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Effect of Copper Ion Concentration on Microstructure and Mechanical Properties of Electrolytic Copper Foil

Yanfeng Li[1], Guojie Huang[1], Xiangqian Yin[1], Xi Chen[1], Xiuling Ma[2], Yongzhen Li[2] and Endong Yao[2]

[1]State Key Laboratory of Nonferrous Metals and Processes, GRIMAT Engineering Institute Co. Ltd, Beijing 101407, China
[2]Qinghai Electronic Material Industry Development Co. Ltd, Xining 810006, China
Email: lyfdata@163.com

Abstract. Under the constant condition of controlling the relative electrolytic process parameters, the electrolytic copper foil with 12 μm thickness was prepared by adjusting the time of electrode position under the conditions of different copper ion concentration. The surface morphology, mechanical properties and texture of electrolytic copper foil under different current density were studied by SEM, XRD, EBSD and universal testing machine. The fracture mechanism of copper foil at different current density was analyzed. The results show that when the copper ion concentration is 84g/L, the particles on the copper foil surface are uniform and fine, and the mechanical properties are the best. With the increase of copper ion concentration, the electrode position rate increases, the particle size of copper foil increases, and the tensile strength and elongation of copper foil decrease. The copper ion concentration has little effect on the texture of copper foil.

1. Introduction

Electrolytic copper foil is an important raw material for the electronics and electrical industry.After a special process and subsequent processing, it can also be used as a negative current collector material for lithium ion batteries. Copper foil properties depend primarily on its microstructure, which is influenced by factors such as electrolyte composition, copper ion concentration, current density, additives, and cathode surface conditions [1-6].

A. Ibanez et al [7] studied mechanical and structural properties of electrodeposited copper and their relation with the electrode position parameters, the results showed that optimisation of the current density makes possible totailor films with specific characteristics for different technological applications. M.A. Getrouw et al [8] researched the influence of some parameters on the surface roughness of thin copper foils using statistical analysis; it was shown that the roughness of the thin copper foils is a function of not only the growth process, but also the nucleation process.

In view of the unstable production process of ultra-thin electrolytic copper foils, thickness of 12 μm copper foils were electrodeposited at different copper ion concentrations to study the copper ion concentration on the microstructure and mechanical properties of copper foils.

2. Experimental procedure

In order to systematically study the influence of copper ion concentration on the mechanical properties of electrolytic copper foil, the copper ion concentration selected as 81 g/L, 84 g/L, 87 g/L, 90 g/L, 93 g/L and 96 g/L, and then the copper foils was prepared by controlling the same of other electrolytic process parameters. The sample preparation system is shown in Figure 1. The deposition time is controlled by DC power supply. The liquid pump controls the flow of the electrolyte. The temperature control system is contained in the electrolyzed. The electrolyte in the solution trough is filtered into the electrolytic tank after filter filtration and then flows back to the solution slot. The quantitative electrolysis process parameters are current density of 0.3A/cm^2, sulfuric acid concentration was 90g/L, electrolyte flow was 180L/h, electrolyte temperature was 50 ℃.

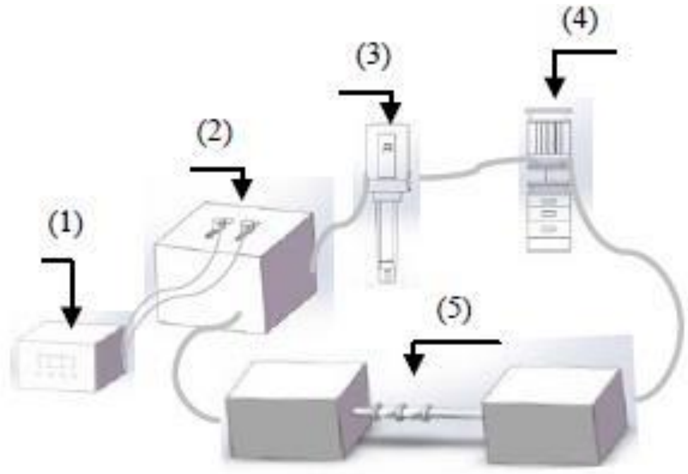

Figure 1. Sample preparation system for Electrolytic copper foils: (1) Power; (2) Electrolytic cell; (3) Filtraor; (4) Pump; (5) Solution tank

The surface morphology and fracture appearance of the copper foil were photographed using a tungsten filament scanning electron microscope (JSM-6010). The copper foil tensile test was performed on a universal testing machine (CMT-4503), field emission scanning electron microscope (JSM-7001F) and backscattering. The electron diffraction probe combination was micro-textured for EBSD testing and the macro texture was tested by an X-ray diffract meter (D/MAX-2550).

3. Results and discussion

3.1. Mechanical properties

Figure 2 shows the tensile properties of the copper foils with different copper ion concentration, and it can be seen that copper ion concentration have a notably effect on the mechanical properties of copper foils. When the copper ion concentration was 84 g/L, the tensile strength was 405 MPa and the elongation was 5.6%.The tensile strength and elongation decreased notably with the copper ion concentration increasing to 96 g/L. When the copper ion concentration was 96 g/L, the strength and elongation was 275 MPa and 1.8%, respectively. The mechanical properties were effect by the microstructure of copper foils.

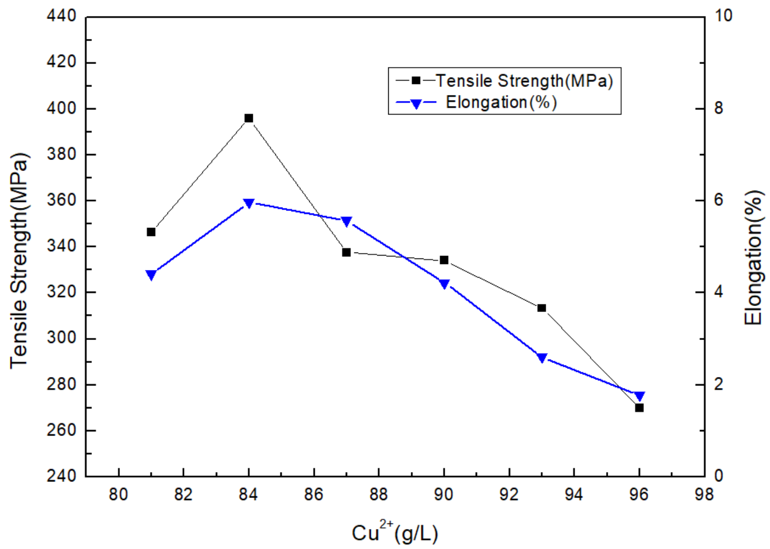

Figure2. The relationship of tensile strength and elongation of copper foils with different copper ion concentration

3.2. Microstructure of copper foils

The surface morphology of copper foil at different concentration of copper ions was shown in Figure 3. When the concentration of copper ions was less than 84 g/L, the surface particles were small, the particles were ellipsoid and the diameter of the particles was about 3.5 microns. The main reason is that the electrolytic deposition rate was slow when the concentration of copper ions was low. When the concentration of copper ion was greater than 90 g/L, the rate of electrolytic deposition was faster, the surface particles become larger, and the needle tip shape appears. The particle size is about 5.5 microns.

At the initial stage of electro deposition, crystal growth can be divided into three stages: initial epitaxy, overgrowth and growth period controlled by electro deposition. In the initial external delay, the copper grains are grown on the surface lattice properties of the titanium cathode surface; the overgrowth period shows that the growth and longitudinal growth occur simultaneously, the grain protruding is the most likely to become a subsequent copper ion discharge nucleation point, and a large number of copper ions are deposited here, accelerating the longitudinal growth of the grain. When copper ion concentration is low, copper ions are deposited at the initial grain protruding point, forming large size grain, which causes the lack of copper ions at the bottom of the grain. The larger the grain, the more easily the copper ions discharge and deposit around them, which further aggravates the lack of copper ions at the bottom of the grain and makes the bottom grain not long.

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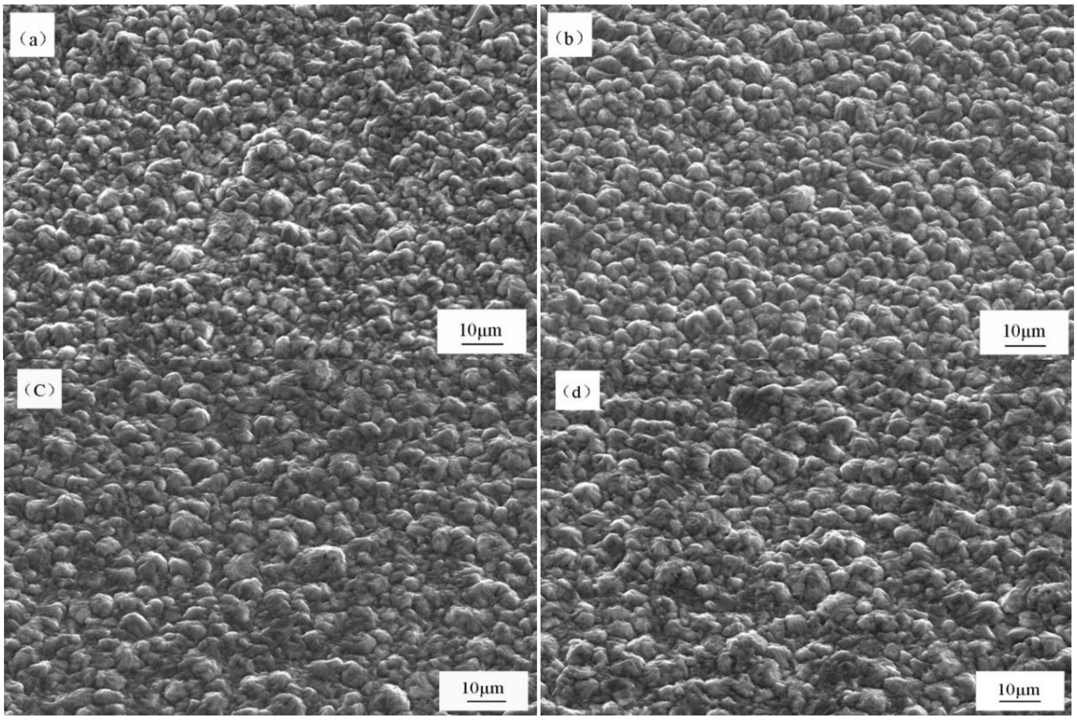
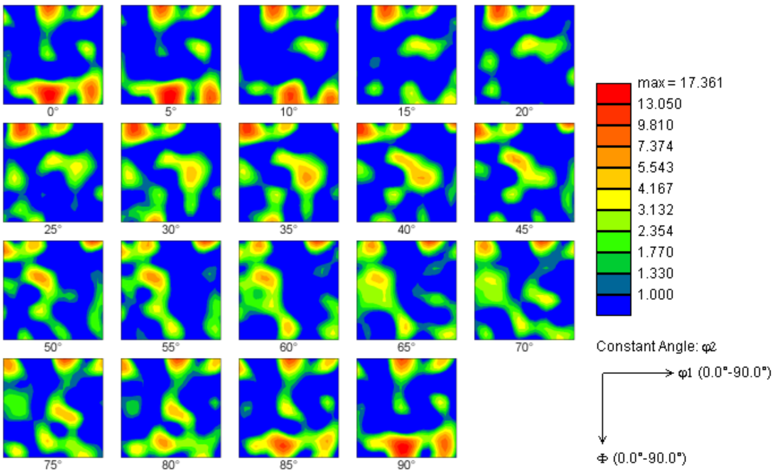
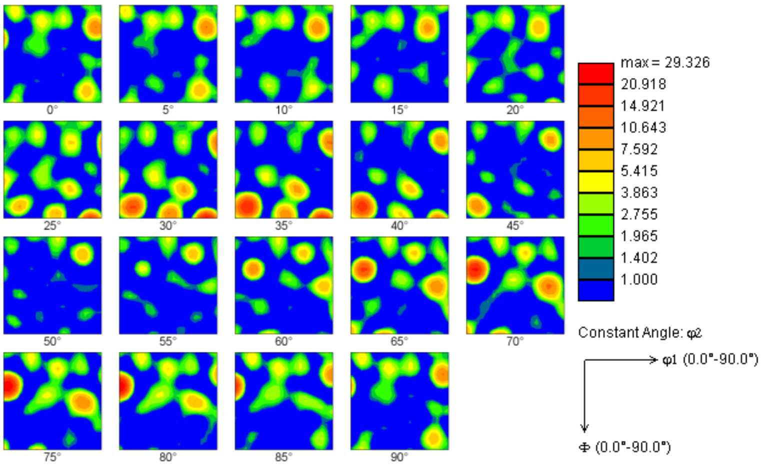


Figure 3. SEM photographs of surface of different copper ion concentration of copper foils: (a) 81 g/L; (b) 84 g/L; (c) 90 g/L; (d) 96 g/L

Figure 4 showed ODF sections of copper foils measured by EBSD. The textures of the copper foils with different copper ion concentration of 84 g/L and 90 g/L have the similar texture. It exhibit a typical cold rolling texture characterized by Cu{112}<111>, and the textures is strong. The formation of preferred orientation of copper foil is due to the competition of crystal face growth direction, growth rate and crystal growth mode. The change of copper ion concentration will only lead to concentration polarization caused by the change of metal ion concentration near the electrode surface. The concentration polarization does not change in energy, so it does not change the equilibrium state of electrochemistry. Therefore, the copper ion concentration has no effect on the growth mode of copper grains, so that the texture characteristics of copper foil cannot be changed.



(a) copper ion concentration of 84 g/L



(b) copper ion concentration of 90 g/L

Figure 4. ODF sections of copper foils measured by EBSD (Cu {112} <111>)

3.3. Tensile fracture of copper foils

Figure 5 was the SEM morphology of copper foil with different copper ion concentration, comparing with different fracture surface. When the copper ion concentration was 84 g/L and 87 g/L, the tensile strength and elongation of copper foil were all high. It was found that there were obvious slip marks and micro holes in the fracture, and there was a small dimple, which leads to the good elongation of copper foil. When the copper ion concentration was greater than 87 g/L, the fracture was typical brittle fracture and the fracture was smooth. Figure 3 showed that when the copper ion concentration was less than 84g/L, the particle size was uniform and small, and the strength and elongation of copper foil were high. When the copper ion concentration was greater than 87 g/L, the surface particles became coarse, resulting in a decrease in strength and elongation. This was also consistent with the above analysis.

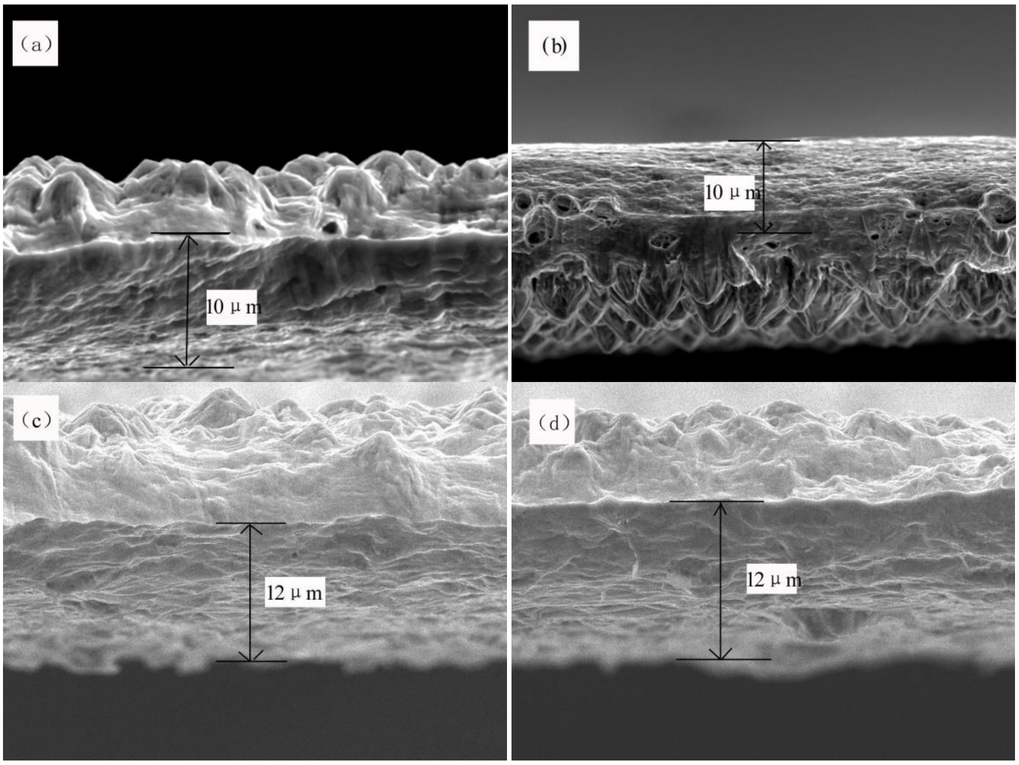


Figure 5. SEM fractographs of different copper ion concentration of copper foils: (a) 81 g/L; (b) 84 g/L; (c) 90 g/L; (d) 96 g/L

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4. Conclusion

The effect of copper ion concentration on microstructure and mechanical properties of electrolytic copper foil were investigated. The important conclusions are as follows:

(1) When the copper ion concentration was 84 g/L, the tensile strength was 405 MPa and the elongation was 5.6%.The tensile strength and elongation decreased notably with the copper ion concentration increasing to 96 g/L.

(2) When the concentration of copper ions was less than 84 g/L, the surface particles were small. When the concentration of copper ion was greater than 90 g/L, the rate of electrolytic deposition was faster, the surface particles become larger. The copper ion concentration has little effect on the texture of electrolytic copper foil.

5. Acknowledgments

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