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Effects of pre-heating treatment on the annealing behaviour of cold-drawn fire-refined coppers

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The influence of hydrogen, oxygen and lead contents on the thermo-mechanical properties of fire-refined copper has been studied and related to the decrease of its hydrogen and oxygen content by the heat treatment known as pre-heating. Fire-refined coppers contain between 0.5 and 0.7 weight ppm of hydrogen, and usually more than 50 weight ppm of lead. The decrease in the hydrogen contents of this material through pre-heating at their optimal pre-heating temperatures, leads to a strong decrease of their annealing temperature for 30% elongation ($\varepsilon_{30\%}$). Fire-refined coppers with a lead content higher than 20–50 weight ppm (and preferably higher than 250 weight ppm) exhibit a microstructure before pre-heating with a low number of voids, as compared to the pre-heated fire-refined copper. Pre-heating also caused a decrease of the hydrogen contents to no detectable values and a decrease of the amounts of dissolved oxygen. These results are related to the possibility that lead increases the solubility of hydrogen in copper. Pre-heating at the optimal temperature develops faceted voids and decreases the hydrogen content to undetectable values by its reaction with the dissolved oxygen, thus forming water. This theory is confirmed by the poor results of pre-heating treatment obtained for oxygen-free high-purity copper, oxygen-hydrogen-free fire-refined coppers and coppers with lead contents lower than 20–50 weight ppm. *© 2001 Kluwer Academic Publishers*

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1. Introduction

Aoyama *et al.* [1] found that pre-heating tough pitch copper with certain amounts of dissolved lead, tin and oxygen, before a 90% cold-working, led to a decrease of the half-softening temperature by 80 K. Similarly, Won *et al.* [2] found that in the same conditions, the recrystallization temperature of tough pitch copper with 55 ppm of dissolved lead fell 90 K.

Fire-refined copper obtained from scrap commonly contains between 100 to 800 ppm ($\mathrm{mg \cdot kg^{-1}}$) impurities. Lead, tin, nickel, zinc, iron and antimony are the most significant ones. In general, these amounts of impurities affect the half-softening temperature, recrystallization temperature and tensile test values of annealed copper, as described in the literature [3–12]. Nevertheless, the interaction of the impurities and their overall effect on these parameters are still unknown.

A pre-heating treatment on fire-refined copper was performed in order to study the possibilities to obtain the annealing temperature for 30% elongation ($\varepsilon_{30\%}$) [13] or half-softening temperatures of the same order as those of electrolytic-refined copper. The results were compared to those for oxygen-free copper, high-grade electrolytic copper and oxygen-hydrogen-free fire-refined copper. Besides, the effect of the pre-heating treatment on the amount of hydrogen and oxygen present on fire-refined copper rods was studied and compared with the amount of these elements present in non-pre-heated samples of the same composition. A hypothesis was formulated in order to explain the decrease in the hydrogen and oxygen content during pre-heating and to account for the differences found in the $\varepsilon_{30\%}$ temperatures and microstructures after pre-heating.

2. Experimental procedure

Copper used in this study was obtained after smelting and fire-refining copper scrap, continuously casting and hot-rolling. Samples of hot-rolled 7.85 mm diameter copper rod were cut in 10 mm long cylinders and pre-heated between 573 and 1073 K for 0.3–7.2 ks, at low pressure (10^{-2} atm) or in salt bath (50% mass of $NaNO_3$ and 50% mass of KNO_3) in order to avoid the surface oxidation. After this treatment, samples were quenched

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in cold water that had previously been slightly acidified with 1 M H_2SO_4 in order to remove copper oxide that could be formed.

The oxygen-free sample (OF) was obtained after smelting, vacuum casting and hot-rolling a 7.85 mm diameter high purity copper rod. This sample was also cut and pre-heated as described above.

Pre-heated and further quenched samples were cold-compressed to a 2.1 mm final length (that is 80% of cold-working). The equivalence between 80% and 90% cold-deformations (this latter used by Aoyama *et al.* [1] and by Won *et al.* [2]) to determine the $\varepsilon_{30\%}$ temperature has been previously established [13]. Cold-compressed samples were annealed in a salt bath (40% mass of $NaNO_2$ and 60% mass of KNO_3) for 3.6 ks at the temperature that gives 75HRF for each different composition (that is the hardness value equivalent to 30% deformation [13]), and further quenched in cold water. The $\varepsilon_{30\%}$ temperature was established by Rockwell-F hardness measurements in a Centaur durometer on annealed samples. The values of $\varepsilon_{30\%}$ temperature were also established by tensile test with a Hounsfield Tensometer with a constant elongation speed of 0.1 $mm{\cdot}s^{-1}$, on test pieces of 100 mm gauge-length obtained after 80% of cold-drawing of the 7.85 mm diameter copper rod.

Oxygen-hydrogen-free samples were prepared by melting each sample in a graphite crucible under nitrogen atmosphere for one minute, thus removing oxygen as CO_2 and hydrogen as H_2O.

In order to study the microstructure of fire-refined and OF samples following exposure to different thermal treatments, some specimens were ground, polished with diamond paste to 1 micron and with silica gel, and finally etched with alcoholic $FeCl_3$ (etchant for copper and copper alloys ASM N° 11). Microstructures were observed with a Scanning Electron Microscope (SEM).

Oxygen and hydrogen concentrations were measured by Fusion Technique with a LECO hydrogen analyzer and with a LECO oxygen analyzer.

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.

3. Results and discussion

Compositions of fire-refined microalloyed copper rods (containing small amounts of different alloying elements) and OF copper rod, established with an optical emission spectrophotometer SPECTROLAB-S, are shown in Table I.

Fig. 1 shows the evolution of $\varepsilon_{30\%}$ temperature vs. the pre-heating temperature (T_H) for each sample studied.

TABLE I Compositions (ppm) of the studied samples

Sample	Pb	Ni	Sn	Ag	Sb	Fe	Zn
1	10	3	20	15	—	13	7
2	15	25	82	20	8	30	16
3	460	14	23	18	20	21	15
4	68	40	133	42	19	30	23
5	543	46	43	54	16	49	37
OF	0.2	5	6	8	3	3	2

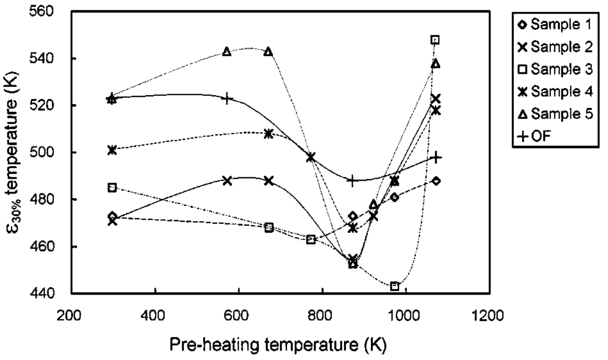

Figure 1 $\varepsilon_{30\%}$ temperature vs. pre-heating temperature for each studied sample.

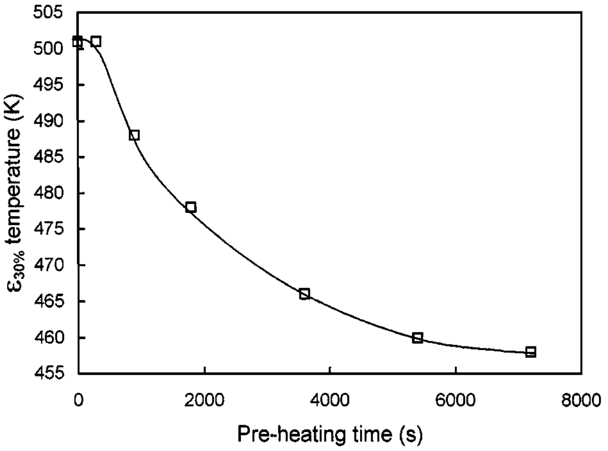

Figure 2 $\varepsilon_{30\%}$ temperature vs. pre-heating time for sample 4 at its T_{H0} (873 K).

For samples 2, 3, 4 and 5, a pre-heating treatment at 873–973 K for 3.6 ks makes their $\varepsilon_{30\%}$ temperature to decrease 16–70 K; for sample 1, the $\varepsilon_{30\%}$ temperature was not significantly reduced by the pre-heating treatment in the range of temperatures studied, compared to the $\varepsilon_{30\%}$ temperature of the non-pre-heated sample with the same composition. These results agree with those obtained by Aoyama *et al.* [1] and Won *et al.* [2].

Table II summarizes the $\varepsilon_{30\%}$ temperatures of the samples described in Table I, the pre-heating temperature that gave their minimum $\varepsilon_{30\%}$ temperature (T_{H0}), their minimum $\varepsilon_{30\%}$ temperature reached after pre-heating for 3.6 ks at T_{H0}, and their electrical conductivity measured before and after pre-heating at T_{H0} for 3.6 ks. In all cases, pre-heating does not affect or increase the electrical conductivity of the studied samples.

Fig. 2 shows the evolution of $\varepsilon_{30\%}$ temperature of sample 4 vs. pre-heating time at its T_{H0} (873 K). As the pre-heating time increased, the $\varepsilon_{30\%}$ temperature decreased asymptotically, reaching a minimum and constant value for this composition during long pre-heating periods. Similar results were also obtained by Aoyama *et al.* [1]. According to this author, the results associated to the pre-heating treatment seem to depend on the presence of at least one impurity, such as tin, lead or both. As the effective solubility of tin and lead in copper is 15.8% and 20–50 ppm respectively [14], the most probable element causing this phenomenon is lead, as Won *et al.* [2] proposed.

TABLE II $\varepsilon_{30\%}$ temperature, electrical conductivity and T_{H0} before and after pre-heating at T_{H0} for 3.6 ks of the studied samples

	Before pre-heating			After pre-heating at T_{H0} for 3.6 ks	
Sample	$\varepsilon_{30\%}$ temperature (K)	Conductivity (%I.A.C.S.)	T_{H0} (K)	$\varepsilon_{30\%}$ temperature (K)	Conductivity (%I.A.C.S.)
1	473	101.7	773	463	101.7
2	471	101.8	873	455	101.9
3	485	101.5	973	443	101.6
4	501	101.1	873	468	101.3
5	523	100.9	873	453	101.1
OF	523	—	873	488	—

Figs 3–5 show the microstructure obtained by SEM of sample 5 with different treatments. Fig. 3 corresponds to the recently hot-rolled specimen. Fig. 4 is the micrography of sample 5 pre-heated at its T_{H0} (873 K) for 3.6 ks and quenched. It reveals the presence of a high number of faceted voids in all the grains, giving it the appearance of "Swiss cheese". Fig. 5 corresponds to a different cylinder from sample 5 pre-heated at 1073 K for 3.6 ks. The number of voids, compared with Fig. 4, has strongly decreased.

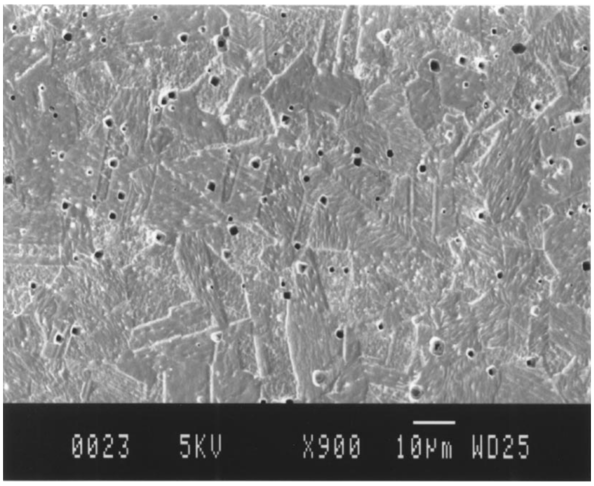

Figure 3 Microstructure by SEM of non-pre-heated sample 5.

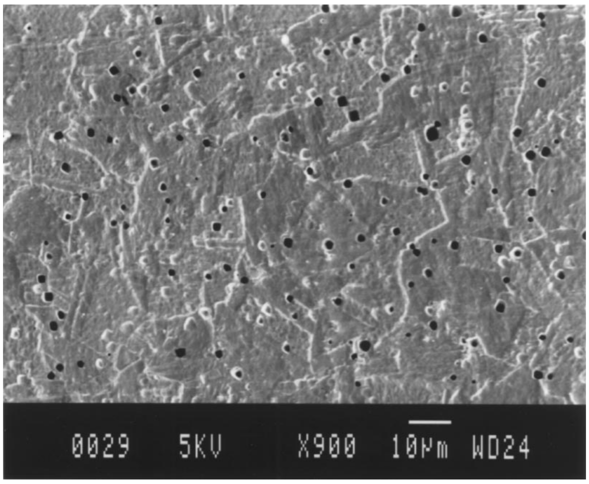

Figure 4 Microstructure by SEM of sample 5 pre-heated at its T_{H0} (873 K) for 3.6 ks.

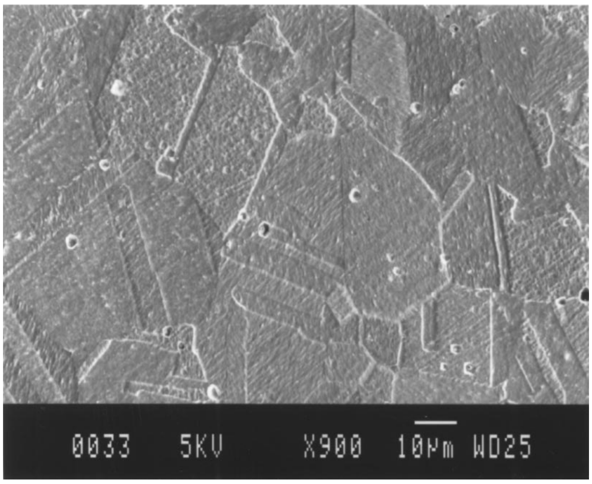

Figure 5 Microstructure by SEM of sample 5 pre-heated at 1073 K for 3.6 ks.

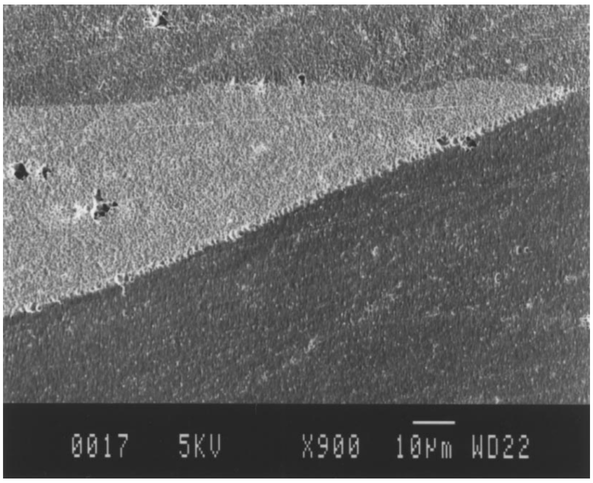

Figure 6 Microstructure by SEM of non-pre-heated sample OF.

Figs 6 and 7 show the microstructure of the OF sample before and after pre-heating at 873 K for 3.6 ks and further quenched respectively. In this sample the look of "Swiss cheese" also appears after pre-heating (Fig. 7), while before it a low number of voids is observed (Fig. 6). Fig. 8 shows the microstructure of the OF sample after pre-heating at 1073 K for 3.6 ks. This figure shows a low number of voids, that are preferably located at the grain boundaries.

Table III shows the hydrogen and oxygen concentrations, analysed by LECO, of all the samples that were pre-heated for 3.6 ks at the T_{H0}, and of the same samples without pre-heating. Hydrogen concentrations before pre-heating for fire-refined samples ranged between 0.13 and 0.72 ppm and for the OF sample was

TABLE III Hydrogen and oxygen concentrations before and after pre-heating treatment at T_{H0} for 3.6 ks of the studied samples

	Non pre-heated samples		Pre-heated samples at T_{H0} for 3.6 ks	
Sample	Oxygen (ppm)	Hydrogen (ppm)	Oxygen (ppm)	Hydrogen (ppm)
1	215	0.21	198	<0.01
2	89	0.13	79	<0.01
3	163	0.72	140	<0.01
4	165	0.58	152	<0.01
5	194	0.66	175	<0.01
OF	5	1.50	<0.01	<0.01

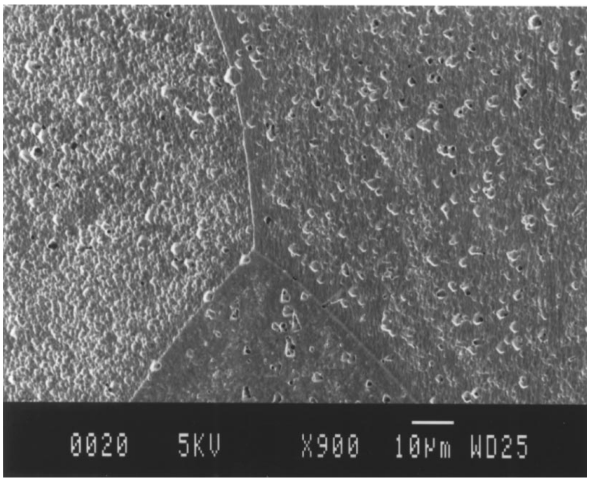

Figure 7 Microstructure by SEM of sample OF after pre-heating for 3.6 ks at its T_{H0} (873 K).

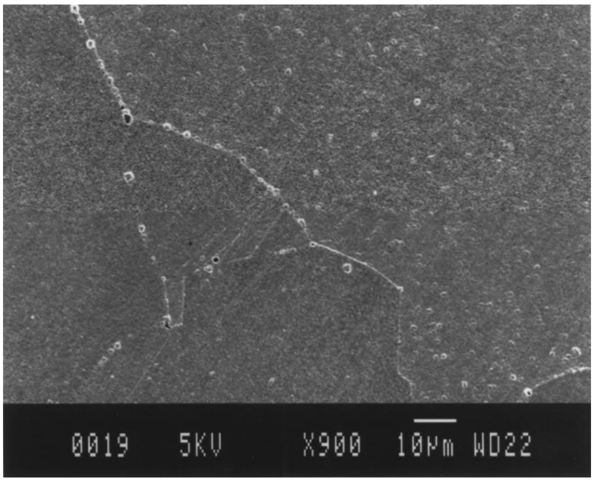

Figure 8 Microstructure by SEM of sample OF after pre-heating for 3.6 ks at 1073 K.

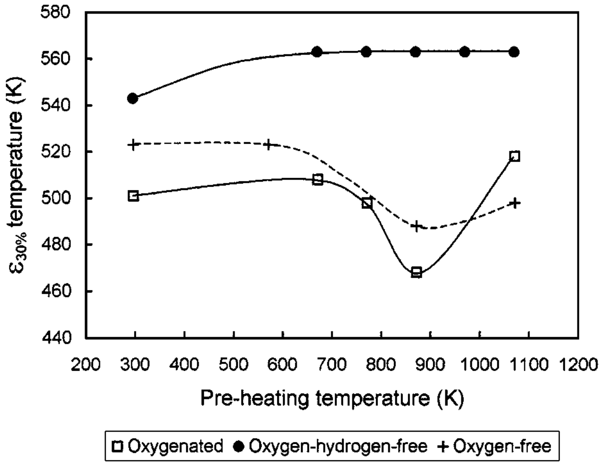

Figure 9 $\varepsilon_{30\%}$ temperature vs. pre-heating temperature for high-grade OF sample and for oxygenated and oxygen-hydrogen-free sample 4.

1.5 ppm, whereas pre-heated samples presented no detectable hydrogen concentrations. Oxygen concentrations also decreased when samples were pre-heated at their respective T_{H0}.

The effect of the presence of oxygen and hydrogen on the $\varepsilon_{30\%}$ temperature reached after pre-heating sample 4 between 298 and 1073 K for 3.6 ks is depicted in Fig. 9. The influence of the pre-heating temperature on the $\varepsilon_{30\%}$ temperature of the OF high-grade copper sample, is also depicted by the discontinuous line.

The fire-refined samples with lead content higher than 20–50 ppm and the OF sample decreased their $\varepsilon_{30\%}$ temperature with pre-heating, whereas the respective oxygen-hydrogen-free samples underwent no decrease in their $\varepsilon_{30\%}$ temperature after a pre-heating treatment in the range of temperatures studied.

Therefore, a pre-heating treatment, for 3.6 ks at the respective T_{H0} of each composition, decreased the hydrogen and oxygen contents present in the specimen, but the oxygen content is still considerable for fire-refined samples.

As the Ellingham diagram [15] reflects, microalloying elements such as Pb, Zn, Ni, Sn, Fe or hydrogen are more stable as oxides than copper at the T_{H0} temperature. Nevertheless, other impurities such as Ag are more stable as elements. Pre-heating the different materials to their optimal T_{H0} helps oxygen to combine with those elements that are more stable as oxides, thus decreasing the amount of oxygen and hydrogen dissolved in the crystalline structure of copper, and finally lowering its $\varepsilon_{30\%}$

The hydrogen in copper is trapped during the process of smelting and fire-refining or during the electrolytic-refining and its presence is unavoidable in industrial practice. Hydrogen seems not to be randomly distributed in the copper net, but remains surrounding lead atoms. When copper contains small amounts of lead (less than 20–50 ppm), hydrogen promotes the appearance of internal bubbles and superficial defects that often lead to the breaking of copper rod during rolling. When lead content is higher than 250 ppm this defects are not observed and copper can be rolled without any problem. Therefore, lead seems to increase hydrogen solubility as defects and bubbles nearly disappear when the amount of lead is high. The higher volume of lead compared to copper could explain this fact as lead atoms should place stress on the crystalline structure creating room for hydrogen atoms to dissolve and remain in it.

The most probable mechanism for hydrogen removal seems to be the formation of water in the case of fire-refined copper samples with more than 20 ppm lead, and this would also explain three other phenomena: the decrease in oxygen content caused by a pre-heating treatment at T_{H0} for 3.6 ks (see Table III), the fact that a pre-heating treatment has practically no effect on the $\varepsilon_{30\%}$ temperature of the studied samples when they are free of both oxygen and hydrogen in the studied range of T_{H} (see Fig. 9), and the constant and minimum $\varepsilon_{30\%}$ temperature achieved at long pre-heating times at T_{H0} for each microalloy composition (see Fig. 2).

A pre-heating treatment at T_{H0} on rods with lead content higher than 20–50 ppm, and specifically higher than 250 ppm, facilitates the removal of the dissolved hydrogen from the crystalline structure as water. As a consequence, voids are formed due to the diffusion of hydrogen, that reacts with oxygen forming water, leading to the higher decrease in the $\varepsilon_{30\%}$ temperature for all the studied samples.

Solubility of gases in solid copper should increase with temperature. Although it seems that the $\varepsilon_{30\%}$ temperature tends to rise with the pre-heating temperature, between 673 and 1023 K water is formed, thus decreasing the $\varepsilon_{30\%}$ temperature until a minimum value and further recovering. When hydrogen content is low (samples 1 and 2) this variation is not so great, whereas when the lead content is high (more than 250 ppm), the variation of the $\varepsilon_{30\%}$ temperature is strong. For coppers with low oxygen content, this recovering is not observed.

In any case, and independently of the mechanism that develops during pre-heating, the results obtained here indicate the influence of dissolved oxygen, hydrogen and lead content on the decrease in the $\varepsilon_{30\%}$ temperature and increase in the electrical conductivity observed after pre-heating at the T_{H0} of each microalloy composition.

4. Conclusions

Pre-heating treatment at the optimal temperature according to the copper composition decreases the hydrogen concentration until no detectable values on high-grade oxygen-free copper, fire-refined coppers and on electrolytic copper.

Pre-heating also affects the thermo-mechanical properties of these coppers, strongly decreasing their $\varepsilon_{30\%}$ temperature when samples were pre-heated at their optimal temperature. The variation of the $\varepsilon_{30\%}$ temperature obtained with this treatment for fire-refined coppers were higher than for high-grade oxygen-free copper and for electrolytic copper. Fire-refined coppers present a strong variation of the $\varepsilon_{30\%}$ temperature for lead contents higher than 250 weight ppm, and their oxygen content also decreases. The variations in the $\varepsilon_{30\%}$ temperature observed for conventional fire-refined copper are not so great when both oxygen and lead are not present (high-grade oxygen-free copper, despite its high hydrogen concentration), or when lead is in a concentration lower than 20–50 weight ppm (electrolytic copper). When both oxygen and hydrogen are not present on fire-refined coppers, no decrease on the $\varepsilon_{30\%}$ temperature is observed.

Conventional fire-refined coppers and high-grade oxygen-free copper present a microstructure with a high number of faceted voids when pre-heated at their respective optimal temperatures. Before pre-heating as well as after pre-heating at temperatures higher that the optimal, microstructures found present a low number of voids.

All these results can be related to a possible theory in which pre-heating at the optimal temperature helps hydrogen to diffuse out of the sample, thus decreasing the $\varepsilon_{30\%}$ temperature and increasing the electrical conductivity.

These phenomena are enhanced when oxygen and lead are also dissolved in the sample in a content higher than 250 weight ppm, decreasing the $\varepsilon_{30\%}$ temperature. Oxygen combines with hydrogen forming water, while lead seems to create enough place for hydrogen to be solved in the crystalline structure of copper, and helps it to diffuse when pre-heated. Formed voids during pre-heating can be explained by the variation of volume produced by the elimination of dissolved hydrogen and oxygen.

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