JOURNAL OF MATERIALS SCIENCE 31 (1996) 2393–2399

Effects of small additions of lead, sulphur and oxygen on annealing characteristics of cold-drawn pure copper

S. AOYAMA
Power System Laboratory, Hitachi Cable Ltd, 4-10-1 Kawajiri, Hitachi 319-14, Japan
M. KANNO
Department of Materials Science, Faculty of Engineering, The University of Tokyo, Tokyo 113, Japan

Softening of cold-drawn wires of a tough pitch copper containing a small amount of lead as well as oxygen and sulphur is enhanced when hot-rolled rods of the copper are heated at 600 °C before cold-drawing. Enhancement causes were examined using wires of pure Cu, Cu–O, Cu–S, Cu–Pb, Cu–Pb–O, Cu–Pb–S, Cu–Pb–S–O. The softening enhancement appearing in the Cu–Pb–S–O specimen was attributed to the decrease in the amount of dissolved Pb and S in the copper matrix due to precipitation during heating at 600 °C. The addition of lead in the presence of oxygen was shown to decrease the solid solubilities of S in the copper matrix.

1. Introduction

Softening of cold-drawn wires of a tough pitch copper containing a small amount of impurity lead has been reported to be enhanced when the hot-rolled copper rods were heated at 600 °C before cold-drawing [1]. The softening enhancement of the tough pitch copper wire containing Pb, S and O as major impurities was more remarkable than that of oxygen free copper wire, which contains only S. The enhancement was attributed to decreased amounts of impurities dissolved in the copper matrix due to the formation of Pb and S precipitates during heating based on results of specific electrical resistivity measurements and energy dispersive X-ray spectroscopy (EDS) analyses of the precipitates [2]. The present study was undertaken to elucidate more clearly the reasons why heat at 600 °C provided softening enhancement of cold-drawn wires.

2. Experimental procedure

Seven kinds of copper ingots (ϕ20 mm × 250 mm) such as pure Cu, Cu–O, Cu–S, Cu–Pb, Cu–Pb–O, Cu–Pb–S and Cu–Pb–S–O were prepared. This choice was based on the fact that the enhancement is most marked in the TPC55 copper rod, which contains ~ 20 at.p.p.m. Pb, ~ 20 at.p.p.m. S, and ~ 1300 at.p.p.m. O [1]. The ingots were made from the following materials: high purity copper (Cu(6N), 99.9999 mass % purity), 99.999 mass % Pb, 99 mass % Cu_2O and a master alloy made from the high purity copper and 99 mass % Cu_2S. Copper ingots of low oxygen concentration were prepared by vacuum melting (< 0.01 Pa) and casting, using a high purity graphite crucible (ash content < 2 mass p.p.m.). Ingots of high oxygen concentration were prepared by melting and casting in an Ar atmosphere, using a high purity alumina crucible of 99.5 mass %. Their chemical compositions are given in Table I.

Each ingot was swaged to a rod 8.2 mm in diameter (reduction in area, 83%), subsequently pickled in HNO_3, and then washed in water. Each rod was heated at 950 ± 10 °C for 86.4 ks and then cooled at a rate of 0.083 $°C\,s^{-1}$ in Ar. After that each rod was divided into two parts. One part was cold-drawn into a wire 2.6 mm in diameter (reduction in area, 90%), and the other part was heated at 600 ± 15 °C for 3.6 ks and then cooled and cold-drawn into a wire 2.6 mm in diameter as described above. These wires were subjected to isochronal annealing at temperatures below 400 °C for 3.6 ks in oil or salt baths and subsequently water quenched.

Tensile tests of cold-drawn or annealed wires were carried out at a tension speed of 0.167 $mm\,s^{-1}$ for a gauge length of 100 mm. Values of half-softening temperature (T_H) were determined from tensile strength versus annealing temperature curves; i.e. after annealing at T_H the specimen gave the mean tensile strength value of the cold-drawn wire and fully annealed ones. The specific electrical resistivities (ρ) for wires of 1 mm diameter were measured at − 196 °C by the four-probe method (distance between potential terminals: about 100 mm).

Structural observations using a transmission electron microscope (TEM) and a scanning electron microscope (SEM, Hitachi-S-800 with KEVEX DELTA 4) were also carried out. In order to facilitate

TABLE I Chemical compositions of specimens (at.p.p.m.)

	O	S	Pb	As	Sb	Ni	Ag	Fe	Bi	Sn	Si
Cu	< 20	< 2	0.3	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	< 0.5	< 2
Cu–O	1390	–	0.9	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	< 0.5	< 2
Cu–S	< 20	18 ± 2	0.3	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	< 0.5	< 2
Cu–Pb	< 20	–	17 ± 3	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	< 0.5	< 2
Cu–Pb–O	1290	–	22 ± 2	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	< 0.5	< 2
Cu–Pb–S	< 20	20 ± 1	22 ± 1	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	2	< 2
Cu–Pb–S–O	1420	14	20 ± 1	< 0.8	< 0.5	< 1	< 0.6	< 1	< 0.3	2	< 2

TABLE II Half-softening temperatures (T_H) of copper wires. The diameter of each copper wire was 2.6 mm

Specimen	Heating conditions (ϕ8 mm)	
	9.50 °C, 86.4 ks	950 °C, 86.4 ks → 600 °C, 3.6 ks
Cu	133	133
Cu–O	136	136
Cu–S	192	186
Cu–Pb	218	207
Cu–Pb–O	240	215
Cu–Pb–S	324	300
Cu–Pb–S–O	181	155

the observations of very small amounts of precipitates, the surface layer of the SEM specimens was removed by electropolishing using an aqueous solution containing 70% H_3PO_4 [2]. Electropolishing was applied after mechanical polishing with SiC or Al_2O_3 powders, because SEM observations of precipitates were hindered by the presence of any residual powders. The nucleation sites of these precipitates were closely examined after etching the specimens in $NH_4OH–H_2O_2$ aqueous solution. Analyses were made on the SEM-observed precipitates by EDS. Most of the observations were done by SEM as mentioned above because it was extremely hard to observe a sufficient number of precipitates by TEM because of their quite low distribution density.

3. Results

3.1. Effects of additions on half-softening temperature

Table II lists the T_H values obtained from isochronal annealing curves of wires 2.6 mm in diameter. The T_H value of pure copper wire (no additives) is 133 °C, independent of the heating conditions before cold-drawing and thus it is the lowest T_H of all the specimens. This experimental T_H is the same as the T_H value for copper wires (99.999 mass % Cu, reduction: 75%) reported by Bigelow and Chen [3]. The T_H value of Cu–O wires is similar to that of pure copper wire, and independent of the heating conditions before cold-drawing. This experimental T_H is almost the same as the literature T_H value of 135 °C for Cu–O wire (350 mass p.p.m. oxygen was added to 99.999 mass % Cu, reduction: 75%) [3]. Therefore the T_H value is hardly affected by oxygen addition to pure copper. The T_H values of all wires containing additives other than oxygen are higher than that of pure copper wire, and the T_H values of all these wires heated at 600 °C before cold-drawing are lower than those of wires heated at only 950 °C before cold-drawing. With respect to the T_H of wires heated at 600 °C before cold-drawing, Cu–Pb–S–O wire shows the lowest T_H except for Cu and Cu–O wires. In other words, softening of the Cu–Pb–S–O wire is most enhanced, compared to that of Cu–S, Cu–Pb, Cu–Pb–O and Cu–Pb–S wires. The T_H value of Cu–Pb–S–O wire (2.6 mm diameter) heated at 600 °C before cold-drawing is 155 °C, and this is higher than the T_H of 144 °C in the previous paper [1], which is obtained by heating of the hot-rolled rod (8 mm diameter) at 600 °C before cold-drawing. Therefore softening enhancement is more marked in the latter wires than the former ones.

In order to clarify the reason for the difference in T_H between the two Cu–Pb–S–O wires, their microstructures just before heating at 600 °C were compared. TEM observations revealed that sub-boundaries are present in the hot-rolled rod and that the dislocation density is higher in the hot-rolled rod than the one heated at 950 °C.

Generally the dislocations influence precipitation behaviour and T_H of wires is affected by the remaining elements dissolved in the copper matrix. Therefore evaluation of the amount of dissolved elements by means of ρ measurements is needed, but it is impossible to measure the ρ value of the hot-rolled rod precisely, because of their large diameter (8 mm diameter). Instead of using a hot-rolled rod, the effects of cold-drawing on the precipitation of S and Pb were examined next using cold-drawn wires (1 mm diameter).

3.2. The effect of cold-drawing on precipitation of Pb and S

First, copper wires (1 mm diameter) prepared for specific electrical resistivity measurements and their heating conditions are given in Table III. The ρ values, which are affected by solute additives in the copper, are shown in Fig. 1. The ρ of the high purity copper wire (Cu(6N)), used as the reference material (Table III (E)), is 1.96 nΩm. For condition (A), the high ρ values of Cu–S and Cu–Pb–S–O wires are due to S and Pb being dissolved in the copper matrix because of water quenching after heating at 950 °C. The ρ of Cu–Pb–S–O wire is slightly higher than that

TABLE III Heating conditions of copper wires (1 mm diameter) prepared for electrical resistivity measurements (WQ: water quenching)

	Heating conditions	Copper wires (ϕ1 mm)
(A)	$\boxed{\phi 8\ \text{mm}} \rightarrow \boxed{950\,^\circ\text{C}\ 86.4\ \text{ks}} \xrightarrow{\text{Cold-drawing}} \boxed{\phi 1\ \text{mm}} \rightarrow \boxed{950\,^\circ\text{C}\ 86.4\ \text{ks}\ \text{WQ}}$	Cu Cu–S Cu–Pb–S–O
(B)	$\boxed{\phi 8\ \text{mm}} \rightarrow \boxed{950\,^\circ\text{C}\ 86.4\ \text{ks}} \xrightarrow{\text{Cold-drawing}} \boxed{\phi 1\ \text{mm}} \rightarrow \boxed{950\,^\circ\text{C}\ 86.4\ \text{ks}\ \text{WQ}} \rightarrow \boxed{600\,^\circ\text{C}\ 3.6\ \text{ks}\ \text{WQ}}$	Cu Cu–S Cu–Pb–S–O
(C)	$\boxed{\phi 8\ \text{mm}} \rightarrow \boxed{950\,^\circ\text{C}\ 86.4\ \text{ks}} \xrightarrow{\text{Cold-drawing}} \boxed{\phi 1\ \text{mm}} \longrightarrow \boxed{600\,^\circ\text{C}\ 3.6\ \text{ks}\ \text{WQ}}$	Cu Cu–S Cu–Pb–S–O
(D)	$\boxed{\phi 8\ \text{mm}} \rightarrow \boxed{950\,^\circ\text{C}\ 86.4\ \text{ks}} \xrightarrow{\text{Cold-drawing}} \boxed{\phi 1\ \text{mm}} \longrightarrow \boxed{600\,^\circ\text{C}\ 10.8\ \text{ks}\ \text{WQ}}$	Cu Cu–S Cu–Pb–S–O
(E)	$\boxed{\phi 1\ \text{mm}} \rightarrow \boxed{400\,^\circ\text{C}\ 3.6\ \text{ks}}$	Cu (6N)

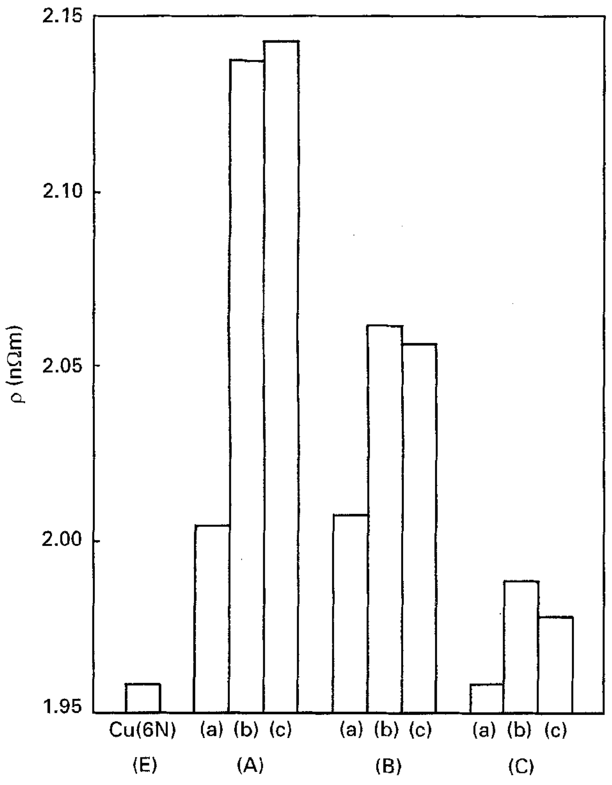

Figure 1 Specific electrical resistivity versus heating conditions of copper wires (1 mm diameter). (a) Cu; (b) Cu–S; (c) Cu–Pb–S–O. Conditions, (A), (B), (C) and (E), are described in Table III.

of the Cu–S wire. The ρ of Cu for conditions (A) and (B) are higher than that of Cu(6N); this is due to a slight contamination through processing. (Cu(6N) specimen was almost free of any contamination because the 1 mm wire was made from an as-received rod through cold-drawing without melting and casting.)

For condition (B), the ρ of Cu–Pb–S–O wire is lower than that of Cu–Pb–S–O wire for condition (A); this means the amounts of S and Pb dissolved in the copper matrix have decreased. The ρ of Cu–Pb–S–O wire is slightly lower than that of Cu–S wire in spite of the presence of Pb, O and S in the former wire. This indicates that the amount of dissolved S of Cu–Pb–S–O wire is lower than that of Cu–S wire. The ρ values of pure Cu, Cu–S and Cu–Pb–S–O wires made under condition (C) are remarkably lower than those made under condition (B) and they approach the ρ of Cu(6N) wire. This shows the amounts of S and/or Pb being dissolved in the copper matrix are much less in each wire for condition (C) than for condition (B). This is because the high density of dislocation promotes precipitation of S and/or Pb.

To confirm the results described above, changes in ρ of wires with heating time at 600 °C were examined using copper wires (A), (C) and (D) (Table III). The changes are plotted in Fig. 2 and they confirm that the precipitation of S in Cu–Pb–S–O wire is more enhanced than that in Cu–S wire.

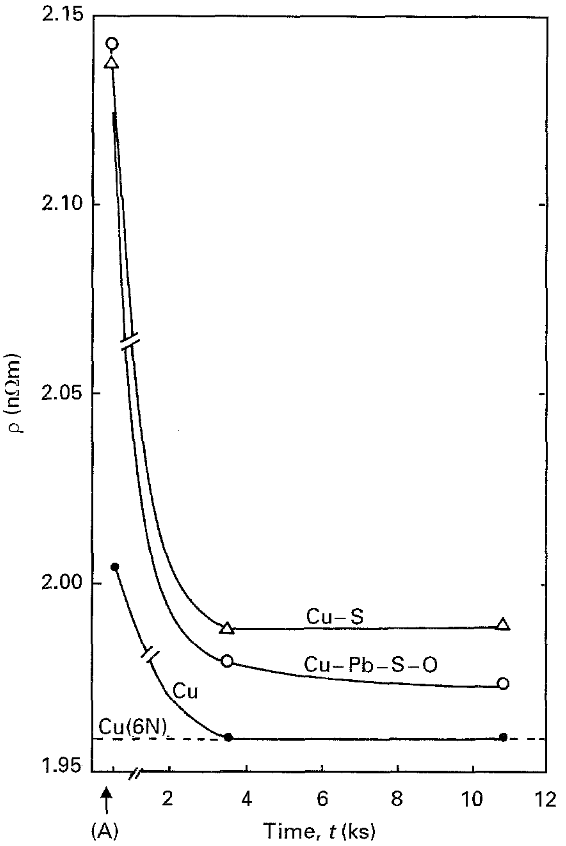

Figure 2 Changes in specific electrical resistivity of cold-drawn wires (1 mm diameter) with heating time at 600 °C. Condition (A) is described in Table III.

Secondly, SEM observations were carried out for Cu, Cu–S and Cu–Pb–S–O wires (1 mm diameter) after heating at 950 °C for 86.4 ks. No precipitates containing S and/or Pb appear in any wire heated at 950 °C for 86.4 ks. This supports the specific resistivity measurements which showed that all of the solutes (S and Pb) are dissolved in the copper matrix of that wire. Then, structural observations were carried out for three kinds of wires (1 mm diameter) after heating at 600 °C for 10.8 ks (Table III (D) and Fig. 2). Precipitates containing S appear in Cu–Pb–S–O and Cu–S wires. Fig. 3a and b show SEM images of a precipitate including Cu_2O in the Cu–Pb–S–O wire. Fig. 3c reveals that the fine particle shown in Fig. 3b contains Pb and S. Particles of Cu_2O are considered to act as precipitation sites for this kind of precipitate. Fig. 4a and b show SEM images of a precipitate observed inside a grain. Fig. 4c shows the results of EDS analysis on the particle indicated in Fig. 4b. The precipitates, containing Pb and S, are observed in triangular etch pits which correspond to edge dislocations [4]. These precipitates, of about 0.2 μm diameter are regarded to form randomly on the dislocation inside the grain.

Fig. 5a and b show SEM images of precipitates in Cu–S wire and Fig. 5c shows EDS analysis results on a particle of about 0.7 μm diameter precipitated on the grain boundary. Elements S and Cu appear in the EDS spectrum obtained from the precipitate. These elements are also detected on the smaller precipitates with etch pits shown in Fig. 5b. Therefore the precipitates are identified as Cu_2S. The mean particle size of Cu_2S observed inside the grain is 0.05 μm, which is smaller by one order of magnitude than the particles on the grain boundary. This may be due to the fact that diffusion of S in the grain boundary is faster than that of S inside the grain. The distribution density of Cu_2S precipitates inside the grain of Cu–S wire is about $1.5 \times 10^{11}\ m^{-2}$, which is lower by one order of magnitude than the dislocation density of $10^{12}\ m^{-2}$ [5] for a cold-worked specimen. This may be due to

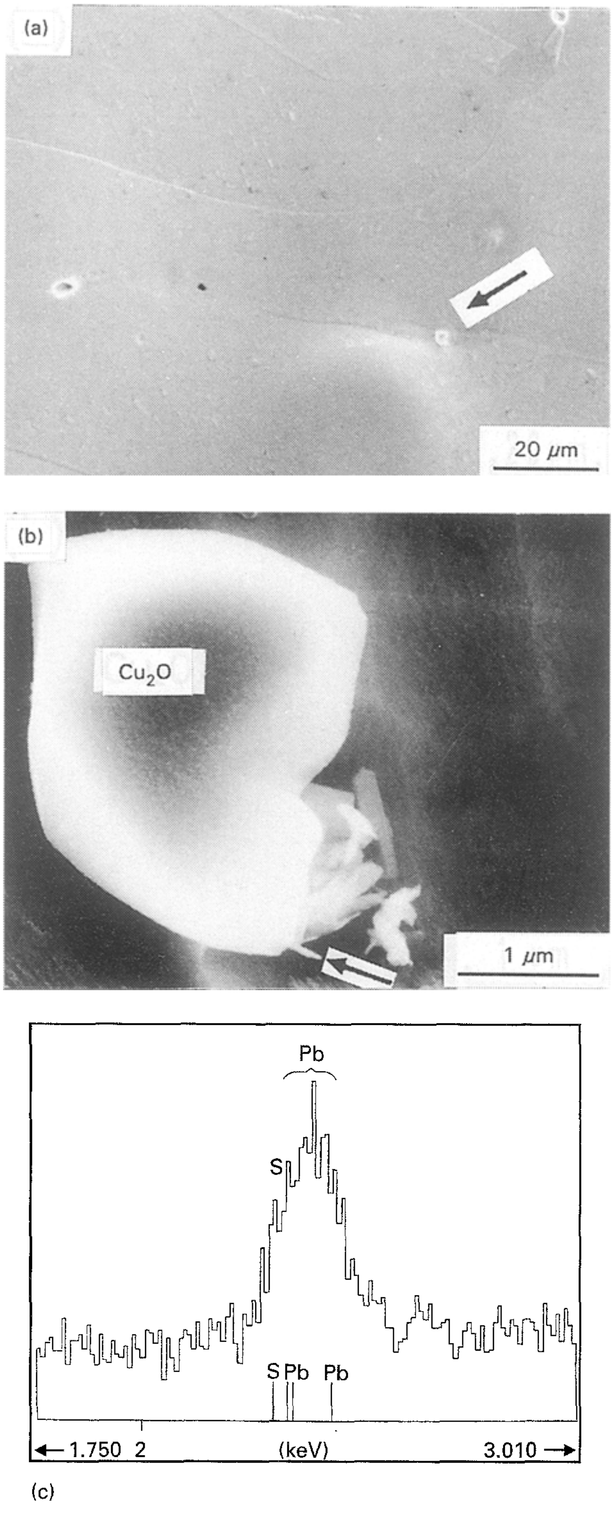

Figure 3 SEM images and results of EDS analysis on a particle. Cu–Pb–S–O wire (1 mm diameter) was heated at 600 °C for 10.8 ks and then water quenched. (a) Low magnification. (b) High magnification. (c) Results of EDS analysis on arrowed particle in (b).

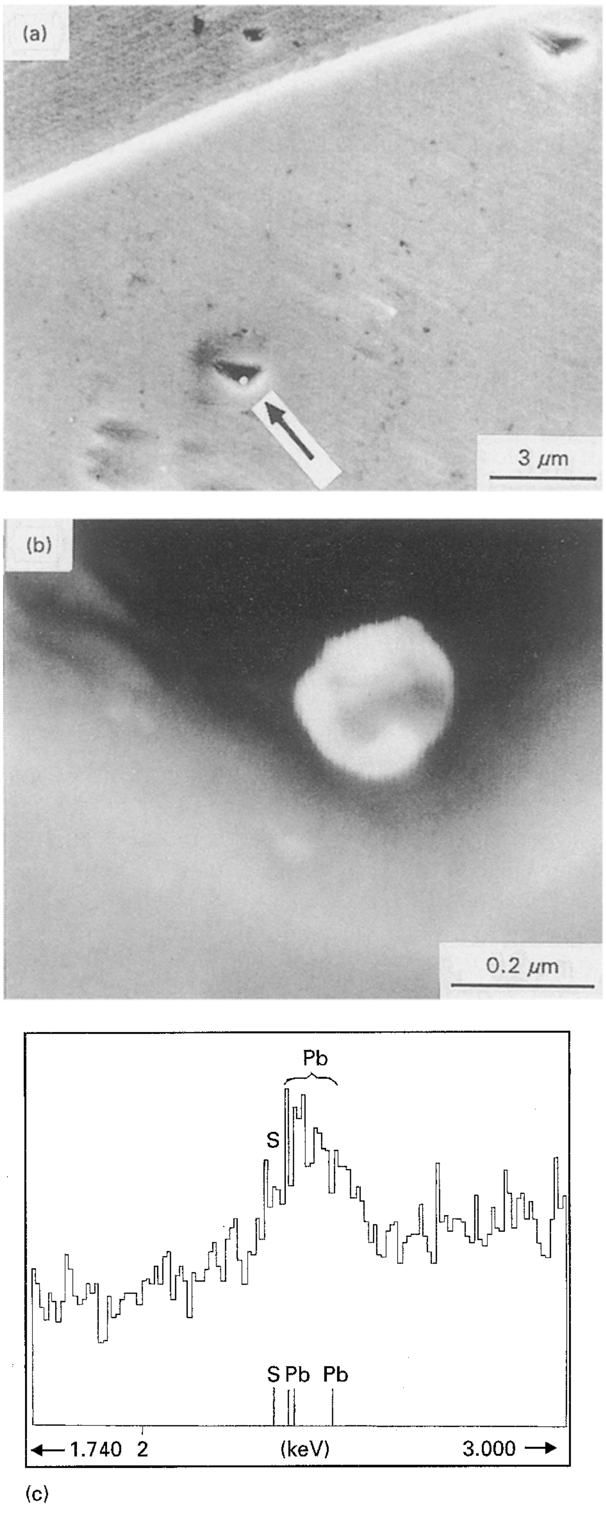

Figure 4 SEM images and results of EDS analysis on a particle. Cu–Pb–S–O wire (1 mm diameter) was heated at 600 °C for 10.8 ks and then water quenched. (a) Low magnification. (b) High magnification. (c) Results of EDS analysis on particle in (b).

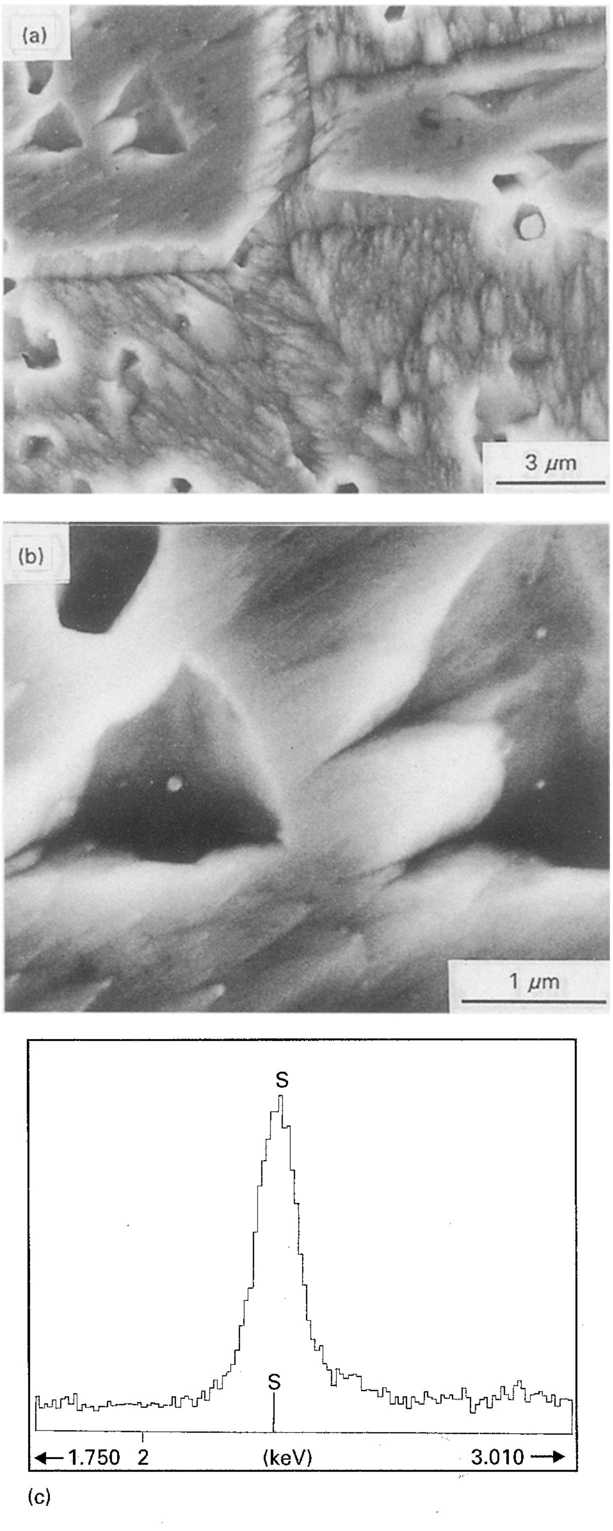

Figure 5 SEM images and results of EDS analysis on a particle. Cu–S wire (1 mm diameter) was heated at 600 °C for 10.8 ks and then water quenched. (a) Low magnification. (b) High magnification. (c) Results of EDS analysis on the particle on grain boundary in (a).

recovery occurring in an early stage of heating at 600 °C.

Finally, the solubility limit of each element in copper was examined. The solubility limit of S in copper has been reported as 2 at.p.p.m. at 600 °C [6], but the limits of O and Pb in copper are not clearly known yet. Therefore the amounts of dissolved O and Pb in copper were evaluated. The ρ values of Cu(6N), Cu–O, Cu–Pb and Cu–Pb–O wires (1 mm diameter) were measured after heating them at 800 and 600 °C for 86.4 ks and the results are shown in Fig. 6. The values must reflect the solubility limits at these temperatures because the heating time is long enough according to the results shown in Fig. 2. The ρ values of Cu(6N) and Cu–O wires do not change with heating temperature, but those of Cu–Pb and Cu–Pb–O wires heated at 600 °C are lower than the ρ values of these wires when heated at 800 °C.

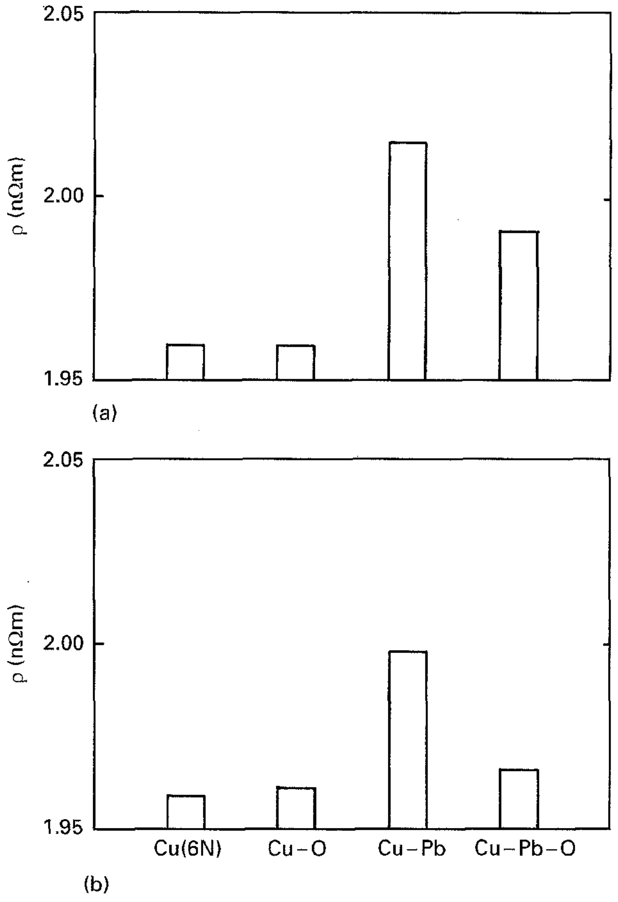

Figure 6 Relation of heating temperature and specific electrical resistivity of cold-drawn copper wires (1 mm diameter). (a) Heated at 800 °C for 86.4 ks and then water quenched. (b) Heated at 600 °C for 86.4 ks and then water quenched.

These results show that the amount of Pb dissolved in copper heated at 600 °C is smaller than that in copper heated at 800 °C. The amount of solute O in the copper matrix is calculated to be below 1 at.p.p.m. at 600–800 °C based on literature data [7]. This concentration of solute O in copper is much lower than the reported value (67.5 at.p.p.m. O at 550 °C [8]). Therefore, the effect of oxygen on ρ is regarded to be negligibly small. The ρ of Cu–Pb–O wire is also unaffected by O itself; the main effect is due to Pb. For the 600 °C heated wires, the solubility limit of Pb in Cu–Pb–O wire (2.3 at.p.p.m.) decreases to about one sixth of that in Cu–Pb wire (12.9 at.p.p.m.). This demonstrates that the added element O decreases the solubility limit of Pb in copper.

Following the same line of reasoning, it can be pointed out that the presence of O and Pb decreases the solubility limit of S in the Cu matrix of the Cu–Pb–S–O system, since the Cu–Pb–S–O wire shows lower ρ values than the Cu–S and Cu–Pb wires after heating at 600 °C as shown in Figs 1, 2 and 6. In other words, the amounts of dissolved Pb and S are decreased by the presence of O. The presence of O as well as that of Pb is said to be indispensable to the marked softening enhancement of cold-drawn Cu–Pb–S–O wires.

TABLE IV Standard free energies of formation (ΔG^*) of several sulphides

Compounds	ΔG° at 600 °C (kJ mol^{-1})	Reference
FeS_2	− 18	
CuS	− 41	
PbS	− 87	[9]
Cu_2S	− 104	
FeS	− 105	
$CuFeS_2$	− 178	[10]

4. Discussion

It was found that the softening enhancement in the quarternary Cu–Pb–S–O cold-drawn wires was due to the decreased amounts of dissolved Pb and S. Therefore, the softening enhancement in cold-drawn wires of the tough pitch copper containing a trace impurity Pb could be attributed to the decrease in solubility limits of S and Pb in the copper matrix. It has been shown that the presence of O decreases the solubility limit of Pb in the Cu–Pb–O system and the solubility limits of Pb and S in the Cu–Pb–S–O system. The decreased amounts of dissolved Pb and S are directly brought about by the precipitation of compounds heated at 600 °C. This precipitation must be caused by heterogeneous nucleation, since these precipitates are observed on etch pits which are regarded as corresponding to dislocations and on grain boundaries and at interfaces between Cu_2O particles and the matrix.

Next, consideration was given to whether the precipitates which contained Pb and S were PbS or not. Table IV [9, 10] lists standard free energies (Gibbs free energy ΔG° at 600 °C) of formation of several kinds of sulphides. According to the listed ΔG°, PbS cannot exist in copper because PbS is unstable compared with Cu_2S. Therefore the precipitates cannot be PbS. On the other hand, the ΔG° value of ternary $CuFeS_2$ is lower than the binary compound FeS_2. Thus there must be a possibility that the ternary element X stabilizes the compound which contains Pb and S. Presumably the precipitates may be a Pb–S–X (X = Cu or O) complex. In a previous paper [2], the elements Sn and/or Fe together with Pb and S were also detected from the precipitates in hot-rolled rod of tough pitch copper.

5. Conclusions

Reasons were examined as to why softening of cold-drawn wire of a tough pitch copper containing small amounts of Pb, S and O was enhanced by heating at 600 °C prior to cold-drawing. Detailed resistivity measurements and structural observations were made for pure Cu, Cu–O, Cu–S, Cu–Pb, Cu–Pb–O, Cu–Pb–S and Cu–Pb–S–O cold-drawn wires before and after heating. The softening enhancement was attributed to the decrease in the amount of dissolved Pb and S due to precipitation during heating at 600 °C. It was shown that addition of a small amount of lead caused a large decrease in the solid solubility of S in the presence of oxygen.

References

1. S. AOYAMA, M. ONUKI, Y. MIYAKE and R. URAO, *J. Mater. Sci.* **26** (1991) 3775.
2. S. AOYAMA and M. KANNO, *J. Jpn Inst. Metals* **58** (1994) 1126.
3. L. K. BIGELOW and H. H. CHEN, in Proceedings of the CDA-ASM Conference on Copper, October 1972 (COD-ASM, Ohio, 1972) p. 16.
4. S. KITAZIMA, *Bull. Jpn. Inst. Metals* **13** (1974) 105.
5. S. KARASHIMA, in "Strength of Metallic Alloys", edited by K. Monma (The Japan Institute of Metals, Sendai, 1972) pp. 70–76 (in Japanese).
6. R. P. ELLIOTT, in "Constitution of Binary Alloys", First Supplement (McGraw Hill, New York, 1964) pp. 381–383.
7. P. GREGORY, A. J. BANGAY and T. L. BIRD, *Metallurgia*, **71** (1965) 207.
8. M. HANSEN and K. ANDERKO, in "Constitution of Binary Alloys", 2nd Edn (McGraw Hill, New York, 1958) pp. 604–605.
9. R. P. ELLIOTT and M. GLEISER, in "Thermochemistry for Steelmaking", Vol. 1, edited by C. Morris (American Iron and Steel Institute, Addison Wesley, Massachusetts, 1960) pp. 243–246.
10. E. T. TURKDOGAN, in "Physical Chemistry of High Temperature Technology" (Academic Press, New York, 1979) pp. 10–18.

Received 23 January
and accepted 17 October 1995