Research on the Surface Performance of Copper after Siliconizing Treatment

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Abstract. In order to improve the surface properties and extend service life of pure copper, siliconizing of copper was carried out by penetrating silica powder. Three new phase were formed in layer, they are Cu0.83Si0.17, Cu7Si, and Cu6.69Si, respectively. The highest micro hardness of the layer reaches up to 340HV0.05, which is 5 times higher than the substrate. The corrosion resistance and oxidation resistance of copper after siliconizing in different solution were studied, such as, the corrosion resistance have improved 2.3 times in H2SO4 solution, 3.8 times in NaCl, and 4.4 times in artificial seawater separately. The oxidation resistance of the siliconized copper is 18 times than that of pure copper. The above experimental results show that, the siliconizing layer will improve the performance of pure copper dramatically.

Commercially pure copper is a widely used material in engineering because of its good electrical and thermal conductivity, but it still has shortcomings in strength, corrosion resistance, oxidation resistance, etc., so that the life of pure copper products is short and cannot meet certain Required under working conditions. Copper can form alloys with metals such as Zn, Sn and Pb. However, the conductivity of pure copper decreases sharply with the intervention of alloying elements. Therefore, copper-based materials encounter the contradiction that conductivity and strength are incompatible. In order to improve the surface properties while maintaining the excellent conductivity of the substrate, the surface chemical heat treatment and surface coating of commercially pure copper were studied to change the microstructure and physical and chemical properties of the copper surface[1-2].

Commercially pure copper infiltration has long been studied and applied[3], but the early silicon infiltration uses ferrosilicon or silicon powder as the infiltration agent. In this paper, silica is used as the infiltration agent, and the active silicon is obtained by reduction reaction for silicon
infiltration (3SiO₂ + 4Al → 2Al₂O₃ + 3Si). At present, there are few reports on the properties of silica infiltrated siliconized layer\(^4\). Therefore, the corrosion resistance of siliconized layer is studied.

1. Experimental materials and method

1.1. Experimental Materials
Pure copper is used as the base material, and the sample size is 20mm×20mm×3mm. The infiltration agent is selected by using silica as the main infiltration agent, Al as the reducing agent, and adding an appropriate amount of NH₄Cl and NaF as an activator, and Al₂O₃ as a filler. Table 1 show the ratio of osmotic agent.

| Component | SiO₂ | Al₂O₃ | Al | NaF | NH₄Cl | CeO₂ |
|-----------|------|-------|----|-----|-------|------|
| Mass fraction (%) | 45.5 | 18.2  | 27.3 | 2.7 | 4.5   | 1.8  |

1.2. Silicon infiltration process
The powder embedding method was adopted, the siliconizing temperature is 850°C, and the temperature were hold for 12 h. Using Stepwise heating, the heating rate is maintained at 3~5°C/ min.

1.3. Organizational structure analysis
Alcohol solution with 3% FeCl₃ was used as corrosive liquid for the metallographic analysis. Etching time is 3 to 5 minutes. The morphology of the siliconized layer was observed under an optical microscope. X-ray analysis was carried out using the Japanese science company 2RGAKU2500/PC. Test conditions: Cu target Kα radiation, Ni filter, tube voltage 40kV, tube current 40Ma, slit size DS=10mm, RS=0.3mm, SS=10mm, sweep speed 8°/min, scan range 10°~80°.

1.4. Hardness Testing
Under the macro hardness HRF of the HR-150DT Rockwell hardness tester, the load was 588.4 N (60 Kgf) and the indenter was 6.35 mm (1/4 inch) steel ball. The microhardness were tested using a HV-1000Z microhardness tester, with was 50 g load, every 50μm was choosen from the edge (siliconized layer) to the core (copper substrate) for testing position, and the loading time was 10 s.

1.5. Corrosion performance test
The main means of testing the corrosion resistance of the material during the immersion corrosion test can intuitively reflect the corrosion phenomenon and corrosion resistance of the material in the corrosive liquid. In order to test the corrosion resistance of the siliconized layer in the liquid corrosive medium, each group of samples was immersed by using three etching solutions of acid, salt and artificial seawater. The test specifications for the immersion corrosion test are shown in Table 2. The soaking corrosion test was measured by the weight loss method. For all corrosive solutions, a new corrosive solution is required after the test has been weighed once. Weigh after drying every 24h, five times in total for all testing. Contents of artificial seawater is shown in Table 3.

Table 2. Immersion corrosion test specification
| solution | Acid  | Salt  | Artificial sea water |
|----------|-------|-------|----------------------|
| solute   | H₂SO₄ | NaCl  | Artificial recipe    |
| Mass fraction | 15%  | 3.50% |                      |

**Table 3. Artificial seawater solution components**

| molecular formula | NaCl | MgCl₂ | MgSO₄ | CaCl₂ | NaHCO₃ | KCl | NaBr | H₃BO₃ | Na₂SiO₃ | H₃PO₄ | AlCl₃ | NH₄ | LiNO₃ |
|-------------------|------|-------|-------|-------|--------|-----|------|-------|---------|-------|-------|-----|------|
| Unit: g/L          | 26.726 | 2.26 | 3.248 | 1.153 | 0.198  | 0.721 | 0.058 | 0.058 | 0.0024 | 0.002 | 0.013 | 0.002 | 0.0013 |

1.6. Antioxidant performance test

The sample is placed in a crucible, placed in a drying oven to be dried until constant temperature, and then the total mass is m. After the box-type resistance furnace was heated to 700℃, the sample and the crucible were placed together, and the mixture was kept at 700℃ for 2 hours in a furnace temperature environment, and then the mass was weighed every 2 hours. Ten samples were selected for each set of tests and the average was tested as the final data.

The oxidation resistance test uses the "weight gain method" to test the oxidation resistance of the layer. The calculation formula of the unit area oxidation amount W(t) is:

\[ W(t) = \Delta m/s \]  \hspace{1cm} (1)

W(t) is the mass gain weight per unit area (g/m²), \( \Delta m \) is the weight gain (g) of the sample, and S is the sample area (m²).

2. Experimental results and analysis

2.1. Microstructure of siliconized layer

Fig.1 shows the metallographic structure of the silicon dioxide siliconized layer. It can be seen from the Cu-Si phase diagram[5] that the siliconized layer is a columnar (α+γ) dual phase structure, α is a solid solution of Si in Cu, and γ is a copper silicon compound. The substrate is an industrial pure copper equiaxed grain. The thickness of the siliconized layer was measured to be 650μm.

The phase structure of the siliconized layer was analyzed by an X-ray detector, and Fig.2 is an X-ray diffraction pattern. In the process of silicon infiltration, as the temperature increases, the silica is reduced by aluminum powder to produce active silicon atoms, deposited on the surface of the substrate, and then diffused into the interior of the group to produce a siliconized layer of a certain thickness. It can be seen from the XRD diffraction pattern that the silicon atom is solid-dissolved into the matrix to form an α phase, and a copper silicon compound such as Cu₀.₈₃Si₀.₁₇, Cu₀Si, Cu₆.₆₉Si is formed. These phases are mostly hard phases and are dispersed in the matrix. Among them, Cu₀.₈₃Si₀.₁₇ has a complex cubic lattice, which is hard and brittle, similar to the osmotic body in pearlite. It can be seen from the copper-silicon phase diagram that it belongs to the γ phase.
Figure 1. Morphology of the siliconized layer

Figure 2. X-ray diffraction of the siliconized layer

2.2. Hardness analysis of siliconized layer

The microhardness test data of the siliconized layer is shown in Fig. 3. It can be seen from the figure that the microhardness of the siliconized layer is about HV349, and the microhardness of the substrate is 5.8 times higher than that of the copper matrix. In the siliconized layer, a new phase such as Cu$_{0.83}$Si$_{0.17}$, Cu$_9$Si, Cu$_{6.69}$Si is formed, which is dispersed in the α matrix, which can significantly increase the strength and hardness of the matrix. The peak of hardness does not appear at the extreme edge, which is due to a certain degree of oxidation of the surface of the layer, resulting in a decrease in microhardness.

Figure 3. Micro-hardness of the siliconized layer
2.3. Corrosion resistance to salt solution

The mass loss curve of the sample in the 3.5% NaCl etching solution is shown in Fig. 4, and the average salt corrosion rate and the corrosion resistance increase factor are shown in Table 4.

![Corrosion resistance curve of siliconized copper in NaCl solution](image)

**Table 4.** Average corrosion rate of siliconized copper in NaCl solution

| Sample            | Average corrosion rate /g.m\(^{-2}\).h\(^{-1}\) | Corrosion resistance increased by several times |
|-------------------|-----------------------------------------------|-----------------------------------------------|
| Pure cooper       | 0.226                                         | 1.00                                          |
| Siliconized layer | 0.060                                         | 3.77                                          |

It can be seen from the above data that the corrosion resistance of pure copper in 3.5% NaCl etching solution is poor, the average corrosion rate is 0.226g.m\(^{-2}\).h\(^{-1}\), and the average corrosion rate of siliconized layer is 0.060, which is higher than pure copper. 3.77 times; indicating that the siliconized layer effectively improves the corrosivity of pure copper.

As the time of corrosion increases, the weight loss of the sample increases, and the corrosion rate of pure copper is higher than that of the siliconized layer. Halogen salts such as NaCl solution corrode various metal materials very seriously. This is because Cl\(^{-}\) ions and salts can destroy the passivation film of the metal. After the surface metal passivation film is destroyed, the metal matrix is exposed to the corrosive medium. Medium, and then the metal will be severely corroded. After osmosis, the surface of pure copper forms a stable and salt-resistant corrosion. The compound phase is dispersed on the surface of the substrate. In addition, the surface of the siliconized layer is easy to form a silicon dioxide film, which can hinder the occurrence of uniform corrosion and local corrosion, thereby improving the salt corrosion resistance of the sample.

2.4. Corrosion tolerance to acid

In this paper, the sulphuric acid corrosion test uses sulfuric acid. In order to prevent the infiltration layer or metal from intensifying the passivation reaction, the experimental results are affected. The experiment dilutes concentrated sulfuric acid into 15% dilute sulfuric acid solution as the etching solution. Fig. 5 shows the acid corrosion mass loss curve, and Table 5 lists the sample average corrosion rate and acid corrosion resistance improvement factor.
It can be seen from Fig. 5 that as the corrosion time increases, the mass loss per unit area of the sample increases, but the increase rate of the pure copper sample is larger. During the test, the surface of the pure copper sample after 24h corrosion had a layer of black attachments, and the color of the deposit gradually deepened with the extension of time. The sample after silicon infiltration did not have this phenomenon. It can be seen from the data in Table 5 that the average corrosion rate of pure copper is 0.138 g.m\(^{-2}\).h\(^{-1}\), and the average corrosion rate of the siliconized layer is 0.061 g.m\(^{-2}\).h\(^{-1}\), which is 2.26 times higher than that of pure copper. It shows that siliconizing can improve the acid corrosion resistance of pure copper.

![Figure 5. Weight lose curve of the sample in H\(_2\)SO\(_4\) solution](image)

**Table 5. Average corrosion rate in H\(_2\)SO\(_4\) solution**

| Sample               | Average corrosion rate /g.m\(^{-2}\).h\(^{-1}\) | Corrosion resistance increased times |
|----------------------|-----------------------------------------------|-------------------------------------|
| Pure cooper          | 0.138                                         | 1.00                                |
| siliconized layer    | 0.061                                         | 2.26                                |

2.5. *Corrosion resistance to artificial seawater*

The mass loss curve of the sample in artificial seawater is shown in Fig. 6. The average seawater corrosion rate and corrosion resistance increase factor are shown in Table 6.

![Figure 6. Weight lose curve of the sample in artificial seawater](image)

It is shown in Fig. 6 that the mass loss per unit area of pure copper is significantly higher than that after siliconizing in the same etching time. Table 6 shows that the average corrosion rate of pure copper is 0.368 g.m\(^{-2}\).h\(^{-1}\); The average corrosion rate is 0.084 g.m\(^{-2}\).h\(^{-1}\), which is 4.38 times higher than that of pure copper. Therefore, silicon infiltration can improve the seawater corrosion resistance of pure copper.

The corrosion mechanism of copper in seawater is similar to that in sodium chloride solution, and has a great relationship with Cl\(^-\) [6]. The good seawater corrosion resistance of the siliconized sample is mainly due to the formation of a uniform and dense protective film on the surface of the sample. The protective film is composed of Cu oxide and Si oxide and copper silicon compound. Synergism occurs
to avoid local corrosion, and the penetration of Cl⁻ and the like into the copper matrix in seawater is effectively reduced, so that the corrosion resistance is improved.

![Graph showing weight loss curve of specimens in seawater](image)

**Figure 6.** Weight lose curve of specimens in seawater

| Sample               | Average corrosion rate /g.m⁻².h⁻¹ | Corrosion resistance increased times |
|----------------------|----------------------------------|-------------------------------------|
| Pure cooper          | 0.368                            | 1.00                                |
| siliconized layer    | 0.084                            | 4.38                                |

**Table 6.** Average corrosion rate in seawater

2.6. *High temperature oxidation resistance*

Copper alloy has good thermal conductivity and is widely used in the smelting industry, such as blast furnace tuyere, slag mouth, lance tube head, electrode holder, continuous casting mold, etc. These parts are key components of metallurgical equipment, and poor work. The environment not only requires good thermal conductivity, but also needs to have a certain resistance to high temperature oxidation.

This experiment tested the high temperature oxidation resistance of each sample at 700° C. The oxidation weight gain curve is shown in Figure 7. The average oxidation weight gain rate and the increase factor, from are shown in Table 7.
Figure 7. Oxidation weight increase curve of the sample

Table 7. Average rate of increased oxidation weight

| Sample              | Average rate of increased oxidation weight /g.m².h⁻¹ | Improved |
|---------------------|-----------------------------------------------------|----------|
| Pure cooper         | 42.293                                              | 1.00     |
| siliconized layer   | 2.322                                               | 18.00    |

It can be seen from Fig. 7 that the high temperature oxidation resistance of pure copper is poor, and the weight gain is very obvious with the extension of the oxidation time, and the weight gain rate of the siliconized sample is relatively flat. The oxidized weight gain of the pure copper sample after oxidation for 12 h was 529.20 g/m², while the oxidized weight gain of the siliconized sample was only 34.81 g/m². It can be seen from Table 7 that the average oxidation weight gain rate of pure copper at 700°C is 42.293/gm².h⁻¹, and the average oxidation weight gain rate after siliconizing is only 2.322/gm².h⁻¹. Pure copper has increased by 18.00 times. It shows that siliconizing can effectively improve the high temperature oxidation resistance of pure copper.

During the experiment, pure copper is easily oxidized at room temperature, mainly due to the large affinity of Cu and O, and it is easy to form the corresponding oxide. The oxidation rate increases at high temperature, the oxidation weight gain of pure copper is very obvious, and a very thick scale is formed. A large amount of black scale peeling occurs when weighing each time, and a thin layer of scale is formed after the siliconized sample is oxidized for 6 hours. There is a little peeling off. This is because, after infiltration of alloying elements, according to the selective oxidation theory at high temperature[7], the lower the free energy of oxide formation, the easier it is to oxidize. The standard free energy of oxides formed by Si and Al at 700°C is lower than that of Cu. On the surface of the infiltration layer, stable and dense oxide films such as SiO₂ and Al₂O₃ are preferentially formed, which effectively reduces the diffusion rate of oxygen atoms in the infiltration layer, hinders direct contact with the copper of the substrate, thereby slowing the weight gain and improving the matrix. High temperature oxidation resistance.
3. Conclusion
(1) Silica powder was used as the silicon source, aluminum powder was used as the reducing agent, and a small amount of activator was added. After incubated at 850℃for 12 h, a 650μm thick siliconized layer was obtained on the surface of pure copper.
(2) The α phase is formed in the siliconized layer, and new phases such as Cu_{0.83}Si_{0.17}, Cu_9Si, Cu_{6.69}Si are formed and dispersed in the α phase solid solution.
(3) The microhardness of the siliconized layer is up to HV349, while the microhardness of the copper matrix is about HV60 and the microhardness is increased by 5.8 times.
(4) The corrosion resistance of the siliconized samples is higher than that of the substrate. Its acid resistance is 2.26 times higher than that of the substrate, the salt corrosion resistance is improved by 3.77 times, and the artificial seawater corrosion resistance is improved by 4.38 times.
(5) The oxidation resistance of the siliconized sample was significantly improved, and the multiple was increased by 18.00 times.

4. References
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