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Investigation on Effects of Plasma Treatment as a Surface Preparation Step on Copper Plating Line

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Abstract

The continuous electrolytic copper plating process traditionally includes degreasing and acid baths before copper plating baths. These baths add difficult-to-control parameters to the process. Besides they contain various alkaline chemicals and acids that are harmful to the environment. The plasma surface treatment is a controllable alternative surface cleaning method which is used in various fields. Also it can be used for surface activation to improve plating performance. Another important aspect of the plasma process is its environmental friendliness. It has a high potential to make plating preparation stages environmentally friendly and efficient. In this study a plasma surface treatment system is attached on a traditional copper plating line which is used for cold rolled low carbon steel sheets. It was determined that plasma surface treatment had a positive effect on the quality of copper plating.

Key words: plasma treatment, copper plating, surface cleaning, degreasing, continuous plating

1. Introduction

Electrolytic metal coatings are economical surface deposition method that are widely used in variety of industrial applications. It functions for protection from corrosion, decorative and functional purposes. Pre-surface cleaning, surface activation and surface preparation steps are the most critical processes in terms of coating quality and performance in electroplating applications on metals. Insufficient cleaning of metal oxides, lubricants and paint residues on the metallic surface causes surface defects in the coating structure and spalling problems of the coating. Before the electroplating of metals, surface cleaning baths containing various chemicals such as alkalis and solvents are used. In addition, acid baths that contain various acids are used to provide surface activation to the substrate metal in order to prepare its surface for electroplating [1]. The troublesome disposal procedures of these chemicals and their harmful effects on the environment are the negative aspects of this technology. In addition to the environmental effects, these processes are difficult to control and they may cause surface contaminations and irregularities if they cannot controlled well enough. It is also known that, substrate surface contaminations and surface defects play important roles in the metal plating defects [2]. Therefore developing different technologies for the surface preparation step of electroplating process is very important both in terms of improving environmental effects and improving the products quality. The industry has a great interest in surface preparation methods, and plasma-based surface technologies provide advantages in many ways.

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Plasma surface treatment technology is already used in many fields such as semiconductor production, optics, medical and food packaging [3]. Plasma technology is a high-energy surface treatment application and activates the surface by changing the chemical structure of the surface at nanoscale without damaging the material surface. It is a cost-effective surface treatment technology without using any chemicals. There are examples of success in the application of plasma surface treatments on coating lines under mass production conditions. This point has strengthened the thought that it can be effective in the production of copper platings, which is our study subject. The effect of insufficient surface cleaning in the root cause search process of surface defects encountered in production lines from time to time is very critical. Pre-cleaning is a vital issue considering the contaminations transferred from the bath to the bath, unsuitable bath impurities, and lubricant residues carried to the surface from machining during the electrolytic coating application process. Under unsuitable conditions, it causes heterogeneity in coating thickness, blistering, delamination, insufficient corrosion life, unsuitable paint and adhesion problems [1-8].

A problem named “spotting”, which is a type of failure associated with the steel surface, has been reported in a continuous copper electroplating line of DC03 steel. It is characterized as small, dark colour spots on the copper plating surface. It is also reported that the spotting problem is one of the most common problem encountered in copper electroplating process, which may increase the production scrap rates and break downs. Also this problem can only be detected after the steel is coated. For these reasons, it is of great importance to prevent this problem in terms of production efficiency.

In this experimental study, the main aim was to examine the effect of the plasma surface cleaning system on the spotting problem. It has been foreseen that the treatment of DC03 steel with a plasma nozzle, just after conventional methods are applied, may have positive effects on the copper plating quality.

2. Materials and Method

The steel used in experimental studies is DC03 (1.0347) and its chemical composition is given in Table 1. The non-alloy steel DC03 acc. to DIN EN 10130 is suitable for cold forming of simple profile forms and components. Its easy weldability, formability and economy allow it to be widely used in the production of automotive parts. It can be easily used in pipe and tube forming works in different wall thickness (0,1-1mm) ranges.

Table 1. Chemical composition of DC03 steel strip

C	Mn	P	S	Fe
max 0.1	max 0.45	max 0.035	max 0.035	Bal.

In the production process, cold rolled sheets are subjected to electroplating operation after a series of pre-surface chemical treatment. These sheets, which are formed as coated, take the form of

products in the form of tubes. As can be seen in figure 1, a plasma nozzle was placed on the production line to increase the performance of the chemical cleaning process and to examine the effect of the plasma surface treatment. It is located between surface preparation and coating baths. If the acid bath is not effective in cleaning the surface, residual acid can cause corrosion on the surface. So the low carbon steel (DC03) strip can be treated with the conventional degreasing and acid baths first, after that it is treated with plasma. Plasma surface treatment has been applied in order to remove residual acids from the surface and to expose the surface to plasma effectively.

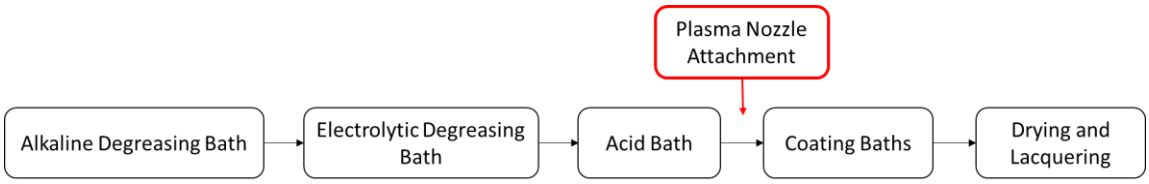

Figure 1. A schematic diagram of the copper plating line and the plasma nozzle attachment.

An open atmosphere air plasma system was used in the preliminary trials. At constant dry air pressure, 1kW of plasma power was applied to the surface at a constant distance. By synchronizing with the speed of the production line, it was tried to reduce the contamination on the surface and to provide surface activation. The ability of the process to be controlled, its speed and being environmentally friendly are quite advantageous. Plasma surface treatments can be used effectively in the aluminum and steel sheet or plate industry, in paint and coating applications, in order to increase the effective surface cleaning and adhesion strength.

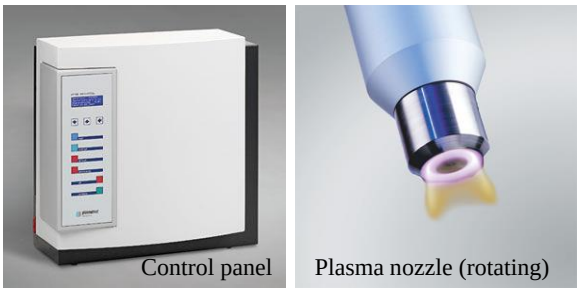

Figure 2. Plasma surface treatment unit (openair plasma; Plasmatreat GmbH)

3. Results and Discussions

The surface problem, which is the subject of the study, is clearly seen in Figure 3. Surface defects, color mismatches and spots are evident on the sheet coil. Periodic surface defects can be detected on copper-coated coil surfaces produced under standard production conditions. Such problems are critical as they cause poor quality, the need for additional cleaning operations, and production downtime.

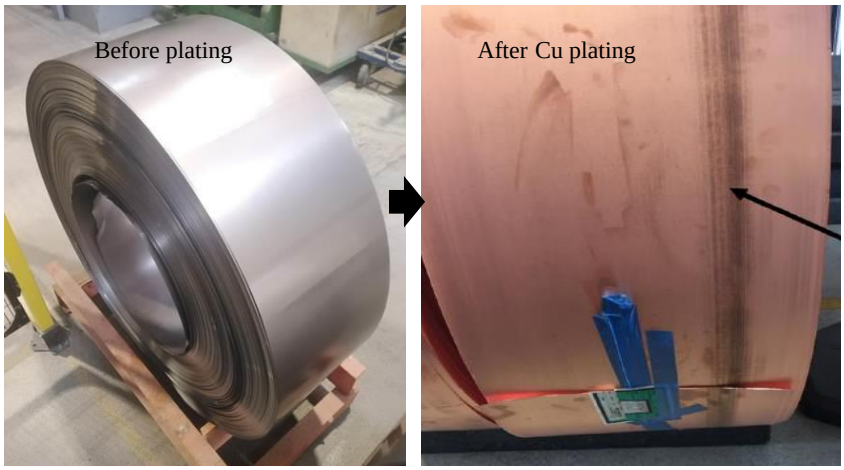

Figure 3. Unsuitable coil surface quality (coil: 333x0,35mm)

A steel coil known to have a spotting problem was fed into the plasma attached continuous copper plating line, and the line was operated. The application aimed to create a contrast between the region with and without plasma application. In order to understand the effect of plasma, an application was carried out in a local area and the results were compared. In Figure 4 the effect of the plasma treated region can be seen with naked eye even before the copper coating baths.

Figure 4. The application of plasma treatment on the continuous copper plating line (9-13m/min).

The plasma application treats only a 5 cm width area. So the treated area is a 5 cm width line on the continuous steel loop. A significant difference in surface quality was observed on the surfaces that were checked at the end of the production line. In Figure 5, it can be seen that the surface defect is decreased by plasma surface treatment. It has been determined that the amount of spot decreases after plasma, becomes smaller and is effective in its general disappearance.

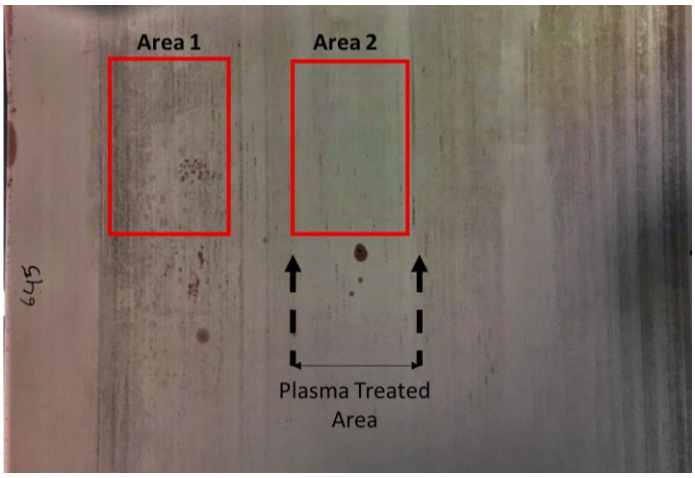

Figure 5. The copper plated steel surface of the strip.
The spotting problem (dark spots) is reduced in the plasma treated area (area 2).

It is seen that the spotting problem is reduced in the region where plasma treatment is performed. This difference can also be seen in the dark field contrast images of the optical microscope (OM) in figure 6.

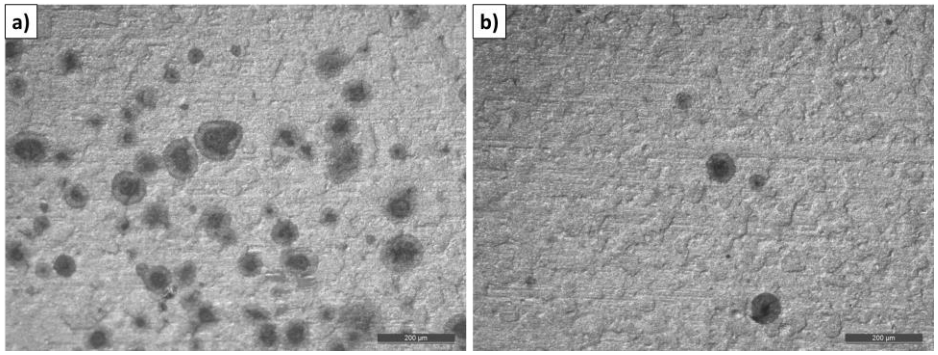

Figure 6. The optical microscope surface images of the copper coated steel surfaces (dark field contrast). a) only cleaned by conventional method, b) plasma treated after conventional cleaning

In the optical microscope cross section images seen in figure 7, blisters between the copper-steel substrate interfaces, which are a characteristic indicator of the spotting problem, seems to reduce by the application of plasma surface cleaning before copper coating baths.

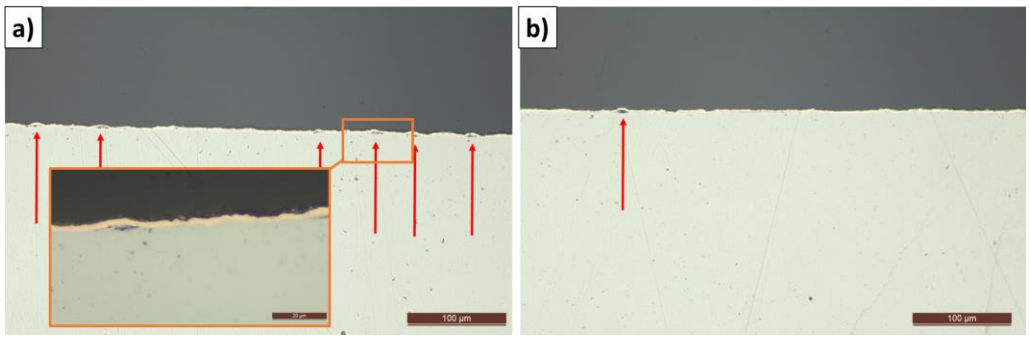

Figure 7. The optical microscope section images of the copper coated steel surfaces (bright field contrast). Red arrows show surface defects of the samples of a) chemical cleaned, b) chemical cleaned then plasma treated strips.

In figure 8, the spot regions on the coating surface were examined under the electron microscope and EDX analysis was performed. In the EDX analysis, copper oxide spots were clearly detected on the surface. In the samples taken after the plasma treatment, it was determined that the surface defects could be significantly reduced.

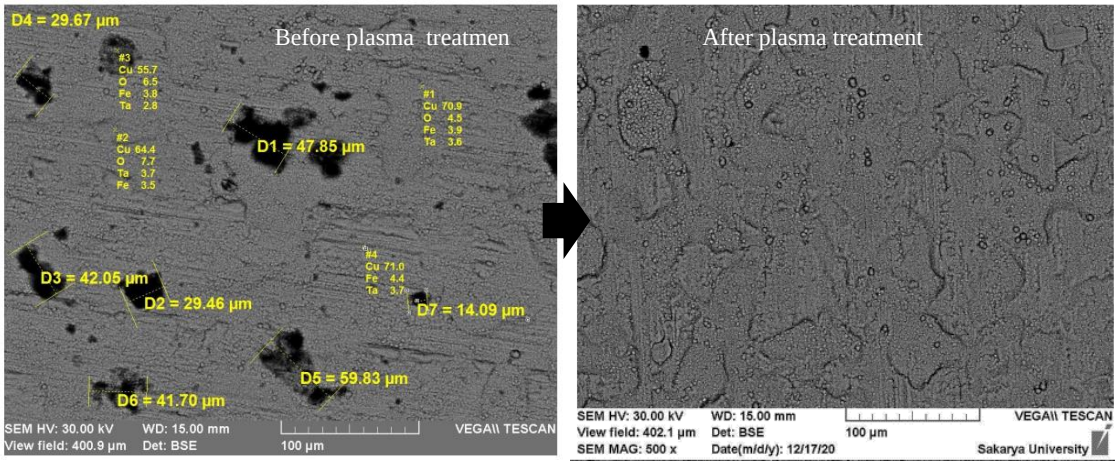

Figure 8. The electron microscope images of the copper coated steel surfaces before and after plasma treatment

In the tests for wettability, the form of the water drop on the surface is observed in Figure 9. Contact angle measurements were carried out for the effect of the plasma on the surface wettability. The contact angle measurement results statistically are shown in the figure 10. The variation of the application time with the contact angle can be clearly seen. As the application time increases, the wetting angle decreases. This helps the coating to adhere to the surface more homogeneously by increasing the wettability of the surface. The reduction of coating bath contaminations on the metallic surface and the more effective plasma activation also increase the coating quality. In order for the plasma to provide an effective activation, it is necessary to determine the appropriate duration of action. It can be seen that the contact angle can be reduced from 80^{o} to 10^{o}.

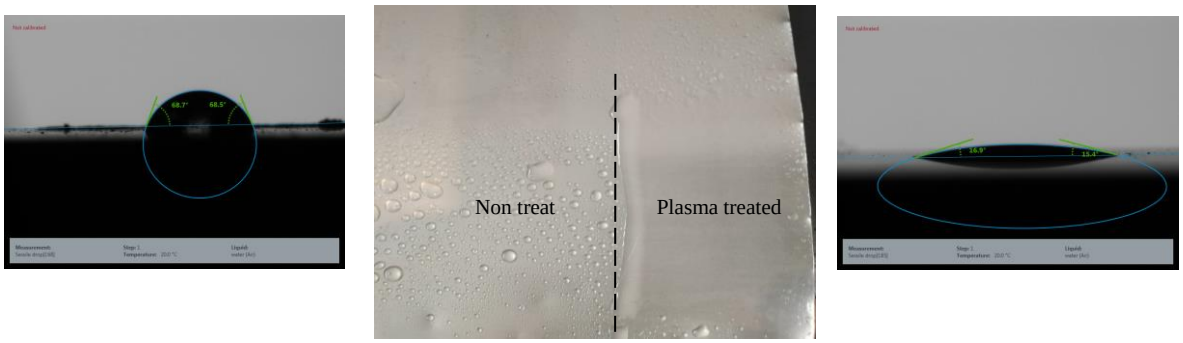

Figure 9. Wettability after plasma treatment, drop shapes

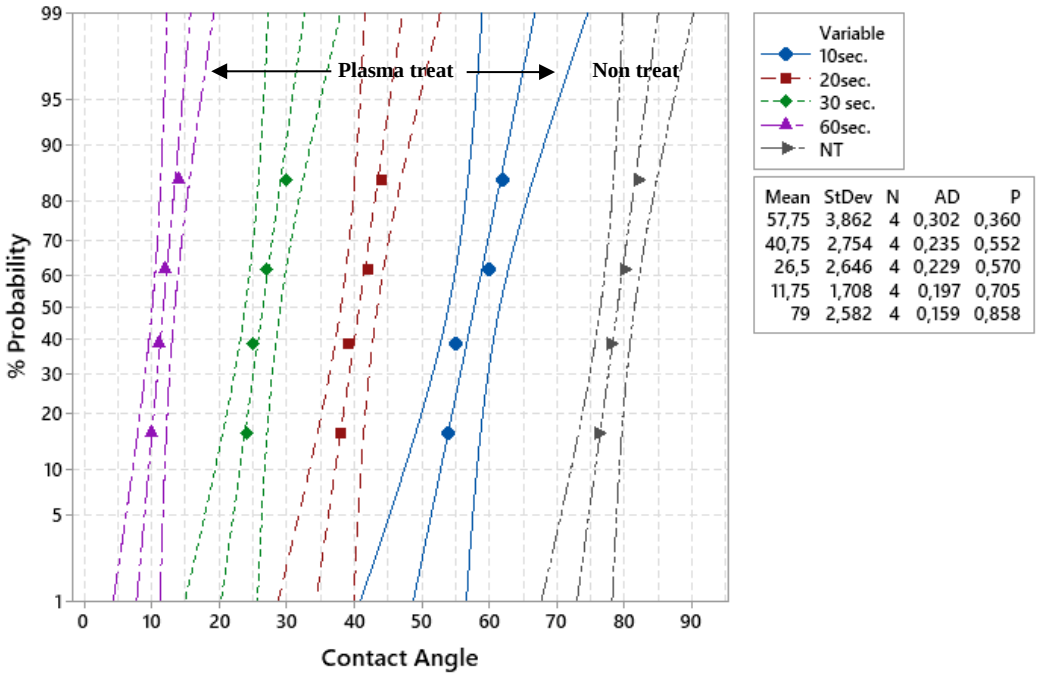

Figure 10. Contact angle test results before and after plasma treatment

4. Conclusions

Pre-surface preparation and cleaning processes in electrolytic coatings determine the coating quality. It is observed that plasma processes give effective results in producing more homogeneous and defect free coatings. There are many current and emerging wetting and adhesion issues which require an additional surface proc-essing to enhance interfacial surface properties. Plasma treatments can activate and clean the steel surface quickly and environmentally. Process control can be done easily with the plasma treatment time, the number of plasma nozzles and the plasma power. With the determination of the optimum plasma time, the surface gets wettability. With the appropriate system design, integration into the production line can be made. Plasma treatments represents an efficient, non-polluting and economical way to clean, activate, and thus to increase the adhesion properties of metallic surfaces.

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