

Study on New Process of Composite Rare Earth Passivation on Surface for Copper Alloy Materials

1st Xuefei Lv

College of Mechanical & Electrical Engineering
Jilin Institute of Chemical Technology
Jilin City, China
108825021@qq.com

2nd Shukun Gan

College of Mechanical & Electrical Engineering
Jilin Institute of Chemical Technology
Jilin City, China
49141544@qq.com

Abstract—In order to improve the surface properties of copper alloy materials, in this paper, a new process for surface passivation treatment of copper alloy materials with composite rare earth salts was obtained by orthogonal test. The corrosion resistance of the new process was evaluated by the nitric acid drop method and the salt spray test method. The morphology of the copper alloy was characterized by JSM-6490LV type scanning electron microscope. The results show that the copper alloy material treated by the new process has a nitric acid resistance time of 22 seconds, and the surface is still bright after 16 hours of salt spray experiment. The new process can change the surface characteristics of the copper alloy material, thereby improving the corrosion resistance of the copper alloy.

Keywords—copper alloy, surface passivation, new process, nitric acid spot, salt spray test

I. INTRODUCTION

Copper alloy has good mechanical properties, thermoplasticity, easy cutting and weldability, and is used in the manufacture of valves, water pipes, air-conditioning internal and external machine connecting pipes and radiators. However, in high humidity and corrosive media, severe corrosion is likely to occur [1], resulting in a greatly shortened service life of copper alloy workpieces. The use of surface passivation film formation technology is a cost-effective method for corrosion protection of copper and alloy surfaces. In recent years, rare earth salts have been widely used, and the research work on rare earth conversion coatings on the surface of copper alloy workpieces is limited to the preliminary research on the single rare earth passivation process. In this paper, a new process of composite rare earth passivation is obtained by orthogonal test. The surface of the copper alloy workpiece is treated to form a composite rare earth conversion coating on the surface, and the corrosion resistance is evaluated.

II. TEST

A. Materials and Processes

The material test piece is H62 brass (commercially available), that is Cu-Zn alloy, the main chemical composition (Wt%): 61.811% Cu, 35.662% Zn, and the rest are impurities. The sample size is 20mm × 10mm × 2mm, and the top side has a 2mm aperture for easy suspension.

The treatment process is: sanding and polishing → distilled water flowing water washing → chemical degreasing → flowing water washing → chemical polishing → flowing water washing → pickling → flowing water washing → rare earth passivation → flowing water washing → drying and drying [2].

B. Experiment Method

The chemical immersion method was used, the reagents used were of analytical purity, and the new process conditions were obtained by orthogonal test.

1) Pretreatment

a) *Grinding and polishing*: The metallographic sandpaper is polished to the working surface to 2000#, the original metal surface is removed, and then washed and dried.

b) *Chemical degreasing*: The immersed sample is immersed in the chemical degreasing liquid to remove oil. The main reagent components and processes are shown in Table I [3].

TABLE I. CHEMICAL DEGREASING PROCESS PARAMETER

Name	Reagent				Temperature (K)	Time(s)
	NaOH(g/L)	Na ₃ PO ₄ (g/L)	Na ₂ CO ₃ (g/L)	Na ₂ SiO ₃ (g/L)		
parameter value	30	70	30	10	348-358	120-300

c) *Chemical polishing*: The sample to be used is placed in a chemical polishing solution, repeated polishing in the same total polishing time to make the sample mirror bright, the main reagent components and process are shown in Table II [4].

TABLE II. CHEMICAL POLISHING PROCESS PARAMETERS

Name	Reagent		Temperature (K)	Time(s)
	H ₂ O ₂ (ml/L)	OP-10 Active Agent(ml/L)		
parameter value	180	2-4	308-313	180-300

d) *Sulfuric acid pre-acid washing*: The polished and dried sample is immersed in a 10% sulfuric acid solution for activation to remove the oxide film on the surface of the alloy. The process parameters are shown in Table III. [5]

TABLE III. CHEMICAL POLISHING PROCESS PARAMETERS

Name	H ₂ SO ₄ /(ml/L)	Temperature (K)	Time(s)
parameter value	50-150	room temperature	300-600

2) *Passivation new process*: Based on the literature [5,6], the initial process components were determined, and the optimal process conditions were obtained by orthogonal test. The components were: barium salt, barium salt, sodium molybdate, citric acid, sulfosalicylic acid, surfactant, and the parameter temperature and time.

C. Film performance test

The evaluation criteria for film properties are as follows, according to the orthogonal test table, the pretreated samples were passivated, and the layers obtained in each group were analyzed and scored [6].

a) *Appearance color*: The surface of the coated copper alloy should be a rainbow color mainly composed of gold, the film layer should be continuous and complete, and there is no brown and dark yellow loose film layer which can be wiped off by the absorbent cotton.

b) *Surface brightness*: The surface of the coated copper alloy should have a smooth surface and high brightness without marble-like fogging.

c) *Evaluation of corrosion resistance of the film*: Using a 1:3 (volume ratio) or 25% nitric acid solution, drop a drop of the rare earth conversion film of the copper alloy obtained under different process conditions, and select 3 samples for each measurement 5 times. Make a note of the time from the time the solution is dropped until the start of bubbling, and average the time [7, 8].

III. RESULT

A. Optimal process

The above three film layer scoring standards were scored in a ratio of 3:3:4 by a percentage system, and the optimal formula of the double rare earth salt obtained by the orthogonal test is shown in Table IV.

TABLE IV. OPTIMAL PROCESS PARAMETERS

Factor name	Parameter
La(NO ₃) ₃ (g/L)	4
Ce(NO ₃) ₃ (g/L)	4
Benzotriazole (g/L)	14
Na ₂ MoO ₄ (g/L)	3
Citric Acid (g/L)	14
Sulfosalicylic Acid (g/L)	10
surfactant (g/L)	0.1
temperature (K)	323
time (s)	300

B. Nitric acid resistance

The corrosion resistance of the film obtained by adding the double rare earth salt, the single rare earth salt (cerium nitrate, cerium nitrate) and the passivation solution without adding any rare earth salt was tested by the nitric acid drop test, as shown in Fig. 1.

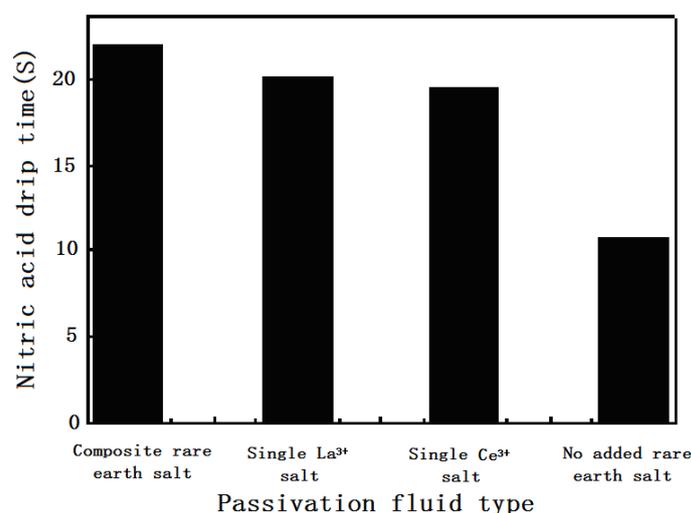


Figure 1. Corrosion resistance of samples after treatment with different passivation solutions

It can be seen from Fig. 1 that the membrane layer with no rare earth salt added is only 11s, and the corrosion resistance is the worst. The corrosion resistance time of adding cerium nitrate salt layer is 19s, followed by cerium nitrate salt, only 18s. The film with the addition of the double rare earth salt (La/Ce) salt has a nitric acid resistance up to 22s, indicating that the film has the best corrosion resistance.

C. Neutral salt spray resistance

According to GB/T3826-1999, the experiment uses NaCl solution in the RK-60 salt spray test chamber. Table V shows the salt spray test results of different samples in a salt test fog machine.

TABLE V. NEUTRAL SALT SPRAY TEST RESULTS

Sample type time(s)	Blank sample	Not added rare earth salt	Single cerium salt	Single lanthanum salt	New process of mixed rare earth salt
14400	corrosive discoloration, speckled	no change	no change	no change	no change, the surface is still evenly bright
28800	brown strip corrosion, Surface tarnish	surface edge corrosion turns green	no change	no change	no change, the surface is still bright
43200	corrosion area is further expanded	block corrosion point near the crack of the turtle	yellow-brown spots appear bright at the crack	very few spots visible to the naked eye, bright surface	no change, the surface is still bright
57600	the surface is completely covered by cracked green cracks, shedding at the edges	large cracks and white haze on the surface	obvious brown spots, matte	1/3 area discoloration, uneven color without light	a small amount of fog marks appear locally, still brighter

It can be seen from Table V that the copper alloy after the new process has been subjected to a neutral salt spray test for more than 57600 s.

a) *Blank sample*: The surface of the blank sample is completely covered by the cracked green crack, and the edge is peeled off.

b) *No rare earth salt sample*: There are large cracks and white misty plaques on the surface of the sample without added rare earth salt.

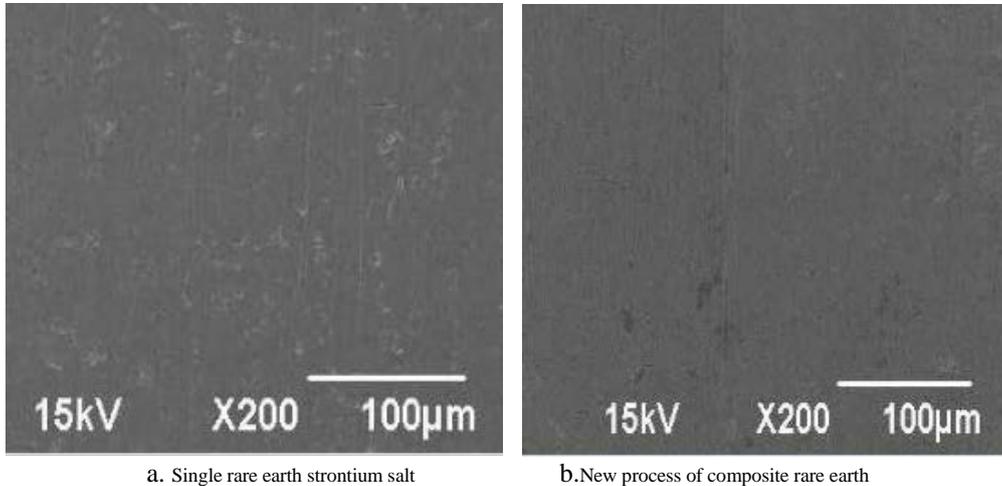
c) *Single strontium salt sample*: The surface of the single strontium salt sample has obvious brown spots and the surface is dull.

d) *Single strontium salt sample*: The 1/3 area of the surface of the single strontium salt sample is discolored, and the color is uneven and there is no light.

e) *Samples after treatment of composite rare earth new process*: A small amount of fog marks appear on the surface of the sample treated by the new compound rare earth process, which is still bright.

D. Membrane performance characterization

The surface morphology of copper alloys obtained by different formulations was characterized by JSM-6490LV scanning electron microscopy[9,10] . Fig. 2 is a comparison of the morphology of each conversion film under the different conditions of 200 times magnification. According to the picture, the surface of the single rare earth strontium salt sample (Fig. a) has a lighter color, and there are pitting defects and cracks that are not allowed to exist, and the substrate is bare. The surface of the sample treated with the new compound rare earth process (Fig. b) has a uniform golden color, and the film layer is smooth and dense with no defects.



a. Single rare earth strontium salt

b. New process of composite rare earth

Figure 2. SEM comparison of different passivation film layers

IV. CONCLUSION

- The optimal formula for the new rare earth composite process of copper alloy obtained by orthogonal test is: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{g/L}):4, \text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{g/L}):4, \text{BTA}(\text{g/L}):14, \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}(\text{g/L}):3, \text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}(\text{g/L}):14, \text{C}_7\text{H}_7\text{O}_6\text{S} \cdot 2\text{H}_2\text{O}(\text{g/L}):10, \text{C}_{18}\text{H}_{29}\text{NaO}_3\text{S}(\text{g/L}):0.1$, passivation temperature(K): 323, passivation time (s): 300.
- The nitric acid drop test was used to test the corrosion resistance of the comparative film under different passivation conditions. The results show that the new composite rare earth process can significantly improve the corrosion resistance of the copper alloy surface and has the strongest corrosion resistance.
- The results of neutral salt spray test show that the surface of the copper alloy neutral salt spray after the new rare earth composite treatment is still bright after 16h.
- The morphology of each film was characterized by scanning electron microscopy. The results show that the composite rare earth conversion film is more uniform and dense than the single rare earth salt film, the strong binding force with the matrix is copper alloy, the surface provides corrosion protection.

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