Formation of Porous Stainless Steel Surface by Al Electrodeposition and Dissolution in the Molten Salt and Sliding Properties

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A porous surface layer was formed by Al electrodepositing and Al dissolving on the surface of stainless steel using molten salt. Furthermore, the relationship between the morphology of the alloy layer produced by Al electrodeposition and the porous layer was clarified. As a result, Fe aluminide with high Al concentration was formed on the surface by lowering the Al electrodeposition potential. Then, in order to investigate the dissolution behavior of Al, the anodic polarization curves of the Al electrodeposited sample and the untreated sample were measured. An increase in the anode current was observed from around $-1.2$ V in the Al electrodeposited sample. On the other hand, an increase in the anode current was observed from around $-0.8$ V for the untreated sample. Therefore, the dissolution experiment was performed at $-0.9$ V, where Al dissolution occurs and SUS304 dissolution does not occur. The lower the potential during Al electrodeposition, the thicker the porous layer with higher porosity formed. As a result of point analysis of the composition of the porous layer, it was recognized to be an austenite phase having a lower Cr concentration than untreated SUS304. It is considered that Fe remains in the porous layer as Al is dissolved and that Fe diffuses at high temperature to form a porous layer. Thus, the sliding characteristics of the stainless steel with the porous layer and the untreated stainless steel were evaluated. The porous sample showed better characteristics than the untreated sample.

KEY WORDS: Al electrodeposition; Al dissolution; molten salt; stainless steel; porous layer; sliding characteristics.

1. Introduction

From the viewpoint of reducing fuel consumption and protecting the global environment, it is required to reduce CO$_2$ emitted from transportation equipment. In order to solve this problem, it is required to improve the fuel efficiency of transportation equipment. Then, in order to improve fuel efficiency, it is necessary to suppress friction loss in the sliding part. Many surface treatment methods have been reported to suppress friction loss. Tachikawa has reported that DLC (diamond-like carbon) is coated on the sliding material to improve friction characteristics. Suzuki et al. investigated the hardness and friction properties of Cr–Mo–N coating. Pawlak et al. reported the results of measuring the friction coefficient by adding boron nitride to modify the surface of the bearing. However, these methods are difficult to deal with sliding materials with complicated shapes. Therefore, the authors considered that electrochemical treatment using molten salt should be used as a method for treating the surface of sliding materials with complex shapes. As a result, it is possible to handle complicated shapes. In addition, the authors considered that low friction could be achieved by making the surface porous by using molten salt and absorbing oil in the porous part. Until now, there have been many methods to make the material surface porous, but few reports have made the alloy porous. The authors considered making the alloy stainless steel porous by the method shown in Fig. 1. First, Al is electrodeposited using the molten salt as a medium. So far, the authors have been studying the electrodeposition of Al using molten salt as a medium. It has been clarified that an alloy of the substrate material and Al is formed by electrodepositing Al using a high temperature molten salt. Therefore, it was thought that if only Al in the alloyed electrodeposited layer could be dissolved, it could be made porous. Since Al is a less-noble metal rather than the constituent elements of stainless steel, Fe, Cr, and Ni, only Al can be preferentially dissolved. There is a method
of dissolving Al alloy with acid or alkali as a method of making it porous, but in that case, there is a problem that the base material is also dissolved. Therefore, if a molten salt is used, the metal that is electrochemically dissolved can be controlled by the potential. And finally, a porous surface layer can be generated.

In this study, Al is electrodeposited using molten salt as a medium to form an alloy of the electrodeposited metal with the substrate, which is then melted and made porous. Such a method is a novel method, and since the electrodeposition method is also used, the surface can be made porous even with complicated material. A friction test was conducted to evaluate the friction coefficient of the porous layer.

2. Experimental Method

Stainless steel (SUS304) was used as the sample. Table 1 shows the composition. The surface of the sample was polished by emery paper No. 800 and then sonicated in acetone.

The Al alloy layer was formed by Al electrodeposition. The electrodeposition was performed using a molten salt as a medium. For the electrolytic bath, an equimolar composition of NaCl–KCl mixed salt with 3.5 mol% AlF₃ was used. Before mixing NaCl and KCl, they were vacuum dried at 543 K for 86.4 ks. As shown in Fig. 2, the same electrolysis cell was used as in the previous report. The reference electrode was a mullite tube containing NaCl–KCl–AgCl (45:45:10 mol%) mixed salt and Ag wire immersed in it. The bath temperature during the experiment was 1 023 K. During the experiment, Ar gas was flown into the cell at a flow rate of 3.3 × 10⁻⁶ m³·s⁻¹. The cathode polarization curve was measured by the potential sweep method using stainless steel as the sample electrode. The sweep speed was 1.7 × 10⁻³ V·s⁻¹. The Al electrodeposition experiment was carried out by potentiostatic polarization to the reduction potential of Al ions which was cleared by the cathode polarization curve. Al electrodeposition was carried out by constant potential electrolysis in the range of −1.4 to −1.8 V. After the Al electrodeposition treatment, it was polarized at a constant potential to form a porous material. The potential of the potentiostatic polarization was set to the potential at which the untreated sample did not dissolve, which became clear from the anodic polarization curves of the Al-deposited sample and the untreated sample. The anodic polarization curve was measured at a potential sweep rate of 1.7 × 10⁻³ V·s⁻¹. After the treatment, the sample was taken out of the bath and the salt on the sample surface was removed by washing with water. The cross section of the sample after the electrodeposition treatment was observed and analyzed by a field emission scanning electron microscope (JEOL JSM-7800F) and an X-ray microanalyzer (JEOL JXA-8230). Furthermore, the treated layer was identified by the X-ray diffraction method (Rigaku RINT2200VK). CuKα rays were used as the X-ray source.

A friction test was conducted to evaluate the friction performance of the sample after the porous treatment. The measurement method was a ball on disc as shown in Fig. 3. SUJ2 (diameter 6 mm) was used for the ball. The sample size was 20 × 20 × 2 mm, and the load was 1 N and 3 N. Furthermore, the test was performed with and without lubricating oil. The radius of gyration of the ball was 3 to 7 mm, the speed was 10 mm·s⁻¹, and the sampling frequency was

![Fig. 1. Schematic diagram of the porous layer formation. (Online version in color.)](image)

![Fig. 2. Schematic diagram of the electrolysis cell. (Online version in color.)](image)

| Table 1. Chemical composition of the SUS 304 stainless steel. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Fe   | C    | Si   | Mn   | P    | S    | Ni   | Cr   | Mo   | Al | N   | (mass%) |
| Bal.            | 0.01 | 0.52 | 0.97 | 0.03 | 0.002| 9.58 | 18.15| 0.20 | 0.002| 0.043|     |

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3 hz. Finally, the surface of the sample after the friction test was observed and analyzed by SEM.

3. Results and Discussion

3.1. Formation of Al Electrodeposited Layer

In order to investigate the behavior of the Al electrodeposited layer, experiments were carried out in NaCl-KCl-3.5 mol% AlF₃ at 1 023 K in Ar gas atmosphere with an electrodeposition time of 3.6 ks. The deposition potentials were −1.4 V, −1.5 V, −1.6 V, −1.7 V and −1.8 V. The test was performed at a constant potential to investigate the effects of the thickness and composition of the aluminide produced by changing the amount of Al electrodeposition. Figure 4 shows the cross-sectional structure of the electrodeposited layer of SUS304 steel. Figure 4(a) is the result at an electrodeposition potential of −1.4 V. It can be confirmed that an electrodeposited layer of about 10 μm is formed on the surface. As a result of the analysis, FeAl₂ was formed in the electrodeposited layer. Figure 4(b) is the result at an electrodeposition potential of −1.5 V. It can be confirmed that two electrodeposited layers are formed on the surface of the substrate and the thickness is about 50 μm. The outer layer of the electrodeposited layer was Fe₂Al₅, and the second layer was FeAl₂. Figure 4(c) is the result at an electrodeposition potential of −1.6 V. It can be confirmed that three electrodeposited layers are formed on the surface and the thickness is about 65 μm. As a result of the analysis, the outer layer of the electrodeposited layer was Al, the second layer was a mixed layer of Fe₂Al₅ and FeAl₂, and the third layer was FeAl₂. Figure 4(d) is the result at an electrodeposition potential of −1.7 V. It can be confirmed that three electrodeposited layers are formed on the surface and the thickness is about 67 μm. As a result of the analysis, the outer layer of the electrodeposited layer was Al, the second layer was a mixed layer of Fe₂Al₅ and FeAl₂, and the third layer was FeAl₂. It was confirmed that the thickness of the 2nd and 3rd layers did not change and the outer layer was thicker than that of the sample deposited by Al electrodeposition at −1.6 V. Figure 4(e) is the result
at an electrodeposition potential of $-1.8 \text{ V}$. It can be confirmed that three electrodeposited layers are formed on the surface and the thickness is about $0.85 \mu\text{m}$. According to the analysis, the outer layer of the electrodeposited layer was a mixed layer of Al and NiAl$_3$, the second layer was a mixed layer of Fe$_2$Al$_5$ and FeAl$_3$, and the third layer was FeAl$_2$. It was also confirmed that the outer layer of the sample under these conditions was thicker than the outer layer formed at $-1.7 \text{ V}$.

### 3.2. Formation of Porous Layer

After Al deposition, a porous surface is prepared by dissolving only Al. Dissolution of Al is performed by measuring the anodic polarization curves of untreated SUS304 and SUS304 on which Al was deposited, and in the potential range where Fe dissolution does not occur. Figure 5 shows the results of the anodic polarization curve. An increase in the anode current (dissolving current) was observed from $-1.2 \text{ V}$ for Al-deposited SUS304. Therefore, it can be seen that the dissolution reaction of Al occurs from $-1.2 \text{ V}$. On the other hand, in untreated SUS304, an increase in anode current (dissolving current) was observed from around $-0.8 \text{ V}$. Therefore, it can be seen that the dissolution reaction of Fe occurs from this potential. From this, it is possible to determine the potential range in which only the deposited Al is dissolved. In this experiment, the Al dissolution poten-

![Fig. 5. Anodic polarization curve for SUS304 and Al electrodeposited SUS304 in NaCl-KCl melts at 1 023 K. (Online version in color.)](image)

![Fig. 6. Current density-time curves of Al deposition at $-1.5 \text{ V}$ and Al dissolution at $-0.9 \text{ V}$ in NaCl-KCl-3.5 mol%AlF$_3$ melt at 1 023 K. (Online version in color.)](image)

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**Fig. 7.** Cross-sectional SEM images of SUS304 after Al deposition at $-1.4 \text{ V}$ to $-1.8 \text{ V}$ and Al dissolution at $-0.9 \text{ V}$ for 7.2 ks in NaCl-KCl-3.5 mol%AlF$_3$ melt at 1 023 K.
The potential was set to $-0.9 \ V$.

Figure 6 shows the current density-time curve when Al was electrodeposited at $-1.5 \ V$ and Al was dissolved at $-0.9 \ V$. The cathode current (deposition current) flows when polarized at $-1.5 \ V$. Therefore, it can be seen that the Al electrodeposition reaction is occurring. A large cathode current was shown at the beginning of electrodeposition, and then gradually decreased. It can be seen that the anode current (dissolution current) flows when the anode is dissolved at $-0.9 \ V$ after Al deposition. This shows that the dissolution reaction of Al is occurring. Similar to the electrodeposition, a large anodic current flowed in the initial stage and then gradually decreased. In the 1-hour melting experiment, the value of current density was close to zero. Therefore, it can be seen that the dissolution of Al is almost complete.

Al was electrodeposited at $-1.4 \ to -1.8 \ V$ to form an alloy layer with Al. After that, Fig. 7 shows the cross-sectional microstructure of the sample with anodic polarization at $-0.9 \ V$ to dissolve Al and make the surface porous. It can be seen that a porous layer is formed in all samples. The adhesion between the porous layer and the substrate was good. Large cracks were observed in the porosity at $-1.5 \ to -1.7 \ V$, but at other potentials, no such cracks were observed.

Figure 8 shows the potential dependence of the porous layer thickness obtained from the cross-sectional microstructure shown in Fig. 7. It can be seen that the porous layer becomes thicker by lowering the potential. At $-1.5 \ V$, the thickness suddenly increased. It is considered that a large amount of Al is electrodeposited at a low potential and a thick Al alloy layer is formed. Therefore, it is considered that when the Al is dissolved, the porous layer also becomes thicker accordingly.

Figure 9 shows the surface morphology of the porous sample. It is clear that all the samples have small voids of $1 \ \mu m$ or less. Finer voids were observed in samples with higher Al electrodeposition potential. It was found that a porous surface can be formed by Al dissolution treatment after Al electrodeposition.

Figure 10 shows the potential dependence of the porosity measured from the surface morphology in Fig. 9. It can be seen that the porosity increases as the electrodeposition potential decreases. The amount of electrodeposition increases as the potential decreases. Then, the electrode:

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<td>(e) $-1.8 \ V \ to -0.9 \ V$</td>
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Fig. 9. Surface morphology of SUS304 after Al deposition at $-1.4 \ to -1.8 \ V$ and Al dissolution at $-0.9 \ V$ for 7.2 ks in NaCl-KCl-3.5 mol%AlF$_3$ melt at 1023 K.
Fig. 10. Porosity of porous layer after potentiostatic polarization in NaCl-KCl-3.5 mol%AlF₃ melts at 1 023 K as a function of polarization potential. (Online version in color.)

Fig. 11. Experimental isothermal section of the Fe–Cr–Ni ternary system at 1 023 K.15) (Online version in color.)

Fig. 12. Anodic polarization curve for SUS304 and Al electrodeposited SUS304 in NaCl–KCl melts at 1 023 K. (Online version in color.)

The deposited layer becomes thicker and the Al concentration also rises. As a result, it is considered that the porosity increased when Al was dissolved. For Fig. 4, it was observed that Fe aluminide with a high Al concentration was formed as the potential decreased. It is considered that the porosity increased due to the dissolution of Al from Fe aluminide, which has a relatively low Fe concentration.

3.3. Effect of Porous Layer on Electrodeposition Potential

Figure 11 shows the Fe–Cr–Ni ternary phase diagram and the composition of the point analysis of the porous layer by EPMA. It is presumed that the metal structure of the porous part is an austenite phase. It can be seen that the Cr concentration is reduced in all the treated samples compared to the untreated sample. It is considered that Cr is dissolved at the same time when Al is dissolved.

Figure 12 shows the anodic polarization curve obtained by adding the results of Ni and Cr to the results of Fig. 5. As a result, the current density of the Al-deposited sample increased at the lowest potential. It can be seen that at low potentials, only Al dissolves and other metals do not. Further, in this study, Al was dissolved at −0.9 V. Although the dissolution of Fe and Ni does not occur, the anode current density of Cr is slightly increased. Therefore, it is considered that the dissolution of a small amount of Cr caused the change to austenite with a low Cr concentration, as shown in the ternary phase diagram of Fe–Cr–Ni in Fig. 11.

3.4. Mechanism of Surface Porosity

The surface morphology with micro-ligaments and pores was confirmed by performing Al electrodeposition on the stainless steel surface using molten salt and then performing Al dissolution. Figure 13 shows a schematic diagram of the porous mechanism of the stainless steel surface.10) For Fig. 13, the Fe atom and Al atom are combined on the stainless steel surface by Al electrodeposition to form an Fe–Al alloy layer. The electrodeposition temperature in this experiment is as high as 1 023 K. It is considered that the electrodeposited Al diffused into the stainless steel and formed an alloy layer. After that, Al atoms are dissolved in the molten salt by applying a dissolution potential. As is clear from the results of the anodic polarization curve in Fig. 11, only Al can be dissolved. As the Al atom dissolves, the Fe atom diffuses on the surface as shown in Fig. 13 and bonds with the Fe atom. By repeating this process, a ligament due to the bond of Fe atoms is formed as in Fig. 13. It is considered that the surface morphology shown in Fig. 9 can be obtained.

3.5. Friction Test Results

A friction test was conducted to evaluate the performance of the porous sample. Figure 14 shows the results of the friction test. The coefficient of friction between the porous sample and the untreated sample was measured. The friction coefficient was lowered by the treatment. In particular, in the environment with oil, the friction coefficient of the untreated sample showed an unstable value, whereas the
treated sample showed a stable low value. The porous part contains oil. Therefore, it is considered that the low friction coefficient was maintained for a long time.

**Figure 15** shows the surface morphology of the sample after the friction test shown in Fig. 14. It can be seen that the surface of the untreated sample is scraped due to friction.
It is considered that the friction coefficient became unstable due to such scraping and showed a large value. On the other hand, no significant change was observed in the morphology of the porous sample after the friction test. It is considered that the wear of the material was suppressed by the reduction of the friction coefficient.

4. Conclusions

In this study, Al was electrodeposited on the surface of stainless steel using a molten salt as a medium, and then Al dissolution was attempted to make the surface porous. Furthermore, the coefficient of friction was evaluated by performing a sliding test on the surface of the formed porous stainless steel. The results obtained are as follows.

(1) As a result of measuring the anode polarization curves of Al-deposited SUS304 and untreated SUS304, an increase in the anode current was observed in the Al-deposited sample from around $-1.2$ V. On the other hand, the untreated sample increased from around $-0.8$ V. Therefore, it was found that the dissolution of Al occurs from $-1.2$ V.

(2) The surface morphology with micro-ligaments and pores was formed on the stainless steel surface by performing Al dissolution at $-0.9$ V after the Al electrodeposition.

(3) It was found that the porous layer became thicker and the porosity increased as the electrodeposition potential decreased.

(4) From the evaluation of the friction coefficient by the sliding test, the porous sample showed lower friction coefficient than the untreated sample regardless of the presence or absence of lubricating oil.

(5) Especially in an environment containing lubricating oil, a low friction coefficient was maintained for a long time.

REFERENCES