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Influence of Impurities in Cathodic Copper on the Ductility of Copper Wires

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The main characteristic of cathodic copper is its concentration of impurities because this determines the mechanical properties, i.e., ductility, of the derived copper wires. However, the results of standard mechanical tests to evaluate ductility show that there is no clear correlation between the content of impurities in the cathodes and the ductility of the copper wires. In this study, from traction tests on copper wires and observation of their fracture surfaces by means of scanning electron microscopy and energy dispersive spectroscopy, it has been concluded that the principal impurity affecting the ductility of the copper wires is oxygen, which is mainly incorporated during the melting of the cathodes and casting of the rods. In addition, to discriminate the effect of oxygen concentration in copper ductility, the used probes or wires must have the same previous deformation and must not have been annealed. When copper wires are annealed, cuprous oxide particles are also more dispersed in the matrix, and not only segregated and concentrated as occurs in the non-annealed condition, thus diminishing the mechanical fragility effect of the oxide.

Keywords cathodic copper, ductility copper wires, impurities, mechanical test and deformation hardening

1. Introduction

Copper cathodes are the input material in the production of electrical wires, in which impurities are considered detrimental. For this, producers around the world try to obtain copper cathodes with lower impurities content, ideally zero. In practice, however, all copper have certain level of impurities; in the case of grade A cathodic copper, the maximum admissible impurities concentration is regulated by the international standards ASTM B115 or its equivalent BSEN 1978-1998 as can be seen in Table 1 (Ref 1). Codelco standards for impurity contents are significantly lower due to the expertise of the company in the whole of the production process, particularly in the steps of electro-winning and electro-refinement that permit a rigorous control of the impurity content in cathodes. These concentrations are due more to historic operating conditions in copper refineries or to the tightening of environmental restrictions, than to the effect they have on the properties of the copper, namely, the diminution on the ductility and, as its consequence, during the drawing of copper wires.

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Proof of this situation is considerably higher maximum admissible impurities for continuous casting rods of 8-mm diameter used for the drawing of electrical wire, which are also shown in Table 1.

The deleterious effects on the ductility of copper and on copper alloys with individual impurities that segregate at grain boundaries, such as selenium, lead, bismuth, antimony, oxygen, etc., are well known (Ref 2, 3). Selenium forms brittle sulfides and oxides, and the presence of these compounds at grain boundaries fragilizes the copper (Ref 4). Lead, apart from segregating to grain boundaries at lower concentrations, diminishes the initial temperature of copper brittleness (Ref 5). In addition, its fragilizing effect is strengthened when other impurities such as Sn and Bi are present (Ref 6). With respect to bismuth, a concentration of over 20 ppm produces severe brittleness manifested by a loss of cohesion in the matrix when it segregates preferentially at the grain boundaries (Ref 7-9) and by changes on the electronic structure of copper (Ref 8). Antimony shows the same behavior: it also segregates to the grain boundaries because of being practically insoluble in solid copper, showing an average segregation capacity of 0.38 (Ref 10) and increasing the annealing temperature of copper (Ref 11). With respect to oxygen, contents of over 36 ppm produce segregation of the cuprous oxide onto the grain boundaries of the copper, diminishing its ductility (Ref 12), to such an extent that concentrations as low as 10 ppm may have some effect on ductility (Ref 13). However, when oxygen concentration is higher and there are also other impurities present, a positive effect is generated in copper. In fact, oxygen contents between 175 and 450 ppm would be beneficial for controlling the gas-metal reactions in the foundry because of the formation of undissolved oxides with other impurities that have a deleterious effect in copper ductility lower than oxygen, and for inducing low grain size during recrystallization of copper when it is rolled into rods before wire drawing (Ref 14). On the other hand, oxygen content higher than 400-450 ppm creates diffi-

Table 1 Internationally acceptable impurity levels (ppm) in cathodic copper grade A and 8-mm copper rods

Impurity element	Copper cathodes		Copper rods 8 mm diameter
	International standard	Codelco (Chilean) standard	
Selenium (Se)	0.5	0.01	2.0
Tellurium (Te)	1.0	0.05	2.0
Bismuth (Bi)	0.1	0.005	1.0
Antimony (Sb)	0.5	0.02	4.0
Arsenic (As)	0.5	0.005	5.0
Tin (Sn)	10.0	1.8	No information
Lead (Pb)	0.1	0.01	5.0
Iron (Fe)	3.0	3.4	10.0
Nickel (Ni)	2.0	0.19	No information
Sulfur (S)	12.0	3.4	15.0
Silver (Ag)	10.0	0.22	25.0
Oxygen (O)	100.0	10.0	500.0

culty in the wiredrawing process, when the remainder segregates in grain boundaries forming cuprous oxide and producing brittleness in the wires (Ref 14).

Nevertheless, when the impurities in copper are present at the lower ppm concentrations as shown in Table 1 for cathodic copper, no conclusive studies are available in literature showing the influence of these impurities on ductility of the copper. Nowadays, the characterization and certification of impurity levels for cathodes are carried out by means of chemical analyses and by mechanical assays. In the case of the Chilean copper refineries, these mechanical tests, such as quick elongation test (AR) and spiral elongation test (SEN), are carried out at a foreign laboratory to wires of 6.3 mm obtained by the melting of the cathodes, continuous casting to a 8 mm rod, wire drawing and annealing of the wires at 270 °C for 10 min. The chemical analyses and mechanical tests performed by several laboratories show that there is not a clear correlation between the amount of impurities present in the cathodes and ductility of the resulting wire, ignoring which impurities or precipitates became source of premature fracture in the wires. So, it is common to obtain more ductile wires from cathodes with higher impurities contents, as shows Fig. 1(a). Likewise a poor correlation exists among tests that determine ductility, normally the quick elongation test and spiral elongation test, as shown in Fig. 1(b) (Ref 15).

These facts lead to conclusion that despite the need to consider the later drawability of rods, the maximum acceptable impurity levels in cathodes are ignored; also the mechanical tests used at present are unable to correlate the ductility of copper with various concentrations of impurities at ppm level. Therefore, the objective of this study was to determine which impurities or precipitates are the real causes of the ductility loss in copper wires and to develop a mechanical test that correlate between differences in the copper ductility associated with concentration variations at ppm level, for cathodes and for wires.

2. Experimental Details

The starting materials in our investigation were grade A copper cathodes of 8-mm thickness. They were analyzed chemically and mechanically. Sampling was made in agreement with international standard ASTM B115, in the commonly named "X-shape." Analyzed cathodes were melted in an induction furnace in a carbon-nitrogen protective atmosphere, and cast in a stainless steel permanent mould to obtain cylindrical samples (27 mm in diameter and 100 mm long). These samples were machined to 16 mm, wiredrawn in three passes with an intermediate annealing at 450 °C for 30 min to produce rods of 8-mm diameter, and the samples were also analyzed chemically and mechanically.

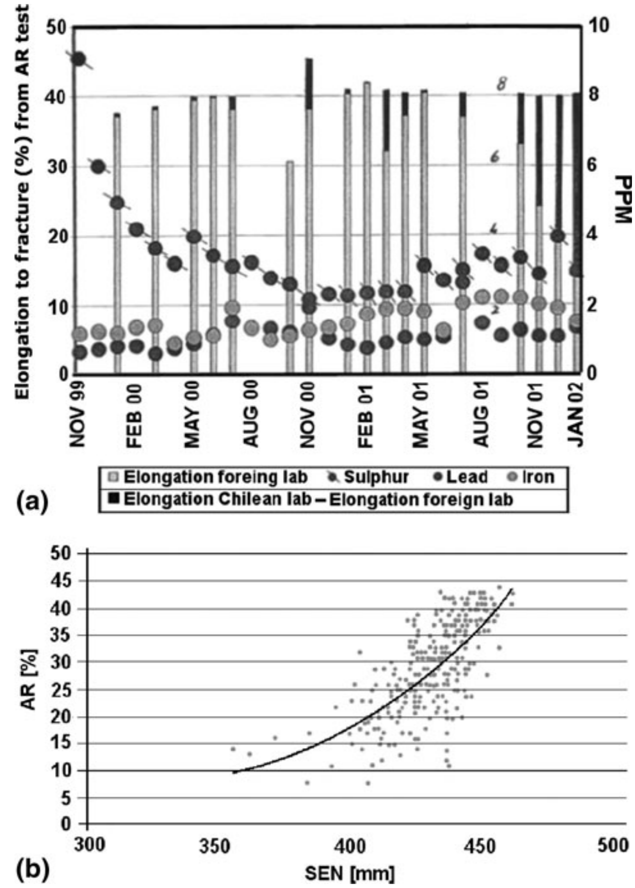


Fig. 1 (a) Data from Chilean laboratory showing no correlation between concentration of impurities and ductility; (b) data correlation between quick elongation (AR) and spiral elongation (SEN) tests from foreign laboratories

Chemical analysis was carried out using x-ray fluorescence. For oxygen content determination, a specific oxygen analyzer LECO was used.

Mechanical property analyses consisting of traction tests were carried out on different specimen shapes. For copper cathodes, three differently shaped specimens of 5-mm nominal diameter were tested: standard (ASTM E8), standard with neck and standard with reduced gage length. These different shapes were used to identify the specimens that permit obtaining a higher ductility in a same material (copper), thus making the traction test more sensitive to the effects of small variations in the impurities concentration on ductility of copper wires. Traction tests were performed using an Instron machine, a strain rate of 10^{-3} s^{-1}, and the ductility as elongation to fracture (%) is reported. Before the traction test, as is the usual practice in mechanical tests of copper rods, the samples were annealed at 270 °C for 10 min.

Finally, fracture surfaces of the samples that underwent the mechanical analysis test were analyzed by means of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The aim was to identify whether the failure occurred at a particular location during the traction tests, i.e., see whether the presence of impurities or precipitates could be found that caused fracture.

3. Results and Discussions

3.1 Chemical Analysis

The results of the chemical analyses were very similar for the copper cathodes and the copper rods for all elements except oxygen. The average chemical compositions are shown in Table 2, and oxygen concentrations, for both cathodes and rods, can be seen in Table 3. As was expected, the oxygen concentration was higher in the copper rods because oxygen from air penetrated into the liquid copper, mainly during casting.

3.2 Mechanical Analysis of Copper Cathodes

The purpose of this analysis was to determine the shape of the specimen to permit higher values of elongation to fracture in a same material, thus obtaining a test specimen more sensitive to the effects that small differences in impurities concentrations could have on the ductility of copper wire. Table 4 shows the elongation to fracture, the gage length L_0, and a schematic representation of each specimen.

From Table 4, it is clear that the 5-mm diameter and 10-mm gage length specimen we proposed had more elongation to fracture than the other two tested shapes and, consequently, is better for determining the effect of the impurities on the ductility. This result comes from the fact that, for a specimen with lower gage length and equal gage diameter, the same localized elongation produced during necking is measured in a lower longitude and thus the material shows a higher ductility value. It is possible that other geometries for traction test specimen can still show higher values of ductility but, in our case, all the mechanical assays made on the wire rods were done with specimens machined with an L_0 of 10 mm.

Table 2 Chemical composition of copper cathodes and wires

Element	Fe	Pb	As	Sb	Bi	S
ppm	≤ 2	≤ 2	≤ 0.2	≤ 0.2	≤ 0.05	≤ 25

3.3 Mechanical Tests of Copper Wires

Traction test curves for specimens annealed 10 min at 270 °C, taken from wire rods with different oxygen contents (5-626 ppm), are shown in Fig. 2. From this figure, it is surprising that the elongation to fracture of the wires is practically the same, i.e., 60-65% and so is independent of the oxygen content, Fig. 3 shows a typical SEM-EDS analysis of the fracture surface for all the specimens. Only oxygen particles, in the form of Cu_2O oxide, were present on the fracture surfaces. This result is relevant because indicates that for any grade A cathodic copper, with the other impurities concentrations shown in Table 1, only oxygen can influence the ductility of the derived copper wires.

Figure 4 shows traction curves for oxygen-free-high-conductivity (OFHC) copper (5 ppm O) and a sample with 377 ppm O both cases presenting a 36% of previous deformation, annealed and without annealing. Note the significant effect of annealing on the ductility. In particular, for the sample with 377 ppm O, the elongation to fracture in the sample without annealing was 22% compared to 60% for the annealed material. For the OFHC copper, these values were 42 and 65%, respectively. The difference in the elongation to fracture between the non-annealed OFHC copper, 42%, and a sample with 377 ppm O, 22%, is only due to the high segregation and concentration of Cu_2O oxide in the latter (see Fig. 5a), which has a deleterious effect on the ductility. Since the previous deformation on both samples is the same, no difference in ductility exit caused by work hardening. In the annealed condition, as a consequence of the recrystallization, some of the Cu_2O particles were more dispersed at the interior of the grains (see Fig. 5b), and so the effect of the oxygen on the ductility of copper wires was less marked. In the shape of cuprous oxide segregated and concentrated at grain boundaries, the deleterious effect of oxygen on copper ductility was also found for the fire-refined copper, with oxygen content being similar to that sampled in our study but with larger amount of other impurities, which confirms the results obtained in this study (Ref 16, 17).

4. Conclusions

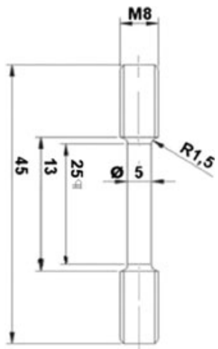
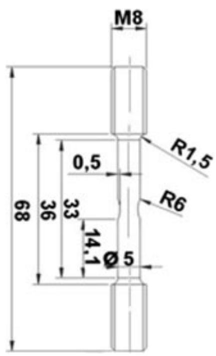
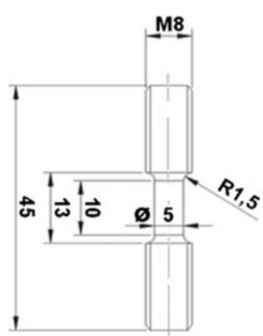
Two main conclusions were drawn from this study:

- The only impurity that affects the ductility of copper wires obtained from grade A cathodic copper is the oxygen in the form of Cu_2O oxides since this is the only element present in the fracture surfaces of the wires. In the annealed conditions and up to 626 ppm of O, the samples showed the same elongation to fracture, since the Cu_2O oxides are more dispersed at the interior of the grains and so the deleterious effect on the ductility of copper when these oxides are segregated and concentrated is avoided.

Table 3 Oxygen concentration (ppm) in copper cathodes and copper rods: two measurements (M1, M2) and the average (Av) are recorded

	Lower zone			Central zone			Upper zone		
	M1	M2	Av	M1	M2	Av	M1	M2	Av
Copper cathode	22	30	26	72	67	70	16	23	20
Copper rods	364	364	364	366	370	368	363	356	360

Table 4 Gage length and elongation to fracture of the three different specimens shown, obtained from copper cathodes

Specimen	L_0, mm	Elongation, %	Sketch of specimen
(a) Standard	25	29.6	
(b) Standard with neck of 2.5 mm diameter	5	27.0	
(c) With reduced gage length	10	55.1	

- Current mechanical tests for determining the ductility of copper cathodes and the derived copper wires are not adequate, and a new specimen shape with reduced gage length was designed for ductility measurements in a simple traction test. Using this design, small differences in ductility due to changing impurity levels can be determined. In addition, to detect the negative effect of oxygen in copper ductility samples, this must be tested with the

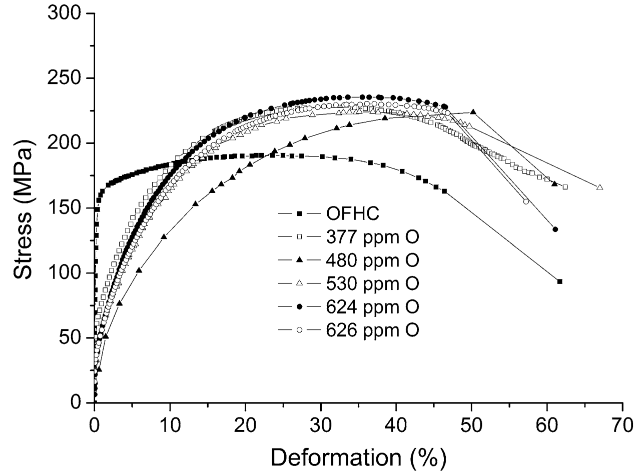


Fig. 2 Traction test for specimens from copper wires with different oxygen contents

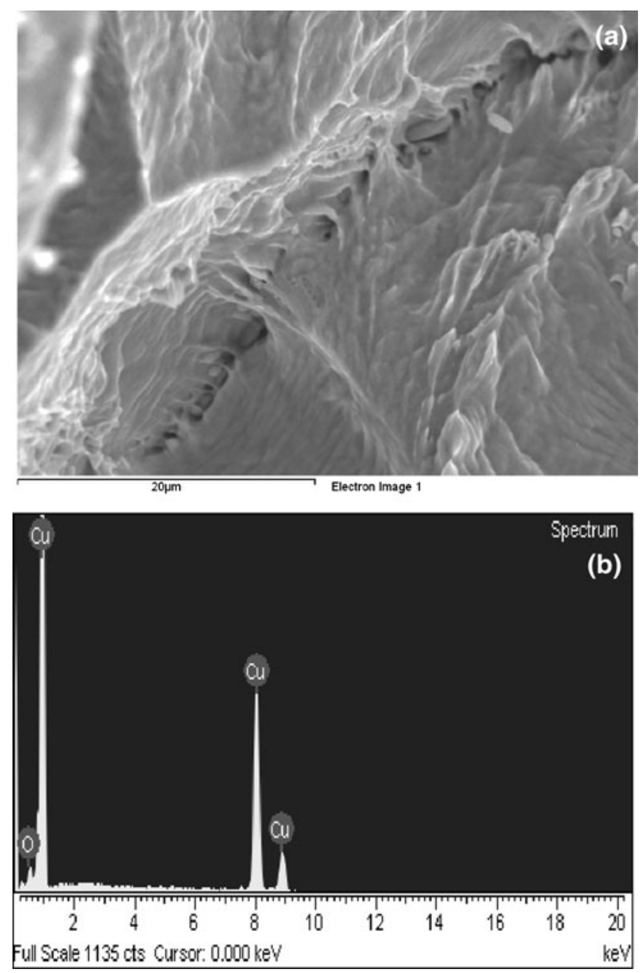


Fig. 3 Scanning electron microscopy and energy dispersive spectroscopy analysis of fracture surfaces of wire rods that had undergone traction tests (see Fig. 2)

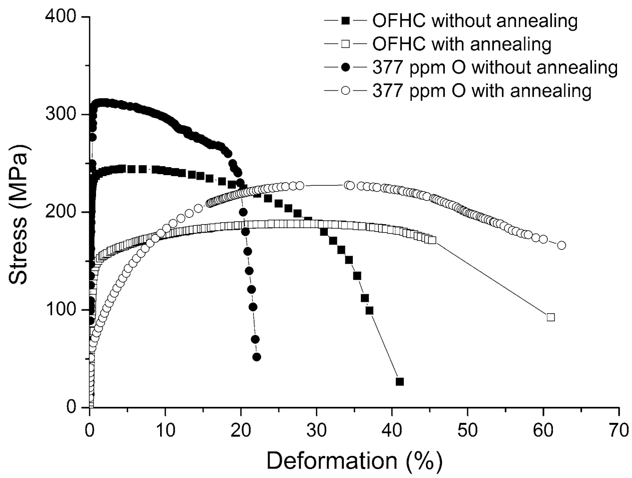


Fig. 4 Tensile curves for copper wires with and without annealing

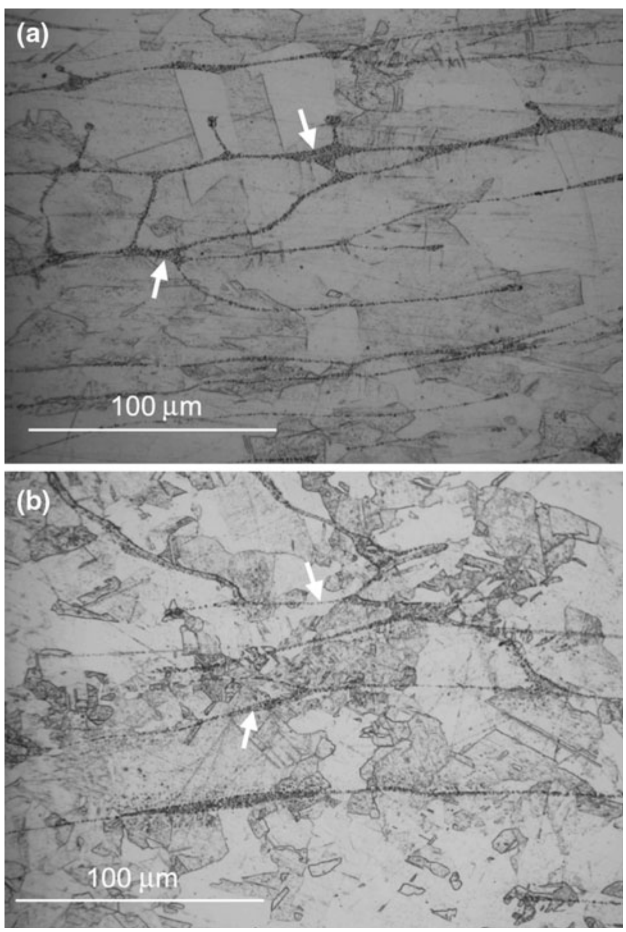


Fig. 5 Micrographs (200×) of copper wire with 377 ppm O. (a) Without annealing, white arrows show the Cu_2O particles segregates and concentrates. (b) With annealing, white arrows show the Cu_2O particles more dispersed in the interior of grains

same previous deformation, i.e., with the same deformation hardening, and without annealing. This treatment partially disperses the cuprous oxide inside the grains, thus avoiding the fragility due to the presence of oxygen. Besides, in this sense, after annealing, copper ductility is independent of oxygen concentration, at least, in the concentration range studied in this study.

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References

1. M. Ignat, Problemas de fragilización y certificación de cobre (Problems in Fragilization Certification of Copper), *Seminar Proceedings, Minor Contaminants in Copper, 2007* (Concepción, Chile), University of Concepcion, 2007, p 14–19
2. A. Liu, *Mechanics and Mechanisms of Fracture: An Introduction*, ASM International, Materials Park, OH, 2005, p 76–77
3. G. Joseph and K. Kunding, *Copper: Its Trade, Manufacture, Use and Environmental Status*, International Copper Association, New York, 1999, p 72
4. J. Davis, *Copper and Copper Alloys*, ASM International, Materials Park, OH, 2001, p 492
5. O. Takashi, O. Takayuki, and O. Keiichiro, Influence of Pb, Bi and Si Impurities in Free Cutting Copper Alloys on the Embrittlement at the Intermediate Temperature Range, *J. Jpn. Copp. Brass Assoc.*, 2001, **40**, p 147–152
6. M. Sadayappan, M. Letts, and M. Sahoo, *Impurity Limits in Aluminum Bronzes*, Material Technology Laboratory, Canada, 2005
7. V. Keast and D. Williams, Quantitative Compositional Mapping of Bi Segregation to Grain Boundaries in Cu, *Acta Mater.*, 1999, **15–16**, p 3999–4008
8. G. Dusher, M. Chisholm, U. Alber, and M. Ruhle, Bismuth Induced Embrittlement of Copper Grain Boundaries, *Nat. Mater.*, 2004, **3**, p 621–626
9. D. Armstrong, A. Wilkinson, and S. Roberts, Micro-Mechanical Measurements of Fracture Toughness of Bismuth Embrittlement Copper Grain Boundaries, *Philos. Mag. Lett.*, 2011, **91**, p 394–400
10. F. Otto, J. Frenzel, and C. Eggeler, On the Influence of Small Quantities of Bi and Sb on the Evolution of Microstructure During Swaging and Heat Treatment in Copper, *J. Alloys Compd.*, 2011, **508**, p 4073–4080
11. B. Bohstein and A. Sminov, Grain Boundary Segregation in Cu-Sb Alloys, *Mater. Lett.*, 2003, **57**, p 4501–4504
12. E. Nieh et al., Embrittlement of Copper Due to Segregation of Oxygen to Grain Boundaries, *Metall. Trans.*, 1981, **12**, p 893–901
13. N. Panosus, B. Wonsiewics, and C. Condra, Oxygen Embrittlement of Copper Leads, *IEEE Transactions on Parts, Hybrids and Packaging*, 2003, p 127–132
14. H. Pops, The Metallurgy of Copper Wire, *Innovations*, 1997. Available on-line http://www.copper.org/publications/newsletters/innovations/1997/12/wiremetallurgy.html; Accessed March 2010
15. Technical Report from GMBH, 2002
16. C. Camurri et al., Rheology and Metal Forming of Fire Refined Copper, *Mater. Charact.*, 2001, **47**, p 253–257
17. C. Camurri, et al., Influence of the Oxygen Content on the Ductility of Fire Refined Copper Between Ambient Temperature and 800 °C, *Rev. Métall., Sci. Génie Matér.*, 1994, p 1797–1803 (in French)