Regular article

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Silver nanoparticles in the thermal silver plating of aluminium busbar joints

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Abstract: Thermal silver plating method by means of nanosilver-based paint could be an alternative to electrochemical processes. Electrochemical silver layering on aluminium is typically achieved with an intermediate layer, which provides very good adhesion of the layer to the aluminium surface but increases the resistance of the whole junction system. In the method of silver plating promoted by the authors, the intermediate layer is eliminated. The layer of silver paint was applied directly on the aluminium surface by spraying using aerograph. Procured silver layers, according to ISO 2409, prove proper adhesion to aluminium. The value of contact resistance with a pressure of 300 N cm^{-2} and current load of 200 A is $0.03 \mu\Omega \text{ mm}^{-2}$, which is comparable to the contact resistance of layers generated by electrochemical means. This new method decreases the level of toxic waste emission

and therefore is less harmful for the natural environment. It is also cheaper and simpler than the electrochemical process. An additional advantage is the possibility of silver plating of the chosen surfaces with various shapes.

Keywords: aluminium busbars; conductive layers; nanosilver; silver layers; thermal silver plating.

1 Introduction

The materials chosen for busducts should possess suitable electrical properties. This condition in the highest possible quality is displayed by copper, which has an electrical resistivity of $1.7 \times 10^{-8} \Omega \text{ m}$ [1, 2]. However, because of financial requirements, producers of busducts successfully use aluminium, instead of copper, as base material [3, 4]. The contact surface of clean base material such as aluminium is subjected to years of functioning in often unfavourable weather conditions, which become the cause of corrosion degradation that results in the failure in current transmission [5]. In order to prevent the formation of the alumina layer, the process of electrochemical application of atomic silver can be adopted [6]. It generates conductive layers on aluminium surfaces, additionally securing them from oxide passivation [7, 8]. Electrochemical processes are conducted by submerging the material in electrochemical bath. The bath consists of chosen salts of metals that are to become the layer itself and both organic and inorganic compounds influencing the solution's conductivity. Additives are chlorides, cyanogen, sulfides, and other derivatives of elements toxic to organic matter, human life, and health [9]. During the electrochemical processes, hydrogen compounds are intensively produced, which leads to the punctual deformation of the layer [10, 11].

Thermal silver plating on aluminium surfaces could be an alternative to electrochemical processes. This technology generates significantly less harmful waste and allows to cure silver layers on aluminium without the necessity to apply an intermediate layer between silver and aluminium. The obtained silver layers exhibit the

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desired adhesion to aluminium surfaces, surface roughness, tightness, thickness, and lifespan [12]. All this is due to the nanometric silver particles procured by means of precursor thermal reduction [13]. This method was selected because of its repeatability and applicability in industrial production [14]. The technology is based on metalorganic synthesis and thermal reduction of precursor prepared in dedicated thermic reactors, in atmosphere of inert gas. Nanoparticles obtained by thermal decomposition of precursor have appropriate grain size and can be procured in large quantity. Proper ratio of the metallic phase to the organic phase in nanosilver particles enables silver plating paint production [14–16].

As research shows, the smaller the particles are, the lower the demand for energy to achieve their conjunction within the grain is [17, 18]. Appropriate composition of paint containing organic solvent and micrometric and nanometric phases results in the abovementioned parameters and secures better removal of the heat produced during current transmission through contact surfaces [19].

The authors elaborated a new technology of silver plating using innovative composition of silver plating paint obtained in a Polish laboratory. The parameters of the new layers are comparable to the layers made by an electrochemical process. To confirm the developed method's usability, research on adhesion, structure, thickness, and current characteristics of the obtained silver layers was conducted.

2 Technology of aluminium surface silver plating

The technology of thermal silver plating was based on the authors' surveys and research. It consisted of the

development production technology of silver nanopowder and micropowder, choosing appropriate paint ingredients, and obtainment of proper rheology for the spray application. As a result of these works, silver plating paint and technology of its application were created. The list of paint ingredients includes silver nanopowder with grain size of approximately 10 nm as in Figure 1A, silver micropowder with grains (Helioenergia, Poland) as big as 10 μm as in Figure 1B, non-polar solvent, stabilizing agents preventing particle aggregation (Sigma Aldrich, Germany), and organic nickel salts (Helioenergia, Poland) [20]. The content of pure silver in the paint is ~18 wt.%. Nanometric size of silver grain allows considerable decrease of layer sintering temperature [21]. Nickel was added in order to improve the mechanical durability of silver layer as well as its continuity and cohesion [22, 23].

Silver nanopowder and silver micropowder were both pulverized in mortar RM200 produced by Retsch (Germany). Next, the following ingredients were added while stirring continuously: non-polar solvent, dispersing agent, and organic nickel salts. The ingredients were then ground for 60 min. The paint was supplemented with non-polar solvent in order to reduce viscosity and then stirred at 700 RPM for 24 h on magnetic stirrer (Chem-Land, Poland).

In order to procure an even layer of silver on the aluminium, a mechanical treatment of surface was performed beforehand. The aluminium material of EN 6060, EN 1050A, and EN 5754 types was used in the presented tests. Surfaces for coating were ground with sandpaper with grit size of 320 and later polished. All leftover aluminium dust was removed roughly by spraying with compressed air. The preparation of the surface was finalized by cleaning with paper towels wetted with petroleum ether, which removed the dust and grease left.

The layer of silver paint was applied by spraying using aerograph (Badger Patriot, USA Airbrush Supply, USA)

Figure 1: Structure of silver powder: nanosize and spheric shape (A), microsize and flake shape (B).

with a 0.5 mm nozzle. The whole process of spraying was conducted in a ventilated spray chamber from a 100 mm distance and under 90° angle to the aluminium surface. After that, the surface was installed at 45° angle to the working plane of the table. The applied layer was left to dry in ambient temperature. Next, the sample was put in muffle furnace with chamber heating of 4.5 kW. During the sintering process, the chamber was ventilated with an atmospheric airflow of 10 dm³ min⁻¹. Sintering of the silver layers was performed in two stages. First, the painted aluminium sample was heated to 200°C, which took 60 min, and left in this temperature for 30 min. This is done in order to evaporate the entire solvent. The second stage included heating the joints to 500°C within 60 min and sintering in this temperature for 30 min.

3 Silver layer quality research

To confirm the appropriate quality of the obtained silver layers, test of adhesion, thickness research, microscopic analysis, and current characterisation were carried out. The main purpose of the selected research was to determine the layer applicability in the electro-energetic sector.

3.1 Test of silver layer adhesion to the aluminium surface

The adhesion of the silver layer to the aluminium surface is a necessary condition, and it was measured using ELCOMETER 121-3-(PIG) according to ISO 2409. The test consisted of making a series of cuts on the silver layer at 90° angle with T99913700-1C blade and cleansing the cuts with an adhesive tape. As a result, a lattice of cuts formed a pattern

of squares measuring 1×1 mm with sharp and even edges as in Figure 2A. The appearance of the lattice on which some chips appeared as a result of faulty sintering process was compared with the patterns in the standard [24]. The surface with the chips was presented in Figure 2B.

3.2 Microscopic analysis of silver layers

Because of the nanosilver presence, the layer applied on the surface will sinter in 500°C. During this process, the nanoscale grains will sinter with one another and therefore create strong and permanent connections between the sinter and microne phase. In order to procure a homogenous layer with bigger grains such as a micro silver, a much higher temperature of sintering is needed. That is why nano and micro silvers are mixed in specific proportions. The silver layers were tested under a digital microscope and under the scanning electron microscope LEO 1530. The layer procured as a result of thermal silver plating was compared with the silver layer obtained from the galvanizing plant. In Figure 3A, the layer is homogenous and pore-free, and it covers the aluminium surface evenly, which prevents it from passivation. The layer received as a result of electrochemical process had an incoherent structure, which is displayed on Figure 3B. The layer does not cover the whole surface evenly.

3.3 Silver layer thickness research

The silver layer thickness research was performed to confirm that the layers applied by the spray method have the desired thickness of 10 µm, which is necessary because of the durability and the ability to protect the

Figure 2: Lattice of silver layer cuts on the aluminium surface: class 0 (A) and class 4 (B).

Figure 3: Layer procured as a result of thermal silver plating compared with the silver layer obtained from the galvanizing plant. (A) SEM picture of a sintered silver layer on the aluminium surface. (B) SEM picture of the silver layer procured in the electrochemical process on the aluminium surface.

layer against corrosion [25–27]. To define the precision and accuracy level of the thermal silver plating method, the thickness research was performed also to thinner layers – 3 and 5 μm . The thickness of the procured layers was measured by Fischerscope® XRAY XDLM 237. The number of readings for all layers was 100, and the time of measuring each layer was 10 s. The average thickness of the layer desired as 3 μm was 3.138 μm ; the standard deviation for this layer was 0.155 μm – the minimal reading was 2.73 μm , and the maximal reading was 3.55 μm . For the layer desired as 5 μm , the average thickness was 5.511 μm with a standard deviation 0.262 μm . The minimal reading for this layer was 4.88 μm , and the maximal reading was 6.28 μm . For the 10 μm layer, the average thickness measured by the Fisherscope was 10.59 μm with a standard deviation of 1.169 μm – the minimal reading was 8.93 μm , and the maximal reading was 15.1 μm . As is shown, the average thickness measured by the Fischerscope for the silver layers is similar to the desired thickness, so it could be concluded that the precision of the spray application method is about 0.5 μm .

3.4 Current characteristics of silver layers

Contact resistance was measured by the Kelvin bridge method, which is suitable for testing low-resistance materials. The tests utilized the digital low resistance ohmmeter Megger DLRO200. The silver layers were procured on aluminium surfaces EN 6060, EN 1050A, and EN 5754 according to PN-EN 573-1 classification. A low-resistance measuring station was prepared. A four-point probe was connected to the digital ohmmeter. The tests were conducted for thermally silver-plated aluminium, electrochemically silver-plated aluminium, and uncoated

aluminium samples directly after mechanical cleansing and repeated after 7 days. Silver-plated aluminium samples were covered in petroleum jelly CAS 8009-03-8 in order to protect them from excessive moisture penetration and sulfur oxide settlement. The whole system was then assembled so that the silver layers would overlap in the pattern. Aluminium surfaces were pressured by pneumatic piston of 67.5 mm diameter, which also removed the excess petroleum jelly. Because of this, a potential layer damage during assembly was eliminated. A schematic of the measurement station is shown in Figure 4.

A series of measurements on forced current flow of 200 A were taken. The tests included measurements of contact resistance of silver layers on aluminium, both obtained by utilizing the spray-on paints and by electrochemical process, as well as uncoated aluminium. Pure aluminium surfaces were tested after 15 min from mechanical cleansing and then repeated after 7 days. The coated surfaces were tested with and without petrolatum (Figure 5).

It was observed that all the silver layers obtained by means of the thermal method (TS1 and TS2) were characterized by lower durability than the pure aluminium base surface left aside for 7 days (AL2). After that time, the oxide layer was thick enough to elevate resistance. Contact resistance of the plate-on-plate pattern is characterized by lower resistance along with greater pressuring force. The same characteristics are observed in the measurements taken on the pure aluminium (AL1). However, when the pressure was slowly subtracted, only the aluminium cleansed just before the measurements (AL1) and silver layer (TS1 and TS2) kept the resistivity on the same level. It may be concluded that a silver layer (TS1 and TS2) assumes similar current characteristic as pure aluminium without the oxide layer (AL1), and it does not have any negative influence on the aluminium surface operation

Figure 4: Schematic of the low-resistance measuring station.

Figure 5: Paint SilverCon – current of 200 A (AL1: cleaned AL-AL and AL2-AL-AL after 7 days, TS1: thermal silver-plated Al interface, TS2: thermal silver-plated Al with petrolatum, ES1: electro silver-plated Al interface, ES2: electro silver-plated Al interface with petrolatum).

and can provide protection from surface degradation of the base material. Measurements of contact resistance of the silver layers procured electrochemically were also taken (ES1, ES2). As can be seen in Figure 5, the silver layers procured by means of thermal sintering of spray-on paints show lower contact resistance than that of the layers procured by electrochemical means. The difference is negligible when the petroleum jelly interface is used, but significant without the interface.

4 Conclusion

As described in this report, the thermal silver plating of aluminium, which utilizes spray-on paints, allows the production of durable and functional silver layers. Thanks to the paint composition, containing silver nano- and micropowder suspended in organic solvent, the sintering of the layer can be conducted in a temperature as low as

500°C, which does not degrade the aluminium surface. Correctly deposited layers display adhesion matching that deposited by electrochemical methods. The silver layer procured by this method is coherent. Its thickness can be controlled by selecting the right amount of paint, taking the loss factor according to the base area and the effectiveness of painting into account. The studied method does not use any galvanizing baths. Moreover, thermal silver plating with the SilverCon paint also allows precise and selective generation of silver plates that saves silver. Procured coating is fully functional and gives a positive effect of lowered contact resistance.

Thermal silver plating on aluminium surfaces could be an alternative to electrochemical processes. This technology does not generate much harmful waste and allows to cure silver layers on aluminium on budget without the necessity to apply an intermediate layer between silver and aluminium. It is due to the nanometric silver particles that are procured by means of precursor thermic reduction. The research team set the aim of their

work on thermic silver plating on aluminium and creating solid silver layers as well as technological process for the method. The obtained silver layers may constitute an alternative to layers created electrochemically. They perform better in adhesion to aluminium surfaces, surface roughness, tightness, thickness, and lifespan.

The development of technology cannot ignore the impact it has on the natural environment. Electrochemical methods of silver plating require vast amount of water and energy, as well as chemicals, such as chlorides, sulfides, or cyanides. If spilled to the environment, these chemicals are a threat to nature, and within electrochemical plants, they create a hazardous work environment. Compared with them, spray-on paints for thermal silver plating are relatively harmless. Organic compounds are easily burned, resulting in water and carbon dioxide, and thanks to the possibility of selective plating, the waste of silver compound is minimized.

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