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Effects of lead on annealing properties of cold-drawn copper wire

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Cold-drawn copper wires were made by cold-drawing after hot-rolling tough pitch copper rods which had been pre-heated at 673–973 K. The wires were annealed at 293–673 K to study their annealing properties. The effects of pre-heating the hot-rolled tough pitch copper rods, including lead, on the recrystallization behaviour of the cold-drawn copper wires were investigated by tensile tests, electrical resistivity measurements and structural observations. The half-softening temperature of annealed cold-drawn copper wires decreased when the hot-rolled copper rods were pre-heated at 873 K before cold-drawing. This behaviour was attributed to separation of lead dissolved in the copper matrix which is known to lower the half-softening temperature.

1. Introduction

It is well known that some properties of metallic materials are influenced by not only the final annealing temperature, but also intermediate working conditions and heat treatments. In copper wires used for magnet coils, the recrystallization temperature or the half-softening temperature of the cold-drawn copper wires is also influenced by casting conditions, hot-working conditions [1–5] and impurity contents [6–21].

As copper wires for industrial use contain small amounts of impurities and are produced by different processes, changes in their recrystallization temperature are complicated. In the present study, the recrystallization behaviour of cold-drawn tough pitch copper, containing lead and tin, was investigated after pre-heating hot-rolled copper rods. Comparisons were made with copper rods formed by different processes.

2. Experimental procedure

Hot-rolled copper rods of three kinds of raw material, i.e. Southwire continuous copper rod (SCR), oxygen-free copper (OFC) and hot-rolled tough pitch copper (TPC1 and TPC55), were used to make cold-drawn copper wires. Their chemical compositions are given in Table I.

A flow chart of specimen preparation is shown in Fig. 1. Before cold-drawing, hot-rolled copper rods were pre-heated at 673–973 K for 0.6–3.6 ks in air, and were pickled in dilute H_2SO_4 to remove the surface oxide layer. The pre-heated rods were cold-drawn into 2.6 mm diameter wires and annealed isochronally at 293–673 K for 3.6 ks. The obtained wires were quenched after annealing with oil and salt baths.

Tensile tests of annealed wires were carried out at a strain rate of $0.3\ mm\ s^{-1}$ for a gauge length of 250 mm. Half-softening temperature was determined by measuring the tensile strength as a function of the final annealing temperature. The half-softening temperature is given by the annealing temperature at the average tensile strength of the cold-drawn and fully annealed wires. Electrical conductivity of the pre-heated copper rods was measured at 293 K by the four-probe method for resistivity (distance between potential traps: 500 mm). The structure of the copper rods was observed by scanning electron microscopy (SEM) and analysed by energy and wavelength dispersive X-ray spectroscopy (EPMA).

3. Results

Cold-drawn copper wires made from the hot-rolled copper rods which were pre-heated at 673–973 K for 3.6 ks were annealed at 293–673 K.

Fig. 2 shows the changes in tensile strength and elongation of the TPC1 copper wires as a function of annealing temperature of cold-drawn copper wire, T_A, and pre-heating temperature of hot-rolled copper rod, T_H. The decrease in tensile strength and increase in elongation at low annealing temperature are marked in the cold-drawn copper wire pre-heated at 873 K before cold-drawing.

Fig. 3 shows these changes for TPC55 copper wires. The tensile strength and elongation of cold-drawn TPC55 copper wires change remarkably with T_H. The abrupt fall in tensile strength is caused by recrystallization [2]. The half-softening temperature was remarkably low when the hot-rolled copper rod was pre-heated at 873 K. The cold-drawn copper wire

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TABLE I Chemical compositions (mass p.p.m.) of the hot-rolled copper rods for cold-drawing

Specimen	O	Pb	Sn	Fe	S	Ag	Sb	Ni	As	Se	Te	Cr	Co	Mn	P	Cd
TPC1	200	1	1	5	11	8	< 1	1	2	0.3	0.3	< 6	< 4	< 2	< 1	< 1
TPC55	320	55	57	16	9	6	8	4	2	0.7	0.6	< 6	< 4	< 2	< 1	< 1
SCR	310	1	1	5	11	7	< 1	1	< 1	1.7	0.7	< 6	< 4	< 2	< 1	< 1
OFC	3	2	1	6	10	6	1	1	< 1	0.4	0.5	< 6	< 4	< 2	< 1	< 1

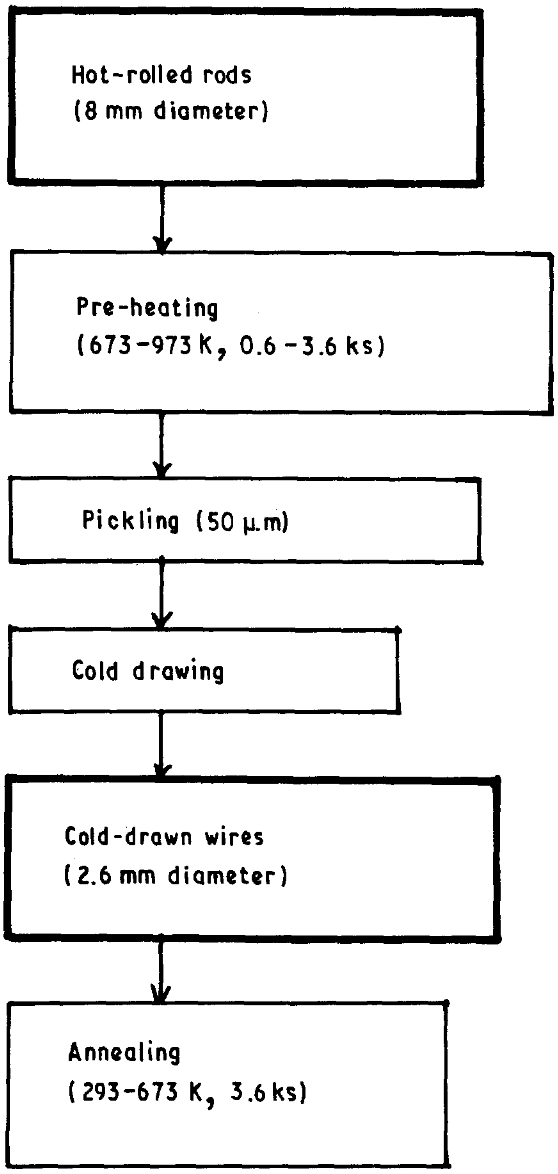

Figure 1 Specimen preparation.

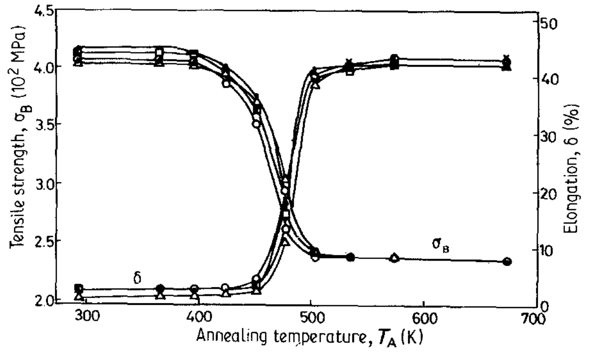

Figure 2 Changes in tensile strength and elongation as a function of T_A and T_H (TPC1). (●) As-hot-rolled, (△) $T_H = 973$ K, (□) $T_H = 773$ K, (×) $T_H = 673$ K, (○) $T_H = 873$ K.

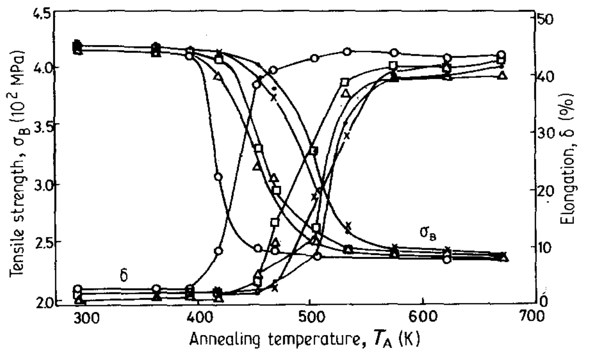

Figure 3 Changes in tensile strength and elongation as a function of T_A and T_H (TPC55). For key, see Fig. 2.

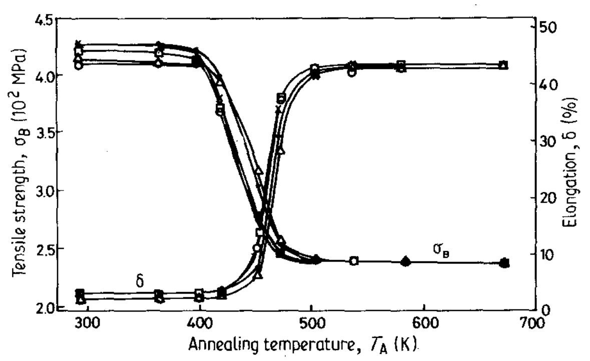

Figure 4 Changes in tensile strength and elongation as a function of T_A and T_H (SCR). For key, see Fig. 2.

without pre-heating has the highest half-softening temperature. The softening curves of the TPC55 copper wires which were pre-heated at 673, 773 and 973 K are between the curves of hot-rolled copper rod without pre-heating, and that pre-heated at 873 K.

Fig. 4 shows the tensile strength and elongation changes for SCR copper wires. The softening of cold-drawing copper wire without pre-heating takes place at a higher annealing temperature than for pre-heated copper wires. The softening of cold-drawn copper wire pre-heated at 873 K takes place at a comparatively lower annealing temperature than those of other pre-heated copper wires. However, the changes in the softening curves of cold-drawn SCR copper wires with pre-heating are small.

Fig. 5 shows the changes of OFC copper wires. This wire recrystallizes at a higher annealing temperature than TPC1, TPC55 and SCR copper wires.

The half-softening temperatures obtained from isochronal annealing curves of the four kinds of copper wire are summarized in Fig. 6 as a function

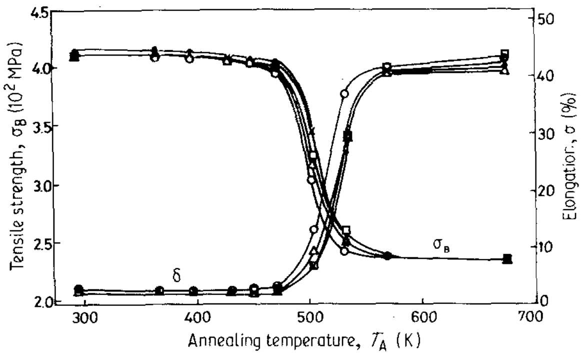

Figure 5 Changes in tensile strength and elongation as a function of T_A and T_H (OFC). For key, see Fig. 2.

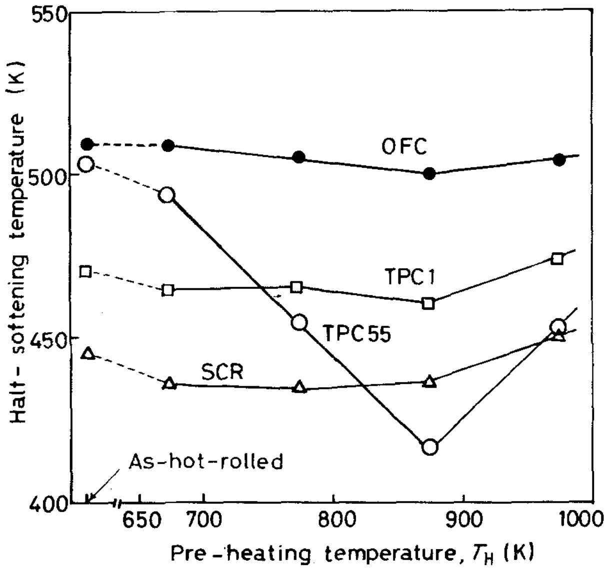

Figure 6 Changes in half-softening temperature as a function of pre-heating temperature of hot-rolled copper rods.

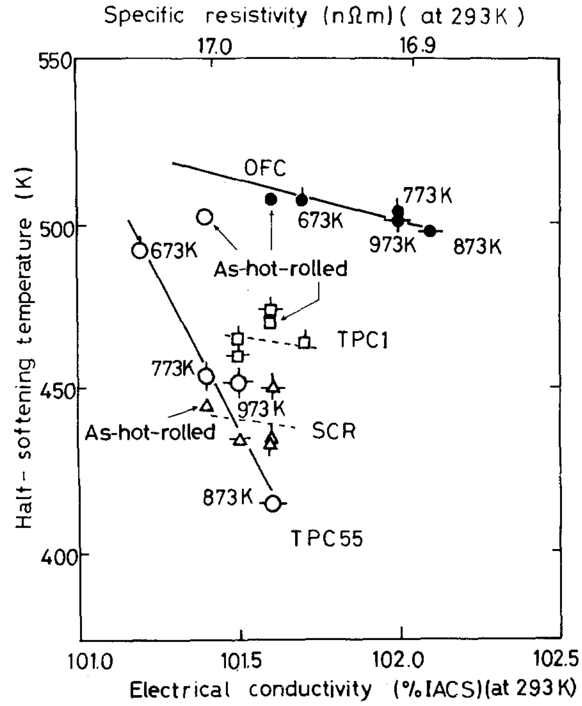

Figure 7 Relations between half-softening temperature and electrical conductivity of pre-heated copper rods.

of the pre-heating temperatures, T_H, of hot-rolled copper rods. The half-softening temperatures of the copper wires without pre-heating are OFC > TPC55 > TPC1 > SCR. The reasons why the half-softening temperature of cold-drawn OFC copper wire without pre-heating is the highest are attributed to small amounts of sulphur and oxygen being contained in the rods [6] and its large crystal grains [2]. The half-softening temperature of cold-drawn SCR copper wires is the lowest because these wires have a much smaller crystal grain size than the others, and they contain much oxygen and many Cu_2O particles. The value of cold-drawn TPC55 copper wires is as high as the cold-drawn OFC copper wires. The changes in half-softening temperature of cold-drawn OFC, TPC1 and SCR copper wires by pre-heating, are small, but the change of cold-drawn TPC55 copper wires is remarkably large, as shown in Fig. 6. Therefore, lead and tin in the TPC55 copper can affect the half-softening temperature.

4. Discussion

Hot-rolled copper rods of TPC55, containing lead and tin, have a low half-softening temperature when they are pre-heated at 873 K. In order to analyse this phenomenon, the half-softening temperatures have been plotted in Fig. 7 as a function of the electrical conductivity of pre-heated copper rods. Pre-heating temperatures of hot-rolled TPC55 and OFC copper rods are also shown in the same figure. The half-softening temperature decreases with increasing electrical conductivity of the pre-heated copper rods, generally becomes lower when the solute impurities in the copper rods are precipitated or separated by pre-heating. In TPC55 and OFC, the hot-rolled copper rods pre-heated at 873 K have a higher electrical conductivity and lower half-softening temperature than the copper rods pre-heated at 973 K. In TPC1 and SCR, the ranges for changes in half-softening temperature and electrical conductivity are narrow. It is considered that some metallic impurities had already precipitated or separated before pre-heating of the hot-rolled copper rod. The half-softening temperature of cold-drawn TPC55 copper wires decreases rapidly with pre-heating time in comparison with cold-drawn TPC1, OFC and SCR copper wires, as shown in Fig. 8. It seems that impurities such as lead migrate and precipitate or separate within the pre-heating time of 1.2 ks.

The effects of impurities of tin, lead and iron on recrystallization of cold-drawn copper wires are discussed for TPC55. Lead, tin and iron in tough pitch copper can separate or precipitate as oxides [10, 15–18], and lead and iron can also precipitate as PbS [20] and $Cu_2SFe_2S_3$ [20], respectively. However, precipitates of lead, tin and iron have not been detected in previous works, so the precipitates in TPC55 copper rod were examined by SEM.

Fig. 9 show typical examples of the scanning electron micrographs and EPMA line scanning profiles on the longitudinal section of a TPC55 copper rod pre-heated at 873 K for 3.6 ks. The Cu_xO particles in the

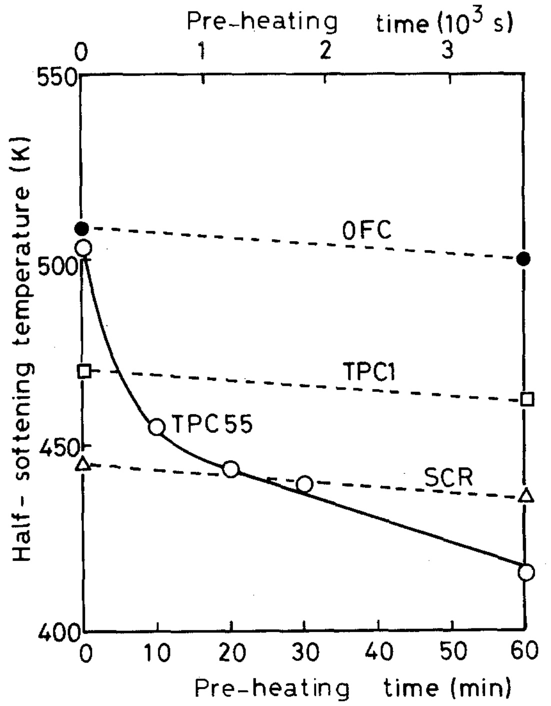

Figure 8 Changes in half-softening temperature as a function of pre-heating time of hot-rolled copper rods at 873 K.

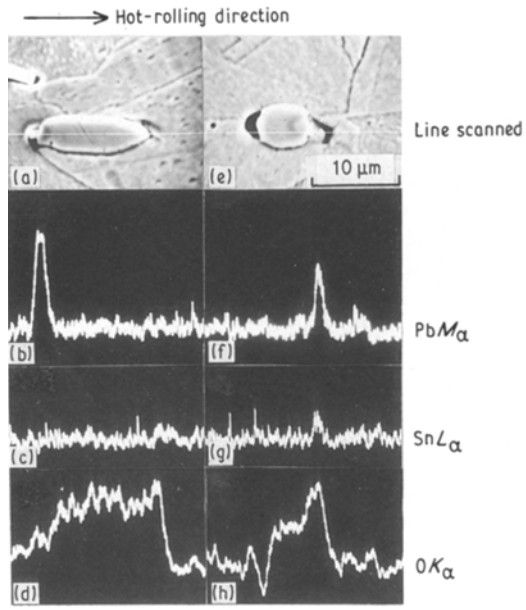

Figure 9 Scanning electron micrographs and EPMA line scanning profiles on the longitudinal section of a hot-rolled TPC55 copper rod pre-heated at 873 K for 3.6 ks. (a, e) Scanning electron micrographs, (b, f) PbM_α, (c, g) SnL_α, (d, h) OK_α.

copper rod were identified by wavelength dispersive EPMA and a polarization microscope, i.e. the characteristic X-ray of OK_α was detected from the particles by EPMA, and red particles showing Cu_2O were observed by polarization microscopy. In Fig. 9 a–d, PbM_α, but no SnL_α characteristic X-rays were detected from the particle in contact with Cu_2O particle. A weak OK_α characteristic X-ray was detected in the particle which contained lead. In Fig. 9e–h, PbM_α and SnL_α rays were detected, and the particle in contact with the Cu_2O particle seems to consist of lead, tin and oxygen, because PbM_α, SnL_α and OK_α rays were detected from the same position, so that lead oxide and tin oxide must exist in the copper rod.

Dissolved tin cannot precipitate by itself from the copper matrix, because the solubility limit (about 15 wt % at 873 K [22]) of tin in copper is much larger than the tin content in TPC55. Therefore, the observed tin oxides seem to be products formed in the molten copper [10]. Dissolved lead in copper separates according to its known solubility curve, because the lead solubility limit in copper is extremely small at 873 K [19, 22]. In the phase diagram of the Pb–O system [22], molten lead with oxygen coexists with PbO of the solid phase which is stable up to about 1157 K. From listed formation energies of oxides [23], oxides of iron, tin and lead are more stable than cuprous oxide, where iron and tin oxides are more stable than lead oxide. It is considered that some of the lead atoms are cast and hot-rolled in a solute state in copper so that lead has a weaker affinity for oxygen compared with tin. The solute lead separates in the copper crystal boundaries and grains during pre-heating. In particular, lead easily separates in the joint of the three grain boundaries and in the boundary between the Cu_2O particle and copper, so that oxide or lead was often observed adjacent to Cu_2O.

Lead oxide is formed by the interaction of separated molten lead and Cu_2O particles as follows. First, Cu_2O forms by a eutectic reaction. Secondly, the formed Cu_2O becomes small Cu_2O particles by deformation. Thirdly, molten lead including a small amount of copper separates in contact with Cu_2O particles at 873 K. The oxygen of Cu_2O redissolves into the molten lead and forms lead oxide. The half-softening temperature of cold-drawn TPC55 copper wire pre-heated at 973 K is higher than that of cold-drawn TPC55 copper wire pre-heated at 873 K, as shown in Fig. 6. This is due to the decrease in small lead particles in copper pre-heated at 973 K because of the increase in lead dissolved in the copper matrix at 973 K, i.e. the solubility limit of lead in copper at 973 K is larger than that at 873 K. As the solubility of tin in copper is large, it is difficult to explain the difference between the half-softening temperature of cold-drawn copper wire pre-heated at 973 and 873 K by the tin solubility change at the pre-heating temperature. With respect to the effect of tin in copper, several groups [10, 15, 16] have reported that tin in tough pitch copper has no effect on electrical conductivity of copper because tin in molten copper easily forms tin oxide. The enhanced recrystallization is due rather to the separation of lead in copper matrix [21].

5. Conclusions

Changes in annealing characteristics of pre-heated hot-rolled copper rods with lead, tin and oxygen have been studied. The results are summarized as follows.

The half-softening temperature of cold-drawn copper wire, with lead and tin, was significantly decreased when hot-rolled copper rods were pre-heated at 873 K. Cold-drawn copper wires have low half-softening temperature when the electrical conductivity of hot-rolled copper rod was high because of precipitation or separation of impurities. Lead oxide, lead and tin oxides were observed here as particles in contact with Cu_2O particles.

It can be concluded from these experimental results that the decrease in half-softening temperature of cold-drawn copper wire after pre-heating at 873 K may be due to the separation of lead dissolved in the copper matrix.

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