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The microstructures and corrosion properties of polycrystalline copper induced by high-current pulsed electron beam

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ABSTRACT

In order to investigate the corrosion mechanism of pure metal materials containing little impurities, polycrystalline commercial pure (cp) copper was irradiated by high-current pulsed electron beam (HCPEB). The surface microstructures of irradiated samples are characterized by using optical microscopy and transmission electron microscopy (TEM). The corrosion resistance is also investigated by using polarization curves of seawater corrosion and electrode impedance spectroscopy (EIS). The experimental results indicate that the corrosion resistance of cp copper irradiated by 10 pulses is remarkably improved comparing with the original sample. TEM observations suggest that large amount of supersaturated vacancy defects are produced when the material surface is subjected to the HCPEB irradiation. Furthermore, the agglomerations of the vacancy defects cause the formation of the vacancy cluster defects, such as vacancy dislocation loops, the stacking fault tetrahedra (SFTs) and voids. It is suggested that the structural defects on the irradiated surface have some relationships with the corrosion resistance's improvement of the material.

1. Introduction

High-current pulsed electron beam (HCPEB) has drawn widely attention for its great application potential and advantages of being simple, reliable, effective, and low energy consumption [1–9]. Under the action of HCPEB, a high power density (10^6–3×10^7 W/cm^2) is deposited only in a very thin layer (up to several micrometers) within a short time (a few microseconds), and such pulsed electron irradiation produces extremely fast heating and cooling of the surface and induces thermal stresses. As a result, abundant metastable surface microstructures or phase structures, such as supersaturated solid solution [1], ultra-fine grain [3], abundant defect structures, and nanostructures [5,10] are formed within the irradiated surface layer.

In general, craters are inevitably formed on the irradiated surface when metals and alloys are irradiated by intense-pulsed energetic beams, which are believed to deteriorate corrosion resistance of irradiated materials [1,2]. However, many researchers reported that evident improvement of corrosion resistance had been achieved due to intense-pulsed energetic beams irradiation. Zou et al. believed that the improvement of corrosion resistance of irradiated materials was mainly attributed to the surface purification effect [11,12]. Based on this mechanism, special selective surface contained impurities firstly melted or sublimated in the process of crater eruption. The mixing in the eruption process and the subsequent solute trapping effect during fast solidification process resulted in the homogenization of elements in the melted layer. Both crater eruption and composition homogenization contribute to the selective surface purification effect. As a result, the corrosion resistance of materials is significantly improved. Whereas, the influence of the microstructure evolutions induced by HCPEB irradiation on corrosion resistance of the irradiated materials was less involved in the mechanism presented by Zou et al. As we know, the surface properties of irradiated materials are determined by the final structure states. However, limited amount of works has concentrated on detailed microstructural characterization of HCPEB irradiated surface.

In this paper, we applied HCPEB technique to irradiate cp copper which almost contained no impurities. We present a detailed investigation on the microstructures of cp copper samples irradiated by HCPEB. The relationships between corrosion resistance and microstructures, especially defects structure, were explored. The detailed mechanism for the improvement in corrosion resistance of cp copper irradiated by HCPEB was investigated.

2. Experimental

Our experiments were conducted on HCPEB equipment (Nadezhda-2 type). It produced a pulsed (0.5–3 μs), low energy

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(10–40 keV), high current (10^2–10^3 A/cm^2), and high-aperture (~30 cm^2) electron beam. Vacuum conditions during electron beam irradiation also can be supplied.

The commercial pure (about 99.9%) copper was selected as the target material. Specimens were machined with a size of 10 mm in length, 10 mm in width, and 6 mm in height. All the samples were grounded with sandpapers and polished with diamond paste. Prior to HCPEB treatment, the specimens were ultrasonically cleaned in acetone. The polished surfaces of samples were irradiated at room temperature with 5 and 10 pulses, respectively. The HCPEB bombardments were carried out under the following conditions: the electron energy 27 keV, the current pulse duration 1.5 μs, the energy density about 4 J/cm^2, and the vacuum 10^{-5} Torr.

In order to obtain more information about microstructure, especially defects structure, the thin foils for transmission electron microscope (TEM) observation were prepared using mechanical pre-thinning, dimpling, and jet electrolytical thinning from the substrate side. The TEM examinations were conducted with JEM-2100 transmission electron microscope, which was operated at 200 kV and the foils for TEM observation is about 100–300 nm in depth. The microstructure changes of the surface layer were also characterized by using a LEICA DM-2500 M optical microscope, JSM-5600F scanning electron microscope. Corrosion tests were carried out using the conventional three-electrode cell containing the work electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum sheet as the counter electrode. The electrolyte solution was simulated sea water and its chemical components (wt.%) was shown in Table 1. Standard potentiodynamic polarization and electrochemical impedance spectroscopy measurements were conducted after samples exposed to simulated sea water under open circuit potential for 30 min (at room temperature, about 25 °C). Normally, after 30 min immersion in simulated sea water, a fairly stable potential could be achieved, the potentiodynamic polarization was carried out at a scan rate of 0.333 mV/s. The EIS spectra were obtained over the frequency (f) range 10^{-2}–10^5 Hz at the open circuit potential with an AC excitation amplitude of 10 mV. The size of effective testing area exposed to simulated sea water was 5 mm × 5 mm with other non-working surface covered with epoxy resin.

Table 1
Composition of simulated sea water (wt.%).

Compound	Concentration (g/L)	Compound	Concentration (g/L)
NaCl	24.53	$NaHCO_3$	0.201
$MgCl_2$	5.20	KBr	0.101
Na_2SO_4	4.09	H_3BO_3	0.027
$CaCl_2$	1.16	$SrCl_2$	0.025
KCl	0.695	NaF	0.003

3. Results and discussion

3.1. Surface morphology and microstructure

Fig. 1 shows the surface morphologies of both 5-pulsed and 10-pulsed cp copper samples. For the irradiated samples, the surface becomes to be much rougher than original samples and the craters formed on the surface while their sizes range from several micrometers to tens of micrometers. Usually, there is a black "dimple" on the center of crater, as show in Fig. 1(a) and (b). They are formed by the eruptions of melting pool and remain until the last. As some researchers' study, they are sensitive sites for the pitting corrosion, which was easily to be attacked by anions [12]. Compared with Fig. 1(a) and (b), one can see that the crater density of 5-pulsed sample is obviously higher than that of 10-pulsed sample, indicating that the crater density decreases with the pulse number increase in range of 5–10. This result can be attributed to the polishing effect to the material surface of HCPEB irradiation. The preceding formed craters would be fused or eliminated by subsequent pulses [13]. From previous studies, such morphology is the result of local sub-layer melting and eruption through the solid outer surface [2,14]. Surface impurities, second phase particles, and

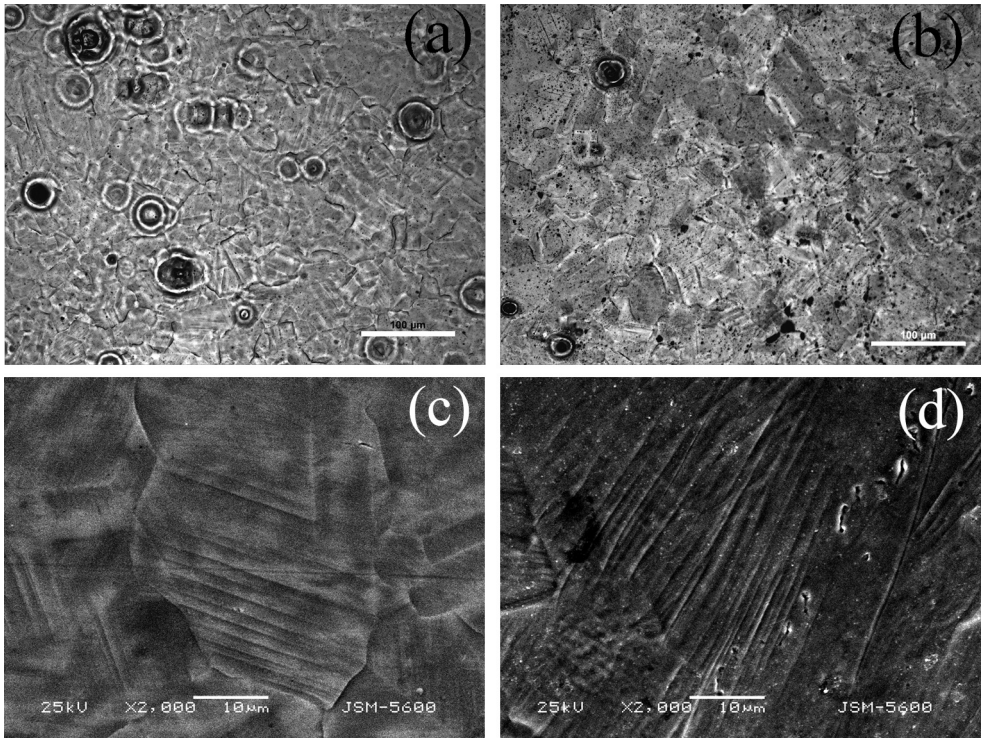

Fig. 1. Surface images of cp copper after HCPEB treatment (a), (c) 5 pulses, (b), (d) 10 pulses.