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Characterization of fire-refined copper recycled from scrap

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Certain properties of fire-refined copper recycled from scrap have been characterized. A method is presented to calculate the half-softening temperature and the annealing temperature that allows 30% elongation to failure, hereinafter referred to as $\varepsilon_{30\%}$ temperature, on the basis of hardness measurements. The relation between ultimate strain and ultimate elongation has been studied and is described by a mathematical expression that seems to be independent of copper composition and annealing temperature. The microstructure of annealed samples reveals that recrystallization begins at half-softening temperature, and is ending at $\varepsilon_{30\%}$ temperature, although grain growth is not observed. An optimal range of oxygen content has been found that gives the minimum $\varepsilon_{30\%}$ temperature for each studied composition, and a mathematical expression with which to calculate those minimum temperatures is developed. The influence of cold-working degree on $\varepsilon_{30\%}$ temperature is also described; these temperatures reach a constant minimum value for each composition at high deformation degrees of cold-working. © *1999 Kluwer Academic Publishers*

1. Introduction

In 1996 total copper production worldwide was 15,604,000 tons, 36% of which was obtained from scrap [1]. Its main application is the production of copper wire, the most important property being its electrical conductivity.

Copper obtained from molten scrap with impurities is commonly sold as fire-refined copper for alloying purposes or cast into anodes for electrorefining [2]. Due to its impurity content, it is rarely used as electrical conductor.

There is general agreement in the secondary copper industry that since the purity of copper scrap is between 95–99.5%, the electrical and mechanical properties required of the final product make electrolytical refining an unavoidable step. Good workability is characterized by low annealing temperatures, low hardness, low tensile strength, a large elongation number and a large elongation to failure. These characteristics, together with an electrical conductivity higher than 101%I.A.C.S., are commonly associated only with electrolytically-refined copper. Two immediate consequences of this general agreement have been the lack of research on the possibilities of fire-refined copper scrap, and few attempts to characterize fire-refined copper.

The literature describes the effects of individual impurities in high purity copper, on annealability and electrical conductivity. The papers of Smart *et al*. are classically considered as the first studies on this subject [3–6]. In 1973, an ASTM joint task group reviewed the experimental data [7].

Fire-refined copper melt from scrap contains between 100 and 800 ppm ($mg \cdot kg^{-1}$) of total impurities, with lead, tin, nickel, zinc, iron, silver and antimony as the most significant. In consequence, it is difficult to establish the relationship between composition, casting conditions, hot working parameters, annealing temperature and electrical conductivity, because interactions between the impurities are still unknown.

This paper presents some of the most significant results, obtained over two years of research, with a systematic characterization of the properties of copper wire recycled from scrap, obtained by smelting, fire-refining and continuous casting at an industrial scale of a hundred tons per day. It also shows that this recycling procedure can, in certain conditions, achieve

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TABLE I Compositions (ppm) of studied samples

Sample	Oxygen	Pb	Ni	Sn	Ag	Sb	Fe	Zn
1	205	5	4	13	13	—	7	7
2	89	15	25	82	20	8	30	16
3	163	460	14	23	18	20	21	15
4	165	68	40	133	42	19	30	23
5	154	236	106	121	59	17	27	57

electrical and mechanical properties of the same order as for electrolytically-refined copper [8].

2. Experimental

Samples of different composition of hot-rolled recycled 7.85 mm diameter copper wire from continuous casting were used to make cold-drawn 1.8 mm diameter copper wires. Initial compositions of copper scrap ranged between 95 and 99.6% copper, usually with 1000–7000 ppm of total impurities such as lead, zinc, tin, iron, antimony, nickel and silver. After smelting and fire-refining, there were selected the studied samples from different castings, whose compositions are shown in Table I.

In tensile tests, strength-elongation values from the 1.8 mm diameter copper wire of each studied sample were determined on test pieces of 100 mm gauge-length after different thermal treatments. A Hounsfield Tensometer with a constant elongation speed of 0.1 $\mathrm{mm \cdot s^{-1}}$ was used.

Electrical conductivities were measured on test pieces of the 1.8 mm diameter cold-drawn wire of 1000 mm length with a Resistomat Mikroohmmeter Typ 2302.

The isothermal treatments of the 1.8 mm diameter cold-drawn copper wires were carried out with 200 mm long test pieces, cut from 1.8 mm cold-drawn wires plunged in a salt bath (40% mass of $NaNO_2$ and 60% mass of KNO_3) for a certain time.

Half-softening temperature (T_H) is the annealing temperature at which the increase in the strength between the maximum (after cold-drawing) and the minimum (after complete annealing) is halved. The specimens studied present, after cold-drawing, ultimate tensile strengths between 372 and 392 MPa, while after annealing the ultimate tensile strength falls to between 186 and 206 MPa.

The study of the microstructure at different annealing temperatures for 1.8 mm diameter wire of the sample number 5 was performed after preparing the sample by grounding and polishing until 1 μm and finally etching with alcoholic $FeCl_3$.

To determine the half-softening temperatures in the 7.85 mm wire, cylinders of 10–20 mm high were cut and subjected to a compressive stress until a given final height in order to obtain different degrees of cold-working, usually from 10 to 2.1 mm height (80% of cold-working). The hardness of these pieces after annealing at different temperatures, determined in a Centaur hardmeter in the Rockwell-F (HRF) scale, was determined and related to the stress-strain properties measured on the cold-drawn 1.8 mm diameter copper wire.

Results and discussion

The ultimate elongation-stress results obtained for all 1.8 mm diameter wires, whose compositions are described in Table I, after annealing at different temperatures for 7.2 ks are plotted in Fig. 1. The experimental values of maximum strain and elongation fit the curve described by the following equation:

$$\sigma = \frac{\sigma_{\varepsilon_0}}{1 + \frac{\varepsilon}{\varepsilon_{\max}}} \tag{1}$$

where σ is the strain value to rupture (in MPa), σ_{ε_0} is the extrapolated value of strain to rupture at null deformation (in MPa), ε (in %) is the deformation corresponding to σ, and $\varepsilon_{\max}$ (in %) is the maximum deformation value obtained among all samples and all studied temperatures, independently of their compositions.

Therefore, it seems that there is no effect of the composition and annealing temperature on the strain-elongation relation.

The half-softening temperature (corresponding to a strain of 284–304 MPa) corresponds to a final plastic elongation between 12 and 16%, and depends on the wire composition. The industrial continuous drawing processes anneal the copper wire until a 30% elongation before going on with the cold-drawing process. Therefore, despite the greater deviation of the experimental points at elongations of 30%, the temperature at which ultimate plastic deformation of 30% ($\varepsilon_{30\%}$) is reached after heating for 7.2 ks is considered as a valid parameter to compare the behaviour of the different samples.

Figs [2–5] show the evolution of the microstructure of sample number 5 with annealing at different temperatures for 7.2 ks and quenching in cold water. Fig. 2 corresponds to 298 K, where copper wire is just cold-worked. Fig. 3 shows the microstructure just at half-softening temperature, where recrystallization is just starting. Fig. 4 corresponds to the $\varepsilon_{30\%}$ temperature, where recrystallization is nearly finishing and Fig. 5

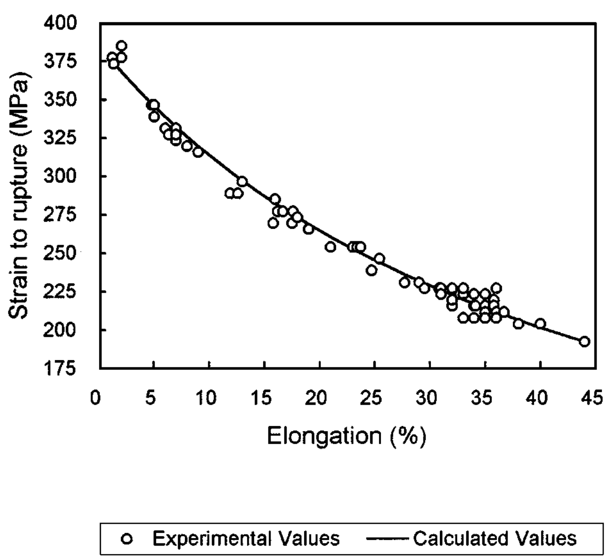

Figure 1 Plot of experimental and calculated values of maximum strain vs. elongation for all the studied samples at all annealing temperatures.

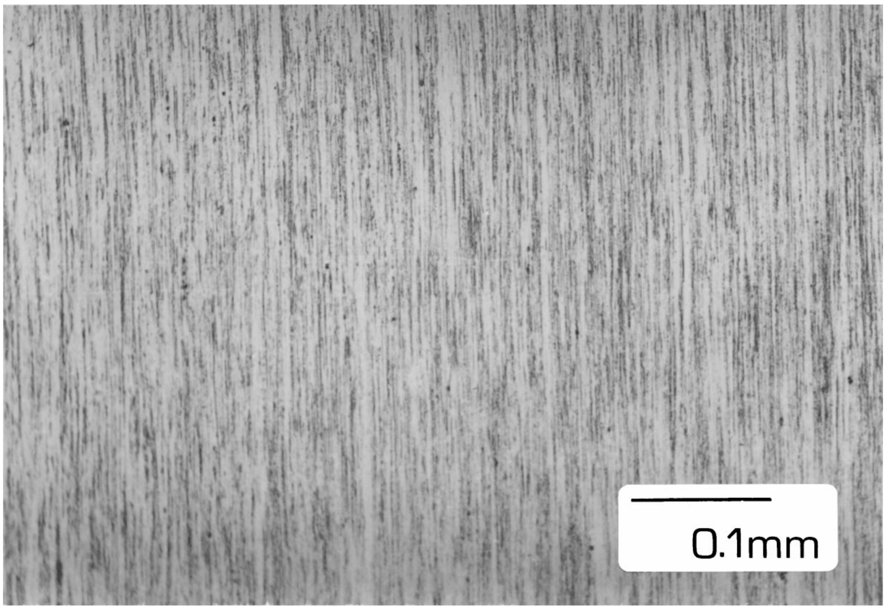

Figure 2 Micrography corresponding to the cold-drawn wire of sample 5 at room temperature with elongation of 1.2% and strain of 377 MPa.

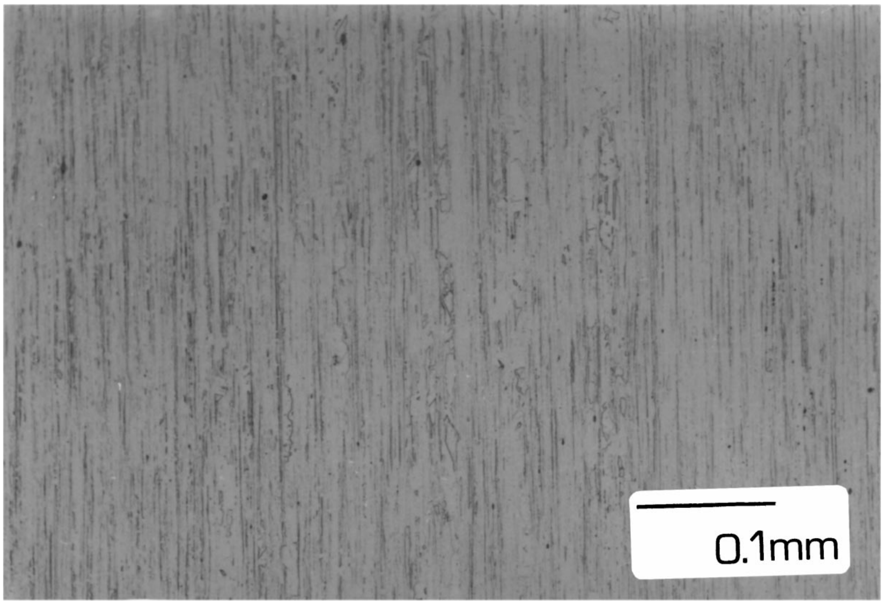

Figure 3 Micrography of the cold-drawn wire of sample 5 after annealing at half-softening temperature (523 K) for 7.2 ks, elongation of 16% and strain of 284 MPa.

shows a completely recrystallized microstructure, in which grain growth is observed.

Table II summarizes half-softening and $\varepsilon_{30\%}$ temperatures for the cold-drawn samples described in Table I, and their electrical conductivities at room temperature in %I.A.C.S. compositions described in Table I can be obtained by fire-refining, attending to the composition of the copper scrap and the to accuracy at which are performed the slagging operations involved. When impurities content increases, as Half-softening temperature and $\varepsilon_{30\%}$ temperature, electrical conductivity decreases, but in all cases is higher than 100.5%I.A.C.S., which is the minimum one required for tought-pitch copper.

TABLE II $\varepsilon_{30\%}$ Temperatures and electrical conductivities of studied samples

Sample	$\varepsilon_{30\%}$ Temperature (K)	Half-softening temperature (K)	Conductivity (%I.A.C.S.)
1	453	448	101.7
2	471	463	101.8
3	485	468	101.5
4	501	488	101.1
5	571	521	100.9

The relationship between hardness of 7.85 mm diameter copper wire after 80% of cold-working with plastic deformation of 1.8 mm diameter cold-drawn copper wire, with the same composition, both annealed at the same temperatures, for samples number 2 and 3 is plotted in Fig. 6.

The $\varepsilon_{30\%}$ temperature for a cold-drawn 1.8 mm wire is the same as that required to soften the cold-worked 7.85 mm wire to 75 HRF, while at half-softening

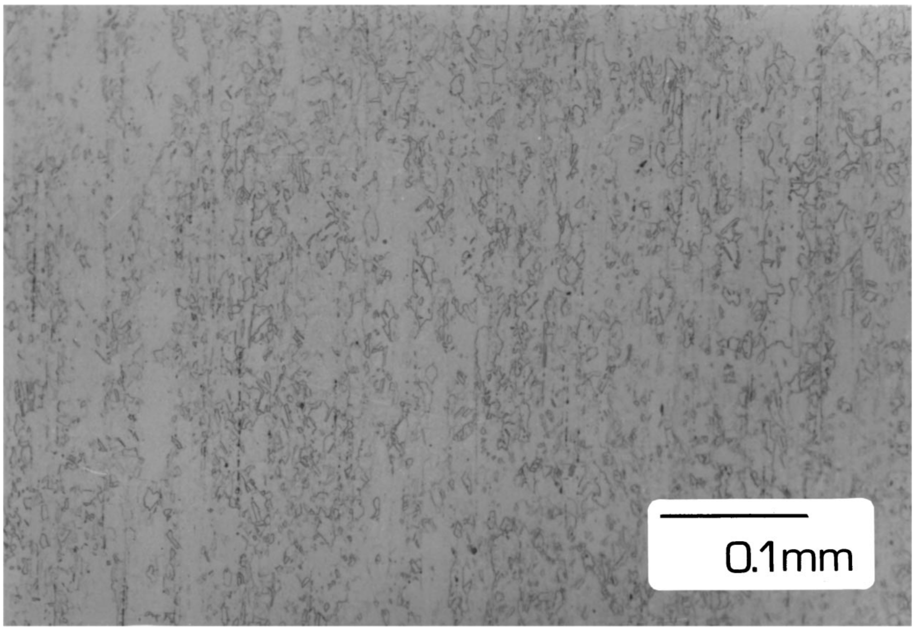

Figure 4 Micrography of the cold-drawn wire of sample 5 annealed at $\varepsilon_{30\%}$ temperature (571 K) for 7.2 ks, strain of 225 MPa.

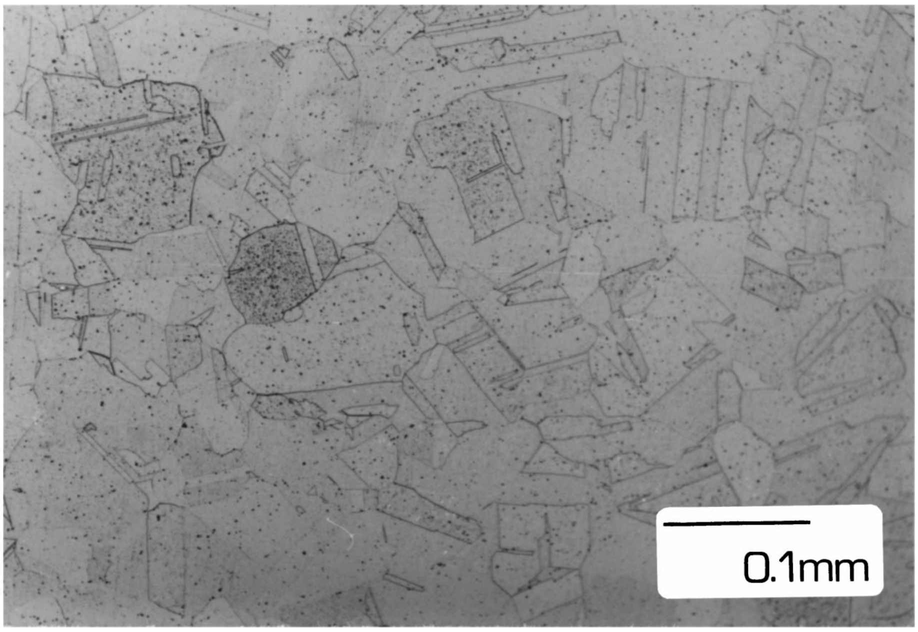

Figure 5 Micrography of the cold-drawn wire of sample 5 completely annealed at 873 K for 14.4 ks.

temperature values of hardness range between 84 and 87 HRF. This correlation is practically independent of the concentrations of impurities in the copper and this technique allows evaluation of the annealability of a 7.85 mm wire before cold-drawing.

The effect of the cold deformation degree on $\varepsilon_{30\%}$ temperature of the cold-compressed 7.85 mm wire for samples number 2, 3 and 4 is depicted in Fig. 7. For cold deformations higher than 75%, the $\varepsilon_{30\%}$ temperature is independent of cold-working degree, and depends only on the composition.

The effect of the oxygen content on $\varepsilon_{30\%}$ temperature was determined for different compositions of cold-worked 7.85 mm diameter copper wire by varying the oxygen content in the continuous casting. Fig. 8 is a plot of the $\varepsilon_{30\%}$ temperature for different oxygen concentrations for sample 4. This curve is representative of the general behaviour found in all cases. At low and high oxygen concentration $\varepsilon_{30\%}$ temperatures are higher than those obtained for intermediate oxygen concentration (between 110 and 180 ppm of oxygen). For each concentration of impurities there is an optimal oxygen concentration that gives a minimum $\varepsilon_{30\%}$ temperature, which is a function of the total amount of impurities. For a wide range of oxygen concentration, when lead and antimony concentrations are higher than 20 ppm, the three ranges are observed.

The effect of the oxygen on the $\varepsilon_{30\%}$ temperature was studied by determining, for several compositions with optimal oxygen contents, the $\varepsilon_{30\%}$ temperature after melting the each sample in a graphite crucible under vacuum. This causes almost complete elimination of

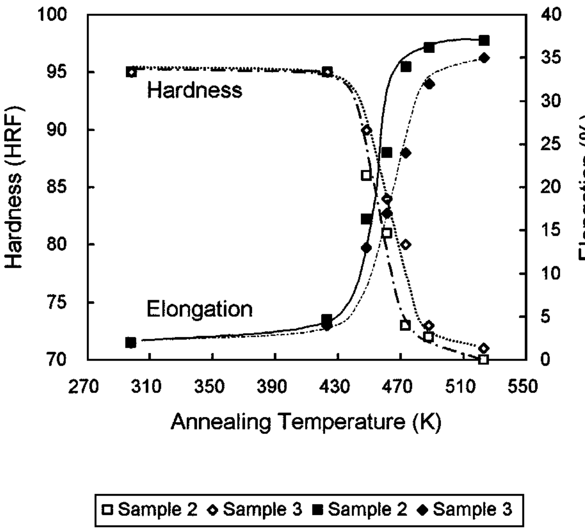

Figure 6 Hardness and elongation vs. annealing temperature for samples 2 and 3.

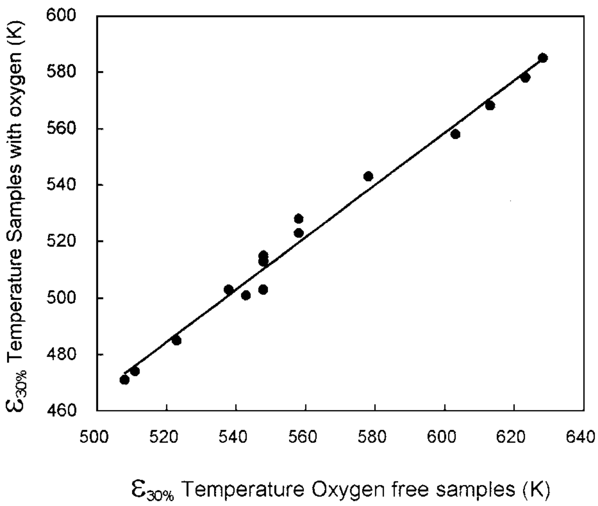

Figure 9 Relationship between $\varepsilon_{30\%}$ temperature of samples with optimal oxygen concentration and $\varepsilon_{30\%}$ temperature of oxygen-free samples.

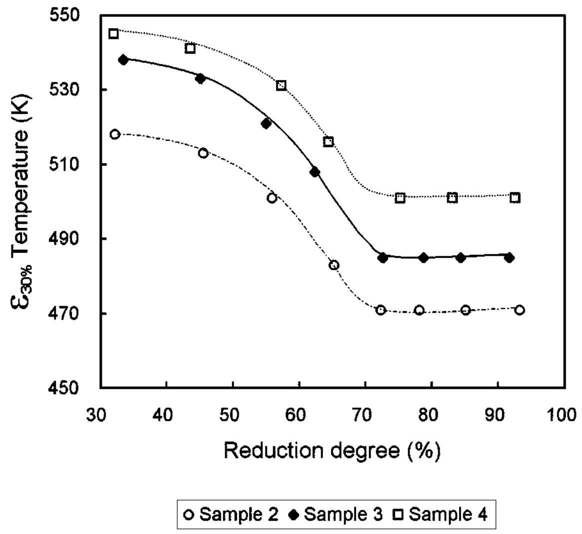

Figure 7 Plot of $\varepsilon_{30\%}$ temperature vs. degree of deformation for samples 2, 3 and 4.

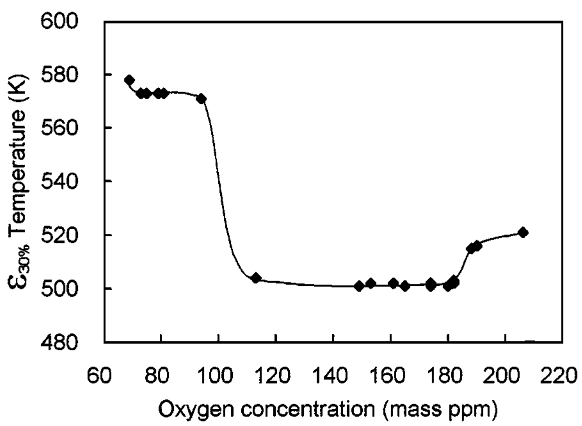

Figure 8 Depiction of $\varepsilon_{30\%}$ temperature vs. oxygen content for sample 4.

oxygen as CO_2. These samples were cold-worked until a cold deformation of 80%, and the $\varepsilon_{30\%}$ temperature was determined in the same way as for the cold-worked 7.85 mm wire.

Fig. 9 shows the $\varepsilon_{30\%}$ temperatures of the samples shown in Table I with the optimal oxygen concentration and oxygen-free samples. A linear correlation is observed, since the experimental points fit the straight line described by the equation:

$$T_{\mathrm{O}} = 0.91 \times T_{\mathrm{f}} + 12 \qquad (2)$$

where T_{O} (in K) is the $\varepsilon_{30\%}$ temperature with an optimal oxygen concentration and T_{f} (in K) is the $\varepsilon_{30\%}$ temperature of the same sample, but oxygen-free.

Copper compositions with an oxygen concentration outside the zone of the plateau in Fig. 8 can be identified by melting the sample in a graphite crucible under vacuum and determining the $\varepsilon_{30\%}$ temperature in oxygen-free conditions. The increase in the $\varepsilon_{30\%}$ temperature caused by an inadequate oxygen concentration is determined by the difference between the $\varepsilon_{30\%}$ temperature of the oxygen-containing sample with an unsuitable oxygen concentration and the temperature corresponding to a correct oxygen concentration (T_{O}), calculated by introducing the experimental temperature obtained with the oxygen-free sample (T_{f}) in Equation 2. For example, sample number 4 with 200 ppm oxygen presents an $\varepsilon_{30\%}$ temperature of 519 K; after treating the melt sample in vacuum, its $\varepsilon_{30\%}$ temperature (T_{f}) is 538 K, corresponding to 502 K (by Equation 2) when the sample has an oxygen content (T_{O}) in the range of the plateau of Fig. 8. This demonstrates that the original oxygen composition of the studied sample (200 ppm) was not the proper one, and should be between 110 and 180 ppm.

Conclusions

A relation between hardness (ranging from 95 to 70 HRF) and elongation (ranging from 1 to 37%) is described, which has been found to be practically independent of the copper composition. This relation allows control of the annealing treatment by hardness measurements, in order to achieve the half-softening or $\varepsilon_{30\%}$ temperatures.

Electrical conductivities of all the studied samples, obtained by fire-refining, are higher than 100.5% I.A.C.S., which is the minimum electrical conductivity required for tought-pitch copper. Nevertheless, when impurities content increases, $\varepsilon_{30\%}$ temperature also increases and the electrical conductivity of fire-refined copper decreases.

Ultimate strain has been related to ultimate elongation for annealed samples, after 80% of cold-working, by an expression that is also a function of the extrapolated strain value at null deformation, and of the higher elongation found (i.e. when the specimen is completely annealed). This relation is independent of the copper composition and of the annealing temperature.

The comparison between the microstructures of the annealed samples at different temperatures, after 80% of cold-working, reveals that at half-softening temperature recrystallization is just starting, while at $\varepsilon_{30\%}$ temperature recrystallization is finishing, although grain growth is not observed.

For each studied composition, between 30 and 75% of cold-working, $\varepsilon_{30\%}$ temperature decreases as cold-working increases, but in the range from 75 to 92% of cold-working, $\varepsilon_{30\%}$ temperature reaches a constant minimum value.

There is an optimal oxygen content, ranging between 110 and 180 ppm, in which, after 80% of cold-working, the $\varepsilon_{30\%}$ temperature reaches its minimum constant value for each composition. It is possible to calculate this temperature from measurements of the $\varepsilon_{30\%}$ temperature for each specimen when it is oxygen-free, because both temperatures are related by a linear expression.

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