SOLUBILITY OF GAS IN COPPER

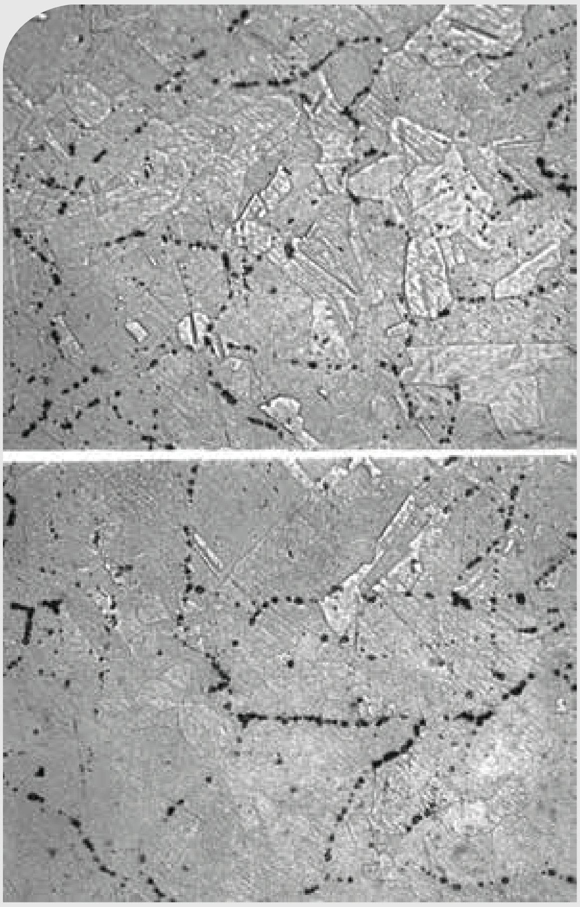

Photo 1 – Interstitial cuprous oxides

Copper has widespread use in various sectors such as electrical, telecommunications and information technologies as well as automotive and construction industries.

The physical and chemical properties that make copper the favored choice include its electrical and thermal conductivity, formability, corrosion resistance and applicability to soldering, brazing and welding.

Even though no single property of copper is the most important, the high electrical conductivity and formability or drawability of the wire are oftentimes among its most appreciated properties due to its various applications within the wire and cable industry.

The above mentioned general properties of copper, mentioned above, are somehow influenced by the gas content which is present. It is interesting to note that the solubility of oxygen in copper is about 70 ppm at a temperature of 1085°C (solidification temperature); whereas the maximum solubility of oxygen in copper at room temperature (25°C) is around 2 ppm as displayed in **Figure 1**.

Electrolytic Tough Pitch (ETP) copper rod is manufactured in such a manner that the copper melt is purposely oxidized; typical Cu-ETP contains oxygen in the range of 200 ppm to 400 ppm.

The Cu-ETP as-cast structure consists of solid solution alpha dendrites. In the eutectic, there are cuprous oxides (Cu_2O), as round precipitates in the solid solution alpha matrix; see **Photo 1**. Also, most impurities have been oxidized in the grain boundaries. The interstitial cuprous oxides will form a very dangerous element for subsequent cold drawing deformation and even for operations such as soldering and brazing.

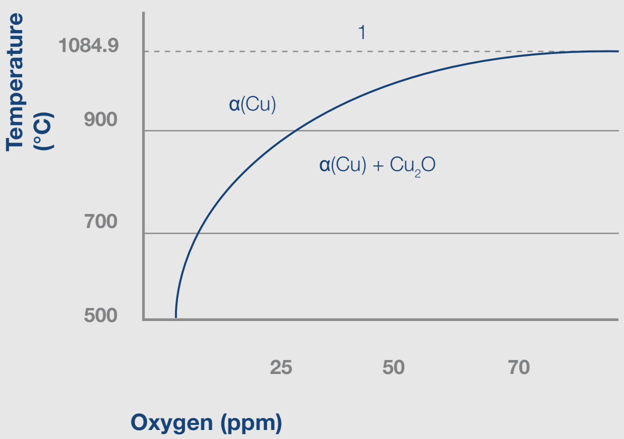

Figure 1 – Solubility of oxygen in copper

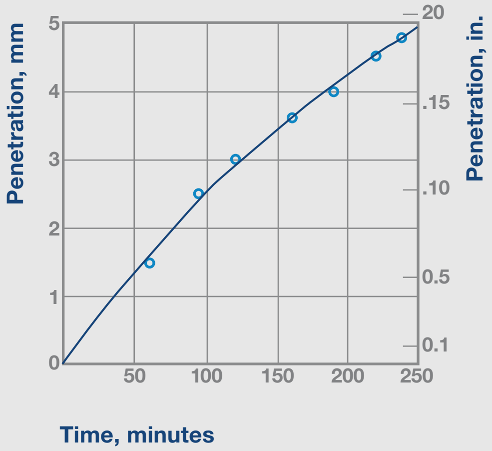

Figure 2 – Hydrogen penetration into the ETP copper hot rolled rod

Photo 2 - Central bursting induced by copper oxide: cone portion of the wire break

Photo 3 – ETP Cu, Ø 8.00 mm: hydrogen embrittlement within the copper structure, after hydrogen atmosphere annealing

The cuprous oxides increase the fragility of copper during the cold drawing processes, especially for fine wires (see **Photo 2**).

Even if the oxygen is present in the copper, as cuprous oxide, and the metal is exposed to a reducing atmosphere at high temperature (over 400°C) such as welding, the hydrogen present in the atmosphere will diffuse through the copper matrix and react with the oxygen and form vapor between the grain boundaries causing embrittlement.

As an example, **Photo 2** shows central bursting induced by copper oxide particles – cone portion of the wire break.

Photo 3 shows the Cu-ETP rod sample after exposure to hydrogen atmosphere annealing. Prior to the hydrogen annealing test, the sample had the following features:

- Grain size: 0.025 mm
- Rm: 230 N/mm^2
- Elongation (A5): 61%
- Oxygen: 225 ppm

Nitrogen, carbon monoxide and carbon dioxide are practically insoluble in copper. However, they may be entrapped during solidification.

The gas having the greatest tendency to dissolve in copper is hydrogen. Recent laboratory works indicate the solubility of hydrogen in copper at various temperatures. At room temperature, the total hydrogen content ranges from 2.5 to 4.5 cm^3 per 100 grams. **Figure 2** shows the penetration of the embrittlement in ETP copper at various oxygen percentages versus temperature.

EFFECT OF OXYGEN CONTENT

From a metallurgical prospective, ETP copper is a binary alloy, even though the alloying element (oxygen) is present in very small quantities.

The equilibrium phase diagram presented in **Figure 3**, indicates that ETP copper is a two phase mixture composed of a copper-oxygen solid solution and the intermediate cuprous oxide (Cu_2O) phase.

The effects of oxygen content upon electrical conductivity are illustrated in **Figure 4**, and has considerable commercial applicability. Conductivity increases for the first 200 ppm of oxygen and then decreases in a linear manner at higher oxygen concentration.

This important increase in conductivity is caused by the interaction between the oxygen and the impurities to form metal oxides, thereby reducing the amount of residual elements remaining in solid solution.

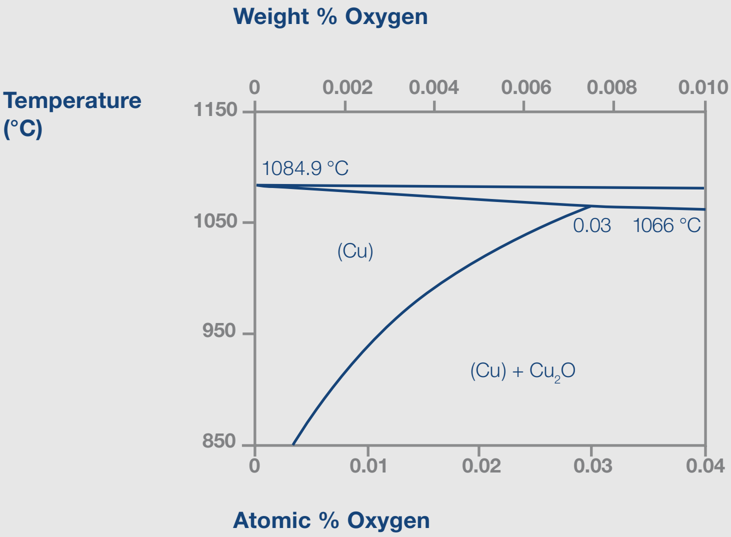

Figure 3 – Equilibrium phase diagram copper-oxygen

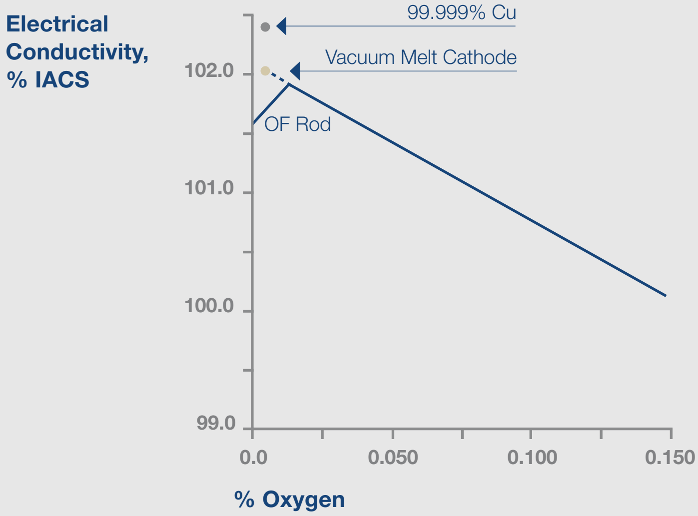

Figure 4 – The effects of oxygen content upon electrical conductivity

Element	Annealing Temperature Increase [°F/ppm]	Spiral Elongation Decrease [mm/ppm]	Resistivity Increase [μΩcm/ppm]
S	15	10	.0016
Se	15	> 50	.0097
Te	10	20	.0034
Pb	6	5	.0009
Bi	15	>> 30	---
Sb	3	3	.00029
As	3	4	.00056
Sn	5		.00016
Fe	1		.0012
Ni	1		.00014
Ag	1	2	.0002

Figure 5 – Unit effects of individual elements upon annealing temperature, resistivity and spiral elongation of fully annealed wires

Figure 5 summarizes the isolated effects of individual metallic elements on fully annealed wires in reference to:

a Annealing temperature
b Spiral elongation
c Resistivity

The simple addition of these isolated effects result in overall values that greatly exceed experimentally measured properties from commercial ETP copper. Oxygen also has a profound effect upon most of the physical and mechanical properties of copper rod as displayed in **Figure 6** including:

1. Breaks per ton
2. Drawing force
3. S.E.N.
4. Cuppy breaks
5. Conductivity
6. Area reduction
7. Twists to failure
8. Energy absorbed

The actual choice of oxygen content used in commercial ETP copper is dictated by a compromise between achieving optimum overall final properties and avoiding drawability problems.

Commercial ETP copper is usually produced by continuous casting and direct rolling systems. All of these systems take advantage of chemical reactions between oxygen and either sulfur or hydrogen to form gases in the melt. Consequently, as-cast bars contain some degree of microporosity which causes slightly reduced bar density. The vertical pouring layout of the Properzi casting machine, however, enables the optimal evolution of those gases. Residual smaller voids are eliminated by hot-rolling during the passes in the tandem rolling mill. *by Alberto Greppi*

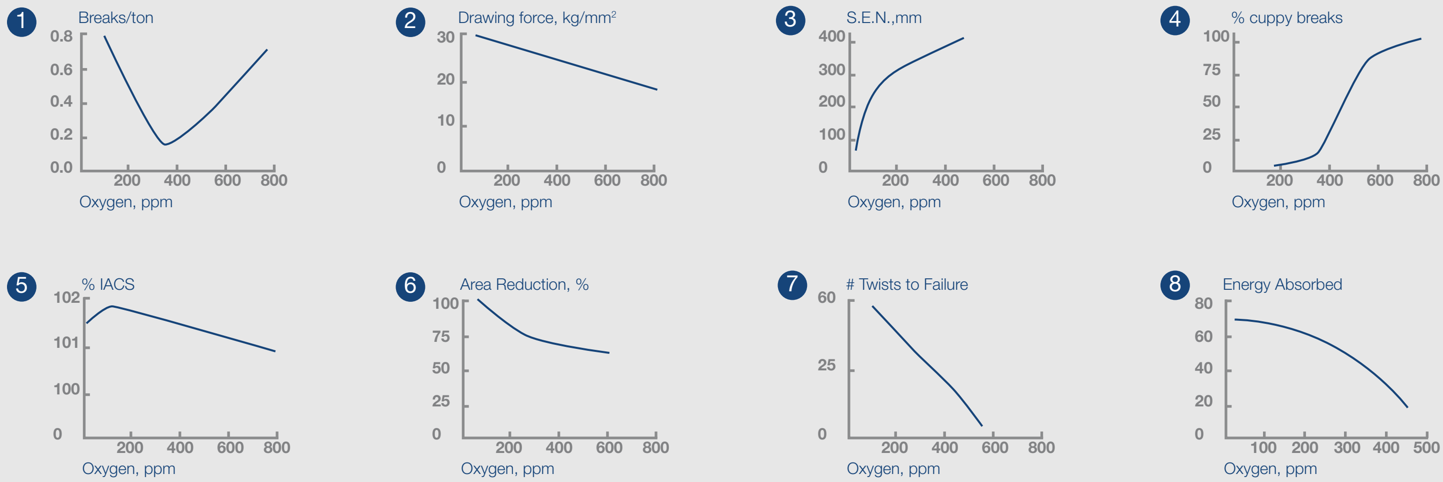

Figure 6 - Influence of oxygen content upon several different physical and mechanical properties of copper