

Preparation of electrolytic copper powders with high current efficiency enhanced by super gravity field and its mechanism

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Abstract: Super gravity field was employed to enhance electrolytic reaction for the preparation of copper powders. The morphology, microstructure and size of copper powders were characterized by scanning electron microscopy, X-ray diffractometry and laser particle analysis. The results indicated that current efficiencies of electrolytic copper powders under super gravity field increased by more than 20% compared with that under normal gravity condition. Cell voltage under super gravity field was also much lower. The size of copper powders decreased with the increase of gravity coefficient (G). The increase of current efficiency can be contributed to the disturbance of electrode/electrolyte interface and enhanced mass transfer of Cu^{2+} in super gravity field. Meanwhile, the huge gravity acceleration would promote the detachment of copper powders from electrode surface during electrolytic process, which can prevent the growth of copper powders.

Key words: super gravity field; current efficiency; copper powders; electrolysis

1 Introduction

Copper powders can be produced by chemical reduction[1], atomization[2] and electrolysis[3–4]. Copper powders produced by electrolysis have many advantages such as high purity, large specific surface area and good compressibility and molding. In order to obtain copper powders, electrolytic reaction must be carried out at high current density or high overpotentials [5] in the solution with low concentration of Cu^{2+} and high acidity, which would induce the concentration polarization of Cu^{2+} at electrode/electrolyte interface. Unfortunately, the concentration polarization of Cu^{2+} would result in serious hydrogen evolution secondary reaction (HESR) and low current efficiency[6]. On the other hand, the size of copper powders can be reduced by the increase of current density, but current efficiency would also reduce further[6]. Meanwhile, considerable hydrogen bubbles produced from HESR cannot separate rapidly from electrode surface and electrolyte under

normal gravity condition. The hydrogen bubbles adsorbing or dispersing on electrode surface or in electrolyte would lead to sharp increase of cell voltage with current density and electrolytic time due to large ohmic voltage drop. Therefore, it is restricted to reduce the size of copper powders by increasing current density under normal gravity condition. The size and current efficiency, the most important criteria for the production of copper powders, are mutual restrictions during electrolytic process. So, it is of vital realistic significance to increase current efficiency and reduce copper powder size simultaneously.

Super gravity can enhance micro mixing and mass transfer[7]; thereby, it would affect the electrolytic process[8]. In our preview works[9–10], it was also found that the crystalline size of nickel foil electrodeposited under super gravity field reduced and the arrangement of crystalline grain became more regular. In addition, the electrodeposition of Pb^{2+} can also be intensified by super gravity field[11]. If electrolytic copper powder process is carried out under super gravity

field, the mass transfer of Cu^{2+} toward electrode surface can be promoted. The concentration polarization of Cu^{2+} becomes small and current efficiency increases. Meanwhile, the huge gravity acceleration and micro disturbance of electrode/electrolyte interface are favorable to the rapid detachment of copper powders from electrode surface, which can prevent the growth of copper powders. In addition, the efficient disengagement of hydrogen bubbles from electrode surface and electrolyte is greatly facilitated[12], which can result in the reduction of cell voltage.

In this work, electrolytic process of copper powder was carried out under super gravity field. The effects of super gravity field on cathodic current efficiency, cell voltage and the size of copper powders were studied. The mechanisms that super gravity enhanced electrolytic copper powder reaction were analyzed.

2 Experimental

2.1 Electrolytic copper powders

The electrolyte consisted of CuSO_4 , 9.8 g/L H_2SO_4 and 1.5 g/L sodium dodecylsulfonate (SDS). The concentrations of CuSO_4 and current density were adjusted according to experimental purpose. All chemical reagents were of analytical grade. Fresh double-distilled water was used throughout.

A cylindrical electrolytic cell with the volume of 100 mL was used. The electrolytic experiments with constant current density were carried out with WYK-3010 DC Power. The pure copper plate with an area of 1.5 cm^2 and nickel foil with an area of 1.0 cm^2 were used as anode and cathode, respectively. A standard three-electrode system was employed for linear sweep voltammetry (LSV) and chronoamperometry in CHI 604B electrochemical working station (CH Instrument Inc.). Nickel foil with an area of 1.0 cm^2 and a platinum plate with large surface area were used as working electrode and counter electrode, respectively. A solid state electrode (GD-IV, Beijing Research Institute of Chemical Engineering and Metallurgy) was employed as reference electrode. All potentials were measured against the solid state electrode in which its potential was 0.185 2 V (vs SHE).

Current efficiency (η) was calculated as follows:

$$\eta = \frac{m}{qIt} \times 100\% \quad (1)$$

where m is the mass of copper powders (g); q is the electrochemical equivalent constant, 1.186 g/(A·h); I is the current, A; t is the electrolytic time, h.

2.2 Super gravity experimental equipment

Super gravity field can be obtained by a centrifuge

with a cylindrical electrolytic cell (Fig.1). The electrochemical signals were transferred by the mercury slip ring (A3S, Shanghai Bige M&E Co., Ltd.) which was fixed on the top of axis. The electrolytic cell was horizontal under super gravity field (i.e. rotating), while vertical under normal gravity condition (i.e. not rotating).

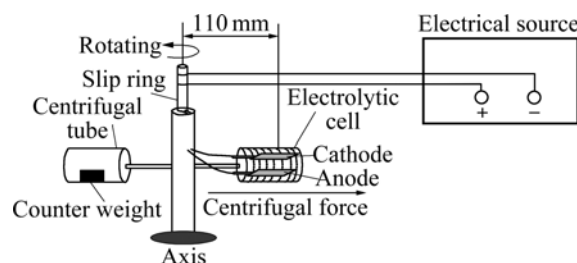


Fig.1 Experimental equipment for electrolytic copper powders under super gravity field

The gravity coefficient (G) value can be adjusted by rotating the electrolytic cell with different speeds and it can be calculated with the following equation:

$$G = \frac{\omega^2 L}{g} = \frac{N^2 \pi^2 L}{900g} \quad (2)$$

where N is the rotating speed, r/min; g is the gravity acceleration, 9.8 m/s^2 ; and L is the distance between electrode center and axis, being 0.11 m in this experiment. The G value is 1 under normal gravity condition.

2.3 Characterization of copper powders

The morphology and crystal structure of copper powders were examined by SEM (JEOL, JSM6700F) and XRD (RIGAKU D/max-RB), respectively. The copper powder sizes were analyzed by laser particle analyzer (LS13320).

3 Results and discussion

3.1 Electrolytic copper powders under super gravity field

The current efficiencies of electrolytic copper powders in 10 g/L CuSO_4 solution at 0.1 A/cm^2 under various gravity conditions are shown in Fig.2. It can be seen that when gravity coefficient (G) was 25, the current efficiency of electrolytic copper powder reached 84.2%, which was much higher than that (61.7%) under normal gravity condition. However, current efficiencies hardly varied with the increase of G value further. Similarly, at 0.2 A/cm^2 , current efficiency also increased from 55.7% under normal gravity condition to 72.7% under G value of 25. In addition, it could be also observed that current efficiency at 0.2 A/cm^2 under super gravity field was

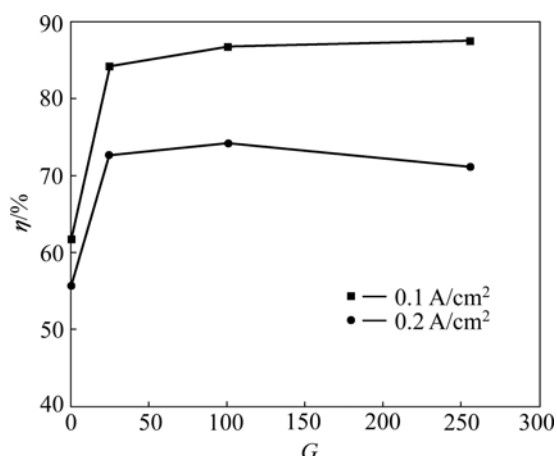


Fig.2 Effect of super gravity field on cathodic current efficiency (Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS)

much higher than that at 0.1 A/cm^2 under normal gravity condition. These results implied that when electrolytic reaction was carried out under super gravity field at larger current density, current efficiency still remained at a higher value.

In order to show more clearly the advantage of super gravity field, electrolytic reaction was carried out in the solution with lower concentration of CuSO_4 (Fig.3). Under normal gravity condition, current efficiency at 0.1 A/cm^2 was only 31.4% in 5 g/L CuSO_4 solution, while current efficiencies were 61.9%, 67.2% and 62.5% under G values of 25, 101, and 256, respectively. When current density was 0.3 A/cm^2 , current efficiency was only 20.5% under normal gravity condition, but the value was up to 56.8% under G value of 25.

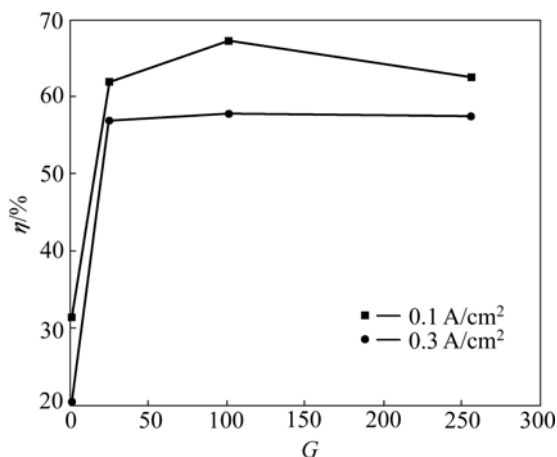


Fig.3 Effect of super gravity field on current efficiency in lower concentration of CuSO_4 (Electrolyte: 5 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS)

According to the results in Fig.2 and Fig.3, it was concluded that current efficiencies for electrolytic copper

powders were increased obviously by super gravity field, and larger current density with high current efficiency could be applied for electrolytic reaction, even in lower concentration of CuSO_4 .

3.2 Analyses of electrolytic copper powders intensified by super gravity field

The cathodic polarization curves of electrolytic copper powders under various gravity conditions are shown in Fig.4. Under normal gravity condition, a reduction peak of Cu^{2+} was found at -0.18 V, and then cathodic current density reduced due to the concentration polarization of Cu^{2+} with negative shift of potential. When potential was scanned to about -0.71 V, cathodic current density began to increase due to hydrogen evolution secondary reaction (HESR). Under G value of 25, similar cathodic polarization curve was obtained, but current density was larger than that under normal gravity condition. With an increase of G value to 101 and 256, no reduction peak of Cu^{2+} was observed, but current density increased further. The results in Fig.4 implied that during electrolytic process, super gravity enhanced the micro disturbance of electrode/electrolyte interface and promoted mass transfer of Cu^{2+} . Therefore, the concentration polarization of Cu^{2+} became small, and then reduction rate of Cu^{2+} increased.

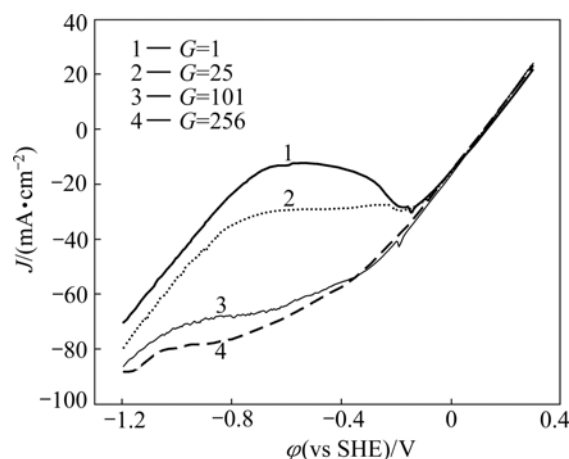


Fig.4 Polarization curves of electrolytic copper powders under various gravity conditions (Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS)

Chronoamperometry measurements were also conducted and the results are shown in Fig.5. Under all gravity conditions, cathodic current densities increased with electrolytic time, but current densities under super gravity field were much larger than those under normal gravity condition. Under G value of 256, in initial stages of electrolysis, current density was larger than that under other gravity conditions, but after about 600 s, current density became smaller than that under G value of 101. The reasons can be explained according to the photo-

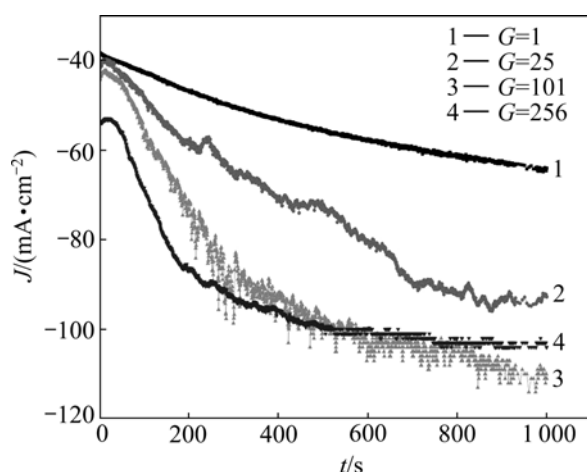


Fig.5 Chronoamperometry curves of electrolytic copper powders under various gravity conditions (Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS; $\phi(\text{vs SHE})=-1.0\text{ V}$)

graphs of cathode surface in Fig.6. After electrolysis, under normal gravity condition, electrode surface was covered by a thick layer of rough copper powders. Due to the large specific surface area of copper powders, real surface area of electrode was much larger than geometrical surface area; thereby, real current density for electrolytic copper powders was much smaller than apparent current density shown in Fig.5. Smaller real current density would reduce cathodic overpotential. With the prolongation of electrolysis time, the mass of copper powders covering on electrode surface and real surface area increased, which resulted in the reduction of

real current density and cathodic overpotential. In other words, at a certain potential, apparent current density increased with electrolysis time, as shown in Fig.5. When G value was 25, it was easier for copper powders to detach from electrode surface due to the effect of super gravity. As a result, the mass of copper powders covering on electrode surface decreased and in partial region copper powders fell off almost completely. In addition, copper powder layer was flatter and more compact, which would decrease real surface area. Nevertheless, apparent current density was still larger owing to the intensified effect of super gravity (Fig.5). When G value increased to 101 further, the region that copper powders fell off almost completely expanded. It must be noticed that only a thin layer of copper powders covered on electrode surface under G value of 256. Due to much smaller real surface area, real current density under G value of 256, especially in last stages of electrolysis, was larger than that under other gravity conditions. As shown in Fig.5, although apparent current density at the initial stage of electrolysis was the largest, it tended to be stable. After 600 s, apparent current density became smaller than that under G value of 101. Table 1 listed the mass and cathodic current efficiencies of copper powders after chronoamperometry measurements. Current efficiency under super gravity field was much larger than that under normal gravity field. The results were similar with those in Fig.2 and Fig.3.

Additionally, during electrolytic process, hydrogen bubbles, produced from serious HESR, cannot be

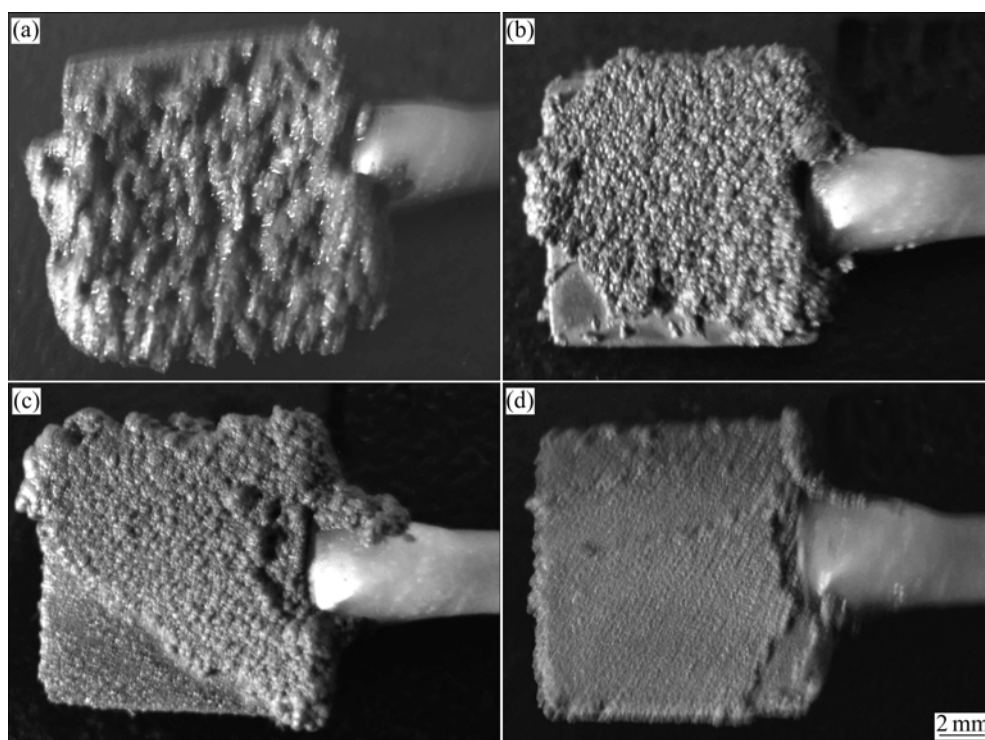
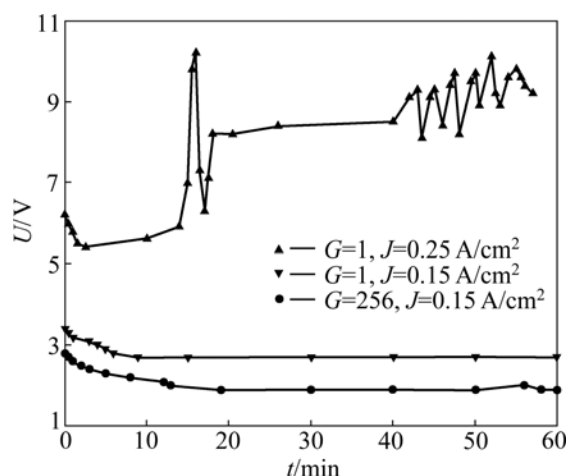


Fig.6 Photographs of cathode surface after electrolysis: (a) $G=1$; (b) $G=5$; (c) $G=101$; (d) $G=256$

Table 1 Mass of copper powders and cathodic current efficiencies after chronoamperometry measurement

G	Mass/mg	$\eta/\%$
1	66.2	67.36
25	113.1	86.35
101	128.1	86.49
256	98.8	79.63

disengaged or spilled rapidly from electrode surface or electrolyte, which would result in high cell voltage. However, it was found in Fig.7 that at 0.15 A/cm^2 , cell voltage under G value of 256 was much lower than that under normal gravity condition. The reasons were as follows. Under super gravity field, large interphase buoyancy term, $\Delta\rho \cdot g$, would enhance interphase slip velocity; thereby disengagement or spillover of hydrogen bubbles from electrode surface or electrolyte can be facilitated greatly[13]. Meanwhile, the convection velocity was enhanced by super gravity and high migration rate of Cu^{2+} was achieved. Therefore, cell voltage reduced under super gravity field.

**Fig.7** Cell voltage of electrolytic copper powders (Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS)

In order to reduce the size of copper powder, it was an efficient method to increase cathodic overpotential by increasing current density. The relationships among overpotential η_k , critical nucleate size h_i , nucleate energy A and nucleate probability W are expressed as[14]

$$nF\eta_k = \frac{2\sigma v}{h_i} \quad (3)$$

$$A = \frac{32\sigma^3 v^2}{n^2 F^2 \eta_k^2} \quad (4)$$

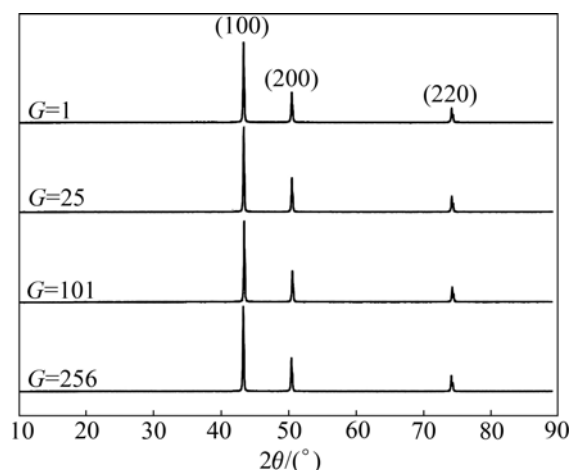
$$W = B \exp\left(-\frac{b}{\eta_k^2}\right) \quad (5)$$

It can be observed from Eqs.(3)–(5) that with the

increase of η_k , the values of h_i and A reduced, and W increased. When the electrolytic copper powder reaction was carried out at higher current density, it was easier to nucleate and the size of copper powders became smaller. Unfortunately, when current density was up to 0.25 A/cm^2 under normal gravity condition, serious HESR occurred and cell voltage increased sharply (Fig.7) due to the severe bubble coverage on electrode surface. Therefore, it was a bottleneck to reduce the size of copper powders by the increase of current density under normal gravity condition. However, under super gravity field, hydrogen bubbles can be separated quickly from electrode surface and electrolyte, which prevented the increase of cell voltage. Electrolytic reaction can proceed stably under super gravity field, even at 0.7 A/cm^2 (no shown in this work).

3.3 Characterization of copper powders

The XRD patterns of copper powders are shown in Fig.8. Under all gravity conditions, copper powders had excellent crystal structure and no oxide or impurity could be found. From SEM images (Fig.9), copper powders were highly branched dendrites under all gravity conditions and the dendrites consisted of agglomerates of copper grains, which was similar with other works[15]. The results in Fig.8 and Fig.9 indicated that the morphology and crystal structure of copper powders were unchanged under super gravity field.

**Fig.8** XRD patterns of copper powders (Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS)

During electrolytic process of copper powders, in order to obtain high current efficiency, it was efficient to reduce current density and increase the concentration of CuSO_4 . However, the size of copper powders would be increased by these methods. Under super gravity field, the micro disturbance of electrode/electrolyte interface was intensified. Therefore, the convection was promoted, which can reduce the concentration polarization of Cu^{2+} .

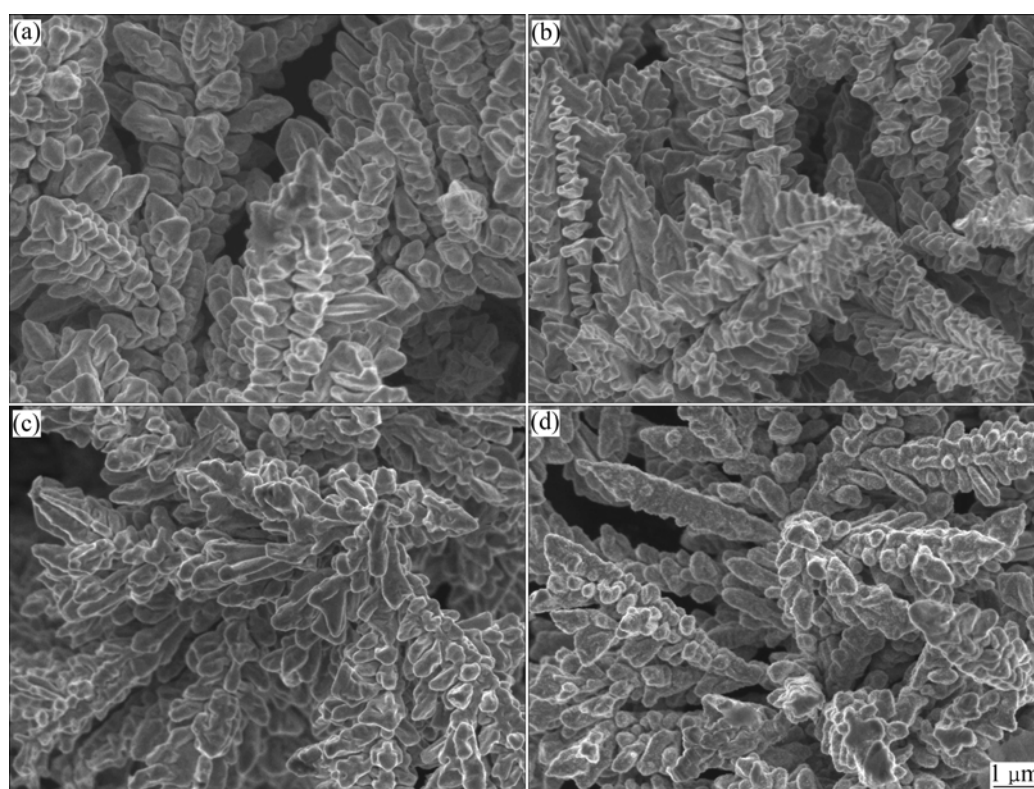


Fig.9 SEM images of copper powders (Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS; $J=0.2 \text{ A/cm}^2$): (a) $G=1$; (b) $G=25$; (c) $G=101$; (d) $G=256$

Consequently, cathodic current efficiency increased, which had been demonstrated by the results in Fig.2 and Fig.3. On the other hand, copper powders produced on electrode surface would suffer from huge gravity acceleration and micro disturbance of electrode/electrolyte interface under super gravity field. It was easier for copper powders to detach from electrode surface, which can prevent the growth of copper powders. The sizes of copper powders obtained under various gravity conditions were analyzed and it was found that the size of copper powders decreased slightly with increase of G value (Table 2). The experimental results gave desirable conclusion that when electrolytic copper powders were prepared under super gravity field, the increase of current efficiency and reduction of copper powder size can be achieved simultaneously.

Table 2 Average sizes of copper powders obtained under various gravity conditions (10 g/L CuSO_4 , 9.8 g/L H_2SO_4 , 0.2 A/cm^2)

G	1	25	101	256
$d/\mu\text{m}$	20.1	19.5	19.2	17.9

The discussion above demonstrated that it was feasible to reduce the size of copper powders by the increase of current density under super gravity field. From Table 3, it can also be observed that the size of

Table 3 Average size of copper powders obtained at different current densities ($G=101$, Electrolyte: 10 g/L CuSO_4 +9.8 g/L H_2SO_4 +1.5 g/L SDS)

$J/(\text{A}\cdot\text{cm}^{-2})$	0.2	0.3	0.4	0.6
$d/\mu\text{m}$	19.2	17.4	14.4	12.9

copper powders, produced under G value of 101, decreased with the increase of current density.

4 Conclusions

1) Compared with normal gravity condition, super gravity can intensify the mass transfer of Cu^{2+} and facilitate the detachment of copper powders from electrode surface. As a result, current efficiencies of electrolytic copper powders under super gravity field increased by more than 20% and the size of copper powders decreased slightly with the increase of G value simultaneously.

2) The disengagement or spillover of hydrogen bubbles from electrode surface or electrolyte can be promoted by super gravity field; thereby, ohmic voltage drop and cell voltage were reduced. When the electrolytic reaction proceeded at higher current density, cell voltage still remained at low level. Under a certain gravity condition, the size of copper powders reduced

with the increase of current density.

3) The copper powders obtained under all gravity conditions were highly branched dendrites and had excellent crystal structure.

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