Microstructure of silver coating of cyanide-free brush plating based on multicomponent coordination system

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Abstract: By using metallographic microscope, scanning electron microscope, X ray diffraction and other test methods, this paper studies the microstructure of brush silver coating prepared by multicomponent coordination systems, such as succinimide, 5,5-dimethyl hydantoin and mono potassium phosphate. The results show that the appearance of silver coating of cyanide free brush is silver white with uniform and even surface and the combination situation between silver coating and copper is great. The coating is the single silver particle structure whose arrangement is tight and size is small and even. It meets the requirements of microstructure of button contact used by high voltage switch and lays the theoretical basis for the development of electric brush plating repair technology of silver coating of button contact used by high voltage switch.

1. Introduction

High-voltage isolators are an important and commonly used electrical device in the domain of electric power systems. Through the opening and closing of dynamic and static contacts, the isolation power supply and switching operation are realized, which is used to connect and cut off the small current circuit. The main performance and life expectancy of switching system are determined by the quality of contact to a large extent. Most of high-voltage switching contacts adopt the copper as basis and its surface is electroplated with silver layer to prevent oxidation corrosion, reduce contact resistance and improve conductivity. Therefore, the quality of silver layer directly influences the reliability and service life of high-voltage isolating switch. However, in the long-term use process, switch heating and power cuts accidents happen usually due to contacts failures and the quality reduction of contact silver layer becomes the commonest issue \cite{1-4}. Presently, for unqualified switch contacts, the spot maintainers apply Vaseline or conductive paste at the surface of the damaged coating to prevent oxidation \cite{5}. After a period of operation, Vaseline or conductive paste hardens or powders, which leads to discharge phenomenon and eventually causes equipment damage. Besides the substitute methods, cyanide plating brush silver plating method is used to repair the site \cite{6}. There are some
reports on non-cyanide plating [7], but it has not been widely popularized and applied. To improve remediation efficiency and realize the reliable, environmentally friendly and efficient repair of silver plating layer, plating operators have made lots of researches on non-cyanide silver plating for many years. At present, the commonly used non-cyanide silver plating technology includes thiosulfate silver plating, imino group disulfonic acid (NS), niacin silver plating, iminazole-aminosalicylic acid silver plating, succinimide silver plating and 5-5 dimethyl glycolylurea silver plating et al. [8-11]. Due to the difficulty of cyanide-free silver plating technology, there are more or less problems in each system that affect the engineering application of cyanide-free silver plating process. This paper comprehensively considers the advantages and disadvantages of each silver plating system and makes the research by using succinimide silver plating system. The coordination ability of the butylenimine is strong, its polarization is large when the silver is deposited, and the silver can be directly electroplated without the need of silver immersion. The existing problem is that butadiimide is easy to hydrolyze, and the plating layer is easy to become yellow and discolored. Combined with application condition of electric contact of high-voltage switch, this paper solves the problem that succinimide solution becomes yellow after hydrolysis and shelving and studies microstructure of silver plating layer, which provides technical data for on-site repair of silver coating of button contact used by high-voltage switch.

2. Experimental material and test method

The succinimide brush silver plating solution selects AgNO₃ as main salt and uses succinimide, 5,5-dimethyl hydantoin (DMH), mono potassium phosphate and ammonia water as multiple coordination system. Moreover, it adds Potassium Methanesulfonate to inhibit the hydrolysis of succinimide, utilizes ammonium acetate as buffering agent to improve cathode polarization, employs potassium carbonate as conducting salt to improve the conductive capability of plating solution and uses Bismuth nitrate to improve the hardness of coating. The bipyridine is used as brightener to make the crystallization of silver coating gloss, thiosemicarbazone is used as surfactants to make the coating crystal fine and promote the normal dissolution of anode and potassium hydroxide is used to adjust the pH value of the plating solution. Silver plating solution is prepared with high purity water at room temperature and the used reagent is analytical purity.

The matrix uses sheet copper as negative pole, whose size is 30mm × 70mm × 5mm. The brush plating applies RePlate-3 current-conducting plate intelligent repair. After brush plating, cleaning and washing, the eye survey is used to measure the appearance quality of silver plating layer. The metallographic specimen is prepared by mechanical machining method and etching is carried out by chrome oxide-sulfuric acid aqueous solution (2gCrO₃+2mlH₂SO₄+800mlH₂O) after grinding and polishing [12]. The metallographic structure of the coating is observed under Olympus GX41 metallographic microscope. Microstructure of the coating is analyzed by ZEISS-SUPRA55 field emission scanning electron microscope, and the chemical composition of the coating is analyzed by its own energy dispersive spectrometer. The phase analysis of coating is carried out by using DX-2700 X-ray diffractometer. The concrete parameters are as follows: the target material is CuKα, measure angle is 20°-100°, stepping angle is 0. 02°, the sampling time is 1s, the voltage of X-ray tube is 40kV and the current is 30mV.

3. Experimental results and analysis

3.1 Quality of silver coating

By using silver coating prepared by succinimide multi-component coordination brush silver plating solution in the research group, the author finds that there are no defects at the surface of solution, such as crack, foaming and shedding. The appearance of coating is silver white and its surface is uniform and even, which meets the requirement of quality. The silver coating and matrix section are shown in Figure 1. The silver coating and matrix are linked tightly and there are no defects in the linking area, such as cavity and crack. The combination situation of silver coating and matrix is good.
3.2 Microstructure of silver coating

After the etching of silver coating by aqua regia solution, microstructure of silver coating is observed with phase-microscope and scanning electron microscope, as shown in Figure 2. Due to the irregular arrangement of atoms at the grain boundary and high free energy, it is corroded preferentially. The grain boundary after corrosion is black under the phase-microscope (as shown in Figure 2a and 2b). The silver coating is uniform in grain structure, its grain size is relatively small and the arrangement between grain and grain is close (as shown in Figure 2c and 2d).

The chemical components of silver coating are analyzed by using energy spectrometer of scanning electron microscope and the results are shown in Figure 3. The main alloy element of particle is Ag element, which suggests that the coating structure is uniform silver tissue.
3.3 Phase composition of silver coating

The phase analysis of silver coating is completed by using X-ray diffractometer and its results are shown in Figure 4. The characteristic of diffraction peak in the silver coating is the same as that in the PDF. The crystal structure is face-centred cubic structure and crystal is preferred along the (111) crystal plane, which is related to the selective adsorption of additives in silver plating solution. From Figure 4, it is seen that silver coating is the single Ag structure and no second phases appear, which shows that the cladding material is fine silver organization.

Figure 4 XRD spectrum of silver coating of succinimide system
4. Analysis and discussions

The standard electrode potential of Ag is 0.799V and it belongs to more electropositive metal. The overpotential of electrochemical reaction of hydration complex-ion is small. To obtain the cladding material with micromesh and compact crystal, the potential of hydration complex-ion needs improving obviously. In the silver plating process, the complex electroplating with strong complexation ability and adsorption on the electrode must be used. According to shab theory of complex [8], Ag⁺ belongs to soft acid, which is easy to form stable complexes with soft bases. Succinimide, 5,5-dimethyl hydantoin and mono potassium phosphate belong to soft bases, which is easy to be adsorbed by the electrode. In addition to forming corresponding complexes with Ag, they are easy to coexist in the inner boundary of the mixed ligands to form a more stable mixed complex due to the symbiosis and produce synergistic and polarized action effect.

The electrolytic deposition of silver includes two processes, nucleation and growth. To obtain fine-grain coating, the forming speed must be larger than the growth speed of grain [8, 13, 14]. When the multi-component complexant is added in the plating solution, the overpotential of negative pole of silvering solution increases obviously, the discharge speed of silver ion slows down, the number of formed grains is more, the grain growth rate is slow, and the grain size of the coating is fine and compact. The usage of bipyridine, sulpho-semicarbazide and other additives could promote the normal dissolution of positive pole and make the silver coating tightly combined with the substrate. The silver-plated crystals are fine, oriented and shiny. The purity of silver coating prepared by multi-component coordination system is high and the coating structure is the single Ag organization. The size of silver particles is fine and the arrangement between particle and particle is close, which meets the requirements for the microstructure of high-voltage isolating switch touch finger silver coating and provides theoretical support for the field environmental protection and reliability repair of touch silver coating.

5. Conclusions

(1) The appearance of silver coating of cyanide free brush prepared by succinimide, 5,5-dimethyl hydantoin and mono potassium phosphate and other multicomponent coordination systems is silver white with uniform and even surface. In addition, the combination situation between silver coating and copper is great, which has no any defects.

(2) The purity of silver coating is high and the coating is the single silver particle structure whose arrangement is tight and size is small and even. It meets the requirements of microstructure of button contact used by high voltage switch and lays the theoretical basis for the development of electric brush plating repair technology of silver coating of button contact used by high voltage switch.

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