Medium Carbon Steel Surface Hardening by Vacuum Arc Cleaning of Oxide Layers

Yusaku ARAI,1) Masaya SUGIMOTO,1) Mitsuhiko KIMURA,2) Shigeaki SUGIYAMA2) and Koichi TAKEDA1)

1) Faculty of Systems Science and Technology, Akita Prefectural University, 84-4 Tsuchiya-Ebinokuchi, Yurihonjo, Akita 015-0055 Japan. 2) Industrial Technology Center, Akita Prefectural R&D Center, 4-11 Sanuki, Araya, Akita 010-1623 Japan.

(Received on June 2, 2008; accepted on July 11, 2008)

In vacuum arc cleaning (VAC) treatment of an oxide layer on a metal surface, the oxide layer is removed evaporatively by movement of high-energy-density cathode spots on it. The action of the cathode spots not only quickly removes the oxide layer on the metal surface; it also causes a rapid temperature variation on the metal surface, which might indicate a change in surface physical features and impart new additional functions. Changes of metal surfaces that had undergone VAC treatment for the oxide layer are investigated using S45C plate. A simple model is suggested and the experiment result is analyzed theoretically.

KEY WORDS: vacuum arc cleaning; cathode spots; surface hardening.

1. Introduction

Cathode spots have very high energy density. They appear and move on the cathode surface when an arc is generated under a low-pressure condition. They play a very important role in vacuum arc cleaning (VAC), which is a new method for metal surface cleaning. The oxide layer is removed preferentially and evaporatively by the cathode spots moving on the oxide layer when a metal surface, which is covered by an oxide layer, is cleaned using VAC.1) Additionally, the completion of the treatment can be recognized by increased the arc voltage. The cathode spot can be called an “intelligent” heat source because of these convenient features for metal surface cleaning. For those reasons, VAC is a promising new technology that uses cathode-spot characteristics not only to clean metal surfaces but also to activate them.2–4) Hardening of the metal surface probably occurs during VAC treatment because it is heated and cooled instantly by the rapidly moving high-energy-density cathode spots.

Major conventional surface hardening treatment processes are thermal spray, diffusion, and quench-hardening methods. The thermal spray method covers the substrate surface with another material; the diffusion method inputs carbon or nitrogen atoms into the substrate from the surface. The very hot substrate is put into sufficient coolant for rapid cooling and hardening in the quench-hardening method. Nonetheless, each of those methods presents some problem. Adhesion of the covering material is not strong because a different substance from the substrate compound is merely attached to the surface in the thermal spray method. The long treatment time must be shortened to make the diffusion method practical. The problem associated with quench-hardening is that not only the surface but the whole substrate is distorted by heating. The surface hardening method using VAC, if it is possible, offers the following advantages over such conventional ones.

1) High energy density and rapidly moving cathode spots harden the material. Therefore, only the surface layer is changed with no interior distortion, and the treatment time is very short compared with conventional diffusive surface hardening treatment processes.
2) Delamination of the hardening layer occurs only slightly because the layers are identical materials.
3) Activation occurs simultaneously with hardening.

For this study, sample surface hardness and internal stress are measured using S45C plate to investigate surface alteration using VAC treatment. Furthermore, the surface cooling rate of S45C test sample after VAC is estimated using a simple model.

2. Experimental Method

The device arrangement for VAC used in this study is shown in Fig. 1. The VAC proceeds in a stainless steel (SUS304) chamber, which is visible through a window of the chamber. A test sample (cathode) to be treated using VAC is a middle carbon steel (S45C): its dimensions are 10 mm x 10 mm x 3 mm and its surface is covered with a 5–10 μm thick oxide layer. All test samples are annealed at 923 K for 2 h to remove residual stress before VAC. The test sample is set in the stainless steel chamber on a water-cooled copper stage; the sample faces a water-cooled, 40-mm-diameter cylindrical copper anode. It is separated from the anode by 50 mm. The stainless steel chamber is exhausted to a few Pascals using a mechanical booster pump combined with a rotary pump. The VAC process is carried out with current of 50 A or 100 A. In addition, two test samples were prepared: one whose oxide layer was removed by grit blasting before VAC, and one to which 10% KOH...
aqueous solution had been applied to the surface before VAC. These samples were prepared to investigate the influences of such pretreatments upon the alteration on the test sample surfaces by VAC. Our previous work shows that the cathode spots' movement rate on the cathode surface to which 10% KOH aqueous solution had been applied is higher than the rate on the surface without it. For these test samples, times of completion of the treatment are determined by the variation of the voltage and visual observations. In addition, to compare the hardness of the VAC-treated samples with those of non-VAC-treated ones, original, grit blasted, and polished samples were prepared. Although the grit-blasted samples retained a thin oxide layer, no oxide layer remained on the polished ones. All of the test samples are designated as A–G, as shown in Table 1.

The samples were embedded, polished, and etched with 3% nital (an etching solution consisting of alcohol and nitric acid) to distinguish the heat-affected layer from the bulk metal. The heat-affected layer thickness in these samples was measured using a microscope. Hardness measurements were performed at depths of 10 μm, 50 μm, and 100 μm from the surface. Additionally, the residual stresses caused by VAC treatment were investigated using X-ray stress analysis. The conditions of X-ray stress analysis are shown simply in Table 2.

### 3. Experimental Results

Figure 2 shows the time of the completion of VAC treatments for the samples A, B, C, and D. At the time of the test sample A, whose treatment current is lower than that of the other samples, is the longest, which indicates that the oxide layer removal rate increases with the treatment current. Although the reason has not been clarified, application of the KOH aqueous solution to the sample surface makes the cathode spots motion faster. In this experiment, the oxide layer under the cathode spot is evaporated and removed in extremely short time and therefore the oxide layer removal rate is determined by the velocity of the cathode spots. Consequently, the completion time of sample C is shorter than that of sample B. Most of the oxide layer is removed by grit-blasting. Therefore, the time of sample D is much shorter.

Figure 3 is a cross-sectional photomicrograph of test sample B after etching with 3% nital. A discolored region near the surface in Fig. 3 is possibly a heat-affected layer.

Therefore, the thickness of the layer that had been discolored by the etching treatment is measured as the thickness of the heat-affected layer by VAC; the result is shown in Fig. 4. It shows a similar tendency to that shown in Fig. 2, which means that the heat-affected layer thickens as the VAC treatment time increases. As mentioned before, the VAC treatment time depends on the displacement velocity of the cathode spots in this case. It means that the increasing treatment time is caused by the smaller velocity of the
cathode spots and the input thermal energy from the cathode spot to the surface in same area increases. That results in thickening of the heat-affected layer as shown in Fig. 4. The change of hardness in test samples B and G for depth from the surface is shown in Fig. 5. The hardness at 10\(\mu\)m from the surface increases remarkably in test sample B. The hardness increase, like that shown in sample B, is observed in all test samples treated using VAC. Consequently, the hardness increase attributable to VAC treatment can be strongly expected. Figure 6 shows the hardness at 10\(\mu\)m under the surface in each test sample. Comparing the hardness of test samples A, B, C, and D with those of the test samples E, F, and G, the hardness near the surface is increased by VAC treatment to be two or three times harder than the original surface. The values of the hardness near the surface of the VAC-treated samples are almost constant. In other words, alteration of the hardness caused by quench-hardening using VAC treatment has no dependence on the treatment time or the treatment current.

The residual stress of each test sample is shown in Fig. 7. The residual tensile stress is shown for test samples A, B, and C: the test sample surface under the cathode spot is melted and the molten layer tends to expand. However, it is cooled down instantly and fixed with the tension when the cathode spot moves away, and it leads such stress generation in the vicinity of the surface. On the other hand, sample F shows residual compressive stress near the surface because grit-blasting pushes down the metallic lattice near the surface. As these results show, VAC treatment and grit-blasting respectively increase the tensile and the compressive stresses. Sample D received both of these treatments; therefore less compressive stress remains compared to those of samples A, B, and C.

4. Discussion

Figure 8 shows a simplified model of the oxide-layer removal process using VAC. The depth profile of the temperature distribution and the cooling rate at the surface are estimated under the following assumptions.

- The heat flux is a one-dimensional flow, which is only in the depth direction.
- The thermal conductivity coefficient of the test sample is always constant.
- Heat loss by the melting phenomenon of the test sample is negligible.
- Material properties of the oxide layer and the bulk metal are equal in this case.

The value of each symbol is shown in Table 3. The heat flux from the arc to the sample in unit time, \(Q_{\text{sample}}\), is written as

\[ Q_{\text{sample}} = \eta (iV) \]  

where the values of \(i\) and \(\eta\) are 20 A and 0.3, respectively, in this estimation. The heat fluxes conveyed away by the vapor of the oxide and the electron flow in unit time, \(Q_{\text{vapor}}\) and \(Q_{\text{electron}}\), are represented respectively as

\[ Q_{\text{vapor}} = - s H \left( \frac{dD}{dt} \right) \]  
\[ Q_{\text{electron}} = i \phi \]

where \(H\) is 1.0\(\times\)10\(^{11}\) J/m\(^2\). The heat flow to the sample substrate by heat conduction in unit time, \(Q_{\text{substrate}}\), is ex-
Table 3. Meaning of each symbol.

| q | Ratio of electric power into cathode to all input electric power |
| v | Current in a spot |
| v | Voltage |
| s | Area of cathode spot |
| \( D \) | Thickness of oxide layer |
| \( H \) | Specific energy for removal of oxide layer |
| \( \phi \) | Work function of oxide layer |
| \( \kappa \) | Coefficient of thermal conductivity of substrate |
| t | Time measured from cathode spot appearance |
| \( t_\alpha \) | Time at which oxide layer reaches evaporation temperature |
| \( t_\beta \) | Time of completion of removal oxide layer at the cathode spot appearance point |
| T | Temperature |
| \( \rho \) | Mass density of substrate |
| \( \varepsilon \) | Specific heat of substrate |
| \( T_{\text{ev}} \) | Evaporation temperature of oxide layer |
| \( T_{\text{melt}} \) | Substrate melting temperature |
| \( T^\prime \) | Representative temperature in molten layer |

pressed in the following form:

\[
Q_{\text{substrate}} = -\kappa \frac{\partial T}{\partial x} \bigg|_{x=0} \quad \text{(4)}
\]

Here, \( x \) is the distance from the surface and \( x=0 \) indicates the sample surface. Because the oxide layer is removed, as shown in Fig. 8, the origin, \( x=0 \), is changing during \( t_\alpha < t < t_\beta \). The following equation is satisfied because of the balance of energy flow at each cathode spot.

\[
Q_{\text{sample}} = Q_{\text{vap}} + Q_{\text{electron}} + Q_{\text{substrate}} \quad \text{(5)}
\]

The equation of heat conduction is represented as

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad \text{(6)}
\]

where \( \alpha \) is the coefficient of thermal diffusivity, written as

\[
\alpha = \kappa / \rho c \quad \text{(7)}
\]

When \( t=0 \) is the initiation time of the heat injection to the oxide layer surface and when it becomes the evaporating temperature at \( t=t_\alpha \), then

\[
\frac{i}{s} (\eta V - \phi) = -\kappa \frac{\partial T}{\partial x} \bigg|_{x=0} , \quad 0 < t < t_\alpha \quad \text{(8)}
\]

is obtained. After the oxide layer temperature becomes higher than that of evaporation, the equation

\[
\frac{i}{s} (\eta V - \phi) = -sH_v \left( \frac{dD}{dt} \right) = \kappa \frac{\partial T}{\partial x} \bigg|_{x=0} , \quad t_\alpha < t < t_\beta \quad \text{(9)}
\]

is satisfied. In addition, the boundary condition of Eq. (9) is given as

\[
T(0,t) = T_v \quad \text{(10)}
\]

When the value of \( t \) is \( 0 < t < t_\alpha \), temperature distribution \( T(x,t) \) is written as

\[
T(x,t) = \frac{E}{\kappa} \left( \frac{2}{\sqrt{\pi}} \frac{\alpha}{\kappa} \right) \exp \left( -\frac{x^2}{4\alpha t} \right) - \frac{x}{2\sqrt{\alpha t}} \text{erfc} \left( \frac{x}{2\sqrt{\alpha t}} \right)
\]

\[
\text{erfc}(y) \text{ represents the complementary error function.} \quad \text{(11)}
\]

Therefore, \( t_\alpha \) is expressed as

\[
t_\alpha = \frac{\pi}{\alpha} \left( \frac{\kappa T_v}{2E} \right)^2 \quad \text{(12)}
\]

using Eqs. (10) and (11), where \( E \) is the energy density of cathode spot:

\[
E = \frac{i}{s} (\eta V - \phi) \quad \text{(13)}
\]

Because the metal is presupposed to be in a solid state, the solution of Eq. (6) under the boundary condition (10) is represented as

\[
T(x,t) = T_v \text{erfc} \left( \frac{x}{\sqrt{4\alpha (t - t_\alpha)}} \right) \quad \text{(14)}
\]

On the other hand, Eqs. (9) and (14) lead to

\[
D(t) = D_0 - \left[ (t - t_\alpha) E \left( \frac{2\kappa T_v}{\pi \alpha} \sqrt{t - t_\alpha} \right) \right] / H_v
\]

\[
\text{(15)}
\]

where \( D_0 \) is the thickness of the oxide layer at \( t=0 \), about \( 5.0 \times 10^{-6} \) m.

In addition, \( t_\alpha \) can be assumed to be nearly 0 when the value of the power density of the cathode spot is \( E = 10^8 \sim 10^{14} \) (W/m²). The time of \( D=0 \) indicates the completion of removal of the oxide layer in the spot. Therefore, \( t_\alpha \) is calculated using Eq. (15). The temperature distribution for various power densities at \( t = t_\alpha \) is calculated using Eq. (11) and is shown in Fig. 9. The material properties of S45C used in this calculation are described in Table 4.

The cooling rate is obtained using Fig. 9. A simple model of the cooling process after VAC treatment is shown in Fig. 10. The temperature distribution shown in Fig. 9 is computed by ignoring the heat loss and alteration of coefficient of thermal conductivity by melting phenomenon.

![Fig. 9](image-url)
However, because the molten layer thickness is necessary to calculate the cooling rate, the region of over the melting temperature of the oxide layer, $T_m$ ($\approx 1540\text{ K}$), is supposed to be the molten layer on the distribution temperature curve.

The internal energy of the molten layer at $t=x/L$, $u$, is represented as

$$u = cpLx^*$$  \hspace{1cm} (16)

where $L$ and $x^*$ are the thickness of the molten layer and representative temperature in the molten layer presumed in this calculation. The heat flow rate to the metal inside through the lower molten layer ($x=L$), $q$, is expressed as

$$q = \kappa \left( \frac{dT}{dx} \right)_{x=L}$$  \hspace{1cm} (17)

Because the internal energy rate of decrease, $du/dt$, equals the heat flow rate,

$$cL \left( \frac{dT^*}{dt} \right) = \kappa \left( \frac{dT}{dx} \right)_{x=L}$$  \hspace{1cm} (18)

is obtained.

In Eq. (18), $(dT/dx)_{x=L}$ can be approximated as

$$\left( \frac{dT}{dx} \right)_{x=L} \approx \left( \frac{dT}{dx} \right)_{x=0}$$  \hspace{1cm} (19)

according to the temperature curves shown in Fig. 8. Accordingly, cooling rate can be estimated as

$$\left( \frac{dT^*}{dt} \right) = \frac{\kappa}{\rho Lc} \left( \frac{dT}{dx} \right)_{x=0}$$  \hspace{1cm} (20)

The estimated cooling rates for various power densities are shown in Fig. 11. The power density of the cathode spot is estimated as about $10^{7}$–$10^{10}\text{ W/m}^2$. Therefore, the cooling rate is approximately $10^{7}$–$10^{10}\text{ K/s}$. This range of the cooling rate enables the molten layer of the substrate to be a martensite state. Because this estimation is based on a simple model and assumptions, the cooling rate calculated here does not indicate a correct value, rather merely the order of that value. However, it can be expected that the increased hardness of the surface by VAC treatment is caused by formation of the martensite layer on the original test sample surface.

5. Conclusions

Some interesting characteristics of VAC treatment are illustrated in this experiment using S45C test sample.

(1) The heat-affected layer thickens with longer VAC treatment time.

(2) The increased hardness near the surface is caused by VAC treatment; the material becomes two or three times harder than original surface.

(3) The hardness near the surface of the VAC-treated samples is independent of the treatment time and current.

(4) The residual tensile stress is generated near the surface by VAC treatment.

(5) The cooling rate of the surface after VAC treatment is estimated as about $10^{7}$–$10^{10}\text{ K/s}$, which implies that the molten surface layer becomes the martensite state; therefore, the hardness is increased.

Results indicate that VAC, a new technology, has a possibility of metal surface hardening and activating coincident with cleaning.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Young Scientists (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

1) R. L. Boxman, P. J. Martin and P. M. Sanders: Handbook of Vacuum Arc Science and Technology, Noyes Publications, New Jersey, (1995), 73.

2) Arifov Institute of Electronics, Patent Application, JP N 2-221389, filed 24 Aug. 1990.

3) K. Takeda and S. Takeuchi: Mater. Trans., JIM, 38 (1997), No. 7, 636.

4) K. Takeda: Surf. Coat. Technol., 131 (2000), 234.

5) M. Sugimoto, A. Mirkarimov, S. Pozharov and K. Takeda: Thin Solid Films, 457 (2004), 168.

6) H. S. Carslaw and J. C. Jaeger: Conduction of Heat in Solids, Oxford University Press, Oxford, (1959), 75.