A Study on the Manufacture of the Cu Powder from Electrochemical Recovery of Waste Rinse Water at the Cu Electroplating Process

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Abstract

A newly designed cyclone type electrolyzer was tested to recover the copper powder from the waste rinse water of Cu electroplating process. Polarization measurements were performed to investigate the electrochemical behavior of copper ions and limiting current density in waste rinse water from copper electroplating processes. Electrowinning was performed at room temperature and the electrolyte was strictly controlled to circulate with a linear velocity of more than 1 m/sec using magnetic pump. More than 99 percent of Cu ion was successfully recovered and the size of the recovered Cu powder ranges from 0.1–0.5 μm . The Cu powder mainly consisted of Cu_2O and Cu. It was easily reduced to pure Cu powder.

Introduction

Such chemical industries as plating, dyeing, refining, and leather, need so much water and discharge much waste water at that rate from several processes. Especially, in case of plating, various waste water is discharged from the most of the processes, like rinsing, degreasing, etching, pretreatment, etc. Most of plating companies in Korea discharge waste water of about 5 tons per day on an average. Almost all plating companies however have no technological and financial ability to treat their waste water and it is a very serious problem for them.

Although waste rinsing water, whose metal concentration is a few hundreds ppm, shows much lower concentration than waste plating solution, it occupies major portion of waste effluent from plating industry. Therefore, it is more important to develop the recovery techniques of various metals from the low concentrated solution considering resource economics and environments.

There are several methods for metal recovery from the waste water containing various metals. Such methods as membrane separation, ion exchange, evaporation, electrolysis can be consid-

ered as representative ones. Among them, electrochemical method is preferred for plating process, because it can be established and operated as an in-line system and it shows a great performance in recovering high purity metals.

It is well known that the recovery efficiency in electrochemical method depends on a kind of metal to be recovered and its concentration. But in general that method has a low efficiency and slow reaction rate. Therefore in order to overcome this weakness, newly designed cyclone type electrolyzer has been developed in this study and used to recover copper ions in waste rinse water of plating industry as a submicron sized powder. Operating parameters like temperature, current density, activity of cathode surface, and linear velocity of electrolyte were established to enhance the performance of this equipment.

Experimental

To obtain the electrochemical behavior and the limiting current density for the reduction of copper ion, which is one of the most important factors, the copper polarization measurements were carried out in various conditions by using an experimental apparatus composed of programmable Potentiostat / Galvanostat and rotating electrode system using 3 electrode. In this system, working

electrode material is SUS316, which is also used as a cathodic material in cyclone type electrolyzer. Rotating disk electrode system enables us to analyze the target system quantitatively, and besides working electrode. This system is composed of reference electrode and counter electrode which are saturated calomel electrode (SCE) and graphite, respectively.

Fig. 1 shows the schematic diagram of cyclone type electrolyzer. It consists of three inlets and two outlets in up and down directions. Overflow enables the electrolyzer to complete the electrical circuit. Synthetic solutions were prepared by dissolving analytical grade CuSO_4 to the desired concentration and pH was adjusted with H_2SO_4 . In the electrowinning experiment with cyclone type electrolyzer, various current densities were applied in the range of 10–35 mA/cm^2 , and the copper concentration was fixed at 100 ppm, which is the average concentration of waste rinse water in PCB copper electroplating process.

Additionally, the linear velocity of influx into the cell was maintained at 5 m/sec which is the best-fitted value obtained from many experiments, and this velocity was adequate for maintaining the turbulent flow.

On the other hand, the microstructures of the powder, such as phase, shape and size, were investigated by using XRD(SIMNS-D5005D), particle analyzer(Photal Otsuka Electronic Co. ELS8000) and FE-SEM(F.E.I. Co, Sirion).

Results and discussion

In this study, the composition of waste rinse water in PCB copper electroplating process was analyzed and the operating conditions affecting the physical properties of copper powder, the shape of the powder, and the recovering rate of

copper ion were verified.

1. The properties of cyclone type electrolyzer

Since there are nothing but copper ions in the waste rinse water, the recovery process is simple and easily achieved by an existing electrolysis method. But the electrolysis efficiency is very low because of very dilute copper concentration of waste rinse water. Existing electrolyzer with parallel type electrodes has several problems, such as low electrolysis efficiency, a long treatment time due to the slow mass transfer of copper ions from bulk to electrode surface and low effective current densities. To alleviate those problems, cyclone type electrolyzer was developed in this study. The newly designed electrolyzer increases the current efficiency and reaction rate due to the fast mass transfer on the electrode surface. Increased mass transfer originated in a turbulent flow formed by the fast inlet into the cell coming up to about 5 m/sec. Reduction reaction on the cathode consists of two steps such as nucleus generation and growth to a specific lattice structure. While the second step is generally considered to be important in electrodeposition process, the nucleus generation is more important step in powder manufacturing process, this is because nucleation step affects the structure and size of primary layer and adhesive strength with electrode.

Nucleus is generated in the surface of electrodes by the large overpotential initially and the density of nucleus depends on the solution conditions such as concentration and pH, and is thought to be very sensitive to electrode potential and current density. The most important factor in nucleus generating process is the relative current density ratio, which is the ratio of current density to limiting current density. It is widely known that since surface diffusion is faster than charge transfer reaction at low current density below the ratio of 0.6, the adsorbed atom can diffuse to a suitable position within lattice and then easily form the structure like screw dislocation. Otherwise, in case of 60–80% of limiting current density, mass transfer is dominant factor and then a “tip”, which has high energy density and minimize IR drop between anode and cathode is formed. When electrodeposition occurred on this tip continuously, copper is electrodeposited as a type of dendrite or whisker. In case of current density over 80% of limiting current density, copper ion is reduced as a copper powder which is weakly electrodeposited on electrode surface. If the current density is over limiting current density, copper ion is recovered as Cu_2O with hydrogen generation reaction. Weakly deposited copper powder can be easily

Fig. 1 Schematic structure of cyclone type electrolyzer

and continuously removed from electrode surface by the turbulent flow.

2. Copper polarization measurements

Fig. 2 shows a reduction behavior of copper ions under the various pH and concentration. From the results, it is known that the limiting current density increases more than 10 times with the decrease of pH from 3 to 1. It is thought that the reason of increase of limiting current density is the higher electrotype owing to the increase of hydrogen concentration. It shows that, with the increase of copper ion, the additional increase rate is very low. From this results, the conditions under pH 3 and at the low copper concentration is preferable for high efficiency of powder recovery process. The relationships between a reduction behavior of copper ion and rotating speed of disk electrode under the condition of pH 3 and 100 ppm of copper ion are shown in Fig. 3. From the results, while the rotating speeds were increased from 900 to 1200 rpm the limiting current density of about 20 mA/cm² was almost unchanged. This means that if rotating speed is more or less high

Fig. 2 Polarization curve for cathodic reaction of the SUS316 in electroplating waste rinse water according to the variation of pH and Cu concentration.

Fig. 3 Polarization curve for cathodic reaction of the SUS316 in electroplating waste rinse water according to the rpm of electrode.

enough, it does not affect the limiting current. In addition, the results also show that the copper powder can be recovered on condition that the reduction current density is over 18 mA/cm². But the cyclone type electrolyzer used in this study has an advantage to recover the copper powder at low current density, because of physical impact effect by the injection of rotating solution with high velocity.

In this study, because we set the linear velocity high enough to form a turbulent, the limiting current density in these experimental conditions are thought to be constant irrespective of flow speed.

3. Recovery of copper powder with the variation of current density

Fig. 4 shows the behavior of copper recovery with changing current density in cyclone type electrolyzer. In this experiment, the copper concentration and the amount of the solution are 100 ppm and 500 liter respectively. The pH is 3 and the area of cathodes is 1230cm². From this result, under the condition of 25 mA/cm² current density, 90% of copper ion can be removed within 7 hours. Especially, in case of high current density (over 40 mA/cm²), 95% of copper ion has been removed within 6 hours. This recovery speed is considered very high and more than 10 times compared to that of the conventional parallel plate type electrolyzer taking 72 hours to get the same efficiency. Fig. 5 and 6 show a SEM image and average particle size of recovered copper powder under 15 mA/cm² current density respectively.

The average size of the recovered powder is 0.146 μm with spherical type, and the 95% of copper powder distribute in the range of 0.1–0.5 μm which is submicron size and has far better com-

Fig. 4 Copper content variation with different applied current density (pH 3, room temperature, Cu 100 ppm).

Fig. 5 SEM photograph of recovered copper powder (pH 3, room temperature, Cu 100 ppm, current density 15 mA/cm²).

Fig. 6 Results of particle size analysis (pH 3, room temperature, Cu 100 ppm, current density 15 mA/cm²).

Fig. 7 SEM photograph of recovered copper powder (pH 3, room temperature, Cu 100 ppm, current density 25 mA/cm²).

mercial values. Fig. 7 shows the shape of the powder obtained under the condition of 25 mA/cm². The shape of the powder changes from spherical type to a regular hexagonal type and the size of the powder is decreased, which somewhat corresponds to the results of elementary electro-

chemical experiments.

This regular hexagonal type powder changes to dendrite with the further increase of current density, as shown in Fig. 8 which is the SEM image of Cu powder obtained with the applied current density of 35 mA/cm². According to the previous studies, whisker and dendrite type copper powder start growth when the current density is larger than 60% of limiting current density. However, in this study, dendrite shape Cu powder was formed above limiting current density, because all the reduction conditions are much different from those of general electrolyzer. From results, it is thought that the powder shape is possible to be controlled with changing experimental conditions.

XRD patterns of the recovered powders under the various current densities are shown in Fig. 9 ~ 11. In all cases, the phase of Cu₂O and Cu coexist. At low current density, 10 mA/cm², the Cu phase is dominant. The peak of the Cu₂O phase, however, is observed as main peak in XRD pattern with

Fig. 8 SEM photographs of recovered copper powder (pH 3, room temperature, Cu 100 ppm, current density 35 mA/cm²).

Fig. 9 XRD patterns of produced powder (pH 3, room temperature, Cu 100 ppm, current density 10 mA/cm²).

Fig. 10 XRD patterns of produced powder (pH 3, room temperature, Cu 100 ppm, current density 20 mA/cm²).

Fig. 11 XRD patterns of produced powder (pH 3, room temperature, Cu 100 ppm, current density 35 mA/cm²).

increasing the current density (Fig. 10 and 11). The reason is considered to be as follows. The recovered powder is located in the easily oxidized solution which has abundant oxygen and is vulnerable to air. Additionally, since the powder size decreases and the specific surface area increases with increasing the current density, the oxidation of powder occur more easily and Cu₂O phase is formed dominantly.

It is known that the copper-oxide exists with two types, like as CuO and Cu₂O, and they are produced by following two equations:

The standard redox potential of reaction (1) and reaction (2) are 0.471 V and 0.558 V (vs. NHE), respectively. Since the reaction (2) has higher redox potential than reaction (1), overpotential for occurring the reaction (2) is larger than the reaction (1), and the reaction (1) occur preferentially.

The results obtained in this work, which oxidation process progress as Cu₂O phase dominantly, are compatible with the results of the reaction theory.

Conclusion

Cyclone type electrolyzer developed in this study could successfully remove copper ion from the waste rinse water and make it possible to recover copper as a various type of powder. The speed of waste water treatment by cyclone type electrolyzer was ten times as fast as that of existing electrolyzer. Cyclone type electrolyzer was also able to recover copper at lower current density as a type of powder due to physical impact effect of fast fluid flow rate, and the shape of the powder could be controlled by changing current density on the cathode.

As cathodic current density increases, Cu₂O phase was observed mainly in XRD pattern. It was due to the increase of the specific surface area of the powder and the redox potential difference between Cu₂O and CuO. Additionally, the average powder size decreases and the size distribution became uniform with the increase of current density. The shape of the powder was changed from spherical type to a regular hexagonal type and then dendrite type with increasing the current density.

The waste water treatment process by using cyclone type electrolyzer developed in this study overcome the many disadvantages of existing electrolyzer, such as low current efficiency and slow reaction rate, less discharge of waste rinse water and additional use of many chemicals for the complete treatment. This newly developed process has additional advantage such recovered copper could be obtained as a nano-sized powder. Being applied to the treatment of waste water from electroplating process, it is thought that this process becomes more economical and environment friendly process in comparison with the other electrochemical and chemical treatment method.

References

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