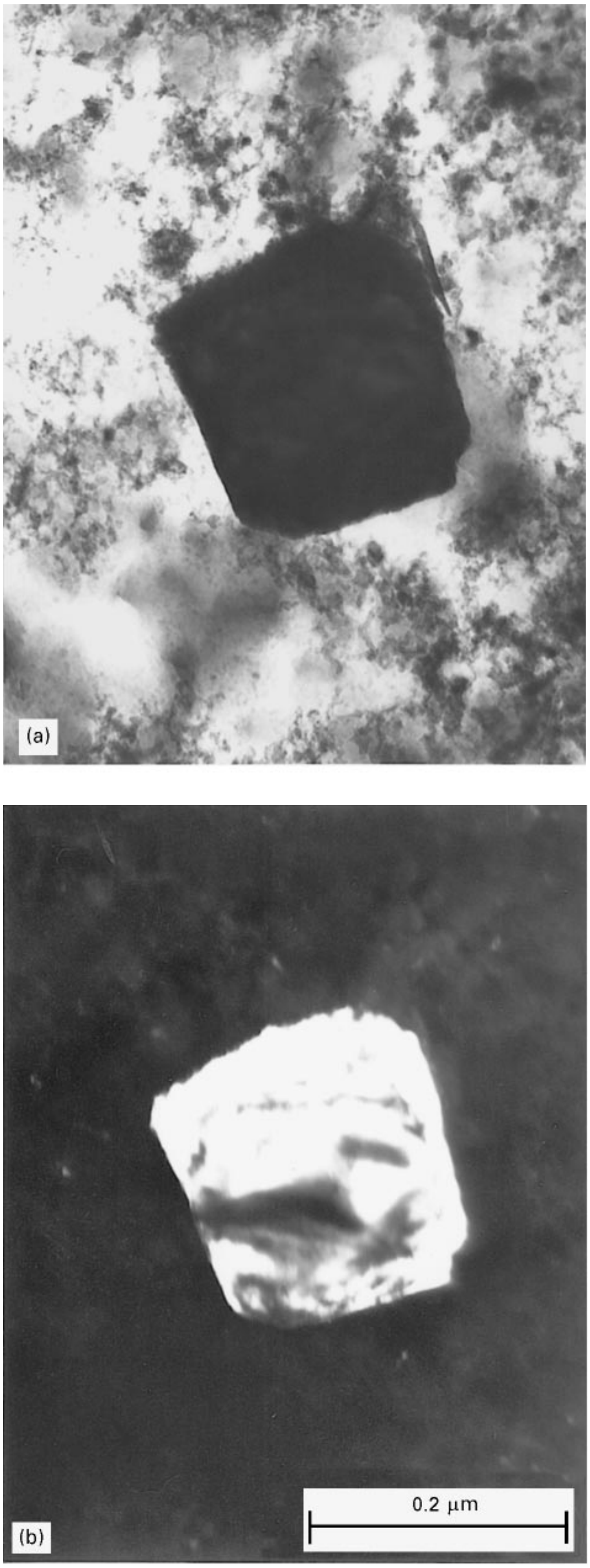

Figure 4 Transmission electron micrographs of Zn_2SnO_4 particle found in a hot rolled copper rod at 1173 K for 1 h. (a) Bright field image, (b) dark field image, (c) electron diffraction pattern and (d) indexed pattern.

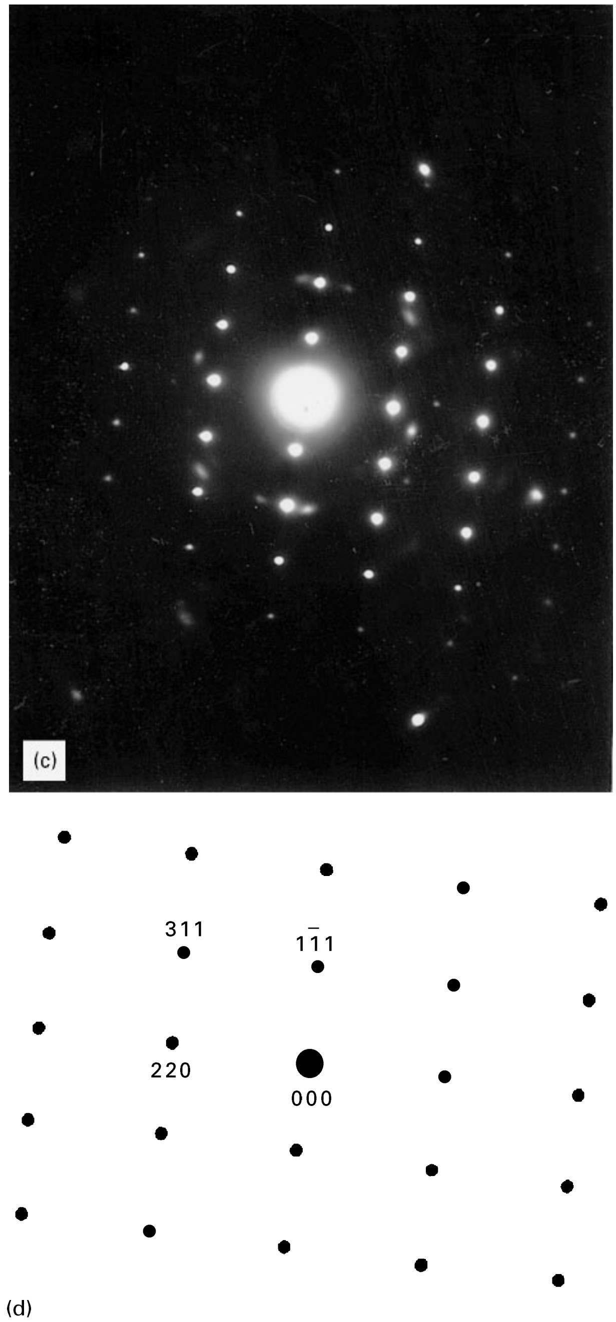

Figure 4 Continued.

a cubic crystal structure with a lattice parameter of 1.0 694 nm and is identified as $PbO–SnO_2$ by comparison with the JCPDS card. Thus the major role of lead seems to be the formation of an oxide particle which removes impurities such as tin, iron, nickel and zinc in molten copper.

Fig. 2(a–f) consists of transmission electron micrographs of $PbO–SnO_2$ particles observed in the hot rolled copper rods preheated at various temperatures for 1 h. The compositions analysed by EDX and the crystal structures are listed in Table II. Fig. 3 shows the size of $PbO–SnO_2$ particles measured from TEM micrographs as a function of preheating temperature. The size of $PbO–SnO_2$ particles in hot rolled copper rod without preheating was 0.05–0.1 μm as is shown in Fig. 2(a). The particle size increased up to 1–2 μm with increasing preheating temperature to 873 K as can be observed in Fig. 2(b and c), and then decreased with further increase in the preheating temperature to 1173 K as can be observed in Fig. 2(d–f). The diameters of PbO–SnO_2 particle clusters in the temperature range between 873–1173 K were measured to be 0.4–1.0 μm as compared to the diameters of individual PbO–SnO_2 particles of 0.1–0.2 μm. The particles mainly had a hexagonal shape up to 873 K, and above this temperature they started to dissolve into irregular shapes. The relative fraction of lead in the PbO–SnO_2 particles increased, whereas the relative fractions of tin, iron, nickel and zinc decreased with increasing preheating temperature between 973–1173 K. These results indicate that the concentration of impurities such as tin, iron, nickel and zinc increases in the copper matrix with increasing the preheating temperature above 873 K.

Fig. 4(a and b) consists of bright and dark field transmission electron micrographs of an oxide particle

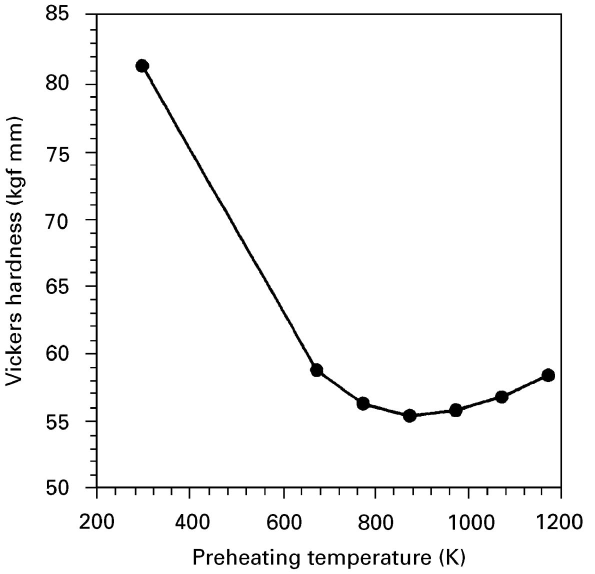

Figure 5 Vickers hardness of copper rod as a function of preheating temperature.

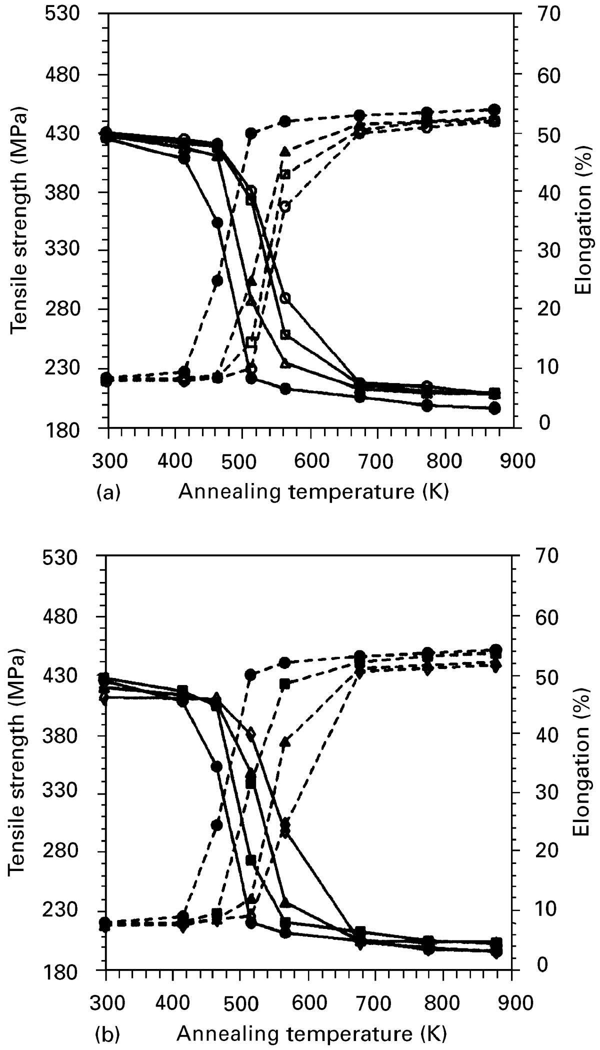

Figure 7 (—) Tensile strength and (– –) elongation of copper wires as a function of annealing temperature at preheating temperatures of (○) As hot rolled, (□) 673 K, (△) 773 K and (•) 873 K and (b) (—) Tensile strength and (– – –) elongation of copper wires as a function of annealing temperature at preheating temperatures of; (•) 873 K, (■) 973 K, (▲) 1073 K and (◇) 1173 K.

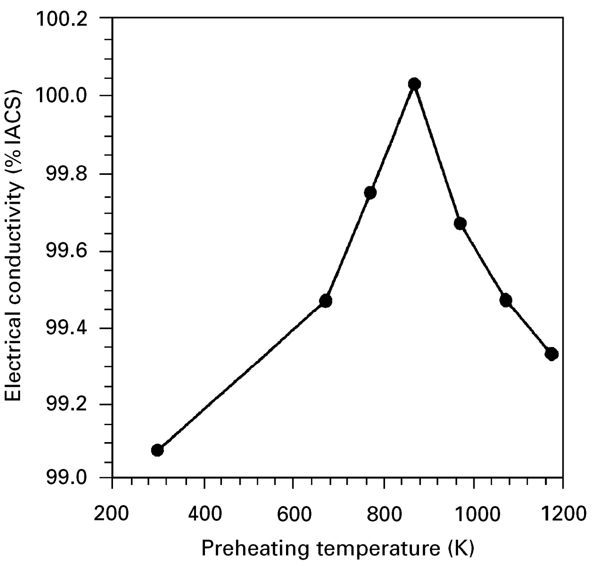

Figure 6 Electrical conductivity of cold drawn copper wire as a function of preheating temperature.

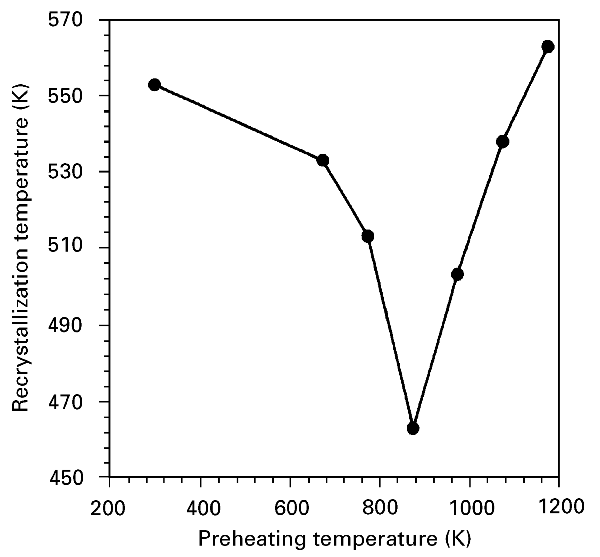

Figure 8 Recrystallization temperature of the 89.4% cold drawn copper wire as a function of preheating temperature.

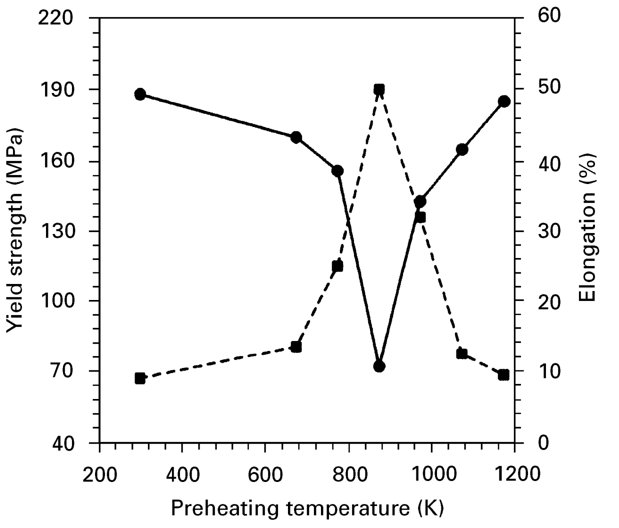

Figure 9 (—) Yield strength and (– – –) elongation of 89.4% cold drawn copper wire annealed at 513 K for 1 h as a function of preheating temperature.

containing tin, zinc, as major elements and also lesser amounts of iron and nickel, which was found in the copper rod preheated at 1173 K. The size of this particle was measured to be 0.2–0.5 μm and its shape was mainly rectangular. The electron diffraction pattern obtained from this particle and its index are presented in Fig. 4(c and d) respectively. It has a cubic crystal structure with a lattice parameter of 0.86574 nm and is identified as Zn_2SnO_4 by comparison with its JCPDS card. The formation of an oxide particle containing significant amounts of tin and zinc and lesser amounts of iron and nickel in the copper rod preheated at 1173 K shows that the amount of tin, zinc, iron and nickel in the copper matrix increases as the preheating temperature is increased above 873 K.

3.2. Mechanical and electrical properties

Fig. 5 shows the Vickers hardness of the hot rolled copper rod as a function of preheating temperature. The Vickers hardness decreased to a minimum value of 55 kgf mm^{-2} at the preheating temperature of 873 K, and slightly increased with further increases in the preheating temperature. When copper rods were preheated below 873 K, impurities in the copper matrix were precipitated into PbO–SnO_2 particles as is shown in Table II and with increasing the preheating temperature, the particle size increased. Thus the amount of impurities in the copper matrix and the hardness of the matrix both decreased with increases in the preheating temperature. However, when the tough pitch copper rods were preheated above 873 K, the amount of impurities such as tin and zinc in the matrix increased as the preheating temperature was increased as discussed in the previous section and the hardness of the matrix also increased.

Fig. 6 shows the electrical conductivity of cold drawn copper wires at room temperature as a function of preheating temperature. A preheating at 873 K produces a maximum value of the electrical conductivity of 100.03% IACS. The electrical conductivity of the 89.4% cold drawn copper wire preheated at 873 K was 1% IACS higher than that of the as hot rolled copper wire.

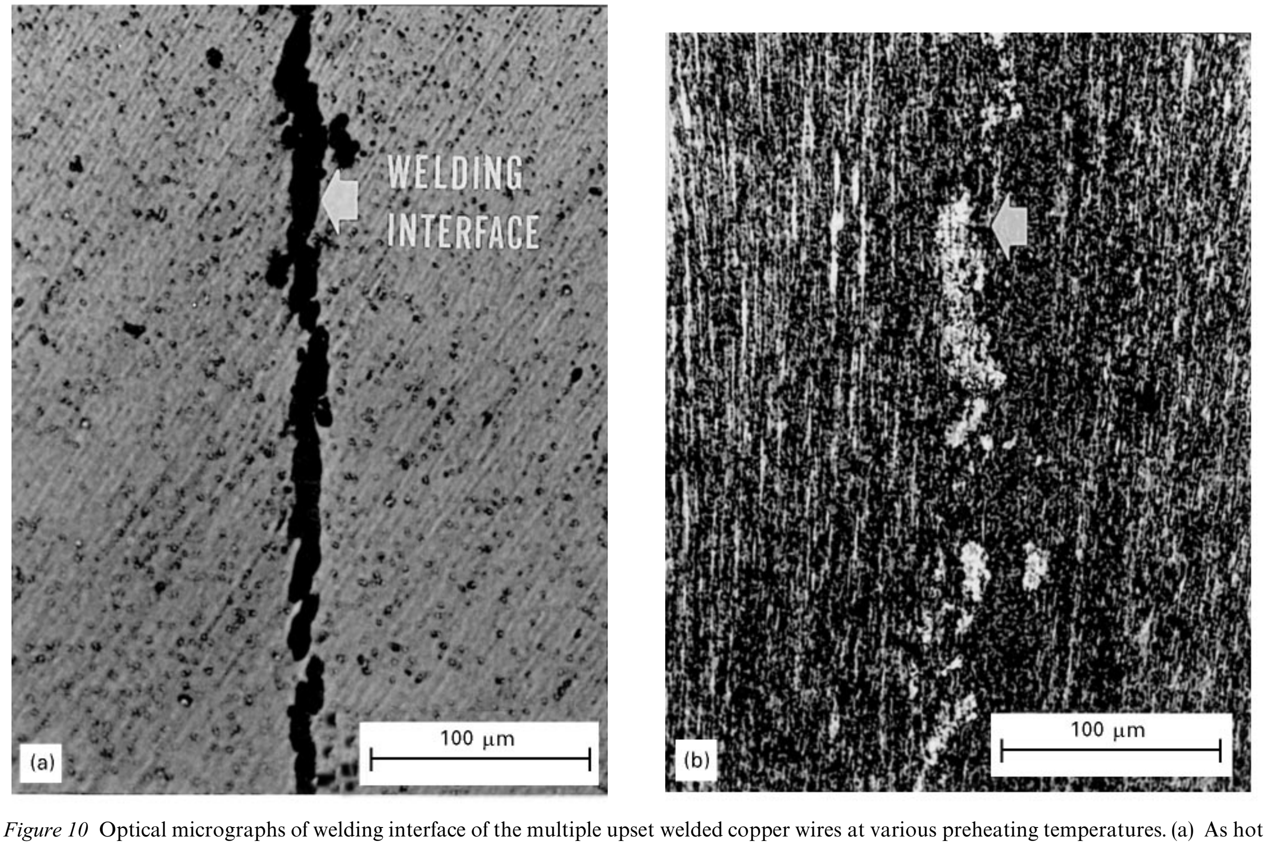

Figure 10 Optical micrographs of welding interface of the multiple upset welded copper wires at various preheating temperatures. (a) As hot rolled, (b) 673 K, (c) 773 K, (d) 873 K, (e) 973 K and (f) 1073 K.

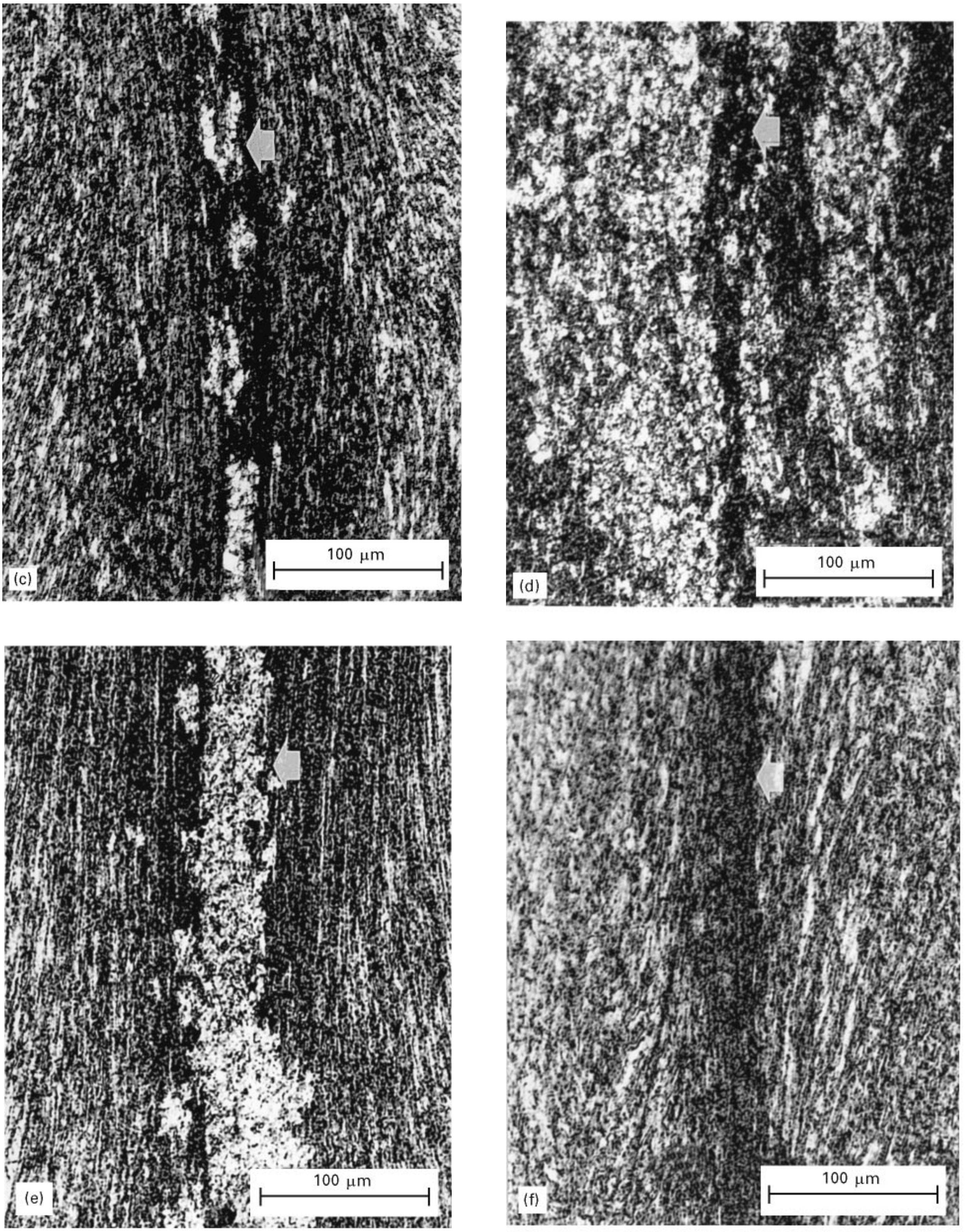

Figure 10 Continued.

Fig. 7(a and b) shows the effect of preheating temperature on the tensile strength and elongation of the 89.4% cold drawn copper wires at various annealing temperatures. Using this data the recrystallization temperature could be obtained as a function of preheating temperature as is shown in Fig. 8. A preheating at 873 K produces the minimum recrystallization temperature of 463 K. The recrystallization temperature of cold drawn copper wire preheated at 873 K was 90 K lower than that of cold drawn copper wire without preheating.

Fig. 9 shows the yield strength and elongation of a 89.4% cold drawn copper wire that had been annealed at 513 K for 1 h at various preheating temperatures. The yield strength and elongation at the preheating temperature of 873 K show the minimum and maximum values, respectively.

The results shown in Figs 3, 5, 6, 8 and 9 consistently show that an increase in the $PbO–SnO_2$ particle size due to preheating up to 873 K produces a decrease in the concentration of impurities dissolved in the matrix. This in turn decreases the recrystallization temperature, the hardness and yield strength, and increases the electrical conductivity and elongation of the copper wires. Therefore, the maximum decrease in recrystallization temperature obtained at a preheating temperature of 873 K can be attributed to the minimization of the impurity content dissolved in the matrix due to the formation of $PbO–SnO_2$.

3.3. Multiple upset weldability

Fig. 10(a–f) are optical micrographs of the upset welded interface of copper wire at various preheating temperatures. The upset welded copper wire without preheating was hardly welded as is shown in Fig. 10(a). At the welded interface, white regions were observed whose size increased with increasing the preheating temperature up to 873 K and then decreased with any further increase in the preheating temperature as is shown in Fig. 10(b–f). Fig. 11 shows the micro Vickers hardness across the welded interface of a copper wire preheated at 873 K. The hardness near the interface shows a lower value than that of copper wire. Fig. 12 shows the micro Vickers hardness in the centre of the welded interface of copper wires at various preheating temperatures. The minimum value of the hardness was obtained for a preheating temperature of 873 K. As shown in Fig. 8, the recrystallization temperature of copper wire has a minimum at the preheating temperature of 873 K. The above result shows that the white regions near the welded interface are a recrystallized region due to plastic deformation during upset welding. The size of the recrystallized region increased to 250 μm with increasing the preheating temperature up to 873 K as is shown in Fig. 10(b–d), but then decreased with any further increase in the preheating temperature. The lower recrystallization temperature would produce a large recrystallized area at the same plastic deformation due to upset welding [16]. The recrystallization temperature of copper wire preheated at 873 K has the minimum value of 463 K and the recrystallized area is the largest, as is shown in Fig. 10(d).

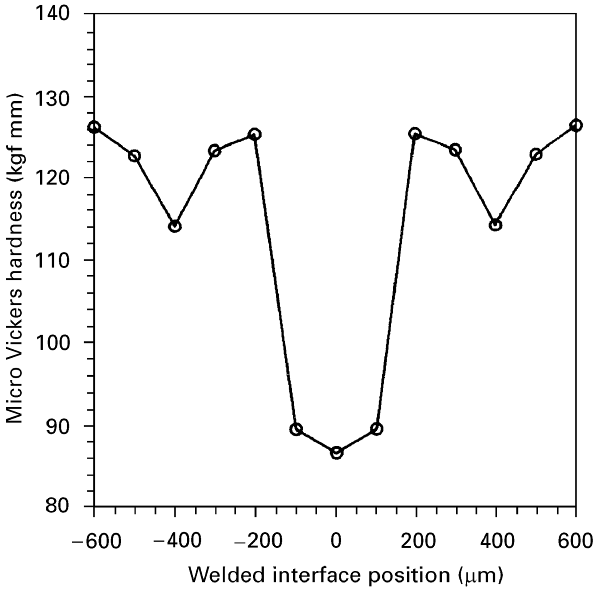

Figure 11 Micro Vickers hardness across welded interface of a copper wire preheated at 873 K.

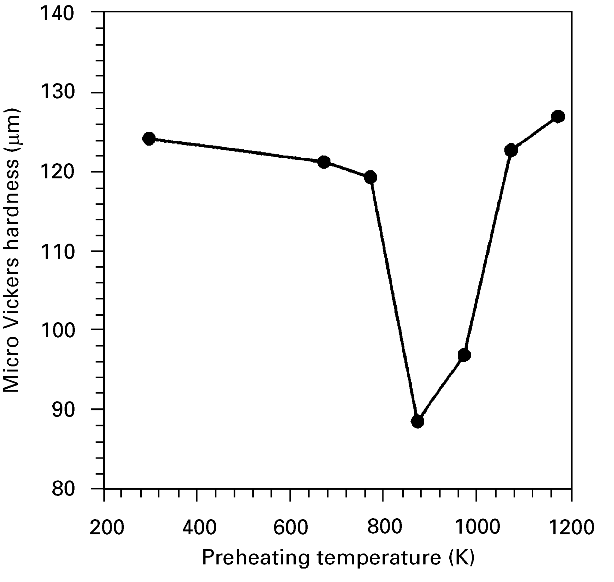

Figure 12 Micro Vickers hardness in the centre of welded interface of copper wires as a function of preheating temperature.

4. Conclusions

In tough pitch copper made from copper scraps, the major role of lead added to the melt seems to be related to removing tin dissolved in the matrix by forming $PbO–SnO_2$. The formation of $PbO–SnO_2$ was influenced by the preheating temperature. The size of $PbO–SnO_2$ particles reached a maximum at a preheating temperature of 873 K, which in turn produced the maximum decrease in recrystallization temperature and the maximum increase in electrical conductivity of the 89.4% cold drawn copper wire.

When preheated above 973 K, the size of the $PbO–SnO_2$ particles decreased, the recrystallization temperature increased and the electrical conductivity decreased due to the dissolution of $PbO–SnO_2$ particles. At a preheating temperature of 1173 K, a Zn_2SnO_4 particle was observed.

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