

Cleaning Copper Beryllium

At room temperature, copper beryllium forms a thin tarnish layer. At the higher temperatures associated with heat treating, heavy oxide layers can occur. These oxides can interfere with subsequent surface operations such as plating or soldering. These oxides can be removed by using the techniques described below.

FORMATION OF SURFACE OXIDES

Heat treating copper beryllium parts produces an oxide film on their surfaces. The surface oxide is a mixture of beryllium oxide (BeO) and several copper oxides. The composition and thickness of this film is dependent on temperature and furnace atmosphere. It is important to remember that beryllium has a great affinity for oxygen and since beryllium oxide is not reduced by hydrogen, there is no heat treating atmosphere that will provide a surface free of beryllium oxide. How much oxide, what type of oxide and ease of cleaning does depend on heat treat conditions and procedures. Heat treating a "clean" surface, free of oils and other contaminants, simplifies cleaning after heat treatment, and should be standard operating practice in any event.

The composition and thickness of oxide films formed on the various copper beryllium alloys will vary somewhat depending on the beryllium content of the particular alloy, but the behavior of Alloy 25 (C17200) is typical. In nominal nitrogen atmospheres (with or without hydrogen) the degree of BeO formation on heat treated Alloy 25 is dependent on temperature, as is the total thickness of the oxide scale. At 700°F and above, the outermost layer is primarily BeO while below this temperature (600°F and 500°F) the outer scale is composed of a mixture of BeO and copper oxides, typically 30% BeO at 600°F and 20% BeO at 500°F. These observations are important from a cleaning standpoint since BeO is not readily attacked by acids. Not only is the oxide thinner at the lower temperatures, but its composition makes it more readily soluble in pickling baths. Time at temperature and type of "inert" atmosphere are also factors in film thickness and composition.

In a typical age hardening heat treatment (2 hours at 600°F) carried out in an "inert" atmosphere, a film thickness of about 300-800 Å can be expected on alloy C17200. Under solution annealing conditions (1450°F), the film can reach

as much as 1000-2000 Å.

OXIDE REMOVAL

These oxide films must be removed prior to stamping, plating, soldering, brazing or welding. The most difficult to remove are the thicker ones composed primarily of beryllium oxide, such as those formed in solution annealing operations. Fortunately, most solution annealing operations are performed only by the copper beryllium producers who have the necessary equipment and expertise to be able to supply an "oxide free" strip to the component manufacturer. Such films require hot, concentrated caustic pretreatment to render them acid soluble.

The component manufacturer, however, frequently age hardens the copper beryllium after stamping and must clean the parts before subsequent processing. There are many acid combinations which can be used, but those proven most successful in removing films containing beryllium oxide are sulfuric/peroxide (20% H₂SO₄, 3% H₂O₂, 125°F) and phosphoric/nitric/acetic (PNA) (38% H₃PO₄, 2% HNO₃, 60% acetic acid, 160°F). Nitric acid alone does not do an adequate job of removing BeO films unless these films are pretreated in hot, concentrated caustic (50-60% NaOH, 265°F).

There are significant differences inherent in the use of these acids for pickling copper beryllium. These will be dealt with in following paragraphs, but a note of caution is advised when dealing with any copper alloy containing lead, such as Alloy M25 (C17300). Nitric acid or PNA is used rather than a sulfuric acid system because of the insolubility of lead sulfate. Also, fluoboric acid (10-25% at room temperature) is frequently used as a preplating acid dip for leaded alloys following alkaline cleaning.

Incidentally, a cyanide copper strike is also recommended

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in the plating procedure as an additional guarantee for good adhesion on any copper alloy, but it is considered essential for leaded alloys. The cyanide strike is a cleaning and activating step.

It has been reported that with alloys containing beryllium, care must be taken to prevent the possibility of cyanide degradation of the substrate by too much exposure to cyanide containing solutions. This can lead to difficulties in adhesion, but is rather easily avoided by omitting cyanide dips or soaks (but not necessarily cyanide strikes) prior to plating.

SULFURIC ACID/HYDROGEN PEROXIDE

The sulfuric/peroxide system has the advantages of easy control and ease of treatment of waste liquors. The pickling action on copper beryllium is gentle with no noxious fumes generated. There may be some entrainment of sulfuric acid vapors, however, in a fume exhaust system. The sulfuric/peroxide bath is what is known as a "bright dip" and leaves the surface with a bright, matt finish. A cold water rinse should be used. The rate of reaction is controlled by hydrogen peroxide (H₂O₂) content and temperature. Sulfuric acid can range from 10 to 20 volume percent, and has little effect on reaction rate. Dissolved copper can be removed from the pickle liquor by cooling to 60°F or so to allow CuSO₄ ~ 5H₂O to crystallize out of solution. The acid can be reused indefinitely. The limited solubility of copper sulfate is sometimes a liability if provisions are not made to properly control the copper ion concentration in the pickle liquor. Hydrogen peroxide in contact with dissolved oxygen must be stabilized or replenished to prevent rapid deterioration of the oxidizing power of the bath. Many proprietary cleaners which are based on the sulfuric/peroxide system contain the proper stabilizers.

NITRIC ACID

The nitric acid system is somewhat cheaper, reaction rates can be varied over a very large range, and the surface finish achieved is bright and shiny, not matt. The disadvantages are the evolution of noxious fumes, the greater difficulty in controlling reaction rates, and waste disposal problems. The fumes can be controlled with the addition of urea to the nitric acid bath (1-2 ounces/gallon), but this complicates control. Reaction rate is dependent on the concentration of acid, urea and copper ion and on temperature. Temperature control is more difficult with urea additions, since the reaction becomes much more exothermic. More

gas is evolved with urea also, which can cause foaming problems if urea concentration gets too high. Urea is not easily analyzed in the bath, but this generally doesn't present a problem since 0.5 pound urea is used up for each 1 pound of copper dissolved, and brown fumes of NO₂ become apparent at concentrations below 1 ounce/gallon of urea. Many production facilities use nitric acid pickling without urea, but good fume removal must be provided. Copper is very soluble in the nitric acid solution, and good pickling can be maintained at concentrations as high as 150 grams/liter. A cold water rinse should be used. It is sometimes beneficial to use a dilute acid rinse (cold) before final rinsing to minimize staining. One to three percent HNO₃ is used.

PHOSPHORIC/NITRIC/ACETIC ACIDS

The phosphoric/nitric/acetic (PNA) system is a "bright dip" which also polishes the surface, leaving it shiny and generally smoother (lower Ra) than before etching. A hot water rinse gives a better looking surface than cold. Concentrations of the three acids can be varied, but less nitric makes the reaction more controllable. Concentrations of 38% H₃PO₄, 2% HNO₃, and 60% acetic at 160°F are ideal for cleaning copper beryllium. Waste disposal may be a problem with this system used on a large scale because of the phosphate ion, as well as the copper ion.

PRETREATMENT

In any acid cleaning or pickling operation, the surface of the metal will be rendered more uniform if it is free of passivated areas beforehand, or quickly becomes so. Generally, this means that the surface should be as free as possible of oils, greases, carbonaceous matter, and other "soils". This can be best achieved by the use of a good alkaline cleaner prior to acid pickling.

If the cleaned surface is not to be immediately plated or soldered, precautions should be taken to prevent tarnishing during storage. Benzotriazole (BTA) is commonly used as a stain inhibitor for copper alloys. The BTA film provides shelf life protection for up to a year as long as the film is not damaged or condensed moisture is not allowed to condense on it. This film can also withstand temperatures up to 300°F before vaporizing.

CONCLUSION

In summary, copper beryllium alloys can be readily electroplated, soldered, welded, or brazed, but extra care

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should be taken in cleaning heat treated alloys to ensure removal of oxide films. This can be accomplished by the use of a hot alkaline cleaner (cathodic or soak) followed by a mildly etching acid such as those described above.

SAFE HANDLING OF COPPER BERYLLIUM

Please refer to the Materion Corporation publications "Safety Facts 104 - Safety Practices for the Chemical Processing of Small Copper Beryllium Alloy Parts", and "Safety Facts 105 - Processing Copper Beryllium Alloys."

Handling copper beryllium in solid form poses no special

health risk. Like many industrial materials, beryllium-containing materials may pose a health risk if recommended safe handling practices are not followed. Inhalation of airborne beryllium may cause a serious lung disorder in susceptible individuals. The Occupational Safety and Health Administration (OSHA) has set mandatory limits on occupational respiratory exposures. Read and follow the guidance in the Material Safety Data Sheet (MSDS) before working with this material. For additional information on safe handling practices or technical data on copper beryllium, contact Materion Brush Performance Alloys, Technical Service Department at 1-800-375-4205.

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