Atmosphere corrosion behavior of plasma sprayed and laser remelted coatings on copper

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Nickel and chromium coatings were produced using plasma spraying and laser remelting on the copper sheet. The corrosion test was carried out in an acidic atmosphere, and the corrosive behaviors of both coatings and original copper samples were investigated by using an impedance comparison method. Experimental results show that nickel and chromium coatings display better corrosion resistance properties relative to the original pure copper sample. The corrosion rate of chromium coating is less than that of nickel coating, and corrosion resistances of laser remelted nickel and chromium samples are better than those of plasma sprayed samples. The corrosion deposit film of copper is loose compared with nickel and chromium.

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A high proportion of the failures in electrical contact materials are due to the overheating of joints, surface contamination caused by atmospheric corrosion is a main reason[1,2]. Atmospheric corrosion leads to oxidation of copper sheet and increase of electrical contact resistance[3−6], particularly in the humid or acidic environment.

In order to improve the corrosion resistance of copper, the coatings was important[7,8]. Plasma spraying and laser treatments have been applied successfully to improve the surface hardnesses and corrosion resistances of ferrous and nonferrous alloys[9−12]. Through plasma spraying and laser cladding with nickel or chromium, one can produce a protective coating on copper and therefore increase the reliability of bolt-together busbar joints that cannot be particularly cleaned.

Usually, atmospheric corrosion test is based on surface observation method, which is subjective in nature. In this letter an objective approach is proposed on the basis of the principle that if the sample surfaces are corroded, their contact resistance will increase. Hence, if joining two corroded samples together, the variation of contact resistance will denote their corrosion degree. We experimentally investigate the corrosion resistance of electrical contact copper through evaluating of the contact resistance of plasma sprayed and laser remelted Ni and Cr joints in the acidic atmospheric environment.

The substrate material was pure copper plate (TU2). The samples were the rectangular plates of $150 \times 25 \times 3$ (mm). After blasting sand, the samples were sprayed using a METCO 3MB plasma spray installation. During plasma spraying, the voltage was 65 V and the current was 500 A. The carrier gas was Ar whose pressure was 0.65 MPa. The feed velocity of the sprayed nickel and chromium powders was 121 g/min, the sprayed distance and area were 120 mm and 25×25 (mm), respectively. The thickness of the chromium and nickel coatings is 250 μm. Laser remelting was conducted using a 5-kW continuous wave CO_2 laser. During the process of laser scanning, the laser power was 3.5 kW and the laser beam diameter was 1.5 mm. The samples were scanned at a speed of 10 mm/s with overlap interval of 0.5 mm. He gas was used to prevent oxidation of the sample, whose pressure was 0.02 MPa. The designation of samples resulting from different treatment conditions were listed in Table 1.

Atmospheric corrosion test was carried out in a closed chamber. Corrosion medium was 5% HNO_3 aqueous solution, which lied on the bottom of the chamber and was refreshed every two days. The chamber temperature was maintained at 35 °C using a 100-W lamp, and relative humidity was 96%. The samples were suspended above the HNO_3 solution. The corrosion area of samples is 25×25 (mm). Besides the corrosion area, the other region of samples was protected by plastic. Figure 1 shows the experimental setup of the corrosion test.

Table 1. Samples under Different Treatment Conditions

Sample	Treatment Condition
P-Ni	Plasma Sprayed Nickel Coating
L-Ni	Laser Remelted Nickel Coating
P-Cr	Plasma Sprayed Chromium Coating
L-Cr	Laser Remelted Chromium Coating
Origin	Original Copper

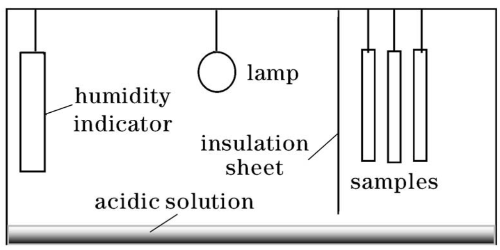

Fig. 1. Experimental setup of corrosion test.

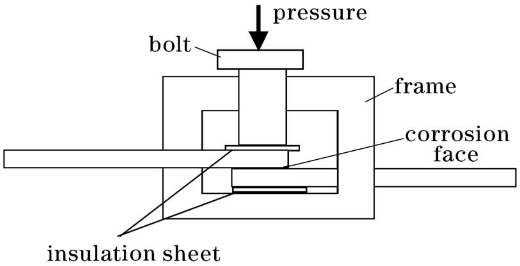

Fig. 2. Schematic of measuring contact resistance.

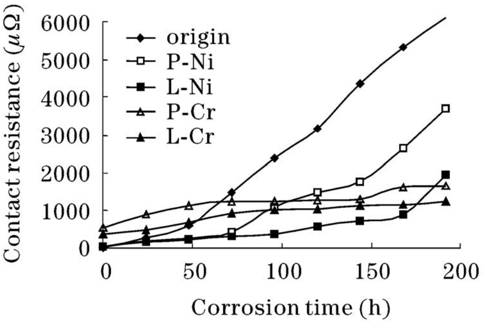

Fig. 3. Contact resistance versus corrosion time under a pressure of 4 kN.

After corrosion, the corrosion faces of samples were joined to each other using a rigid frame with different pressures. The contact resistance was measured using a typical four-probe method. The measuring current was 50 A. The schematic of the measuring contact resistance is shown in Fig. 2.

Figure 3 shows the variation of contact resistances of different samples with corrosion time under a constant pressure of 4 kN. From the figure, it can be seen that with the increase of corrosion time, the contact resistance increases gradually due to the deposition of corrosion product. Assume that there are three stages in the corrosion product deposited process, namely, primary deposit stage, steady deposit stage, and accelerated deposit stage. The contact resistance rises initially in the primary stage, remains almost steadily in the steady deposit stage, and increases rapidly in the accelerated deposit stage. Obviously, the later the accelerated deposit stage appears, the better the corrosion resistance of the sample will be.

It is seen that original sample, copper, shows no steady deposit stage and it reaches the accelerated deposit stage in the shortest corrosion time. The increase in contact resistance of plasma sprayed nickel is less than that in copper, and the steady deposit stage appears. Laser remelted nickel sample displays very small contact resistance and longer steady deposit stage. Although chromium coatings showed higher contact resistance before the corrosion test, both plasma sprayed coating and laser remelted coating showed very low resistance after corrosion. Indeed, the accelerated deposit stage did not appear even corroded near 200 hours. The corrosion resistances of the laser remelted nickel and chromium samples are better than those of the plasma sprayed samples, respectively.

Figure 4 shows the variation of contact resistance of samples with corrosion time under a pressure of 16 kN. It is seen that the accelerated deposit stages of both plasma sprayed and laser remelted nickel coatings appear later than that of the copper sample. Laser remelted nickel coating displays a longer steady deposit stage. However, for the plasma sprayed and laser remelted chromium coatings, the contact resistance remains almost constant at a very low value.

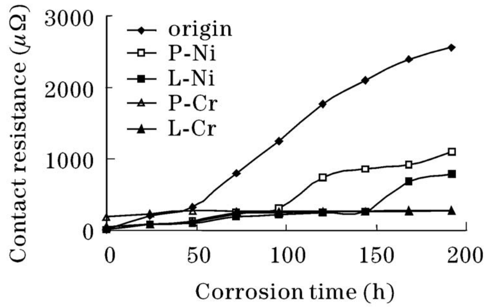

Fig. 4. Variation of contact resistance of samples with corrosion time under a pressure of 16 kN.

From Fig. 3, regression models of the contact resistance in terms of the corrosion time can be developed as

$$R_{\mathrm{Cu}} = -0.0009t^3 + 0.3325t^2 - 0.3808t + 33.05, \quad R^2 = 0.9989, \tag{1}$$

$$R_{\mathrm{P-Ni}} = 0.0003t^3 + 0.0183t^2 + 4.6208t + 15.301, \quad R^2 = 0.9895, \tag{2}$$

$$R_{\mathrm{L-Ni}} = 0.0008t^3 - 0.165t^2 + 12.197t - 18.62, \quad R^2 = 0.9679, \tag{3}$$

$$R_{\mathrm{P-Cr}} = 0.0005t^3 - 0.1508t^2 + 17.57t + 540.2, \quad R^2 = 0.9724, \tag{4}$$

$$R_{\mathrm{L-Cr}} = 9 \times 10^{-5}t^3 - 0.0473t^2 + 10.453t + 315.98, \quad R^2 = 0.9826, \tag{5}$$

where R denotes regression equation, t is corrosion time, and R^2 is square of correlation coefficient.

From Eqs. (1)—(5), the time derivative of contact resistance can be found, which denotes the corrosion rates of

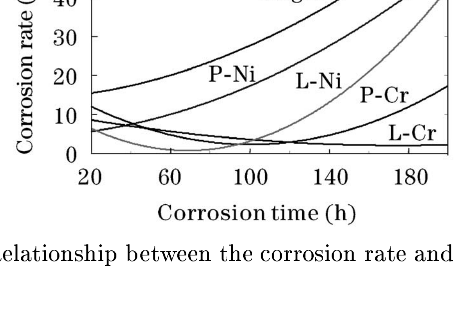

Fig. 5. Relationship between the corrosion rate and corrosion time.

different coatings, as shown in Fig. 5. From it, we can see that the corrosion rate of the original sample is the largest, and increases continuously. Corrosion rate of the plasma sprayed nickel coating shows similar corrosion rate to that of original sample, but at a low magnitude. Corrosion rates of laser remelted nickel coating and plasma sprayed chromium coating decrease first, and then increase. However, the corrosion rate of laser remelted chromium decreases continuously at a low rate. It can be seen that the corrosion rates of samples in a descending order are original sample, plasma sprayed nickel coating, laser remelted nickel coating, plasma sprayed chromium coating, and laser remelted chromium coating.

From the above, it can be seen that after corrosion, the contact resistances of all samples will rise. As the corrosion deposits cause the resistance increase, the change of resistance reflects indirectly the compactness of corrosion deposit film. Before the corrosion, the contact resistances of samples were measured under the different applied pressures. The contact resistance decreases with increasing pressure, however, the magnitude of decrease is different for different coatings. In order to compare behavior of oxide deposits, the original resistance of sample coatings without corrosion under different applied pressures should be removed from corrosion resistance. Figure 6 shows that after corrosion of 96 hours, the relationship between contact resistance increment of different coatings and pressure. We can see that the contact resistance increment deceases with the increase of the pressure. It is because that the corrosion deposit layer is compact at high pressure and electrical contact resistance is reduced. Generally, the larger the contact resistance, the looser the corrosion deposit layer. Therefore, to compare indirectly the compact level of the oxide deposit layer, looseness Ln is established as

$$Ln = \mathrm{d}\Delta R/\mathrm{d}T, \tag{6}$$

where ΔR is the contact resistance increment and T is the pressure.

From Fig. 6, the approximate linear regression equations of the contact resistance increment in terms of applied pressure can be developed. Based on these equations, the loosenesses of different coatings in different corrosion time can be found. Figure 7 shows the relationship between the loosenesses of Ni coatings and corrosion time. From it, we can see that the looseness of original sample decreases quickly with increasing the corrosion time. When the corrosion deposit film is loose, the exposed substrate is easily corroded under atmospheric corrosion. For the nickel coatings, the loose level in a descending order is copper, plasma sprayed, and laser remelted samples. The laser remelted coating shows the smallest loose level.

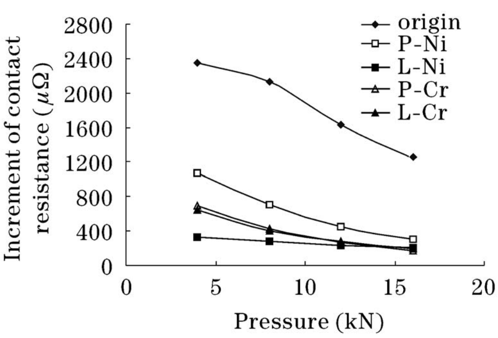

Fig. 6. Relationship between contact resistance increment with pressure (a corrosion of 96 hours).

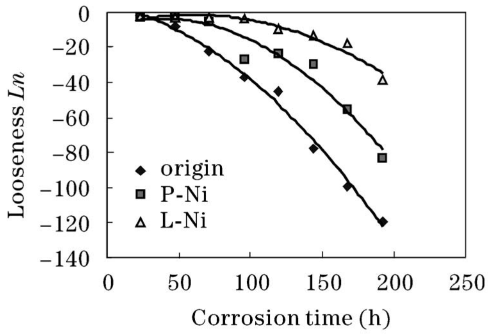

Fig. 7. Relationship between looseness Ln and corrosion time for nickel coatings.

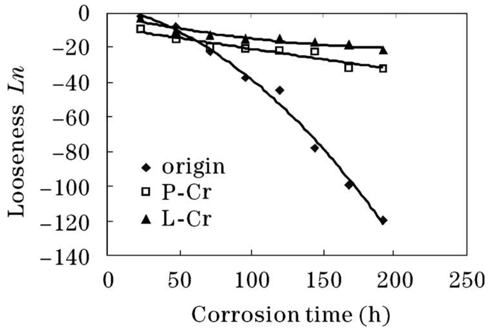

Fig. 8. Relationship between looseness Ln and corrosion time for chromium coatings.

Figure 8 shows the relationship between looseness of chromium coatings and corrosion time. Unlike copper and nickel coating samples, the looseness of chromium coatings increases at a much slower rate and linear manner. This indicates that the corroded films of chromium are more compact, which can lower the corrosion of the substrate. It is also seen that the laser remelted chromium coating shows a smaller loose level in comparison with the plasma sprayed coatings. These results are consistent with those of Figs. 3 and 4.

In conclusion, in this study, corrosion resistances and corrosion rates of plasma sprayed and laser remelted nickel and chromium coatings were compared with those of the pure copper sample using an impedance comparing method. At the same time, the characteristics of oxide corroded films have been analyzed. We find: 1) both nickel and chromium coatings show better corrosion resistance in comparison with copper. The corrosion resistance of chromium coatings is less than that of nickel coatings, and that of laser remelted coatings is less than that of plasma sprayed coatings; 2) the corrosion rates of both nickel and chromium coatings are smaller than that of copper. The corrosion rates of samples in a descending order are copper, plasma sprayed nickel coating, laser remelted nickel coating, plasma sprayed chromium coating, and laser remelted chromium coating; 3) the oxide corrosion deposit of copper is looser than that of nickel and chromium coatings, and the chromium coatings show more compact corrosion deposit film.

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