



Phosphorus Distribution in Copper Anodes And Its Effects Upon Black Film Formation

Introduction

Phosphorus containing copper anodes and chloride additions in the plating bath are employed to cause the formation of a black “protective” film on the anode surfaces during electroplating. This protective film reduces anode sludging and improves the quality and efficiency of the plating process. This paper describes tests done to characterize the best process window in an effort to optimize black film formation. Variables evaluated include: phosphorus content of anodes, chloride content of the bath and anode current density. Anode variables include: anode purity, grain structure and work hardening. “Best operating practice” recommendations concerning these variables are suggested for the plater.

Numerous questions have been raised concerning the distribution of phosphorus in phosphorus containing copper anodes. Phosphorus is added as an alloying element in amounts varying between 0.01% to 0.1% for the purpose of creating a film on the anode during electroplating. This black film protects the anode from acidic electrolyte corrosive attack and thus inhibits grain boundary corrosion and particulate formation in the electrolyte. The problem raised by particulates is that they may settle on the components being plated and cause surface defects.

Copper anodes are manufactured by a variety of methods and processes, including hot casting and cold rolling. Shapes, such as balls, are made by both hot and cold forging and rolling processes. Claims have been made by manufacturers and end users as to the benefits of the particular processes in making superior performing anodes. In particular, phosphorus distribution in the copper anode has been cited as of importance to the electroplating process.

Our work seeks to measure the phosphorus distribution in copper anodes and then determine the effect of this distribution upon anode performance and the plating process.

Phosphorus distribution has been measured in copper anodes of various sizes and shapes manufactured by producers from around the world. Scanning electron microscopy reveals phosphorus segregation in all anodes, reflecting solidification and anode fabrication processes. Laboratory electroplating tests have been performed on these anodes to measure anode sludging and current efficiency.

Findings

We started out by finding a scanning electron microscope equipped to measure phosphorus in a copper matrix in the range found in most anodes, 0.040 to 0.065 percent. We then obtained phosphorus deoxidized anodes from a variety of manufacturers from around the world and subjected them to SEM (scanning electric microscope) analysis. These anodes were both nuggets and balls which ranged in size from 25mm to 60mm in diameter. They were manufactured in a variety of ways.

We found that in every instance, phosphorus exhibited segregation. In the anodes examined by the SEM (scanning electron microscope), that contained an average of 0.005% phosphorus, the SEM measured phosphorus levels from a low of 0.009 to a high of 0.0197 percent.

Segregation is predicted based upon solidification theory and the phase diagram of the copper-phosphorus system. Most impurities in metals segregate during solidification. The extent of the segregation can be estimated from the phase diagram. All copper anodes are initially cast and processed in different ways to achieve the finished shape. Although, treatments such as hot or cold processing, followed by annealing, will cause recrystallization in metal. Recrystallization will not affect the underlying

distribution of impurities. Extensive hot deformation, such as extrusion or high reduction ratios in hot rolling, will also accomplish substantial homogenization.

Phosphorus segregates in the dendritic solidification structure of copper anodes. The segregation occurs over very short distances in the microstructure of the phosphorus deoxidized copper. This distance, from peak to peak, depends upon the solidification rate, but ranges from about 25 to 50 microns (0.001 to 0.002 inches). The relevant question for the planning engineer is: what effect does this phosphorus segregation have upon anode performance in the plating tank? We have performed our tests in order to find the answer to this question.

Discussion

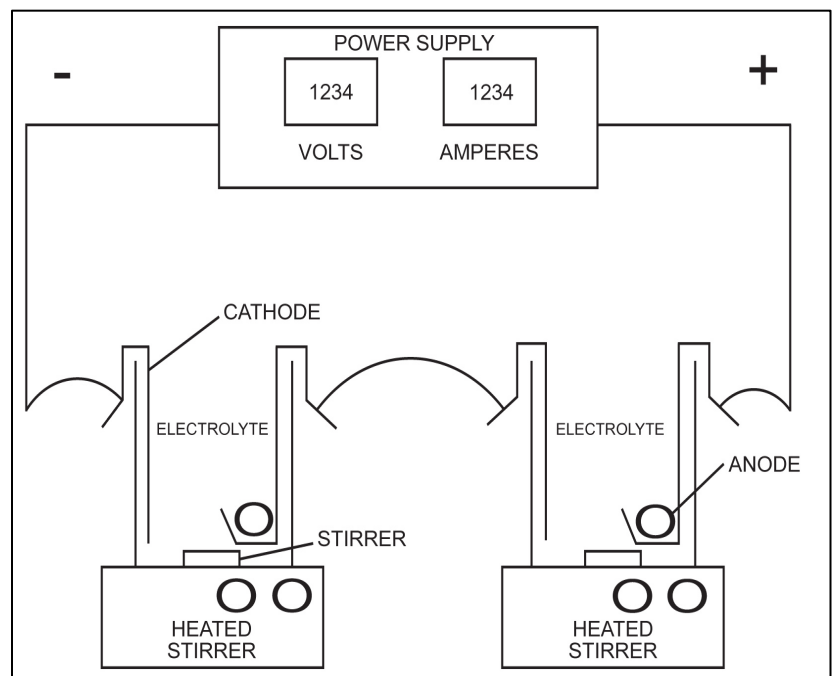
A common industry measure of anode performance sludging. Anodes that film properly, and which generate a minimum of anode sludge, are judged to be good performers. Anodes that generate a lot of sludge are judged to be poor performers. Anode sludge formation is effected by many variables in the plating environment. A list of these variable include:

- ◆ Anode current density
- ◆ Electrolyte composition
- ◆ Electrolyte circulation
- ◆ Anode chemistry & phosphorus content
- ◆ Anode basket geometry
- ◆ Anode bags, bag design & material
- ◆ Chloride content of the bath

It has been well established that the addition of phosphorus to the copper, together with chloride in the electrolyte under controlled electroplating conditions, creates a black phosphorus containing film which retards anode corrosion by the sulfuric acid in the electrolyte. If plating conditions change so that the black film does not form, anode corrosion and sludge formation increase as a consequence. The goal of the plating engineer, when using phosphorized copper anodes in a sulfuric acid-copper sulfate plating environment, is to control the plating process to ensure stability of the phosphorus film. Given a stable plating environment and proper phosphorus film formation, we wanted to find out what effect might be seen related to phosphorus distribution in the anode itself.

We decide to perform corrosion tests in our laboratory using a protocol developed by a brightener manufacturer. This protocol describes a method of corroding anodes in an electroplating environment and described a procedure for calculating the amount of anode sludge formed and the anode current efficiency. It also furnishes a rating scale for anode performance based upon the percentage of anode sludge formed.

To perform these tests we set up four test cells. We used two rectifiers, one for each two cells. The cells were 2000 liter breakers, set atop individual magnetic stirrers for electrolyte stirring. In each cell we hung a titanium "basket". The basket was a sheet of titanium mesh three inches wide, bent on the bottom to form a shelf to hold the anodes. The mesh was bent on the top to allow it to be hung from the edge of the breaker.



The mesh was long enough to ensure that the anodes were well submersed in the electrolyte. For cathodes we used strips of copper sheet cut to the correct width and length to give the desired immersed surface area.

Each rectifier had a variable current and/or voltage and could be set for voltage or current control. The units are rated for 0-30 volts DC and 0-10 amperes current. They were operated in the current control mode with the current set to produce the required current density at the anodes. When two tanks were being operated, they were set up in a series arrangement so that the current flowed through both cells. We were careful to select anodes to ensure the same anode area in both tanks supplied by the same rectifier.

The electrolyte was a basic copper sulfate bath made new for each anode test. The composition was:

Copper sulfate	225 G/L
Sulfuric acid	50 g/l
Chloride content	As planned
Brighteners	Per supplier

A proprietary brightener system was used. Additions were made at startup and daily in accordance with the manufacturers recommendations.

Procedure

The procedure for performing the anode corrosion test was as follows:

1. Prepare new plating solution, stir
2. Select anodes, calculate surface area
3. Make cathodes with required surface area
4. Calculate current required
5. Clean, weigh and insert anodes and cathodes
6. Add brightener
7. Turn on power, set amperes, record voltage
8. Record appearance of anodes hourly for first 4 hours, then at the beginning and end of shift
9. Replenish brightener daily, add distilled water to make up for evaporation at same time
10. Run test for 48 hours, record amperes
11. At power off, record appearance of anodes
12. Rinse anodes with distilled water over tank
13. Weigh filter paper
14. Filter the bath, rinse and dry the filter paper
15. Weigh the anodes, cathode and filter paper
16. Analyze the bath
17. Calculate sludge percentage and anode current efficiency

A total of 88 anode corrosion tests were conducted. Anodes used in the corrosion tests included those for which phosphorus distribution had been measured. These anodes included both nuggets and balls. The anode balls were manufactured by a variety of hot and cold processes and exhibited a variety of microstructures as described above. The corrosion tests were all conducted the same insofar as possible. At the start of the test series, plating tests were performed at several different chloride contents. Based upon these results, most tests were run using a chloride content between 70-115 ppm. Most anodes were tested twice and some three times.

The data included:

- ◆ Anode size, shape, manufacture mode
- ◆ Anode chemical analysis
- ◆ Anode phosphorus, average by spectrograph
- ◆ Phos distribution measured by SEM
- ◆ Bath chemistry
- ◆ Sludge percentage
- ◆ Anode efficiency

The anode sludge percentage was calculated as follows:

$$\text{Sludge \%} = (\text{Weight Sludge}/\text{Anode Weight Loss}) = 100$$

$$\text{Anode CE \%} = \text{Actual Anode Weight Loss}/\text{Theoretical Weight Loss}$$

Where:

$$\text{Theoretical Weight Loss} = 1.2007 \text{ Grams/Ampere} - \text{Hour} \times \text{Amperes} \times \text{Hours}$$

Results

Step 1

Initial tests were performed at several different chloride levels as indicated above. The purpose was to determine a suitable chloride level for the test program. Chloride levels of 25, 90 and 180 ppm were run with the results shown below:

CHLORIDE	RESULTS
25 PPM	thin black film, bath clear
90 PPM	thick black film, bath clear
180 PPM	anodes gray, bath murky

The low chloride test resulted in a thin black film on the anodes. In an actual plating situation, with the anodes in a bagged anode basket, chloride in the electrolyte around the anodes may become depleted relative to the main bath volume, causing film failure. The high chloride test resulted in a gray film on the test anodes. This is not satisfactory black phos film. The bath became murky in appearance indicating particulates in the bath. Sludge measures 0.21 percent, approximately 10 times the average amount observed in the subsequent test.

Based upon these results, the chloride levels used for the test program were programmed in the range of 70 ppm to 115 ppm.

Step 2

We then proceeded with the tests on anodes from manufacturers around the world. What we found surprised us. As long as the black phosphorus film formed well, there was no substantial difference observed in sludging behavior or current efficiency from one anode to another.

The table below shows sludge percentage and current efficiency for the various anodes tested. Each manufacturer is represented by a letter. The numbers are averages of one to four plating tests done on the particular products.



Manufacturer	Product	Percent Sludge	Current Efficiency
A	Large Ball	0.028%	96.9%
B	Large Ball	0.027	98.6
C	Large Ball	0.039	97.8
D	Small Ball	0.025	97.2
E	Small Nugget	0.033	98.6
	Small Ball	0.006	98.2
F	Large Ball	0.034	98.9
G	Medium Ball	0.048	97.2
H	Medium Ball	0.034	97.2
I	Large Ball	0.039	98.6
J	Small Nugget	0.046	96.4
	Small Ball	0.050	98.4
K	Small Ball	0.031	98.0
	Large Ball	0.014	97.5
Overall Average	All Shapes & Sizes	0.030%	97.8%

There does not appear to be a pattern to this data. Moreover, the manufacturers represented in the list above manufacture anodes by different processes. The phosphorus distribution is affected by different manufacturing processes as discussed above. Therefore, phosphorus distribution does not have an effect, which we are able to discern, upon sludge generation and/or anode current efficiency.

Discussion

Numerous variables and process steps must be controlled in order to electroplate successfully. In these tests we have attempted to create a controlled environment in order to isolate the variable of interest, namely anode phosphorus distribution.

We have shown that chloride content of the electrolyte is an important variable which must be controlled. Too much or too little will result in phosphorus film formation failure. When the phosphorus film fails, anode corrosion increases dramatically and sludge formation increases accordingly. Within a range of chloride content, which allows for the formation of good black phosphorus film on the anode, anode performance is rather consistent regardless of size, shape or phosphorus distribution.

Not examined in this work are the detailed effects of other variables, such as anode chemistry (purity), or phosphorus content. The anodes tested had a range of phosphorus within 0.040 to 0.065 percent, which is usually specified by end users. In addition, the anodes tested varied in purity. Our review of this information did not indicate that phosphorus content or anode purity had an observable effect upon sludge formation or anode current efficiency. We would indeed expect to see some effect of anode purity upon anode current efficiency in an appropriate test environment. We would also expect that in a production plating environment, anode purity would affect impurity levels in the electrolyte over time, based upon material balance considerations.

We also recognize that our test procedure does not represent the real world plating environment in which many other process variables play a role in a properly performing plating environment. Electrolyte circulation in and around anodes in a bagged basket environment is very important in the performance of anodes during sustained plating performance. Our simple plating test environment was appropriate for the goals of our test program.

REFERENCES: Procedures for performing Corrosion test on Anode Material, TSA 1049, EnthoneOMI Inc.
CLEPO CUPRAFIN 800 manufactured by the Frederick Gumm Chemical Company