



Comparative Study on Corrosion Resistance Properties of TP2 Phosphorized Copper and Rare Earth Microalloying Pure Copper in HCl Solution

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The microstructure, the second phase distribution and the second phase morphology of TP2 phosphorized copper and 0.1 wt. % Ce microalloying pure copper (Cu-0.1Ce) were investigated by optical microscope and scanning electron microscopy. The corrosion properties of TP2 phosphorized copper and Cu-0.1Ce in 0.5 mol/L HCl solution was studied using potentiodynamic polarization tests. The corrosion surfaces were observed by SEM. Results showed that cerium refined the grain sizes and enhanced the corrosion resistance properties of pure copper in 0.5 mol/L HCl solution. The corrosion potential and corrosion current density of TP2 phosphorized copper and Cu-0.1Ce were -193.57 mv, 3.79×10^{-7} A/cm² and -173.65 mv, 2.06×10^{-6} A/cm², respectively. At last, the mechanisms of cerium refining grain sizes and improving corrosion resistance properties in acid solution were discussed.

Keywords: Phosphorized copper, Pure copper, Cerium, Corrosion resistance property, Microalloying.

INTRODUCTION

Copper and copper alloys have been widely used in machine building industry, electric and electronic industry owing to the excellent thermal conductivity, electric conduction, corrosion resistance property, formability and solderability^{1,2}. Nowadays, TP2 phosphorized copper tubes are often applied in air conditioning and refrigerator (ACR) industry. With the development of ACR tubes, copper tubes with smaller diameter and thin wall become more and more needed. Therefore, the mechanical properties and corrosion resistance of copper are paid more attention. Research showed that the damage of air conditioner was caused mostly by electrochemical corrosion. Rare elements are named as industrial vitamin³, which means that it can improve the properties of a material after a minor addition. Rare earth elements can refine the grain size, purify the matrix, modify the inclusion and enhance the corrosion resistance property, heat resistance property and mechanical property of metal and metal alloys. Rare earth elements have shown beneficial effects on magnesium and magnesium alloys, aluminum and aluminum alloys, weathering resistant steel and heavy rail steel⁴⁻⁶. Researchers have investigated the influences of rare earth on the thermal conductivity, electric conduction and mechanical properties of Cu-Cr-Zr, Cu-Fe-P and Cu-Ni alloys⁷⁻¹¹. They found that rare earth elements improved the properties of various copper alloys. Chen *et al.*¹² studied the effect of rare earth on the corrosion property of Sn brass and

they found that a compact oxide layer was formed on the surface of copper alloy and the addition of rare earth improved the corrosion resistance of Sn brass. Zhang *et al.*¹³ discovered that rare earth cerium increased the corrosion potential of copper alloy and improved the corrosion resistance in thermodynamics. Rosalbino *et al.*¹⁴ studied the influence of Nd and Er on the corrosion resistance of pure copper in alkaline medium. Results indicated that the net structure and the formation of intermetallic compounds, Cu₆Nd, Cu₆Er inhibited the further corrosion of pure copper in alkaline medium after the addition of Nd and Er.

In this study, the effects of the representative light cerium on the microstructure and corrosion resistance properties of pure copper were investigated. Considering the corrosion environment of ACR copper tubes is acid medium, the corrosion resistance properties of TP2 phosphorized copper and cerium microalloying pure copper in HCl solution were studied in order to develop new type ACR copper tubes.

EXPERIMENTAL

TP2 phosphorized copper was obtained from a company. Cerium microalloying pure copper was prepared according to the following procedure. First, pure copper ($\geq 99.9\%$) was melted in the vacuum induction furnace and then 0.1 wt. % Ce wrapped by copper paper were added into the copper melt. The melt was stirred and held for 10 min. At last, the melt was

poured into an iron mould. The chemical compositions of TP2 phosphorized copper and Cu-0.1Ce were determined by SPECTRO direct reading spectrometer, as shown in Table-1.

The microstructures were observed by Zeiss Optical Microscope after etching in a solution of $\text{FeCl}_3\text{:HCl:CH}_3\text{CH}_2\text{OH} = 3 \text{ g} : 2 \text{ mL} : 96 \text{ mL}$. Corrosion behaviour was evaluated in 0.5 mol/L HCl solution by potentiodynamic polarization tests using cs300 electrochemical workstation. A three-electrode cell which a saturated calomel electrode (SCE) is as a reference, a platinum electrode is as a counter and the sample is as the working electrode was used. The samples were mounted by epoxy resins with an exposed area of 1 cm^2 . In the electrochemical tests, the polarization curves were measured at a scanning rate of 0.3 mV/s . The corrosion surfaces were examined by SSX-550 Scanning Electron Microscope (SEM). The back-scattered electron images of Cu-0.1Ce and element composition of second phases were analyzed by SEM and energy dispersion spectrometer (EDS)

RESULTS AND DISCUSSION

Analysis of microstructure: Fig. 1 shows the optical microstructures of TP2 phosphorized copper and Cu-0.1Ce. The cast structure of TP2 phosphorized copper was coarse columnar crystal. After the addition of 0.1 wt. % Ce, the microstructure of pure copper became small equiaxed grains. Cerium reduced the columnar grains of pure copper remarkably. In addition, the grain boundaries of pure copper was more clear than that of TP2 phosphorized copper. There are two important effects of rare earth elements in copper. On the one hand, cerium purified the copper matrix. It is well known that rare earth has active physical and chemical properties, which can react with impurities, O, S, Pb, Bi, Sn and Fe in copper and form rare earth compounds with high melting points and low density. Therefore, these refractory compounds were floated up to the surface of the copper melt and were removed as slag. On the other hand, cerium refined the grain sizes. The solubility of Ce in copper is very limited and the melting point of Ce is lower than that of copper. So, Ce gathered in the front of solid-liquid interphase and increased the degree of constitution undercooling in copper melt. The force of nucleation was increased and the grains were refined. Furthermore, Ce reacted with copper and formed Ce-rich intermetallic compounds, which were dispersed in copper matrix and increased the number of nucleation centers. From this point of view, Ce addition is also beneficial to refine the grain sizes.

Analysis of second phase: Backscattered electron images can reflect the composition of the sample surface. The area with high average atomic number has stronger electronic signal and presents as bright area, while the area with low average atomic number has weaker electronic signal and presents as dark area. Fig. 2 shows the backscattered electron images of Cu-0.1Ce and EDS results of second phase. The atomic number of Ce(58) is higher than that of copper(29). The white areas

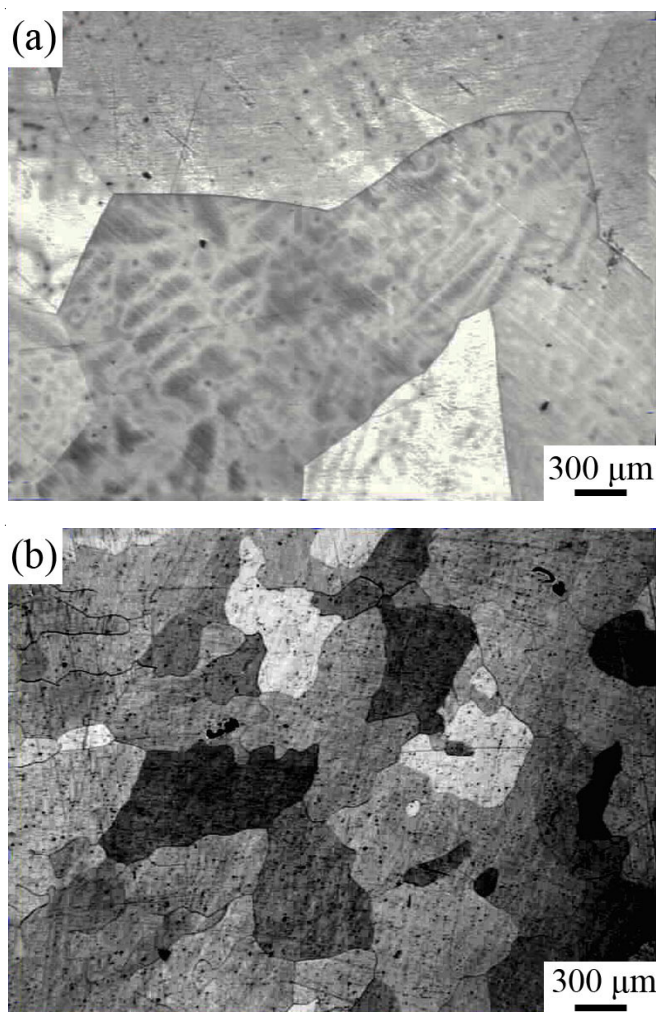


Fig. 1. Optical microstructure of TP2 phosphorized copper and Cu-0.1Ce: (a) TP2 phosphorized copper; (b) Cu-0.1Ce

in Fig. 2 were Ce-rich phase and EDS results showed that the ratio of Cu and Ce was $85.15:14.85 \approx 6:1$ (atomic ratio). This means that second phase particles, Cu_6Ce were formed between Ce and copper. The surface tension between Ce-rich phase and copper matrix was large and Ce-rich phase existed as spherical particles. These spherical Ce-rich second phase particles were dispersed in the copper matrix, which improved the thermal conductivity, electric conduction, corrosion resistance property and mechanical property of pure copper.

Analysis of corrosion resistance properties: Fig. 3 shows the potentiodynamic polarization curves of TP2 phosphorized copper and Cu-0.1Ce in 0.5 mol/L HCl solution. Table-2 gives the electrochemical parameters of potentiodynamic polarization curves. Though the corrosion potential of Cu-0.1Ce was more negative than that of TP2 phosphorized copper, the corrosion current density of Cu-0.1Ce was lower than that of TP2 phosphorized copper. The corrosion current densities and corrosion rates of TP2 phosphorized copper and Cu-0.1Ce were $3.79 \times 10^{-7} \text{ A/cm}^2$ and 0.0045 mm/a , $2.06 \times$

TABLE-1
CHEMICAL COMPOSITIONS OF EXPERIMENTAL MATERIALS

	Cu (%)	Ce (%)	Sb	Bi	Fe	Ni	Zn	S	Ag	Al
TP2	99.972	0	11.0	1.0	27.52	1.64	1.40	8.22	9.87	1.0
Cu-0.1Ce	99.992	0.1	9.22	1.42	26.26	4.70	1.37	6.11	8.96	6.67

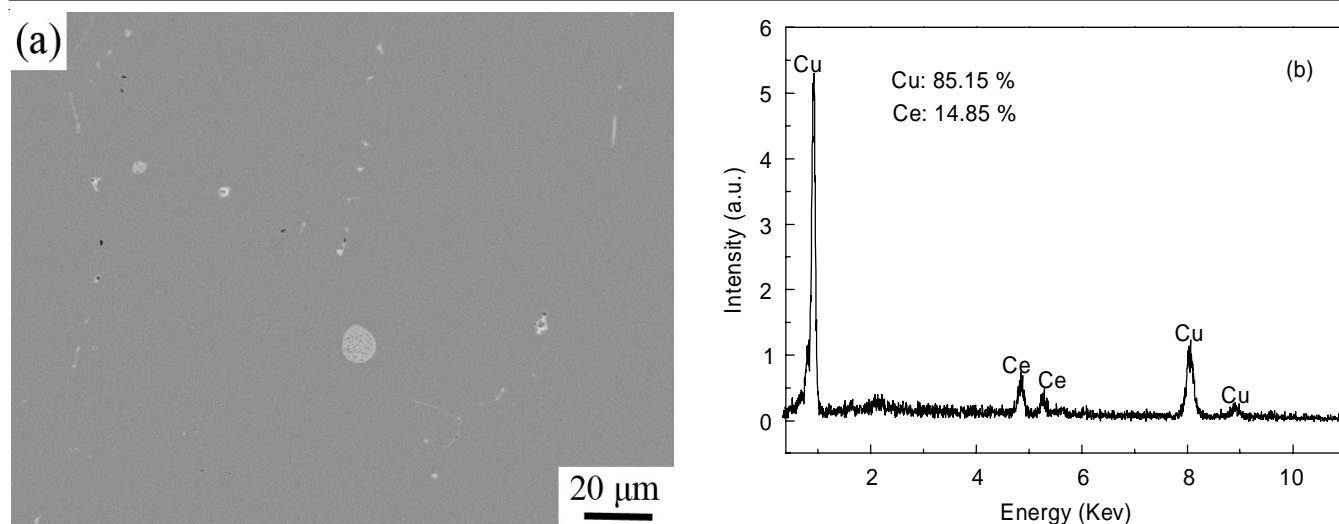


Fig. 2. Backscattered electron images of Cu-0.1Ce and EDS results of second phase

10^{-6} A/cm² and 0.024 mm/a, respectively. The cerium addition improved the corrosion resistance properties of pure copper clearly. The reasons were as follows. First, Ce addition purified the copper matrix and reduced the area of impurities. In corrosive medium, impurities worked as cathode and copper was anode. So, the existing of impurities accelerated the electrochemical corrosion of pure copper. After addition of Ce, the area of cathode was reduced and the electrochemical corrosion was weakened. Second, the second phase particles, Cu₆Ce, acted as dynamic obstacles of electrochemical corrosion and inhibited the further corrosion of copper matrix. Research showed that the content, shape and distribution of second phases would have different effects on the corrosion resistance property of pure copper¹⁴.

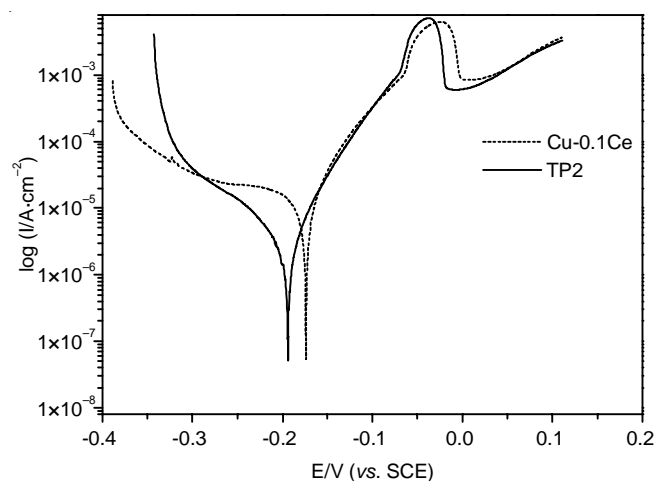


Fig. 3. Potentiodynamic polarization curves of TP2 phosphorized copper and Cu-0.1Ce in 0.5 mol/L HCl solution

Analysis of corrosion surface morphologies: Fig. 4 shows the surface morphologies of TP2 phosphorized copper and Cu-0.1Ce after electrochemical corrosion in 0.5 mol/L HCl solution. The corrosion surface of TP2 phosphorized copper was coarse and loose and a large number of corrosion products covered on the surface, while the surface of Cu-0.1Ce was smooth and compact and there were only few corrosion

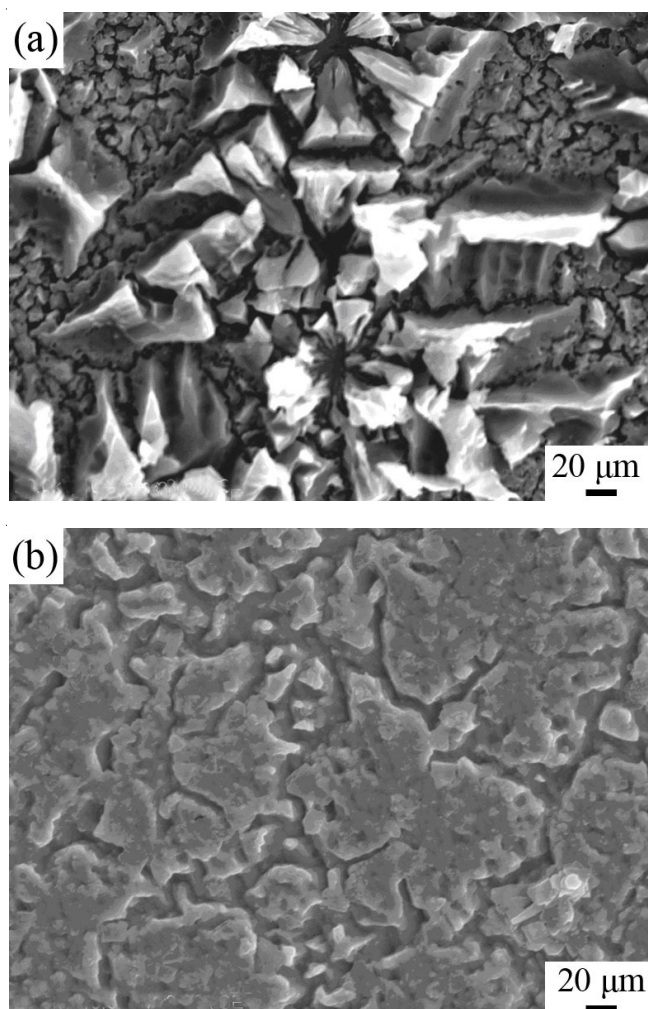


Fig. 4. Surface morphologies of TP2 phosphorized copper and Cu-0.1Ce after electrochemical corrosion: (a) TP2 phosphorized copper; (b) Cu-0.1Ce

products. The addition of cerium changed the corrosion morphologies and a compact oxide film was formed on the surface. As a result, addition of cerium improved the corrosion resistance property of pure copper. This result was consistent well

TABLE-2
ELECTROCHEMICAL PARAMETERS OF POTENTIODYNAMIC POLARIZATION CURVES

Sample	Corrosion current density (A/cm ²)	Corrosion potential (mv)	Corrosion rate (mm/a)
TP2	2.06×10^{-6}	-173.65	0.024
Cu-0.1Ce	3.79×10^{-7}	-193.57	0.0045

with the potentiodynamic polarization curves and Cu-0.1Ce had more excellent corrosion resistance property than TP2 phosphorized copper.

Conclusion

The microstructure of TP2 phosphorized copper was coarse columnar crystal, while the microstructure of Cu-0.1Ce was small equiaxed grain structure. The addition of cerium not only purified the copper matrix but also refined the grain sizes. High undercooling degree and the formation of a large number of Cu₆Ce second phase particles were both beneficial to refine the grain sizes. Electrochemical tests showed that the corrosion resistance properties of Cu-0.1Ce was more excellent than TP2 phosphorized copper. Cu₆Ce second phase particles were dynamic obstacles for the further corrosion of copper. Moreover, the formation of a compact corrosion product film on the surface was useful to improve the corrosion resistance properties of pure copper.

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