Synthesis of silver coatings by brush plating with cyanide-free solution

Baoshuai Du*, Zhongwen Zhang, Shuai Suo, Xinmei Li

State Grid Shandong Electric Power Research Institute, Jinan 250003, China

Abstract. Silver coating can be used to improve the surface properties of components made of copper in terms of corrosion resistance, wear resistance and electrical contact conductivity. A cyanide-free solution based on $Na_2S_2O_3$ is proposed for the brush plating of silver coating on copper substrate. XRD, SEM and microhardness tester were used to characterize the microstructure and properties of the coatings. It is found that this cyanide-free solution can deposit silver coating with high efficiency. Coatings consist of nano-sized grains which present as aggregated nodular morphology. The brush plated coatings show microhardness of 122.47 Hv, which is promising in the engineering application of electrical contact components.

Keywords: Cyanide-free solution, silver coating, brush plating, microstructure

1. Introduction

For electrical contact components made of copper, in order to increase their corrosion resistance and improve their electrical conductivity, a protective coating is normally applied to the surface of the components. It has been proved that silver coating is effective in terms of enhancing the surface properties beyond the capability of the substrate[1,2]. Electrodeposition is often used to perform the fabrication of the silver metallic coating. Moreover, driven by the safety and environment concern, there have been a lot of investigations devoted to the development of cyanide-free electroplating bath[3].

Brush plating, or selective plating, uses an anodic brush to deliver the electroplating solution to the cathodic workpiece. Direct contact between the anode and cathode is prevented by the electrically insulating cathode which covers the insoluble brush. The brushing action disturbs the hydrodynamic boundary layer which results in fast solution movement. Thus, although the brush plating is characterized by the same principle with electroplating, it possesses its own features, such as portability and high efficiency[4,5]. It has been proved that brush plating is promising in the on-site repair of copper electrical contact components with silver coating.

In this study, a cyanide-free solution is developed for the brush plating of silver coating. Phase constituents and microstructure of the coating was characterized. It is expected that the developed bush plating technique can be used for the repair and remanufacturing of copper components used in electric power industry.

2. Experimental material and methods

Copper plates with dimensions of 60 mm×30 mm×2 mm were used for the bush plating process. Cathodic clean with alkaline solution was conducted before the bush plating. This is followed by anodic etch in a weak acidic electrolyte solution in order to improve the coating adhesion. The brush plating solution is composed of $Na_2S_2O_3$(200-220 g/L), K2S2O5(40-60 g/L), AgNO3(30-50 g/L) and additives (1g/L). Solution temperature was kept in the range of 30-40ºC. Electrical brush plating was performed manually at a working voltage of 1.7-2.5 V.

Surface morphology was examined with JSM-7800F scanning electron microscopy (SEM) and micro-zone chemical was conducted using the attached X-ray energy disperse spectroscopy (EDS). Phase constituents were identified using DX 2700 diffractometer with Cu k_α source operated at 40 mA and 35 kV. The step size and scan speed were set at 0.02º and 1º/min respectively and the range of scan angle is from 20º to 100º. Microhardness of the brush plated coating is evaluated using a microhardness tester (Tukon 1102) with loading of 50 g and duration time of 12 s.

* Corresponding author: dubaoshuai@163.com

 https://doi.org/10.1051/matecconf/202235801005

3. Results and discussion

3.1 Appearance and coating thickness

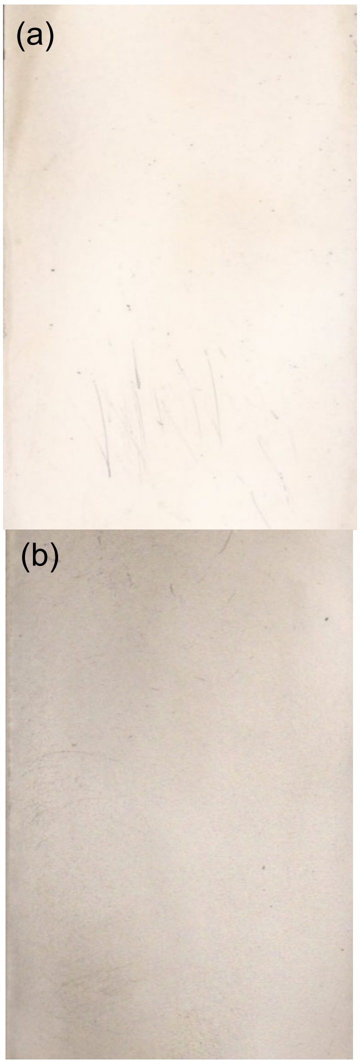

Fig. 1 Typical coating appearance: (a) 1.7 V; (b) 2.5V

The brush plated coatings show smooth and uniform visual appearance with white color, which is different from other cyanide-free electrodeposited silver coatings characterized by a shining mirror bright deposit[3]. Nevertheless, the coating is coherent and defect-free, indicating its potential to be used as protective coating on the copper substrate. Besides, it can be found that coating deposited with higher voltage exhibit a greyer color, which may be induced by the high energy input during the depositing process.

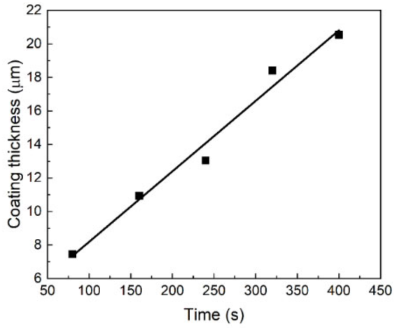

Fig. 2 Coating thickness versus brushing time

The variation of coating thickness with brush plating time is shown Fig. 2. It is apparent that the increase of brush plating time causes a linear increase of coating thickness. The linear fitting function between the brushing time and coating thickness is given by:

$$CT = 3.9836 + 0.04206 \times t \quad (1)$$

where CT is the coating thickness, and t is the brushing time. It ca be found that final coating thickness is more than 20 μm with brushing time within 400 s. Compared with traditional electroplating process, brush plating shows a higher efficiency.

3.2 Phase identification and grain size

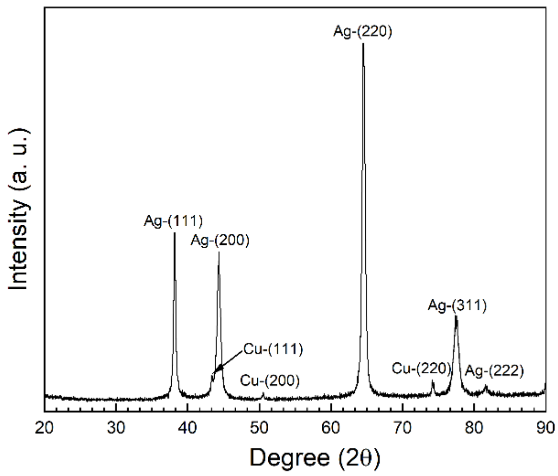

Fig. 3 XRD pattern of the brush plated silver coating

Phase identification is performed using the XRD and diffraction peaks are presented in Fig. 3. XRD pattern of the brush plated coating shows the diffraction peaks of silver and copper. It is evident that the synthesized coating is composed of pure silver with no other phases. Diffraction peaks of copper is originated from the substrate.

Grain size of the brush plated coating was quantified by applying the Scherrer equation of the (111) peaks. The Scherrer equation is known as:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where K is dimensionless shape factor, λ is the wave length of the X ray, β is the line broadening at half the maximum intensity, and θ is the Bragg angle. According to equation (2), the calculated crystallite grain size is 26 nm, which is in the nano-size range. Thus, it shows that with proper solution bush plating can be used to fabricate silver coating with very fine crystal structure.

3.3 Microstructure and microhardness

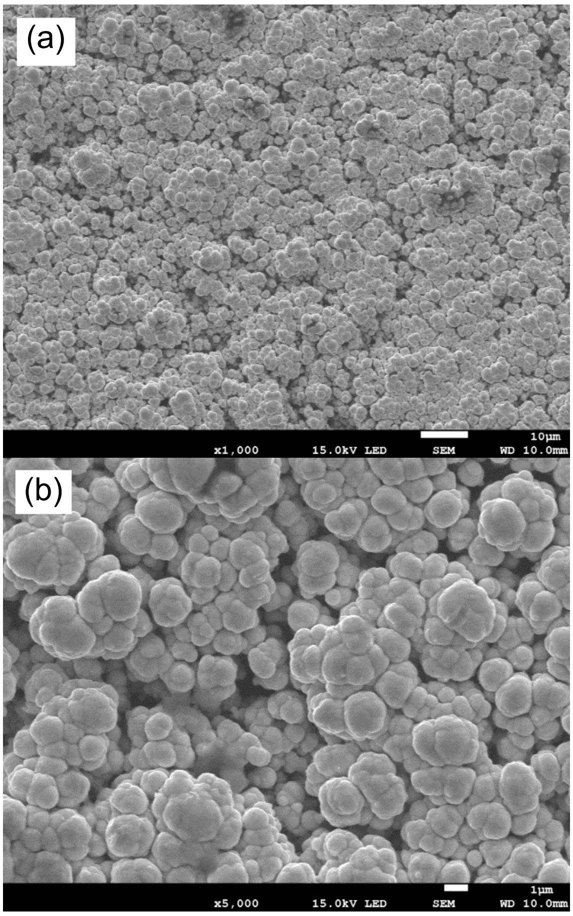

Fig. 4 SEM images of the brush plated coating: (a) ×1000; (b) ×5000

SEM images of the brush plated coating with voltage of 1.7 V is shown in Fig. 4. It can be found the coating surface is homogeneous and covered with aggregated grains. The well-formed silver crystallites are apparent on the surface. The crystallites present as nodular morphology. This kind of appearance is typical for the electrodeposited coatings. For brush plating, the repetitive movement of the brush can effectively interrupt the grain growth of the deposit and motivate the crystal nucleation, thus resulting in finer grain size.

Microhardness measurement shows that the average microhardness is 122.47 Hv and 105.39 for the coating bush plated with 1.7 V and 2.5 V respectively. Compared with other electroplating Ag coatings, this is a relatively higher value[6,7]. This is may be due to the fine crystal size presented in the plated coating. For components used as the electrical contact, adhesive wear resistance is often considered. And it is generally accepted that adhesive wear resistance is governed by the Archard law. According to this law, higher hardness indicates better wear resistance. Thus, conclusion can be made that this brush plated coating shows promising as wear resistant coating for electrical contact components.

4. Conclusion

The brush plated silver metallic coating has been developed for engineering application, which uses a cyanide-free solution. Phase identification shows that the coating consists of pure silver with crystal size of 26nm. The brush plated coating consists of fine aggregations of nodular silver crystallites. The highest microhardness of the brush plated coating is Hv 122.47, which can be used as protective coating electrical contact components.

Acknowledgments

This work was financially supported by Science and Technology Project of State Grid Shandong Electric Power Company (No. 520620210020, Research on Fabrication and Application of Electric Brush Plated High Performance Silver Alloy Coatings).

References

1. Dadvand, Mina, Nazila. Pulse Electrodeposition of Nanostructured Silver-Tungsten-Cobalt Oxide Composite from a Non-Cyanide Plating Bath[J]. Journal of the Electrochemical Society, 2014.
2. Jiao Z B , Schuh C A . Nanocrystalline Ag-W alloys lose stability upon solute desegregation from grain boundaries[J]. Acta Materialia, 2018, 161:194-206.
3. Liu A M , Ren X F , Wang C , et al. DMH and NA–based cyanide-free silver electroplating bath: a promising alternative to cyanide ones in microelectronics[J]. Ionics, 2021, 27(1):417-422.
4. Zhong Z , Clouser S J . Nickel–tungsten alloy brush plating for engineering applications[J]. Surface and Coatings Technology, 2014, 240:380-386.

5. Behera P , Rajagopalan S K , Brahimi S , et al. Effect of brush plating process variables on the microstructures of Cd and ZnNi coatings and hydrogen embrittlement[J]. Surface and Coatings Technology, 2021, 417(3):127181.
6. Bs A, Sj B, Sd A, et al. A comparative study of electrodeposition routes for obtaining silver coatings from a novel and environment-friendly thiosulphate-based cyanide-free electroplating bath[J]. Surface and Coatings Technology, 2021.
7. Wang Y, Tay S L, Zhou X, et al. Influence of Bi addition on the property of Ag-Bi nano-composite coatings[J]. Surface and Coatings Technology, 2017, 349.