Troubleshooting Functional Chromium

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It takes good detective work to troubleshoot any plating process. It takes knowledge of the process, a methodical approach, and patience. In the case of troubleshooting functional chromium plating, what appears to be a simple process can become quite an adventure. This edited version of a presentation from the Chromium Colloquium, held in January 1994 at Orlando, FL, gives some guidelines for finding the answers to plating problems.

As with any plating solution, it is important to stay within operating guidelines for each bath component. Functional chromium consists of chromic acid, and a catalyst (either sulfate, or a mixed catalyst system using sulfate and fluoride, or other materials). It is extremely important to maintain the proper ratio of chromic acid to catalyst.

Bath Parameters

Concentration

The concentration of chromic acid can be determined by a Baumé reading with a hydrometer, noting temperature at the time of reading, then checking the manufacturer's literature to determine concentration. Unfortunately, if the solution contains metallic impurities, it may cause higher readings. The preferred method is by wet analysis, which can be found in any handbook or manufacturer's literature. Normal range for plating is 195–300 g/L (24–48 oz/gal), with the lower end of the range for mixed catalyst formulations.

Some effects of low concentrations are dull or burned deposits, and lack of deposit hardness. High concentrations can cause dull deposits, and a lack of deposit hardness.

A ratio of from 75:1 to 100:1 is common in functional chromium plating, with a conventional chromic acid/sulfate solution. In mixed-catalyst bath ratios, from 100:1 to 200:1 are normal.

An analysis of sulfate and chromic acid should be determined on a regular basis to maintain the proper ratio. Small amounts of 66-degree Baumé sulfuric acid (no more than 0.0013 g/L [0.01 oz/gal] at a time) should be added to raise sulfate, and, in turn, lower the ratio. The g/L of sulfate desired, multiplied by the number of liters of solution, multiplied by 32.636 = mLs of sulfuric acid required. Or, the oz/gal of sulfate required, multiplied by the number of gal of solution, multiplied by 0.543 = fluid oz of sulfuric acid required.

Conversely, barium carbonate is added to lower the sulfate, and raise the ratio. It requires adding twice the amount of barium carbonate than the amount of sulfate desired to be removed. It is much easier to raise the sulfate using sulfuric acid, because it readily mixes into solution. Barium carbonate can take up to four hrs to react before lowering the sulfate.

In mixed catalyst baths, the catalyst should be analyzed by the manufacturer on a regular basis to determine if adjustments are needed, and to make the appropriate recommendations.

A high ratio can cause dull deposits, and reduce deposit hardness. Both high or low ratios can cause deposit roughness.

An incorrect catalyst concentration can cause dull deposits, pitting, and even a misplate (no coverage at all).

Fume Suppressants

The use of fume suppressants in functional chromium plating should be chosen with care. Some suppressants use wetting agents that may cause pitting at a thickness above 25 microinches (0.001 in.). If a higher thickness is required, contact a supplier for the correct recommendation.

Temperature

It is critical to maintain temperature at recommended guidelines. In general, for functional chromium, a range of 49–66 °C (120–150 °F) is required. It is a good idea to have a minimal amount of air agitation to prevent temperature stratification, and possible localized overheating of the solution. Take into account the proper sizing of the tank when considering temperature. Because of the poor efficiency of functional plating (15–25 percent), the bath has a tendency to generate heat. Size the tank to operate at 3–5 A/4 L (1 gal) of solution.

It is important to understand the relationship between temperature and current density in choosing the right temperature. Higher temperatures with higher current densities, as well as lower temperatures with lower current densities, can cause a lack of hardness in the deposit. Other effects caused when temperatures are either too high or too low, are dull deposits, uneven plating thickness, and burned deposits.

Current Density

Average cathode current density for functional chromium plating is in the range of 23–100 A/dm^2 (1.5–6.5 A/in.^{2}). It is important to know the surface area of the part being plated to properly adjust the amperage. If the current density is too high, it can lead to deposit roughness, and a tendency to burn. If the current density is either too high, or too low, it can cause dull deposits and affect the plating rate.

It is also important to avoid current interruption during plating, because it may tend to peel or whitewash. Some causes of interruption are poor racking, poor electrical connections, or, in the case of automatic plating lines, a poor joint alignment in the rail.

Solution Impurities

Metallic impurities in functional chromium plating build up resistance in the bath which, in turn, requires a higher voltage to obtain the proper amperage. Generally, the total metallic impurities should be kept under a concentration of 0.066 g/L (0.5 oz/gal). In some cases, it may be advantageous to raise the concentration of the bath to compensate for the buildup of impurities. Normally, trivalent chromium, chloride, iron, copper, zinc and aluminum are the most common. Some contaminants can be easily removed by electrolysis, while for others, it may be more economical to cut the solution to remove the contaminants.

Trivalent Chromium

Trivalent chromium can be formed by the introduction of organic contaminants to the bath, or by using too low of an anode area. It usually gives the solution a dark—almost black—appearance. It can be removed by electrolysis with an anode-to-cathode ratio of at least 10:1 at 6 V. It takes about 24 hr at 54 °C (130 °F) to remove 7.5 g/L (1 oz/gal) of trivalent chromium. To obtain the best results, try to distribute the cathode area evenly throughout the tank. Trivalent chromium has a significant effect on the efficiency of the solution. It also can cause treeing, or excessive buildup in high-current-densities.

Chloride

As a contaminant, chloride acts as a catalyst in chromium plating. It is about 8–10 times stronger than sulfate or fluoride. For this reason, it is very important to avoid drag-in of hydrochloric acid. Concentrations as low as 0.00053 g/L (0.004 oz/gal) can cause problems. In the past, most shops used silver oxide to precipitate chlorides in chromium solutions. Today, most shops try to electrolyze for chlorides, similar to removing trivalent chromium, because of the high cost of silver. A high anode-to-cathode ratio is necessary to drive chloride off as a chlorine gas at the anodes. Chloride contamination has a destructive effect on lead anodes. It will cause hazes at both high- and low-current-densities, and can cause white blotches.

Iron, Copper, Zinc and Aluminum

As contaminants, iron, copper, zinc and aluminum affect the resistivity of the solution. The presence of metallic impurities can also complex with the fluoride catalyst, and are best removed by ion exchange. Because of recent breakthroughs with resin technology, ion exchange is becoming the economical choice for impurity removal, as apposed to cutting the solution, disposing, and rebuilding it with fresh chromic acid. It is important to keep these impurities below 0.067 g/L (0.5 oz/gal).

Mechanical Causes and Effects

Several mechanical occurrences can cause plating problems that are sometimes overlooked.

Anodes

It is necessary to understand the importance of the anode-to-cathode relationship for uniformity in the chromium deposit. The closer that the anode and cathode are, the better the thickness distribution in the plate. For outside diameter plating, a distance of 10.2 cm (4 in.) is recommended. For inside diameter plating, a distance of no more than 1.3–2.5 cm (1–1.5 in.) is best. The length of the anode should be about 10.2 cm (4 in.) shorter than the cathode. The same holds true with the top of the anode being below the cathode. This will help prevent overplate, or dogbone effect, on the ends of parts. Some jobshops, which plate parts of several different lengths, may mask-off the bottom of the anode with a vinyl tape.

The anodes should be chocolate brown in appearance. If they are coated with a yellowish chromate film, they are inactive. The chromate film is formed from long periods of shutdown, or by the anode current density being too low. In general, three 5-cm (2-in.), or four 3.8-cm (1.5-in.) diameter anodes per 3 dm (1 ft) should give sufficient anode area for the proper current density. For inside diameter plating, use as large an anode as possible to prevent polarization. Anodes should be routinely checked and cleaned, either chemically or electrochemically.

Most functional chromium plating anodes are constructed of 93-percent lead and 7-percent tin. Antimony-tin can be used in a conventional chromium/sulfate solution, but is not recommended for mixed catalyst baths.

Electrical Connection

Anode and cathode leads to the rectifier must be sufficient to carry the required current. If they are hot to touch, they are either inadequately sized, or the connections are poor. If possible, all connections should be silver-soldered, because silver will form silver chromate in a chromic acid environment. If this is not possible, copper bolts should be used.

Fixturing

Because of the high current densities employed in functional chromium plating, and the relatively low cathode efficiency, it is extremely important to ensure that the current reaches the part. Copper is the material of choice. Racks and fixtures should be designed to carry 50 percent more current than required. Contacts should make a positive contact; gravity contacts should not be used. Shields or robbers are frequently used to assure uniform distribution of thickness.

The work being plated should be at least 7.6 cm (3 in.) below the surface of the solution. Hydrogen gas bubbles up to the top from the work, and can cause a diluting effect at the cathode film, which will cause a high current density and burning.

Rectification

As with most plating solutions, it is extremely important to avoid ripple (AC voltage) from being introduced. AC ripple should not exceed 5 percent for chromium plating. The rectifier should not be operated at less than 75 percent of rated amperage.

Pretreatment, Etching And Cleaning

In most cases, pretreatment and surface preparation is the main cause of many problems in functional chromium plating. Chromium will duplicate the surface condition of the base metal. Chromium does not level, so any imperfections in the base metal will be magnified in the chromium bath. That is why work coming into the shop must be free of imperfections.

Mechanical Finishing

In most cases, better finishing techniques can eliminate several problems, such as roughness, pitting and cracking. What appears to be a good plateable surface can come out of the plating solution with pits or slivers of roughness. When that happens, it is usually up to the surface finishing professional to prove that his operation is not at fault. In most of these cases, it would be beneficial for the plater, engineers, and the finishing department to communicate better. Tight controls are necessary in the grinding and finishing stages of mechanical finishing, as well as in the plating process. Engineers are often not sure of how much stock is removed in a single grinding pass. If done improperly, the grinding step can tear the metal and leave smeared slivers. These slivers pop up in the plating solution and become high-current-density areas that cause roughness, or tear off to become pits. It is necessary to ensure consistent practices throughout the process.

Surface Cleaning

It is important to properly clean parts, and obtain a water-break free surface, prior to functional chromium plating. Improper cleaning prior to reverse etching can result in an uneven, patchy chromium deposit. Normal procedures for base metal cleaning should be observed. Care should be taken in rinsing after acid pickle, to prevent the drag-in of hydrochloric or sulfuric acids, because they will alter the solution chemistries. In some instances, because of the size of large parts being plated, a minimal wiping of the surface with a solvent has been sufficient.

Reverse Etching

In functional plating, it is necessary to micro-etch the part prior to plating, to ensure adhesion to the base metal. This is done by reverse etching in a separate solution, typically a chromic acid solution without any catalyst, of 210–240 g/L (28–32 oz/gal), and should be maintained at plating temperature. Reverse etching should not be done in the plating bath, because it will introduce metallic contaminants, such as iron or copper, and reduce the efficiency and life of the solution. The part should be allowed to come up to the temperature of the etch before current is applied, to ensure an even etch. Over-etching may occur when using a catalyst-containing bath because the catalyst will speed up the etching process.

Over-etching can cause deposit roughness and should be avoided. It can expose carbon particles on the surface that cannot accept a chromium deposit. Mechanical finishing after plating may remove these particles and result in a pitted surface.

The proper etch time should be determined based on the basis metal. Most carbon steels, hardened and unhardened, should be etched at 14.4 A/dm^2 (144 A/ft^2) for 15–30 sec, with times up to 60 sec for hardened steels. Aircraft steels containing molybdenum require longer times—3–5 min at 14.4 A/dm^2 (144 A/ft^2). Reverse-etch of cast iron is not recommended. Vapor or dry blasting is usually all that is needed, assuring that the media is properly rinsed prior to chrome plating. Stainless steels, and all nickel-containing alloys, require a cathodic, room-temperature sulfuric acid (10–50 percent by volume) etch at 6 V for 15–30 sec. Non-ferrous alloys are not generally reverse-etched because an excessive amount of metal would be removed. Aluminum usually requires an interlayer of tin or zincate prior to plating. Some cast aluminum alloys, however, may be plated directly with chromium, after the proper pretreatment steps are completed.

These guidelines can be used for troubleshooting functional chromium plating. As all good detectives, or troubleshooters know, "leave no stone unturned in the search for answers." o

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