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Comparative study of electrical and mechanical properties of fire-refined and electrolytically refined cold-drawn copper wires

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Abstract A comparison is made between FRHC (fire-refined high-conductivity) and ETP (electrolytically tough pitch) copper wire in cold-drawn samples. Conductivity and mechanical properties are evaluated as a function of the annealing temperature. The fire-refined copper samples with controlled amounts of impurities show the higher annealing temperatures needed to achieve the 100.0% IACS (International Annealed Copper Standard) required to be an electrical conductor. Nevertheless, FRHC copper keeps its mechanical properties for a wider range of annealing temperatures than ETP copper, thereby becoming an interesting alternative for some industrial applications such as trolley wire or fire detection systems. The applicability as trolley wire is evaluated by comparing ETP copper with commercial grades, and an electrical conductivity-tensile strength chart for this application is presented.

Introduction

In the year 2000, the worldwide production of copper from scrap peaked at 2.13 Mt, and in 2003 it dropped to 1.75 M, constituting about 11.5% of the total of refined copper production worldwide. Copper recovered from refined or remelted scrap (about 78% from new scrap and 22% from old scrap) composed, in 2003, 30% of the total U.S. copper supply [1]. The U.S. recycling rate for copper reflects the decline in old scrap consumption and the increasing substitution of primary refined copper for scrap and secondary refined copper [2], showing an average value of 44% for the 20-year period ending in 1990.

It is well known that the most usual application of copper wire is as an electrical conductor, but mechanical properties are also required for applications related to conductivity; that is why recycled copper is rarely used as an electrical conductor. However, the utilization of fire-refined copper recycled from scrap in the production of copper wire is a reality in Spain, where 100,000 tons of FRHC (fire-refined high-conductivity) copper were produced in 2004 with the COSMELT process developed by LaFarga Lacambra and consisting in melting, fire refining and conventional continuous or semi-continuous casting [3].

For a given composition of fire-refined copper, mechanical and thermal properties such as the $\varepsilon_{30\%}$ temperature may be controlled by the oxygen composition, a parameter adjustable during continuous or semi-continuous casting. The temperature at which the ultimate plastic deformation of 30% is reached ($\varepsilon_{30\%}$ temperature) is an important industrial parameter, directly related to drawability [4–6].

Some properties of fire-refined copper melted from scrap have been previously characterized, and it was established that the annealing treatment may be controlled by hardness measurements [7]. Lead, tin, nickel, zinc, iron, silver, antimony and oxygen are the most common impurities contained in fire-refined copper. The impurities content directly affects the conductivity, the $\varepsilon_{30\%}$ temperature and tensile test values, as described in the literature [8, 9].

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Nevertheless, the interaction and effect of the impurities on these parameters are still unknown.

The aim of this study is to compare the mechanical and electrical properties of pyrometallurgical cold-drawn copper wires with electrolytically refined wire. The variation of $\varepsilon_{30\%}$ temperature could be of special industrial interest, as there are some applications such as electrical contacts, trolley wires or even fire detection circuits for which having a higher $\varepsilon_{30\%}$ temperature may be an additional advantage. If the relationship among the annealing temperature, mechanical properties and conductivity is previously known, the industrial annealing unit becomes the tool to produce a made-to-measure copper wire.

Case study: trolley wires

As a case study, the applicability of FRHC copper as trolley wire is discussed in terms of properties given by the copper base alloys used for this purpose. The main requirement for trolley wires is an elevated wave propagation rate that minimizes the wear rate [10]. This is accomplished with the high-tension stress given by a high mechanical strength, although other properties, such as conductivity, are required to be sufficient. Moreover, the high strength must be maintained without risk of dropping, even if elevated temperatures are occasionally achieved under working conditions, and the electrical conductivity must remain the same. In addition to CuETP, many copper alloys have been described for this application: tin copper alloys that may also have silver as alloying element [11–13]. Two other groups of materials are the Cu–Sn–Fe alloys [14], and the Cu–Cr–Zr–Al alloys [15]. Copper alloys with Ag contents of around 0.1% are reported [16] and described as standard material in the specific materials regulation [17] of Renfe (Spanish national railroad company), and this regulation also describes the minimum characteristics required for copper–magnesium alloys and Cu-ETP to be used as trolley wire.

It was considered of interest to construct a material properties chart (MPC) for copper assimilating conductivity and tensile strength to the axes for this specific application as trolley wire. Properties of several compositions described in the above-mentioned literature were compiled, jointly with the properties measured on trolley wires manufactured with FRHC copper used in this study. The resulting diagram could be useful in a material selection process for this application and may be further extendible to other applications.

Experimental procedure

Cold-drawn copper wires of 1.8 mm diameter were used to make a comparative study between copper recycled from scrap and electrolytically refined copper. Four different samples were used to represent the most significant results. The samples termed PMA1, PMA2 and PMA3 are fire-refined copper obtained by continuous casting, and sample ETP corresponds to electrolytically refined copper. The samples of pyrometallurgical copper correspond to a high-conductivity multicompound copper microalloy with improved heat resistance and strain strength named PMA [6]. The compositions were determined with an optical emission spectrophotometer SPECTROLAB-S and the oxygen concentrations were measured by Fusion Technique with a LECO oxygen analyzer. Composition of the samples used is summarized in Table 1.

Several isothermal treatments were carried out on 1.8 mm-diameter cold-drawn copper wire pieces 100 mm and 1500 mm in length, submerging the samples in a salt bath (40% mass of $NaNO_2$ and 60% mass of KNO_3) at different temperatures within the range of 125–350 °C for 1 h [7]. The longer pieces were previously coiled around a rigid support and heated in that position. After the heat treatment, the samples were quenched in a solution of MeOH:H_2SO_4:H_2O (2:1:10) to eliminate any possible copper oxide. Tensile tests were immediately carried out on the 140 mm test pieces using a Mecmesin tensometer with a constant elongation speed of 0.2 mm s^{-1}.

After each heat treatment, a Resistomat Mikroohmmeter Type 2302 was used to measure the electrical conductivities of the 1500 mm test pieces at 293 K. Conductivity is expressed as a percentage of the standard. 100% IACS (International Annealed Copper Standard) represents a conductivity of 58 megasiemens per meter (MS/m); this is equivalent to a resistivity of 1/58 ohm per meter for a wire

Table 1 Composition (ppm) of studied samples

Sample	Composition (ppm)								
	Sn	Pb	Ni	Fe	Zn	Sb	Σ others	Ag	O_2
ETP	1	1	1	17	1	1	22	11	170
PMA1	232	424	153	25	61	63	958	158	224
PMA2	47	369	19	18	18	41	512	56	203
PMA3	36	546	45	19	22	22	690	31	165

one square millimeter in cross section and corresponds to a free-oxygen pure copper. Any impurity makes conductivity to decrease while some annealing treatments make conductivity to increase up to more than 101% IACS, a usual value for copper wire in electrical applications.

Trolley wire samples made of FRHC copper were characterized in terms of mechanical and electrical properties following the specific standard tests given by Renfe regulation [17].

Results and discussion

Conductivity was measured on all the samples after cold-working. Although the conductivity of the ETP sample was slightly higher than the conductivity of fire-refined copper wires, none of the samples achieved the minimum conductivity required, that is, 100.0% IACS. Thus, thermal treatment is an obligatory prerequisite to accomplish this value. The measured conductivity values corresponding to different annealing temperatures are depicted in Fig. 1. From these data it can be seen that PMA samples need higher annealing temperatures (60–100 °C over heated) to achieve the value of 100.0% IACS.

The cold-worked copper wires studied show a similar tensile response independently of their composition, as is represented in the stress-strain curves of Fig. 2. It is important to notice that pyrometallurgical copper wires show in general higher maximum strength values, this difference being around 50 MPa.

This mechanical response will change after an annealing treatment. To evaluate the dependence of mechanical parameters on the annealing temperature, tensile tests were performed immediately after the heat treatments carried out for different temperatures as described in the experimental

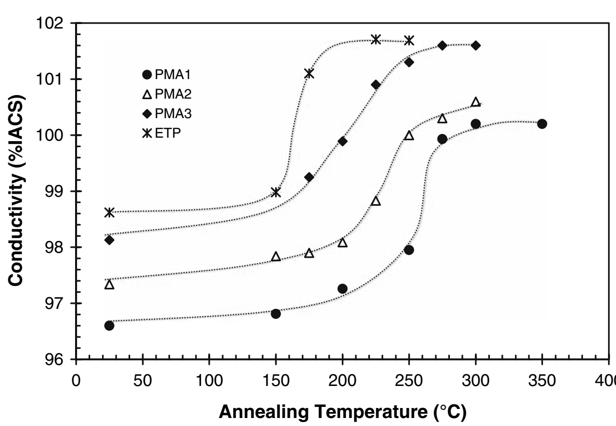

Fig. 1 Conductivity values after annealing treatment at different temperatures for 1 h

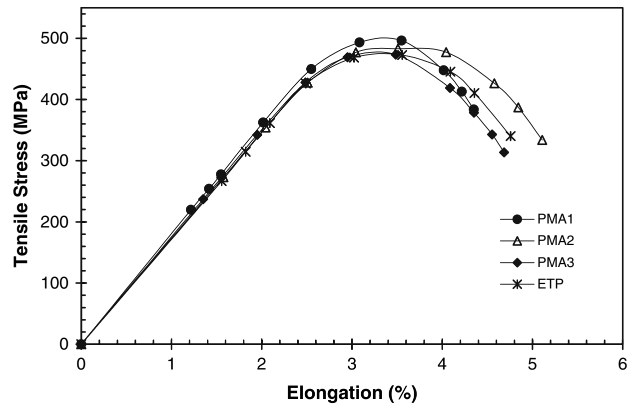

Fig. 2 Strain stress curves for the studied samples after cold-work

procedure. The most significant results are depicted in Figs. 3 and 4.

Figure 3 shows the variation of tensile strength with the annealing temperature for the studied samples. The most

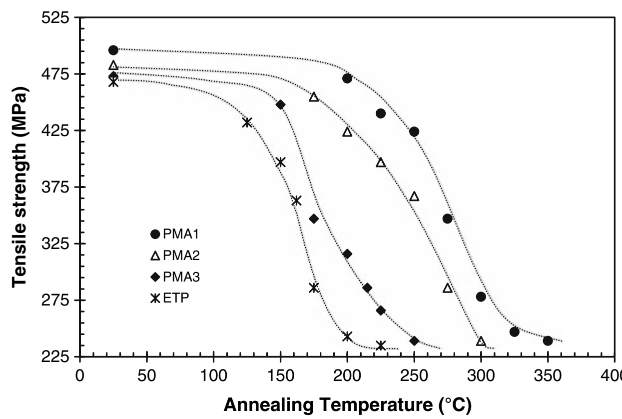

Fig. 3 Tensile strength values after annealing treatment at different temperatures for 1 h

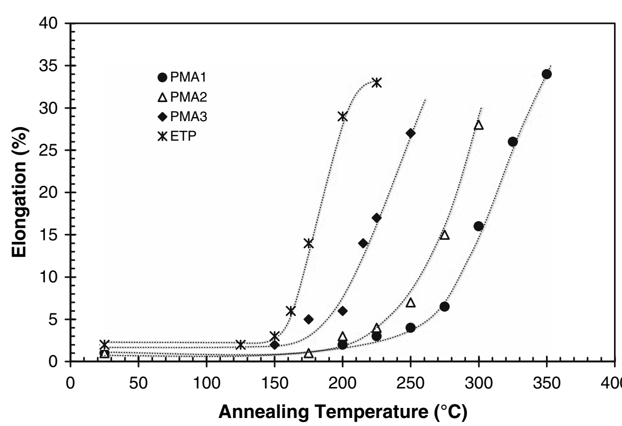

Fig. 4 Elongation values after annealing treatment at different temperatures for 1 h

significant result is that the strength drops more than 200 MPa once the copper wire is completely annealed, independently of the composition. The difference lies in the specific way in which these copper wires anneal. While the tensile strength of the electrolytic wire lessens with a higher slope within a narrow range of temperatures, this range is considerably higher for FRHC copper. These results reveal the flexibility of the annealing conditions of fire-refined copper, compared with the accurate control of the annealing temperature necessary to guarantee certain mechanical properties for an electrolytically refined copper wire.

Figure 4 illustrates changes in elongation with increased annealing temperature. Maximum differences are achieved at the ε30% temperature. The ε30% temperature ranges within an interval of values from 205 to 335 °C. This increase has previously been attributed to the differences in oxygen content [8, 9], as well as hydrogen and lead contents [4], although the composition and the total amount of impurities may also play an important role.

Annealing of copper is a time-temperature transformation. It is predictable that FRHC copper wire will need more time to achieve the same ε30% temperature as an ETP copper wire at a given temperature. The time dependence is currently being investigated. Moreover, having a better knowledge of the variation of $\varepsilon_{30\%}$ temperature with time may help to define the time-temperature transformation of fire-refined copper. Bearing in mind the experimental results and time dependence considerations, an industrial annealing unit was calibrated and is currently running with satisfactory results.

MPC of copper base trolley wires

Table 2 lists the codes grouping several copper base alloys used as trolley wires, as well as the total impurities content in addition to the alloying elements characteristic of each group. The diagram depicted in Fig. 5 was constructed drawing the different regions that contain the referred electrical conductivity-tensile strength values for each group, and reflects the mechanical and electrical behavior of more than 90 alloys used as trolley wire. As expected, the use of alloying elements different from silver increases mechanical strength to the detriment of conductivity. This figure also makes it clear that less than 0.1% alloy is in fact beneficial, because a compromise between mechanical and electrical properties may be achieved, thus improving the results obtained with CuETP or even CuAg.

Table 2 Code designations Fig. 5

CODE	Σ Alloying elements (%)		Σ Others (ppm)	
	min	max	min	max
CuSn	0.27	0.82	0	1000
CuSnAg	0.11	0.77	0	800
CuSnFeP	0.18	0.58	–	–
CuCrZrAl	0.172	1.131	–	–
CuAg	0.08	0.12	23	305
CuMg	0.1	0.7	–	–
CuETP	–	–	37	305
CT USP	–	–	0	1000
FRHC	–	–	662	953

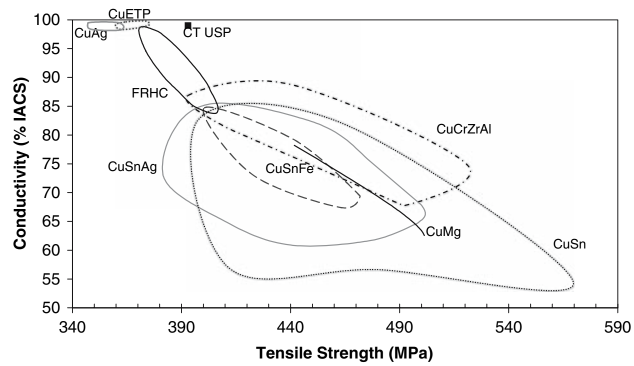

Fig. 5 Electrical conductivity-tensile strength chart. Application of copper based alloys as trolley wire

Conclusions

- The FRHC samples can reach conductivity values that make them suitable for use as electrical conductors.
- The tensile strength of FRHC wires is higher than for ETP wire, even after an annealing heat treatment. The FRHC wires keep their initial mechanical strength for a higher range of temperatures.
- A made-to-measure FRHC copper wire may be obtained by controlling the amounts of impurities and the oxygen content and by varying the annealing temperature.
- FRHC copper may be considered as a suitable material for trolley wire applications.

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