Cathode Spot Behavior Variation in Oxide Layer Removal Caused by Potassium Hydroxide Pre-treatment

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A several-micrometer-thick oxide layer on steel plate samples was removed by high energy density cathode spots appearing on the cathode surface in vacuum arc discharge. The samples’ surface conditions before the oxide layer removal are altered by application of various concentrations of KOH aqueous solution. Such surface condition changes affect cathode spot behavior and improve the energy efficiency of the oxide layer removal.

KEY WORDS: vacuum arc cleaning; cathode spots; removal oxide layer; KOH aqueous solution.

1. Introduction

Results of our and other group’s recent study strongly suggested that the cathode spot in vacuum arc is a convenient metal surface cleaning alternative to conventional mechanical and chemical treatments.1–5) Although the individual cathode spot is tiny, its unique features—extremely high energy density and high mobility—make the vacuum arc a promising method for removal of scale or organic contaminants from metal surfaces.6,7) Its pure effectiveness has already been confirmed as sufficient. It is necessary to prove its practicality as the next stage of research.

The prime application target of this cleaning method, vacuum arc cleaning (VAC), is as a preparation process for actual treatments for surface guarding of metal products such as plating, coating, and painting. The performance of films formed by these treatments depends upon the metal surface’s prior condition. Therefore, the post-cleaning surface-state control technology is important. In addition, from an economical perspective, the treatment’s cost-efficiency is an important determinant of its practical use. This method consumes only electricity; very little hazardous material is emitted. High performance with less electricity is certainly desired to accentuate its advantages over conventional cleaning methods.

To meet these requirements, it is necessary that the cathode spot behavior during VAC be controlled. The motion of the cathode spot while removing the oxide layer is influenced strongly by two factors: discharge pressure and the oxide-layer surface states before cleaning.8–11) Especially, it has been recognized that the work function change of the oxide layer surface causes different behavior of cathode spots and engenders decreases in both the roughness and heat-affected layer thickness of the cleaned metal surfaces when an aqueous solution of potassium hydroxide (KOH) is applied to the oxide layer surface before VAC.12,13) Although the detailed mechanism has not been unveiled yet, this phenomenon must be a key to understanding the roles of the cathode spots in VAC.

For this study, KOH aqueous solutions of various concentrations were applied to change the work function of the oxide layer surface before the VAC. The variation of the moving velocity of the cathode spots and their oxide layer removal performances are investigated. Time evolutions of the arc voltage during VAC are measured and the consumed electric energy variation of the oxide layer removal for different surface conditions is studied quantitatively.

2. Experimental Method

Experiments proceeded through the following procedure: sample preparation, measurement of the sample surface work function variation, and VAC treatment for removal of the oxide layer.

The samples used for this study were 100 mm × 100 mm × 3 mm rolled steel for general structure (SS400) plate, covered with an approximately 5–10-μm-thick oxide layer whose surface roughness (Ra) is about 0.2 μm. Each plate has four open circles to connect to a negative electrode with four bolts. After washing and drying, KOH aqueous solutions of less than 30% concentration were applied on the sample surface as uniformly as possible. Each sample was dried sufficiently on the hot-plate over 100°C until KOH crystals were visible on the surface. Three samples were prepared with each concentration of KOH aqueous solution. The sample work function variation with the applied KOH aqueous solution concentration was investigated using oscillating capacitance method, with a probe (Kelvin Probe 6500; McAllister Technical Services). Regarding this method, because the obtained values are only relative ones to the probe tip work function, only the differences from no KOH aqueous solution of the applied samples were measured. The
measurements were done under the condition of atmospheric pressure air at room temperature. Because the stainless steel (SUS 304) probe tip was of 10 mm diameter, the obtained work function was the mean value in the same size area.

Figure 1 shows a schematic of VAC treatment device arrangement in panel (a) and a photograph of the stainless steel vacuum chamber interior in panel (b). The VAC process was viewed through the chamber window. The prepared sample was set on a water-cooled copper stage, and was connected to the cathode using the bolts, which were unexposed not to be treated. To prevent a breakdown at the outside of the sample, a ceramic plate, which had a larger size than the sample, was inserted between the sample and the stage, as presented in Fig. 1(b). The 100-mm-diameter cylindrical water-cooled anode was also made of copper. A 50-mm gap separated the sample and the anode. The stainless steel chamber was evacuated to 10 Pa using a mechanical booster pump combined with a rotary pump. No additional gas was conducted into the chamber and the samples were treated in the only residual air atmosphere. The VAC discharge was initiated by high-frequency voltage and was sustained with the DC power supply. The VAC treatment current was constant at 100 A. The treatments were continued until all oxide layers had been removed, except for some samples, which were treated for only 30 s to observe the cathode spot tracks.

3. Experimental Results

3.1. Work Function Variation with KOH Aqueous Solution Concentration

Figure 2 presents the variation of the sample surface work function that occurred concomitantly with change in the concentration of KOH aqueous solution applied on the oxide layer surface. Here, the values are differences from those of the sample without KOH aqueous solution; 0% concentration means that no KOH aqueous solution is applied. The measurements of the work function were performed at three different places on a sample surface. Because three samples were prepared with each concentration of KOH aqueous solution, nine values were obtained for each sample surface condition. Therefore, the closed circles and the bars in Fig. 2 represent the average with the maximum and the minimum values of such obtained nine measurement values in each KOH aqueous solution concentration. When the concentration was not high, as in the 10% case, the work function of the sample surface decreased gradually with the KOH aqueous solution concentration. The difference was attained to 0.27 eV at 10%. In contrast, in cases with higher concentration over 10%, the work function difference no longer decreased; the difference was almost constant around 0.27 eV. This result indicates that the KOH led to the lower work function, and extension of the KOH covering area caused the gradual work function decrease in the cases of less than 10% concentration. On the contrary, the KOH covering area saturated in more than 10% concentration cases and thus the work function no longer changed.

3.2. VAC Treatment

Vacuum arc was successfully generated and cathode spots appeared on the sample surface with the KOH aqueous solution application as well as the case of normal surface. Although the work function varied monotonously, the cathode spot behavior changed drastically with concentration of the applied KOH aqueous solution. When the concentration of the applied KOH aqueous solution was low—less than about 10%—the cathode spot motion resembled that of the sample without KOH aqueous solution. However, in the case with high concentration KOH aqueous solution application, which was greater than about 10%, the moving velocity of all cathode spots increased. The pressure in the chamber during VAC treatment increased to about a few times of before the treatment, which was not influenced by KOH aqueous solution on the sample. Because our previous work showed that the cathode spot behavior was affected by the larger pressure difference, the pressure effect can be
neglected in the present work.\textsuperscript{11,14} Consequently, cathode spot behaviors of two types are identifiable, designated herein as slow cathode spots (SCS) and fast cathode spots (FCS). The change between these two-type behaviors seemed to occur discretely. Time evolutions of the discharge voltage during VAC treatment, corresponding to each cathode spot behavior, are depicted in the panels of Fig. 3: (a) without KOH aqueous solution, and (b) with 30\% KOH aqueous solution applied. For the case without KOH aqueous solution, the discharge voltage was almost constant. It was nearly 15 V during VAC treatment, and rapidly increased to between 25 V and 30 V when the treatment was completed, as depicted in Fig. 3(a). In contrast, the discharge voltage changed very rapidly in the case with KOH aqueous solution, as depicted in Fig. 3(b). The variations were between about 15 V and 29 V. The similar variations were observed in the case with over 10\% KOH aqueous solution application and no dependence on the concentration was confirmed. Comparing the discharge voltage and the fluctuation level with those of no KOH aqueous solution case, finishing of the treatment can be found as indicated by an arrow. These experimental results imply that the quiet and the fluctuating voltage variations correspond respectively to the SCS and FCS appearances.

Figure 4 depicts the averaged discharge voltage VAC treatment for various concentrations of KOH aqueous solution applying cases on the sample surface. The closed circles mean the average of obtained three averaged discharge voltage values. And the bars represent the maximum and the minimum values of such three averaged values in each KOH aqueous solution concentration. The average voltages were about 14.9 V, but only SCS appeared during the treatments for which less than 10\% KOH aqueous solution and no aqueous solution had been applied. On the contrary, the average voltages increased to about 18.4 V while only FCS appeared by an application of high concentration KOH aqueous solution over 10\%. When the concentration of KOH aqueous solution was just 10\%, only FCS were observed despite the average voltage was as same as that of SCS case. These results imply that there exists a threshold of work function decrease for the change of cathode spot from SCS to FCS, which is possibly around the case of 10\% KOH aqueous solution. Because the discharge current was constant, these consequences mean that the KOH aqueous solution application and the FCS appearance increase the electric power consumption of the VAC treatment except for the case of 10\% KOH aqueous solution, which is about 23\% higher than the case in which SCS appeared.

Figure 5 presents the removal rate of oxide layer on the sample surface for various KOH aqueous solution concentrations. The closed circles stand for the average of obtained three measurement values and the bars represent the maximum and the minimum values of such three measurements in each KOH aqueous solution concentration. Here, the removal rate is defined as the area of the removed oxide layer in one second, which can be calculated with the whole sample surface area, namely 100 mm $\times$ 100 mm, and the spent time to complete the treatment for that area. The removal rate was approximately 40\% higher when FCS appeared by application of high-concentration KOH aqueous solution than when SCS appeared with application of
low-concentration KOH aqueous solution. According to the observation during discharge, the moving velocity was almost constant in the same type cathode spot. Furthermore, the average number of cathode spot did not change in the same current. Therefore, the removal rate did not change in the case of less than 10% concentration as well as over 10% concentration.

Variation of the electric energy consumption until VAC treatment completion with applied KOH aqueous solution concentrations is portrayed in Fig. 6. The electric energy consumption is calculated with the averaged electric power and the treatment time for the whole of the sample surface. The closed circles are the products of such averaged electric power and treatment time. And, the bars represent the maximum and the minimum values. The necessary electric energy for the removal of the entire oxide layer of the sample was about 8.9×10^4 J, when SCS appeared on the surface by application of less than 10% concentration of KOH aqueous solution. On the other hand, the consumed energy to complete the VAC treatment decreased to approximately 7.8×10^4 J when the FCS appeared on the surface by application of a more than 10% concentration solution. Although electric power with FCS is larger than that with the SCS, as stated in the Fig. 4 caption, the electric energy necessary for completion of VAC treatment with FCS is less than that with SCS. This is because treatment time with FCS was about 71% of that with SCS, and therefore the total energy was greatly decreased. Since the FCS appear and the discharge voltage is almost equal to that of the SCS when the KOH aqueous solution concentration is 10%, the consumed energy is the least as seen in Fig. 6. Because the average voltage and the removal rate do not change in the same type cathode spot as shown in Figs. 4 and 5, the consumed energy is almost constant.

Figure 7(a) presents photographs of the sample surface before treatment. Other panels of that figure portray the sample surface after 30 s VAC treatment (b) without KOH aqueous solution, and (c) with 30% KOH aqueous solution. Before treatment, the sample surface appeared dark, as shown in Fig. 7(a), because of the oxide layer color. However, the region where the oxide layer was removed by the cathode spots appears bright in the figures because of the bulk metal color. Such a cathode spot track as that seen in Figs. 7(b) and 7(c) was changed by application of the KOH aqueous solution. This result indicates that the cathode spot appearance was also varied. For example, according to Figs. 7(b) and 7(c), the track width was about 1 mm in the case of SCS, but approximately 0.3 mm in the case of FCS. Therefore, the SCS and FCS dimensions are expected to be nearly 1 mm and 0.3 mm at most.

4. Discussion

In this study, several changes were observed through KOH aqueous solution application to the oxide layer surface of the sample before VAC treatment: (1) the sample surface work function decreased; (2) the cathode spot moving velocity became larger; (3) many discharge voltage fluctuations occurred during VAC and the averaged discharge voltage increased; (4) the cathode spots appearing during VAC became smaller. The decrease of surface work function by KOH aqueous solution application triggers sudden change in the cathode spot behavior, which results in the changes of averaged voltage, removal rate of oxide layer and consumed electric energy as shown in Figs. 4–6. Although not all mechanisms related to these changes are understood, the following can be inferred as possible explanations.

Regarding the decrease of the work function (1) and the increase of the discharge voltage (3) described above, the existence of many potassium atoms on the sample surface is the likely cause. In fact, the work function of potassium is 2.217 eV, whereas that of iron is 4.60 eV. The low work function of potassium possibly engenders the decrease of that of the oxide layer surface. Although the detailed relation between the low work function and the cathode spot behavior is unclear, the reason for the higher discharge voltage (3) and the smaller cathode spots’ appearance (4) can be...
considered as follows. Because of the lower vaporization temperature and the lower ionization energy of potassium (1031 K and 4.341 eV) than with that values of iron (3 160 K and 7.870 eV), the applied KOH aqueous solution supplies large amounts of positive potassium ion K⁺ to the space between the anode and the sample when the oxide layer is removed. When the concentration of KOH aqueous solution is small, the amount of potassium to be vaporized and ionized is small and therefore the discharge voltage does not changed. However, the voltage must become higher to supply much positive potassium ion K⁺ in the case of higher concentration KOH aqueous solution. This increase of positive ions increases the cathode spot current density for two reasons. Because the mechanism of the electron emission from the cathode surface in the spot is fundamentally thermionic emissions enhanced by Schottky effect, the increase of the positive ions strengthens the electric field near the surface, which reduces the effective work function, and raised the surface temperature through their collision, thereby emitting more electrons.\textsuperscript{15,16} Actually, the reduction of effective work function of cathode, which is considered to be caused by Schottky effect, has been observed in arc discharge.\textsuperscript{17} Furthermore, positive ions weaken the space charge effect of the electrons. According to these effects, the current of the cathode spot is expected to be increased. Additionally, the current increase engenders a stronger pinch effect. For that reason, the cathode spot size becomes smaller and the current density is increased. It is difficult to explain the relations of the faster cathode spot motion (2) and the very frequent fluctuations of the discharge voltage (3) with the small cathode spot appearing (4). However, our previous report described that the heat-affected layer near the VAC-treated surface thinned when the KOH aqueous solution was applied, which seems to be related to the present obtained result described as (2).\textsuperscript{13} Our future work will include more detailed investigations into cathode spot energy density and the treated surface state.

5. Conclusions

This study revealed some interesting changes of VAC treatment characteristics.

1) Application of the KOH aqueous solution decreased the sample work function.

2) By application of a KOH aqueous solution concentrated to more than 10%, the moving velocity of all cathode spots that appeared became large.

3) Regarding the appearance of SCS, the discharge voltage was almost constant. On the other hand, the discharge voltage changed rapidly in cases where FCS appeared.

4) As evidenced by the cathode spot track on the sample surface, the FCS was smaller than the SCS.

5) Although the electric power consumption of the VAC treatment with the FCS was greater than that with SCS, the total energy necessary for VAC treatment completion with the FCS was less than that with the SCS because of the shortened treatment time.

The most important result is that the efficiency of the VAC treatment for removal of oxide layer can be improved by such a simple preparation as the application of KOH aqueous solution to the sample surface.

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