Recovery of Copper Metal in the Continuous Regeneration of Cupric Chloride Etchant

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Abstract

An electrochemical device has been developed that deposits non adherent copper metal powder at the cathode, and generates chlorine gas at the anode. The chlorine is contained within the system, and is used to regenerate the etchant in a continuous closed loop process. Chlorine is generated only when the electrochemical process is underway. There is never any stored chlorine gas. The copper metal powder is deposited on rotating disc cathodes, and continuously and automatically removed and stored. The disc cathodes rotate through the recirculating etchant solution, and the copper powder is deposited approximately 750 amperes per square foot and 5 volts DC. The powder is continuously removed from the cathode disc by mechanical scrappers, and flushed into a collection bin by a recirculating water spray. The anodes are inert DSA anodes. The chlorine generated is continuously transferred to the etchant where it reacts to regenerate the etchant. The rectifier is automatically turned on only when the ORP is below a set point. The rectifier is turned off when the ORP reaches a preset upper ORP limit, thus ending the production of chlorine gas. In order to conduct this study the existing unit has been installed and operated and tested in a real production facility. Because of the chlorine production, the unit cannot be operated or tested unless it is connected to a working etching system. The current high price of copper metal has made this technology very economically viable.

Introduction

The cupric chloride etchant provides an inexpensive, continuous method for etching copper. It is used primarily for inner layer etching because of limitations on the etch resists which can be used. The mechanism of etching involves the reaction of cupric ion with copper to form cuprous ions. This is done in a hydrochloric acid medium to facilitate the solubility of cuprous ion (cuprous chloride). Various oxidizing agents can be used to re oxidize the cuprous ion, thus regenerating the etchant. Common oxidants include chlorine gas, hydrogen peroxide, and chlorate ion, usually alkaline sodium chlorate. The addition of the oxidant can be automated through the control of the oxidation reduction potential (ORP) or through the sensing of turbidity in the solution. The etching process leads to the formation of excess cupric chloride that must be disposed of by the user.

The use of sodium chlorate requires the consumption of hydrochloric acid to neutralize the salt. The mechanism probably involves the formation of chlorine from the acidified chlorate ion. Although the chlorate oxidant method is more costly, it is widely used in order to avoid storage of either chlorine gas or hydrogen peroxide.

There have been many previous attempts to utilize electrolysis to regenerate cupric chloride etchant. The cathodic product is copper metal. The anodic reaction results in the production of chlorine gas. In order to avoid this anodic reaction, most electrolysis approaches utilize membrane technology to separate the anode and cathode reactions. With this technique the anode can be exposed to a low chloride content solution so that the anode reaction is the re oxidation of cuprous ion to cupric ion. The membranes utilized are expensive, and have a relatively short lifetime in the hot acidic environment of the application. Examples of these efforts are given in reference 1, 2, 3.

The use of chlorine gas to regenerate cupric chloride etchant has been common in the past. Chlorine is not widely used at present because of the danger associated with the storage of liquefied chlorine under pressure. Our goal was to develop an electrolytic method, which would operate without the use of membranes. The electrolysis of the etchant leads to the generation of chlorine only when current is flowing. Therefore, the control of this current can limit the generation of chlorine to occur only when the ORP of the etchant is low enough to call for it. There is no stored chlorine. The present effort was directed toward determining whether the chlorine generated during the reaction could be controlled and contained within the system and used to re oxidize the cuprous ions without any of the chlorine escaping into the environment.

In addition, the program was directed toward developing a continuous automated method for removing the plated copper metal from the cathode. We wanted a high efficiency for the formation and removal of the copper from the system. Since the copper is formed in an etching environment, the efficiency will depend, in part, on a rapid removal of the copper from the etchant. In addition, the copper must be very pure, and formed in high efficiency relative to the current utilized. We also wanted to compare the economics of the electrolytic system with the economics of the currently used oxidants and acid.

Design of the System

We chose to utilize discs as the cathodes to maximize the surface area presented to the etching solution. Titanium surfaces are an ideal choice for the discs because titanium is inert in the etchant, and because deposited copper will not adhere to a titanium surface because of the oxide formed on the surface in air. Since titanium is a very poor conductor of electricity, modified discs were used. The discs are mounted to a rotating shaft, and inert scrapers are mounted to continuously remove the copper as it is formed. The anodes are DSA inert anodes, mounted as close as is possible to the rotating disc cathodes. This spacing is dictated by the need to allow solution flow between the electrodes, and the need to allow enough spacing to prevent anode, cathode shorting by the deposited copper. This arrangement is shown in figure 1, and by the photograph of the system, partially assembled, in figure 2.

Figure 1 Cathode Arrangement

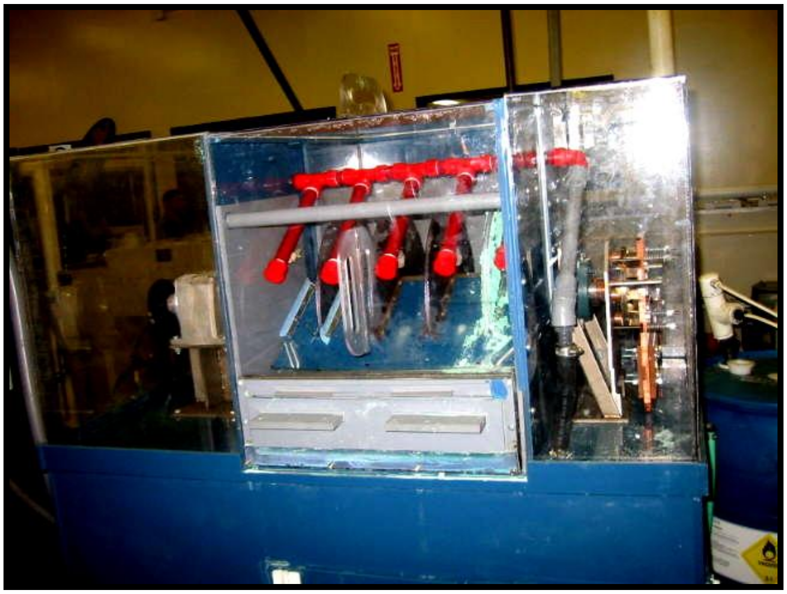

Figure 2 Partially Assembled System

Very high current density will deposit an easily removable copper powder on the cathode discs. Current densities between 65 amperes per square meter (700 amperes per square foot) and 90 amperes per square meter (1000 amperes per square foot) have been employed. The system operates in an on line continuous manner. The etchant is pumped directly from the sump of the etcher, through the plating cell, and back to the etchant sump. The ORP of the etchant is continuously measured, and the plating current is turned on only when the ORP is below a preset level. When the ORP reaches a high preset level, the plating current is turned off, ending the generation of chlorine and the deposition of copper. There is never any stored chlorine. In operation, the cathode discs are rotated at a controlled speed so as to remove the deposited copper from the solution quickly and minimize the etching of the deposited copper. However, rotation must be slow enough to permit the formation of sufficient copper powder for easy removal by the stationary scrappers.

The system is sealed so that the chlorine can be contained. The chlorine is transferred from the plating system to the etchant under vacuum, so there is never any chlorine under pressure. There has been no problem with chlorine escape into the environment. The deposited copper falls into a collection bin inside the sealed system. The system and the bin are shown in figure 3.

Figure 3 Installed System

Copper is removed from the system approximately once per shift. Prior to removal of the copper, the rectifier is turned off for about 20 minutes while the rest of the system continues to operate. This allows time for the vacuum to transfer all of the chlorine to the etchant where it reacts to oxidize cuprous ion to cupric ion. The copper is removed by pulling the bin forward and removing a copper holder. A fresh copper holder is then inserted, the bin is closed, and the system is again ready for operation.

Results

Since the system, in operation, produces chlorine gas, it is not possible to operate the unit unless it is connected to a working etcher. Winonics, in Brea California, agreed to work with us on this program, and the unit was connected to their operating cupric chloride etching system. The Winonics system already had a regeneration capability, and our plan was to supplement that existing system. We also intended to introduce our system gradually so that we could test it in partial operation. We were interested in a number of variables and test results. These included ability to control the evolved chlorine, determine the thermal effects of the plating current, test the copper collection system, verify the ability to control the ORP of the etchant, and determine the purity and collection efficiency of the copper. We planned to study these parameters at various current densities, disc rotation speeds, and solution flow rates. We also wanted to determine the economic advantages of the unit compared to the use of oxidants.

The cathode current density was varied between, 65 amperes per square meter (700 ASF) and 90 amperes per square meter (1000 ASF). An anode current density above 1000 ASF will reduce the anode lifetime, and this determined the upper limit on the cathode current density. At these currents, the DC voltage required was about 5 volts. At higher current density there is more heat generated by the plating operation. The copper deposit is more powdery and easier to remove from the cathode at high current density. At lower current, some of the copper deposit tends to be more foil like, and is more difficult to scrape from the rotating discs. Un removed copper will re dissolve in the etchant, reducing the efficiency of the operation. However, un removed copper will dissolve in the etchant at the end of operation, helping to keep the discs clean. Since we are running multiple anodes from a single rectifier, the total current is limited by the current on the most conductive anode The efficiency of copper collection is best at high current density.

The etchant is brought directly into the plating cell at the temperature of the etchant. The etchant is heated by the plating operation, and is returned to the etcher sump at elevated temperature. The elevation of the temperature plateaus after about 30 minutes. Figure 4 shows this effect as well as the added increase in temperature caused by an increase in current. At 1300 amperes, the added temperature caused no problems with the etching process. This is because the cooling system in the etcher was able to maintain the etching temperature at the set value. At higher current, a chiller is required to control the temperature of the solution as returned to the etchant. This is accomplished by cooling the solution after it is pumped from the etcher, and before it reaches the plating cell. Then, after plating, the solution is returned to the etcher at operating temperature.

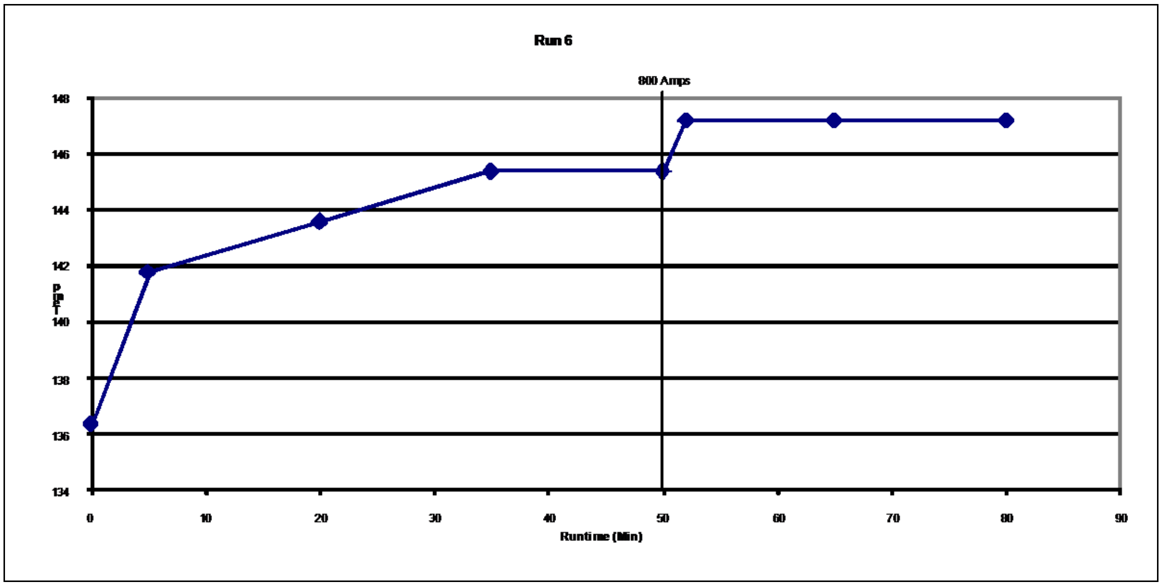

Figure 4

The ability of the system to control the ORP depends upon the balance between the rate of etching and the rate of chlorine production. Figure 5 shows the ORP value over time as the etcher was run. When etching was discontinued, the ORP increased until the unit automatically shut down. This can be seen in the figure. No chlorine was detected outside of the unit during this run. The chlorine detector was set at 0.5 PPM chlorine.

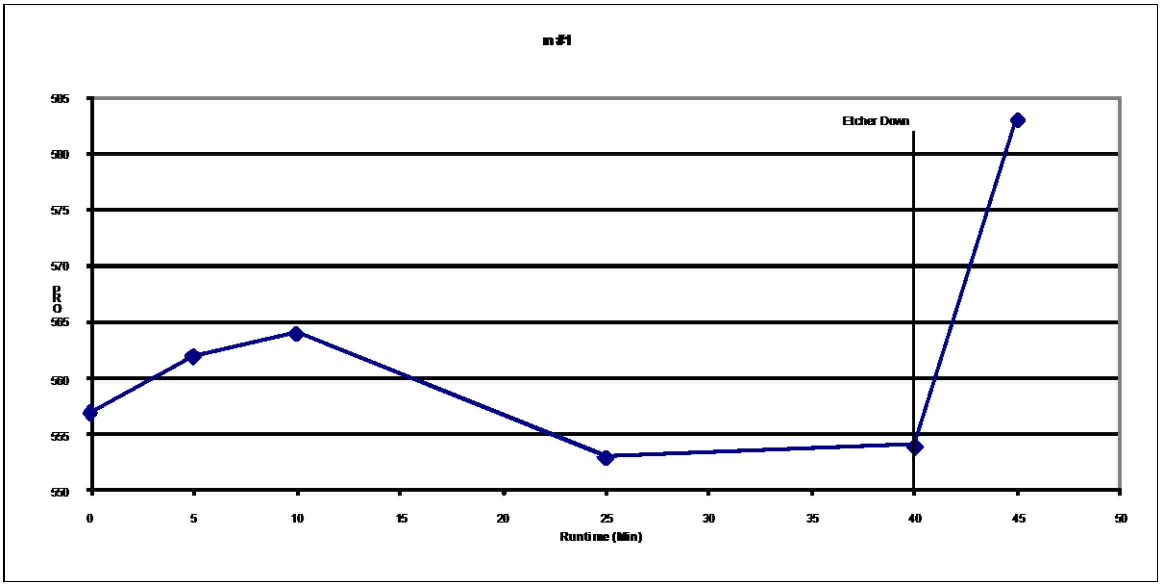

Figure 5

The collected copper was rinsed in 10% hydrochloric acid, water, and dried. Analysis showed it to be 99.8% to 99.9% copper. Based upon theoretical calculations (Coulomb's Law) the copper was collected at 77% efficiency. At 2200 amperes, and at 75% efficiency, we would expect to collect about 3.5 pounds of copper per hour.

Advantages

There are numerous environmental advantages. There is less or no excess cupric chloride to collect and haul away. In some states, this is considered a hazardous waste. The liability for the hauled away cupric chloride is eliminated. The storage of hazardous oxidant and acid is minimized or eliminated.

The etching of copper with sodium chlorate as the oxidant has a cost of about 5.5ç per ounce of copper etched. This includes the cost of oxidant, acid, and waste hauling, and will vary from shop to shop. The cost of power to operate this unit is about 1.2ç per ounce of copper recovered, depending upon the cost of power. Pure scrap copper sells for about 80% of new copper. At the current COMEX price for copper (November 2007), this is about 17ç per ounce of copper. The user will save about 20ç per ounce of copper etched. This should give an acceptable payback on the equipment. .

Acknowledgements

1. The authors would like to thank Winonics for their assistance and for allowing us to operate the unit in their facility.

2. There is a patent pending on the device and process.

3. This work was funded by the EPA under an SBIR Phase II Award Contract No. EP-D-06-085

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1. Electrolytic Regeneration of Acid Cupric Chloride Printed Circuit Board Etchant, J E Oxley, R J Smialek, DOE Final Report, 1996

2. 2 U S Patent 5,705,048 Oxley et.al,

3. 3 US Patent 4,468,305 Hills M R

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Recovery of Copper Metal in the Continuous Regeneration of Cupric Chloride Etchant

- **Introduction**

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- **Introduction (continued)**

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  In addition, the program was directed toward developing a continuous automated method for removing the plated copper metal from the cathode. We wanted a high efficiency for the formation and removal of the copper from the system. Since the copper is formed in an etching environment, the efficiency will depend, in part, on a rapid removal of the copper from the etchant. In addition, the copper must be very pure, and formed in high efficiency relative to the current utilized. We also wanted to compare the economics of the electrolytic system with the economics of the currently used oxidants and acid.

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- **Design of the System**

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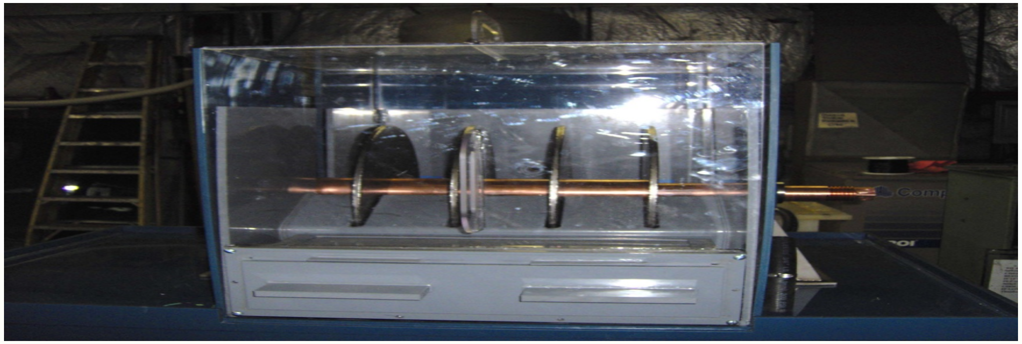

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- **Design of the System (continued)**

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  There is never any stored chlorine. In operation, the cathode discs are rotated at a controlled speed so as to remove the deposited copper from the solution quickly and minimize the etching of the deposited copper. However, rotation must be slow enough to permit the formation of sufficient copper powder for easy removal by the stationary scrappers.

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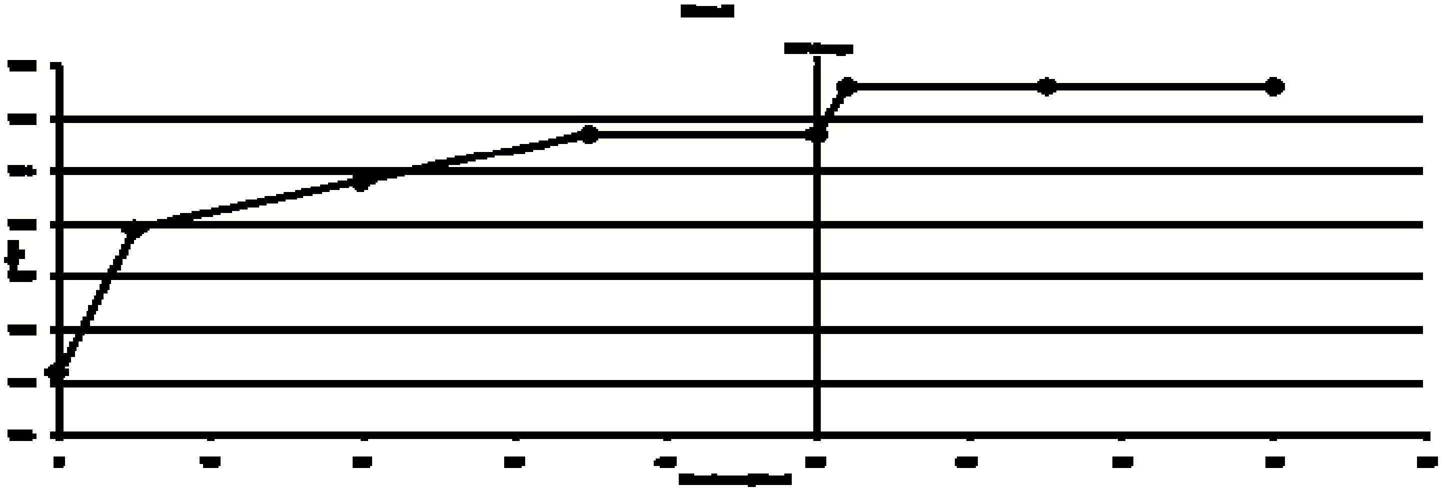

Figure 4

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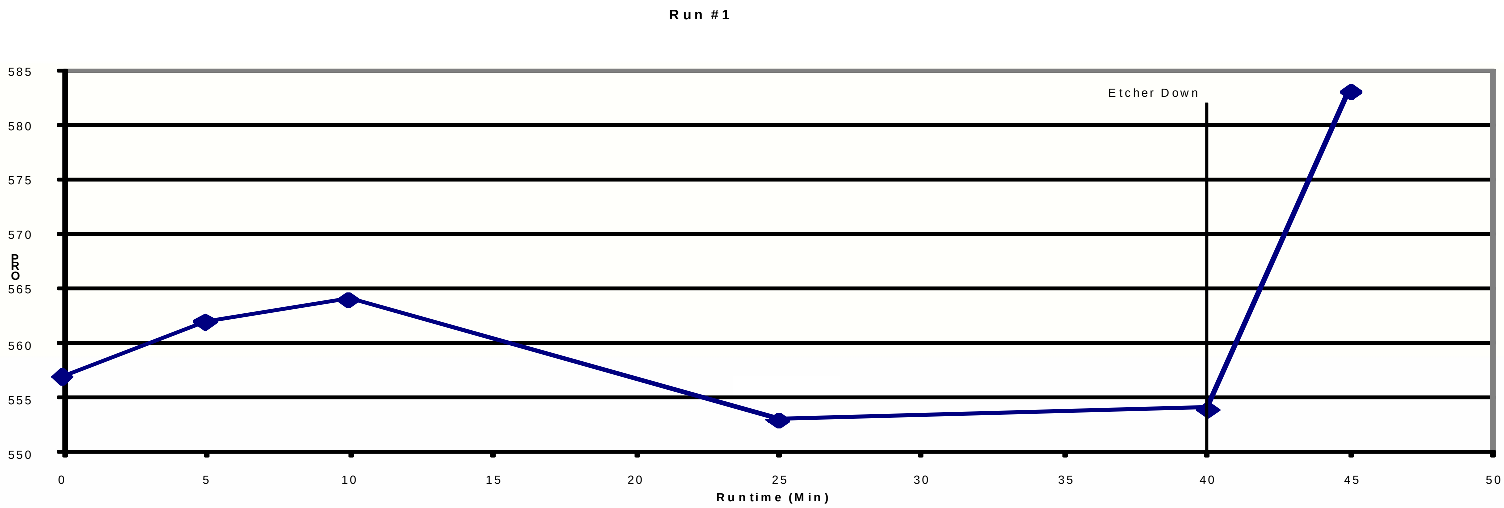

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2. There is a patent pending on the device and process.
3. This work was funded by the EPA under an SBIR Phase II Award Contract No. EP-D-06-085

- **References**

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