

## Effect of mechanical attrition on microstructure and property of electroplating of copper plating in acid solution

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**Abstract.** In this paper, the mechanical attrition(MA) was supplied in a traditional electroplating process by rolling movement of different diameter of glass balls in the acid copper plating electrolyte to study the effects of different diameters of the glass balls on microstructure of copper plating and the properties of carbon-impervious, grain refine and corrosion resistance. The results showed that the grain size of the plating had obviously decreased in the MA process, and with increasing the diameters of the glass balls, the porosity, corrosion resistance and the properties of carbon-impervious of the plating were first increased and then decreased.

### Introduction

Acid copper electroplating with sulfate extensive applied in industrial production bath has a history of more than a century due to its simple composition, stable and cheap electroplating solution and so on[1]. It is known that copper plating has been used as anti-carburizing plating because the copper layer has a high contact and the carbon has the features that don't form solid solution or compound with copper. However, the thick Cu plating is required to be used as anti-carburizing on account of the coarse grain of the Cu plating.

Surface mechanical attrition treatment(SMAT) is an approach to improving comprehensive performance of materials rely on more strong plastic deformation in the metal surface, which can lead materials with nanoscale, submicron and micro of grain size by high frequency and direction of the load[2,3]. The SMAT has the advantages of wide range of application, high toughness, good interface bonding and so on. Based on the deficiencies of traditional electroplated(TEP) copper plating, the SMAT was applied in acidic copper plating by using mechanical attribution to enhance the corrosion resistance and anti-carburizing of the copper plating.

### Experimental methods

The A3 steel samples with dimensions of 20mm ×40mm ×1mm mounted in epoxy resin as cathode. Before plating copper, the A3 steel was electroplated with Ni. Electroplating experiments were carried out with current density of 5A/dm<sup>2</sup> in the traditional sulfate electroplating solution (190g/L CuSO<sub>4</sub>·5H<sub>2</sub>O and 60g/L H<sub>2</sub>SO<sub>4</sub>) at room temperature for 30min. Glass balls, covered about 1/4 surface area of each sample, with diameters of 4mm, 6mm, 8mm and 10mm were used respectively on the cathode surface to provide mechanical impact. A plastic tank filled with plating solution was placed on the top of a vibrator[4], when the vibrator moved vertically with an amplitude of 1 mm, the plastic tank swung around the bearing with 15°. The microstructures of the copper platings plated by MA electroplating at different diameters of glass balls were examined by using scanning electron microscopy(SEM). Stick filter paper method was used to measure the porosity by observing the number of blue dot in each square centimeter. To evaluate the corrosion resistance of the plated copper platings, polarization curves were measured in a three-electrode cell by using a galvano-chemistry Workstation(CHI-660C) in 3.5% NaCl solution at room temperature with a sweep rate of 0.5mV/s. The composition was 15wt% BaCO<sub>3</sub>, 3wt% CaCO<sub>3</sub>, 88wt% charcoal power. The paraments were bured at 820C for 30 min, heated to 900C for 90 min, then cooled at 850C for 30 min and finally quenched. The cross-sectional microhardness of the carburized steel was measured by a digital microhardness tester(HVS-1000) with a load of 0.1N for

20s.

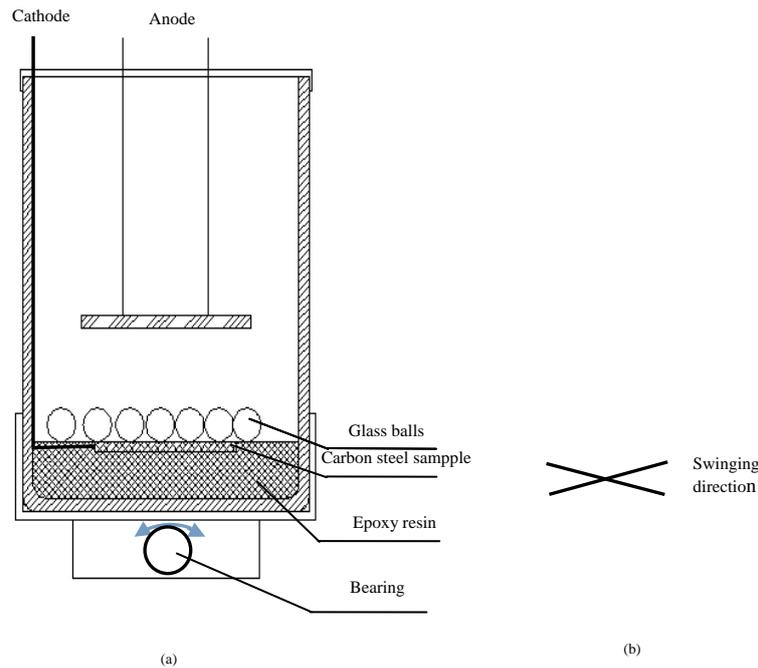


Fig.1 Schematic diagram of mechanical assisted electroplating device and swinging direction (a) MA electroplating device, (b) swinging direction.

## Results

### Surface morphology

Fig.2 presents the surface morphology of copper platings electroplated with different diameter of glass balls. Fig.2(a) shows the surface of copper plating after TEP is rough and uneven. It can be seen that many pyramid-like crystals with size of 1-6  $\mu\text{m}$  form nonuniformly on the surface of copper plating after TEP and coarse grain were surrounded by fine grains. While, from Fig.2(b)-(d), it can be seen that the grain size increase with increasing diameter of glass ball and distribute uniformly on the surface. Compared with copper plating after TEP, the grain on the surface of copper plating with MA process is finer than that of copper plating with TEP. As shown in Fig. 2(e) and (f), it is clear to see there are a little “cauliflower-like” grains with a diameter of 6  $\mu\text{m}$  surrounded by small grains with a diameter less than 1 $\mu\text{m}$  when the glass balls with diameter of 10 mm are used. With MA process, the rolling glass balls enhance convection and limiting current density. However glass balls change the direction of power line while current density of actual area is bigger than the setting current density. It was clear to see that the “cauliflower-like” grains were detected on the surface of copper plating when the glass balls with diameter of 10 mm are used. This would explain when the glass ball with diameter of 10 mm was used in the electroplating process, the actual current density is bigger than the limiting current density.

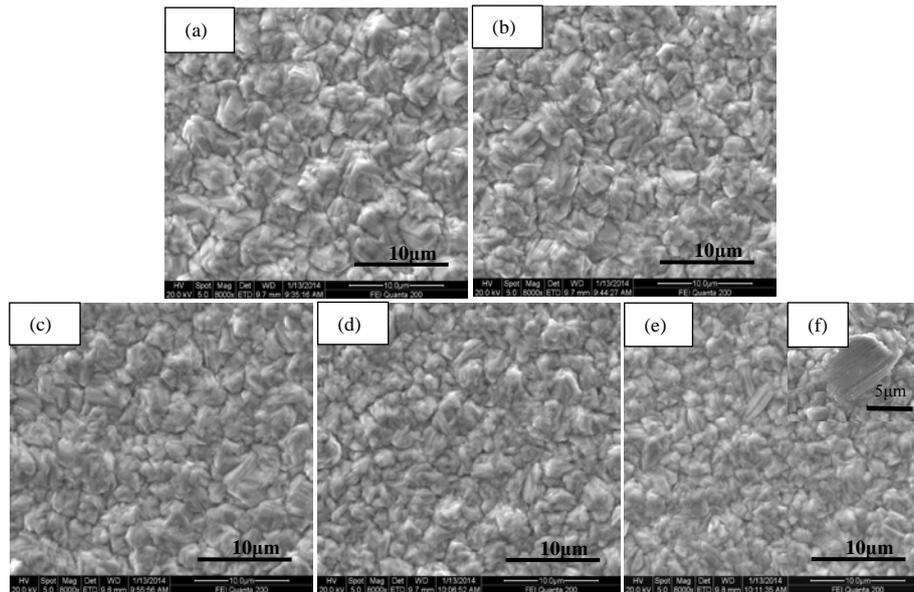


Fig.2 Surface morphologies of copper plating by mechanical attrition electroplating process at different diameter of glass ball: (a) TEP; (b) 4mm; (c) 6mm; (d) 8mm; (e) 10mm; (f) local coarse grains with diameter of 10mm.

### Macroscopic performance

#### Porosity

Fig.3 shows the porosity of copper plating after TEP and with MA process. It is know that the porosity of copper plating after TEP is 1.25 per cm<sup>2</sup>. With MA process, the porosity of copper plating is lesser than that of copper plating after TEP. Therefore, MA action can affect the electroplating process and the porosity of plating. According to Fig.3, it can be seen that the porosity of copper plating decrease as the diameter of glass balls increases from 0 mm to 8 mm. When the diameter of glass balls is 8 mm, the porosity of plating is least. However, when the glass balls with the diameter of 10 mm, the porosity of plating is bigger than that of 8mm. So, the best effect of MA action on the porosity of copper plating is glass balls with diameter of 8 mm.

Table.3 Porosity of copper plating by mechanical attrition electroplating process at different diameter of glass ball

Diameter of glass ball (mm)	0	4	6	8	10
Porosity(per square centimetre)	1.25	0.9	0.85	0.5	0.75

#### Corrosion resistance

Fig.4 shows the polarization curves of carbon steel and mechanically assisted electroplated and TEP copper platings in 3.5% NaCl solution at room temperature. According to polarization curves, the E<sub>corr</sub> and I<sub>corr</sub> of copper plating are obtain, as shown in Table. 2. The E<sub>corr</sub> illustrates corrosion tendency of plating, and the I<sub>corr</sub> shows rate of corrosion. According to Fig.4, it was clear to seen that during electroplating process MA action can lead to enhance the E<sub>corr</sub> of copper plating and decrease the I<sub>corr</sub> of copper plating. Zhaoxia Ping[5,6]etc found similar law by studying mechanically assisted electroplating of Ni-P plating on carbon steel. Polarization curves reveal that the I<sub>corr</sub> of copper plating first decrease and then increase as the diameter of glass balls increase, and I<sub>corr</sub> is smallest when the diameter is 8 mm, as shown in Table.2. Therefore, MA action can be effectively refined grains, decreased porosity and enhanced corrosion resistance of copper plating.

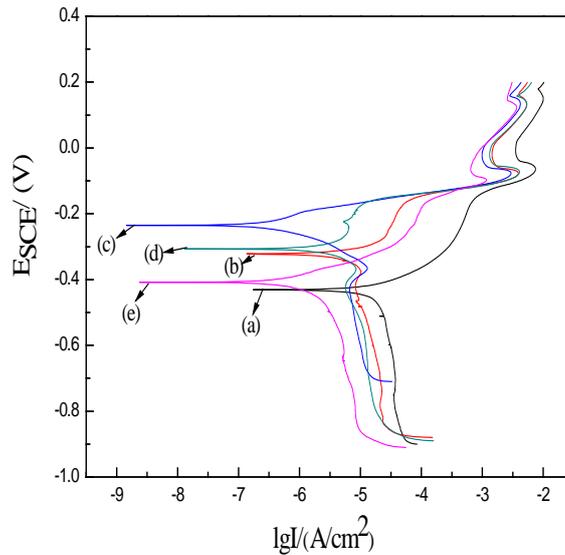


Fig.4 Polarization curves of copper plating by mechanical attrition electroplating process at different diameter of glass ball in 3.5% NaCl solution: (a) TEP; (b) 4mm; (c) 6mm; (d) 8mm; (e) 10mm.

Table 2 Fitting result of polarization curves in the 3.5% NaCl solution at room temperature

sample	Diameter of glass ball(mm)	$E_{corr}/V$	$I_{corr}/(A/cm^2)$
TEP	0	-0.602	$2.104 \times E-5$
MA electroplating	4	-0.357	$3.802 \times E-6$
MA electroplating	6	-0.228	$2.003 \times E-6$
MA electroplating	8	-0.255	$1.323 \times E-6$
MA electroplating	10	-0.517	$2.48 \times E-6$

### The property of anti-carburizing

As the carbon content in the carbon steel increases so does the hardness of carbon steel increase. Therefore, the change in cross-section hardness of carbon steel before and after carburizing evaluate the property of carbon-impervious. Fig.5 shows microhardness of cross-section substrate after carburizing under copper coating by mechanical attrition electroplating process at different diameter of glass ball. It was clear to see that the case depth of carbon steel without copper plating is  $350 \mu m$  by carburizing. Fig.5(b) is the part of dotted line in the Fig. 5(a). As shown in Fig.5(b), the case depth of carbon steel with TEP is  $54 \mu m$ , and with MA process that of carbon steel decrease. It revealed that the case depth decrease with the diameter of glass ball from 4 mm to 8 mm, when the diameter of glass ball is 10 mm, the case depth increase. So, the property of carbon-impervious of copper plating is best one with diameter of 8 mm, and the case depth is  $14 \mu m$ .

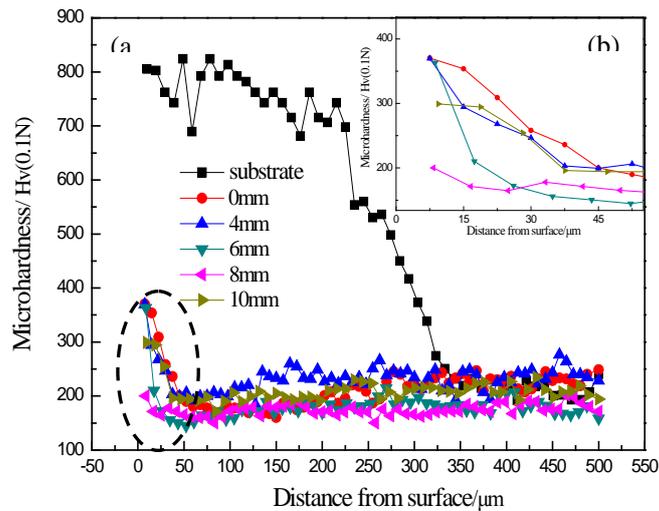


Fig.5 Microhardness of cross-section substrate after carburizing under copper plating by mechanical attrition electroplating process at different diameter of glass ball (a) complete figure, (b) local figure with copper plating.

## Discussion

It has been reported [7,8] that scratches were detected on the surface of copper plating when the vibrator moved horizontally. In the electroplating process, the mechanical assisted electroplating device swung with an angle, most of the glass balls were rolling on the surface of the sample, and the friction is smaller than that of glass ball sliding on the surface of the sample.

i) In the actual electrode process, the rate-determining step is a hybrid control about electron transfer and diffusion step [9]. It used stirring in the electroplating process that could enhance convection strength, reduce diffusion layer thickness and increase the limiting current density. High current density was used in the electroplating process, while the polarization degree increased and nucleation was promoted.

ii) Electroplating copper plating with the MA process improves the adhesion of the substrate and copper plating and reduces the porosity of the plating. Under the compression and shearing load of the glass balls, on one hand, the copper plating meshed together with the copper powder ground down from the copper plating because of displacement and deformation. On the other hand, the atoms on the surface of the plating are close to each other, when the extranuclear electrons of atoms overlap with those of other atoms, two copper atoms are welded together to form a new metallic bond [10,11]. It is obvious that the grain size of the copper plating decreased as the diameter of the glass ball increased. Hydrogen was prevented from adsorbing on the surface of the cathode, and impurities were removed from the surface to prevent the formation of defects by using the MA process in the electroplating process.

## Conclusions

The conclusions are as follows:

i) MA action can affect the electroplating process and lead to a finer surface morphology of the copper plating. The size of the grains decreases as the diameters of the glass balls increase from 0 mm to 8 mm.

ii) The porosity, corrosion resistance, and carbon-imperviousness of the plating first increase and then decrease as the diameter of the glass balls increases from 0 to 10 mm.

## Acknowledgments

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