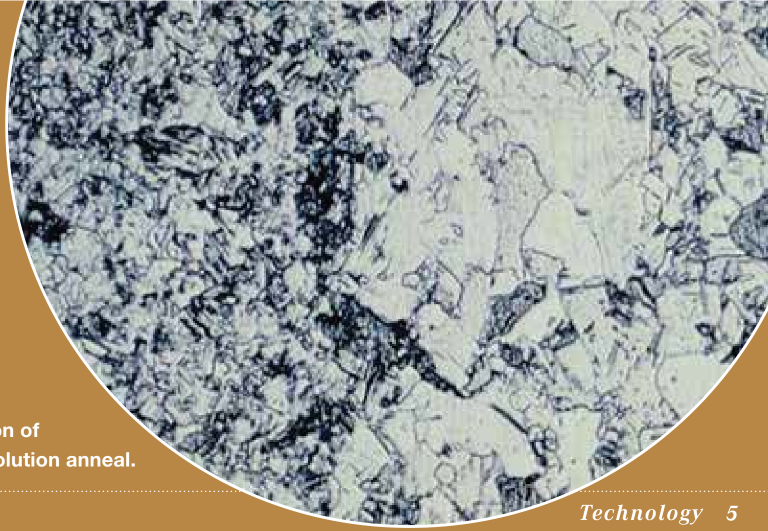
Influence of Oxygen in Copper

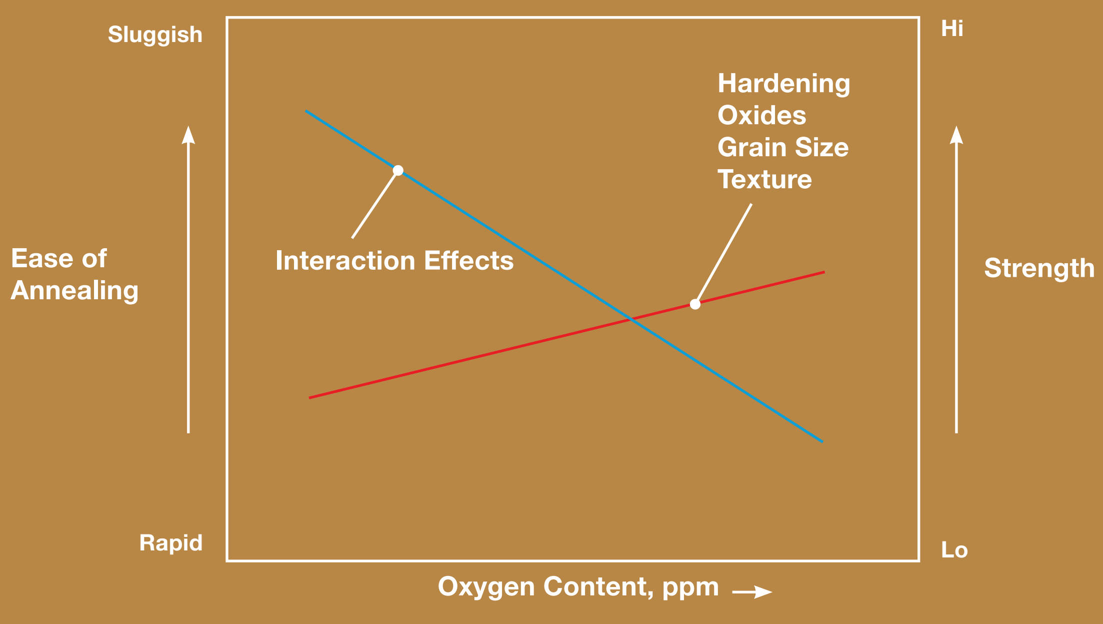


Duplex microstructure caused by dissolution of copper oxides during a high temperature solution anneal.

Metallic impurities cause harmful effects in commercial grade ETP copper such as retarding annealing, increasing stiffness, and impairing conformability during coil winding operations. Oxygen is intentionally added as a gas to molten copper in order to offset these detrimental effects, and is therefore considered as an alloying element. By acting as a scavenger for metallic impurities, many benefits are achieved and will be discussed in this report. Oxygen reacts with hydrogen and sulfur to form gases in the molten copper. These gases offset shrinkage in the cast bar during solidification and prevent the formation of shrink (blow) holes. Oxygen also forms binary or higher order oxides with most of the residual metallic impurities, thereby removing them from solid solution and minimizing their deleterious behavior. Approximately 50 ppm of oxygen is dissolved in the copper at room temperature and a slightly larger amount is needed to tie up any impurities as metallic oxides or gases. As a result of these reactions, electrical conductivity increases during the first ~ 200 ppm of oxygen, but then starts to decrease as more equilibrium copper oxide particles are formed. At the same time the copper is strengthened by these oxide dispersoids and drawability is impaired at much higher oxygen contents. Inasmuch as there are problems at both low oxygen contents (hydrogen embrittlement) and high values (drawability issues), ASTM standard B 49 for ETP copper limits the oxygen content to the range between 100 and 650 ppm. It should be noted, however, that many premium quality rods usually have oxygen contents between 125 and 400 ppm. Oxygen has a beneficial effect upon the annealing behavior of cold worked copper wire by reducing its annealing time, temperature, and activation energy for recrystallization. This reduction occurs because the dissolved impurities are removed from solid solution and tied up as metallic oxides. A lower wire temperature during in-line annealing results in energy savings and improved process controls. These benefits are offset slightly by a concomitant increase in tensile strength that is attributed to the presence of copper oxide dispersoids. The oxide particles not only increase strength at high oxygen contents, they also have a stabilizing effect upon final grain size, which can sometimes be beneficial. The behavioral effects of oxygen content upon annealability and strength of fully annealed wires are shown schematically in the figure below, and indicate two opposing tendencies. Whereas high oxygen values may impair drawability, annealing is more difficult at low oxygen contents. Formation of either abnormally large grains or a duplex microstructure (a mixture of large and small grains) after annealing can be a problem because it oftentimes results in diminished ductility and elongation. Sudden coarsening of grains, sometimes referred to as "secondary recrystallization", is associated with dissolution of oxides during exposure at high temperature and is prone to occur at oxygen concentrations less than 600 ppm. A typical photomicrograph of a duplex microstructure is presented in the figure above.

Most industrial QC laboratories measure oxygen content in both molten copper and the finished rod using commercial analyzers. ASTM standards have been developed for oxygen concentrations between 5 and 400 ppm, and work is in progress by this organization to develop standards having higher oxygen contents. Although industrial probes can be used continuously by inserting them in molten copper, they only measure oxygen that is dissolved in the copper. To be more useful to the rod producer, a correlation would have to be determined between probe data and results obtained using commercial oxygen analyzers. The latter instruments measure total oxygen content, which includes the dissolved value in addition to oxygen that is tied up as entrapped slag, copper oxides, metallic oxides, and surface oxides.

by Horace Pops



Schematic representation showing the effects of oxygen content upon annealing behaviour and hardening of copper.