



Removal of 5,000 Å oxide diagram (temperature/time)

Cleaning Copper Rod

When molten aluminum or copper solidifies during continuous casting, a covering of oxide scale forms on the outer surface of the cast bar. In the casting of copper, however, this scale is non protective and increases in thickness very rapidly prior to entering the rolling mill. A thickness of 100,000 Å or more (0.01 millimeters) is not uncommon. On the other hand, oxide films on aluminum cast bars are very thin, tenacious, and protective. Consequently, they do not grow in thickness with time at elevated temperature because it is difficult for oxygen to diffuse through the scale and then react with the underlying aluminum base metal.

Since copper oxides are very abrasive and resist lubrication bonds, they frequently cause quality problems such as die wear, fines generation, and wire breaks during subsequent drawing of rod into wire. Copper oxides are normally removed quite effectively in the Wire & Cable industry by use of three different processes. First, most of the scale is removed from the hot copper bar by mechanical descaling. The rolling mill emulsion is fed into a high pressure pump and then blasted onto the hot copper inside the roughing mill. When copper is exposed to a temperature of approximately 8000°C, the oxide exhibits very poor adhesion with the contiguous copper interior. Consequently, most of the scale can be effectively removed. Proper direction of the spray prevents recontamination of downstream copper with the exfoliated scale. Most of the residual oxide is then removed from the hot rod after it exits the rolling mill by either acid pickling or alcohol reduction. A hot aqueous solution of sulfuric acid, sometimes with a peroxide additive is used to dissolve the copper oxide constituent. Acid pickling is particularly used in rod plants that are associated with a refinery and/or have large casting rates. Dissolved copper is subsequently recovered from the acid solution, but at a considerable expense.

The third method of cleaning copper rod is continuous immersion of the finish rod into an alcohol solution, which usually contains several percent of isopropyl alcohol (IPA). In theory, almost any other organic material can be used. As alcohol heats up from contact with the hot copper it vaporizes, thereby forming the reducing gases Hydrogen and Carbon Monoxide. These two gases each reduce the copper oxides to copper and steam. Consequently, alcohol cleaned

rod always contains an outer layer of reduced copper and a subsurface mixture of unreduced cuprous and cupric oxides. An alternative method to alcohol cleaning is to directly apply the reducing gases Hydrogen and Carbon Monoxide to the hot copper. The kinetics of cleaning oxidized rod using either an alcohol solution or reducing gases are about the same. As may be seen from the following graph, approximately three seconds at elevated temperature are required to reduce an oxide film that is ~ 5000Å in thickness.

Most rod producers currently measure the residual thickness of copper oxides using a coulometric reduction technique. This method employs an electrolytic cell in which the sample is the negative cathode, and an inert metal is used as the positive anode. Hydrogen ions reduce each oxide constituent at different voltages, and a plot of voltage versus reduction time is generated for further analysis. Both the quantity and thickness of each oxide can be easily determined from Faraday's law. Although ASTM Specification B49 for copper rod drawing stock is considering the lowering of the maximum allowed oxide thickness from 1000Å to 750Å, most copper rod manufacturers are capable of producing copper rod with an outer layer that is less than several hundred angstroms.

Continuous Properzi, working in conjunction with an outside developer, Confident Instruments, will be marketing a new tester called the "Comprehensive Surface Analyzer" (CSA).

Additional details can be obtained at www.confident-instruments.com/surface-oxides.htm. The new combined method instrument will not only increase accuracy and repeatability, but also replaces the electrolyte after a pre-designated number of samples have been run, provides tighter control of current density, analyzes the voltage-time curve, allows the operator to vary current density, and gives more credence to the real surface area of the rod specimen. In addition, patches of embedded oxides that are rolled-in and contiguous with the outer rod surface can be detected. The use of copper foil serves as a secondary standard for purposes of calibrating all surface film analyses with the test equipment. It should also be noted that the thickness of other copper compounds, such as those based upon sulfur or chlorine can also be monitored. *by Horace Pops*