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Effect of Rare Earth Ce on the Inner Oxide Layer and Properties of Copper-Chromium-Titanium Alloy

Rongqun Zhang[a], Xiaohong Chen

School of Materials and Chemistry, University of Shanghai for Science and Technology, Shanghai 200093, China

[a]rqzhang2022@163.com

Abstract

Cu-0.6Cr-0.06Ti and Cu-0.6cr-0.06Ti-0.08Ce alloys were prepared by vacuum high frequency induction melting technology, and the heat treatment processes of internal oxidation, cold rolling and aging were carried out to prepare Cr_2O_3 composites with high conductivity. The microstructure morphology and properties were analyzed by means of metallographic microscope under different processes. The results show that the conductivity, hardness and inner oxide thickness increase with the increase of internal oxidation time. The addition of a small amount of Ce can promote the internal oxidation process of Cu-Cr-Ti alloy. After adding 0.08%Ce to Cu-Cr-Ti alloy with oxygen content of 0.8%, internal oxidation for 8h, internal oxidation temperature of 950°C, the oxide layer depth can reach 796μm, and the conductivity and hardness can be increased to 93.2%IACS, 93.4HV. The main innovation of this experiment is the addition of rare earth elements in the alloy, through the comparison with the non-added rare earth alloy, it is concluded that the rare earth element Ce can improve the hardness of the alloy.

Keywords

Internal Oxidation; Conductivity; Hardness; Cr_2O_3 Composite Material; Rare Earth.

1. Introduction

With the increasing speed of high-speed rail, high-speed rail contact lines require higher electrical conductivity to improve current carrying capacity, as well as higher strength to withstand higher suspension tension. At present, it is difficult to improve the conductivity and tensile strength at the same time. By controlling the microstructure of the surface and the core of the material, the internal oxidation treatment of Cu-CR titanium alloy achieves the performance of high surface conductivity and high core strength, and realizes the high strength and high conductivity of the material [1]. In this paper, the rare earth elements are added to Cu-Cr-Ti alloy, which is treated in different internal oxidation time, and the conductivity and hardness are tested, and the microstructure and properties are analyzed[2].

1.1 Experiment

High purity electrolytic copper, Cu-25Cr alloy, Cu-50Ti and Cu-20Ce intermediate alloys were used as raw materials for high temperature melting in vacuum high frequency induction melting furnace. The calculated raw material is dried before melting and a suitable ultra-high temperature release agent is sprayed on the bottom of the mold. Before melting begins, pure electrolytic copper is placed in a graphite crucible and the temperature is raised until the liquid in the crucible flows evenly and is completely melted. Then, alloy Cu-25Cr, Cu-50Ti and Cu-20Ce are added to the hopper on the rotating crucible to make Cu-Cr-Ti and Cu-Cr-Ti-Ce alloys. After melting is completed, a round steel ingot with a diameter of 80 mm is cast, and the upper and lower incomplete parts of the ingot are cut with a grinding wheel cutting machine.

Cu-0.6Cr-0.06Ti and Cu-0.6cr-0.06Ti-0.08Ce alloys were selected as experimental samples for internal oxidation treatment, and the appropriate temperature for internal oxidation treatment was 950°C, and the internal oxidation treatment time was 2h, 4h, 6h, 8h, 10h. After the internal oxidation treatment, the samples were deformed by 80% and aged at 450°C×1 h, and nitrogen was injected as the protective gas of the experiment.

The microstructure and morphology of the alloy were observed by ZEISS Axio Imager A2M metallographic microscope. DK60 metal conductivity meter was used to measure the inner oxide layer conductivity of the alloy under different internal oxidation processes. AX050 50kN universal testing machine was used to carry out tensile test on the aging state of the sample, and the same sample was tested for 3 times, and the average value was obtained. The microhardness of the alloy was tested by microhardness tester. The loading time was 20s and the loading load was 100g. The average value of the test results was taken.

2. Effect of Internal Oxidation on Internal Oxide Layer and Conductivity

2.1 Effect of Internal Oxidation Time on Internal Oxidation Layer and Conductivity

2.1.1 Effect of Internal Oxidation Time on Internal Oxidation Layer

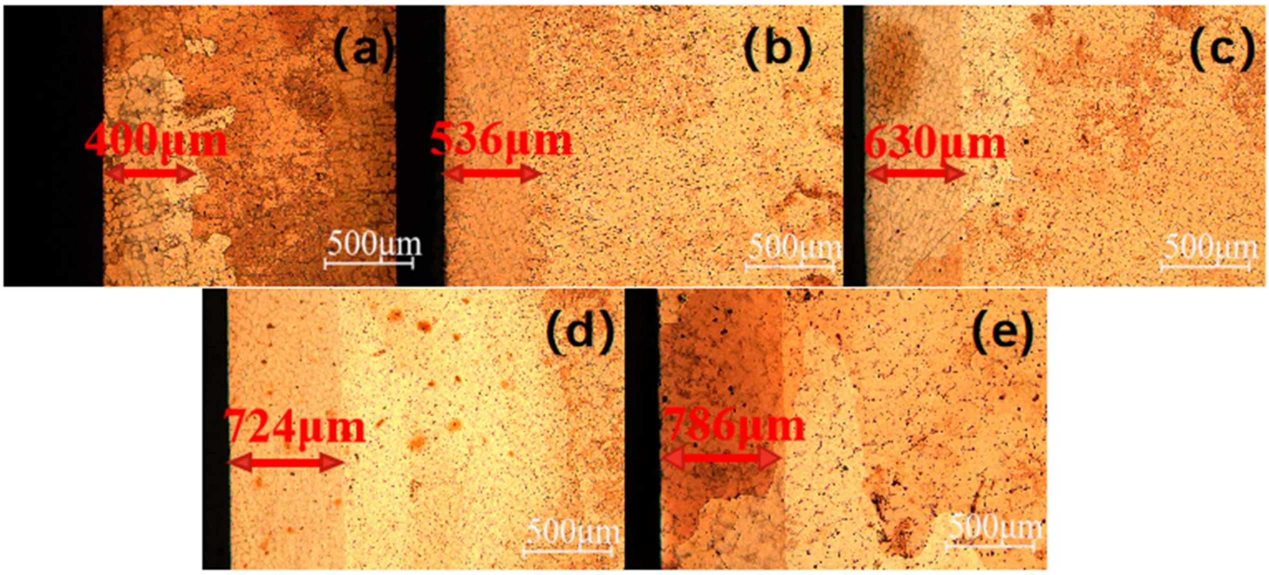

Figure 1. Effect of internal oxidation time (2h, 4h, 6h, 8h, 10h) on the oxide layer of Cu-0.6Cr-0.06Ti-0.08Ce alloy

As can be seen from Figure 1, with the increase of internal oxidation time, the depth of internal oxidation layer gradually increases, and the internal oxidation rate increases from fast to slow, forming a typical parabolic time rule relationship. With the addition of rare earth for 10h, the inner oxide layer thickness reached 786μm, and without the addition of rare earth, the inner oxide layer thickness was 705μm, and the inner oxide layer thickness increased by 81μm. Due to the deepening of the internal oxidation front, the oxygen diffusion distance increases, and the oxygen enters the matrix and consumes a part of the oxygen in the reaction with Cr, resulting in a decrease in the oxygen concentration and further inhibition of the internal diffusion, that is, the addition of Ce also plays a role in promoting penetration, which helps [O] penetrate through the alloy surface into the interior, thus greatly increasing the depth of the internal oxide layer[3].

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2.2 Effect of Internal Oxidation Time on Conductivity

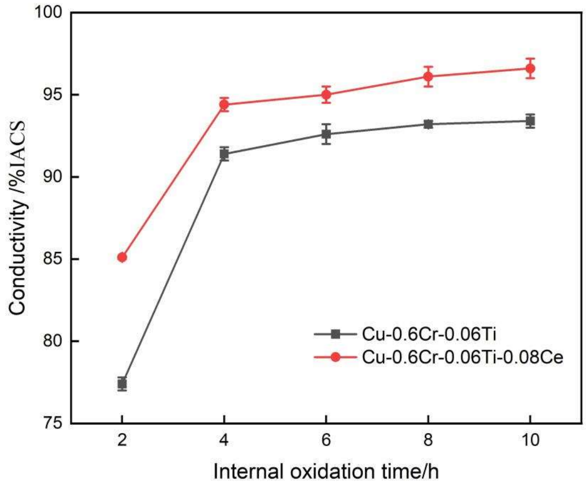

Figure 2. Effect of internal oxidation time on conductivity

Figure 2 shows the change trend of conductivity and hardness under different internal oxidation time with oxygen content of 0.8% and internal oxidation temperature of 950°C. It can be seen from the figure that the electrical conductivity increases significantly with the extension of internal oxidation time, and the electrical conductivity of the inner oxide layer is 77.4%IACS after the addition of rare earth alloy for internal oxidation 2h, and 93.2%IACS after internal oxidation for 8h. After oxidation on the surface of the sample, Cr dissolved in the Cu matrix is precipitated from the matrix in the form of Cr_2O_3, the matrix is purified, and the electrical conductivity is improved. With the extension of internal oxidation time, the hardness will first increase, and then decrease after reaching the peak[4]. The level of hardness is mainly related to the number of oxide particles and the size of oxide particles. In the early stage of internal oxidation, the number of oxide particles and the thickness of the inner oxide layer will increase, and the increase of internal oxidation time will make the grains grow larger. Performance deteriorates, resulting in reduced hardness. After oxidation within 8 hours, the hardness reaches its peak.

3. Conductivity and Hardness Changes after Deformation and Aging

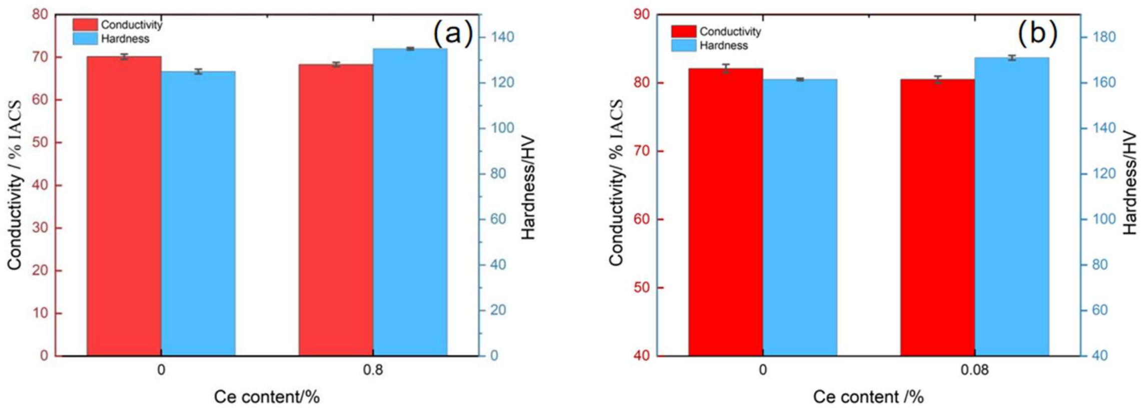

Figure 3. Changes in conductivity and hardness after deformation and aging (a) deformation (b) aging

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The conductivity and hardness increased significantly after aging. The electrical conductivity with 0.08%Ce decreased compared with that without rare earth. The overall electrical conductivity with 0.08% CE was 75.3%IACS and that without rare earth was 81.7%IACS. The hardness of adding 0.08% rare earth is higher than that of not adding rare earth, and the hardness of adding 0.08% rare earth is 171HV, and the hardness of not adding rare earth is 161.5HV. High-speed rail contact wire materials need to cope with high strength and high conductivity, which requires that the conductivity should be higher than 75%IACS, while the need for high strength to withstand higher suspension tension, tensile strength should be greater than 500Mpa[4]. According to Figure 3 (b), the effect of increasing tensile strength is higher than that of decreasing conductivity, so the addition of rare earth with low conductivity and high hardness is better.

3.1 Analysis of Tensile Strength after Aging

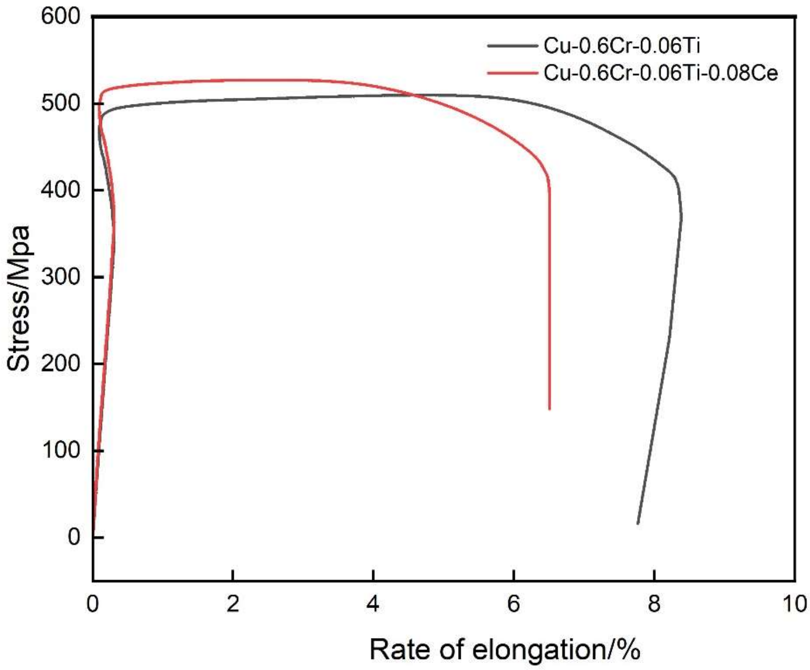

Figure 4. Changes in tensile strength after aging

Figure 4 shows the change of the tensile strength of the alloy after aging treatment. After aging, the tensile strength increases and the elongation decreases. After the addition of rare earth, the tensile strength is increased to 523Mpa and the elongation is 6.5%. The tensile strength without rare earth is 503Mpa and the elongation is 8.3%. The addition of a small amount of rare earth increases the tensile strength of the material, but the rare earth has the effect of refining the grain, thus reducing the elongation of the alloy. As an important source of dislocation growth, Cr_2O_3 particles can significantly increase the dislocation density, and through work hardening, significantly increase the dislocation diffusion rate, showing deformation strengthening effect, and thus significantly improve the strength. And the grain size is reduced, which increases the distance between the grain and the grain boundary, shorters the length of dislocation accumulation within the grain, reduces the stress concentration, increases the grain boundary, makes the grain difficult to crack under the action of external forces, and significantly improves the strength of Cu-Cr_2O_3 (Ce) composite[5] .

4. Conclusion

As the internal oxidation time continues to increase, the thickness of the internal oxide layer continues to deepen, the electrical conductivity rises first and then tends to flatten, and the hardness rises first and then decreases.

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After aging, the electrical conductivity and hardness increased significantly, and the electrical conductivity decreased and the hardness increased with the addition of rare earth.

The tensile strength increased and the elongation decreased after the addition of rare earth.

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