Corrosion Resistance of a Free-Cutting Soft-Magnetic Stainless Steel in Pure Water

Yu Sugawara¹,*, Tatsuya Naruse², Takashi Ebata³, Izumi Muto¹ and Nobuyoshi Hara¹

¹Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
²Engineer of Technical Department, Tohoku Steel Co., Ltd., Shibata-gun, Miyagi 989-1393, Japan
³Corporate Planning Department, Tohoku Steel Co., Ltd., Shibata-gun, Miyagi 989-1393, Japan

The corrosion resistance of a new free-cutting soft-magnetic stainless steel containing Ti₄C₂S₂ instead of MnS was examined by immersion corrosion tests in pure water and anodic polarization measurements in 0.1 M Na₂SO₄. The Ti₄C₂S₂ inclusions hardly dissolved in pure water at 353 K and did not suffer anodic dissolution in the passivity region of stainless steel in 0.1 M Na₂SO₄. In contrast, conventional free-cutting soft-magnetic stainless steels with (Mn,Cr)S inclusions caused the significant release of Mn species during immersion in pure water, and showed a marked increase in the dissolution current of MnS under anodic polarization in 0.1 M Na₂SO₄. The thermodynamic stability of Ti, Mn and Cr oxides films on the inclusions makes the difference in the corrosion resistance of Ti₄C₂S₂ and (Mn,Cr)S, with no dissolution of Ti from Ti₄C₂S₂ and the selective dissolution of Mn from (Mn,Cr)S.

(Received June 1, 2015; Accepted August 17, 2015; Published October 2, 2015)

Keywords: free-cutting soft-magnetic stainless steel, corrosion resistance, Ti₄C₂S₂, MnS, pure water, anodic polarization curve

1. Introduction

Soft-magnetic stainless steels are used as the magnetic core material of solenoid valves for pure water flow systems in polymer electrolyte fuel cells (PEFCs), such as humidification of membrane electrode assembly (MEA) and steam reforming of fuel.¹ In addition to common requirements of high hardness, wear resistance, durability, and soft-magnetic properties, high corrosion resistance is a stringent requirement for the PEFC application since dissolved metal ions in pure water contaminate the MEA, resulting in loss of cell performance.²

The addition of Pb and S has been widely used for improving the machinability of soft-magnetic stainless steels. In the near future, the addition of toxic Pb will be prohibited.³ While S also can be added in the form of MnS,⁴ it causes a reduction in corrosion resistance; MnS inclusions dissolve anodically and act as an initiation site for pitting corrosion in chloride-containing solutions.⁵⁻¹⁰

Recently, a new free-cutting soft-magnetic stainless steel with Ti₄C₂S₂ inclusions rather than MnS has been developed.¹¹ In the case of conventional free-cutting stainless steels, the corrosion resistance of the Ti₄C₂S₂ inclusions is higher than that of MnS inclusions.¹²,¹³ It has been reported that the absence of anodic dissolution of Ti₄C₂S₂ inclusions in a conventional 18Cr-8Ni austenitic stainless steel can be attributed to the formation of a Ti-enriched oxide layer, and that no pitting initiates at the inclusions as a result.¹⁴ The corrosion resistance of the new soft-magnetic stainless steel with Ti₄C₂S₂ is expected to be high. In order to investigate the applicability of the new soft-magnetic stainless steel with Ti₄C₂S₂ to solenoid valves for water systems of PEFCs, the influence of both Ti₄C₂S₂ and MnS inclusions on the corrosion resistance in pure water environments was determined in this study.

2. Experimental

2.1 Specimen preparation

Table 1 shows the chemical composition of the 18-Cr based soft-magnetic stainless steels used in this study. K-M38 was a conventional soft-magnetic stainless steel with high corrosion resistance. K-M38CS was a new free-cutting soft-magnetic stainless steel with Ti₄C₂S₂ inclusions. Steel A was a conventional free-cutting soft-magnetic stainless steel with MnS inclusions. The chemical composition of Steel A is similar to that of Type 430F. The specimens were cut into disks 10 mm in diameter and 1.6 mm in thickness, heated at 1123 K for 3 h, and then air-cooled. Before the immersion corrosion tests, all the specimens were mechanically ground with 1500-grid SiC paper, and cleaned ultrasonically with acetone. The surface of specimens for electrochemical measurements and SEM observations was polished with diamond paste down to 1.0 µm in grain size and degreased ultrasonically with ethanol.

2.2 Immersion corrosion tests in deionized water at 353 K

50 mL of deionized water (18.0 MΩ cm; ORGANO PURIC-ZII) was put into polypropylene bottles with a volume capacity of 100 mL and heated to 353 K in a constant temperature chamber. Each specimen was then put into a bottle such that one of its horizontal surfaces was in contact with the bottom of the bottle. The bottles were tightly sealed and kept at 353 K for 1, 3, 7, 20, and 40 days. After the immersion tests, the amount of dissolved metallic ions in each bottle was measured by Inductively Coupled Plasma-

Table 1 Chemical composition of specimens (mass%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-M38</td>
<td>0.017</td>
<td>2.20</td>
<td>0.23</td>
<td>0.019</td>
<td>0.002</td>
<td>0.72</td>
<td>18.17</td>
</tr>
<tr>
<td>K-M38CS</td>
<td>0.058</td>
<td>2.16</td>
<td>0.23</td>
<td>0.026</td>
<td>0.057</td>
<td>0.56</td>
<td>18.20</td>
</tr>
<tr>
<td>Steel A</td>
<td>0.017</td>
<td>1.37</td>
<td>0.41</td>
<td>0.017</td>
<td>0.320</td>
<td>0.18</td>
<td>17.38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Mo</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-M38</td>
<td>0.36</td>
<td>1.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>K-M38CS</td>
<td>0.36</td>
<td>1.02</td>
<td>0.22</td>
</tr>
<tr>
<td>Steel A</td>
<td>0.06</td>
<td>0.30</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

*Corresponding author, E-mail: sugawaray@material.tohoku.ac.jp
Mass Spectroscopy (ICP-MS: Agilent ICP-MS7500). Ge and In elements were used as the internal standard for the quantitative determination of metallic elements (except Fe) during the ICP-MS analysis. Hydrogen was introduced as the reaction gas during the analysis of Fe to reduce the interference of ArO$^+$.15)

2.3 Anodic polarization measurements in 0.1 M Na$_2$SO$_4$ solution

Anodic polarization curves of the specimens were measured in 0.1 M Na$_2$SO$_4$ solution at 298 K under an aerated condition. An Ag/AgCl (3.33 M KCl) electrode was used as the reference electrode, and all potentials in this study are referred to this standard. A Pt plate was used as the counter electrode. After the settlement of the corrosion potential, the anodic polarization was started from $-0.1$ V at a potential scan rate of $38 \times 10^{-5}$ V s$^{-1}$. The electrolyte was prepared using the deionized water and analytical grade chemicals. The pH of the electrolyte was 5.9.

2.4 Surface observations of the inclusions

Before and after the immersion tests for 7 days and the polarization measurements, the surface observations were conducted using an optical microscope and a scanning electron microscope (SEM: JEOL JSM-7100F) equipped with an energy-dispersive X-ray spectrometer (EDS: JEOL JED-2300). The accelerating voltage was 20 kV.

3. Results and Discussion

3.1 Composition analysis of the inclusions

Figure 1 shows the optical micrographs of surfaces in K-M38, K-M38CS, and Steel A. In K-M38, the number of inclusions was quite small, and those inclusions were less than 3 µm, while a large number of inclusions a few micrometers in size were distributed widely on the surface of K-M38CS and Steel A. The SEM images and EDS maps of typical inclusions observed in K-M38CS and Steel A are shown in Fig. 2. Ti, C, and S elements were concentrated in the inclusion of K-M38CS, while Mn, Cr, and S elements in that of Steel A. Table 2 summarizes the results of EDS analysis of the points marked in Fig. 2. Assuming carbon contamination is uniform over the surface, the actual C concentration at point 2A can be estimated to be 18.8 at% by subtracting the value at 2B from that at 2A. The relative atomic percentage of Ti : C : S at point 2A was 51 : 26 : 23; that is, the inclusion in Fig. 2(a) was confirmed to be Ti$_4$C$_2$S$_2$. In the same manner, the relative atomic percentage of Mn : Cr : S at point 3A was estimated to be 23 : 33 : 44, indicating that a complex sulfide, (Mn,Cr)S was the dominant inclusion in Steel A.

3.2 Corrosion resistance in deionized water at 353 K

Table 3 shows the concentration of dissolved metallic ions in deionized water after the immersion corrosion test at 353 K for 7 days. The limits of detection (LOD) for Fe, Ti, Mn, Cr, Ni, Mo, and Cu by ICP-MS measurement in this study were 3.1, 0.74, 0.48, 1.8, 0.19, 0.09, and 0.88 mass ppb, respectively. The concentrations of metallic ions dissolved from K-M38 were less than the LOD. Those from K-M38CS were also quite small and lower than the LOD. It must be noted that no Ti dissolution was confirmed in K-M38CS despite the existence of Ti$_4$C$_2$S$_2$ inclusions. In contrast, the concentration of dissolved Mn was significantly high for Steel A, indicating dissolution of (Mn,Cr)S inclusions in the deionized water. The dissolution of Mn was not accompanied by an increase in the concentration of Cr. This is evidence that the Mn component dissolved preferentially from (Mn,Cr)S inclusions into the deionized water.

Figure 3 shows the concentration of dissolved Fe, Ti, and Mn ions as a function of immersion time. As shown in Fig. 3(a), the concentration of dissolved Fe ions were almost always lower than the LOD for all specimens. Figure 3(b) indicates that the concentration of dissolved Ti ions was lower than the LOD for all the specimens immersed over 40 days. On the other hand, the concentration of Mn ions dissolved from Steel A increased rapidly with immersion time up to 20 days, as shown in Fig. 3(c), suggesting that the (Mn,Cr)S inclusions dissolved into the deionized water. In addition, even though the solution contained no chloride, after 40 days a ring-shaped rust region with a diameter of

![Fig. 1 Optical micrographs of surfaces of (a) K-M38, (b) K-M38CS, and (c) Steel A.](image-url)
1.5 mm was observed on the surface of Steel A attached to the bottom of the test bottle, as shown in Fig. 4. The rust region was thought to be formed by the deposition of Fe oxides or oxyhydroxides, since the concentration of dissolved Fe ions for Steel A was as low as the LOD. The inset in Fig. 3(c) shows that the concentration of Mn ions for K-M38 was always around the LOD and that, in the case of K-M38CS, it initially increased with immersion time, but did not exceed the LOQ.

The results of the immersion test in deionized water reveal negligible dissolution of the Ti$_4$C$_2$S$_2$ inclusions in K-M38CS in pure water, rendering them harmless, while the (Mn,Cr)S inclusions in Steel A have a detrimental effect in that they pollute the pure water. The corrosion resistance of K-M38CS in pure water is higher than that of Steel A and comparable to that of K-M38.

3.3 Anodic polarization curves in 0.1 M Na$_2$SO$_4$ solution

In order to determine the electrochemical properties of specimens in a neutral solution, the anodic polarization curves in a 0.1 M Na$_2$SO$_4$ solution at 298 K were measured, and are shown in Fig. 5. The polarization curve of K-M38CS was approximately the same as that of K-M38 and exhibited a passivity region in the potential range of $-0.1$ to $0.8$ V, indicating that Ti$_4$C$_2$S$_2$ inclusions have no detrimental effect on the electrochemical stability of the 18-Cr stainless steel. In contrast, a gradual current increase was observed at potentials above $0.2$ V in the polarization curve of Steel A. The increase in the anodic current was attributed to the anodic dissolution of MnS inclusions and the subsequent anodic dissolution of steel matrix around the inclusions by sulfur species dissolved from the inclusions. Figure 6 shows the optical micrographs of K-M38CS and Steel A after polarization. The interference colors observed on the Ti$_4$C$_2$S$_2$ inclusions of K-M38CS suggest the growth of oxide film. The oxide film should have inhibited the dissolution of the inclusions under...
anodic polarization. The black discoloration was observed at some of the (Mn,Cr)S inclusions in Steel A after the anodic polarization to 0.5 V, revealing the dissolution of the (Mn,Cr)S inclusions.

3.4 Thermodynamic discussion on the stability of sulfide inclusions

In order to discuss the thermodynamic stability of inclusions in aqueous solutions, the potential-pH diagrams for Ti$_4$C$_2$S$_2$-H$_2$O, MnS-H$_2$O, and CrS-H$_2$O were calculated. The standard chemical potentials of species, with the exception of Ti$_4$C$_2$S$_2$, Ti$^{2+}$, and Ti$^{3+}$, were derived from the HSC thermo-chemical database. The standard chemical potentials of species, with the exception of Ti$_4$C$_2$S$_2$, Ti$^{2+}$, and Ti$^{3+}$, were derived from the HSC thermo-chemical database. Those of Ti$_4$C$_2$S$_2$, Ti$^{2+}$, and Ti$^{3+}$ were obtained from the literature. The concentration of soluble species was set to $1 \times 10^{-5}$ mol kg$^{-1}$ (H$_2$O). The partial pressure of H$_2$ and O$_2$ for H$^+/H_2$ and O$_2$/OH$^-$ equilibria was set to 0.1013 MPa. For all the inclusions, H$_2$S$_2$O$_3$, HS$^-$, and S$^{2-}$ were assumed to be the dissolved species of S at higher potentials.

Figure 7 shows the potential-pH diagrams for the Ti$_4$C$_2$S$_2$-H$_2$O system at 298 K. The stability ranges of Ti-, C-, and S-related species are shown in the three diagrams. Ti$_4$C$_2$S$_2$ is stable at lower potentials over the pH range examined. Assuming that the corrosion potential of K-M38CS in neutral solutions is $-0.05$ V and the pH of the deionized water in contact with natural air is 5.6, TiO$_2$ was found to have formed on Ti$_4$C$_2$S$_2$ inclusions, and H$_2$CO$_3$ and S$_2$O$_3^{2-}$ were expected to have been produced as the dissolved species of C and S in the pure water. These TiO$_2$ films on the surface of Ti$_4$C$_2$S$_2$ inclusions in K-M38CS are believed to have inhibited the dissolution of Ti ions in the immersion corrosion test, as shown in Fig. 3(b). Since the stable region of TiO$_2$ covers the passivity region of 18Cr stainless steel ($-0.05$ to 0.8 V), the TiO$_2$ formation on Ti$_4$C$_2$S$_2$ surface should be responsible for the high corrosion resistance of K-M38CS in the anodic polarization.
polarization measurement in Fig. 5 and the interference colors of the inclusions in Fig. 6.

Figure 8 shows the potential-pH diagrams for the MnS-H2O system at 298 K. MnS is not stable in neutral solutions. Although Mn-oxide layers are formed on the MnS inclusion surface in the as-polished condition, both Mn oxide and hydroxide (MnO2, Mn2O3, Mn3O4, and Mn(OH)2) are unstable at the corrosion potential of −0.05 V in the deionized water. Thereby, MnS and native Mn-oxide films are expected to dissolve as Mn2+ and S2O32− in the deionized water, as shown in Fig. 3(c). Figure 9 shows the potential-pH diagrams for CrS-H2O system at 298 K. The stable region of CrS surrounded by a dotted line frame appeared only by assuming the absence of Cr2O3, and the region disappeared when Cr2O3 was taken into account in the calculation. The immersion test condition in the deionized water is located in the stable region of Cr2O3. It appears that the Cr-oxide films which formed on the surface of CrS remained after the selective dissolution of Mn from (Mn,Cr)S, and suppressed the dissolution of Cr in the immersion corrosion test of Steel A, as shown in Table 3.

The SEM images and EDS maps of the inclusions observed in K-M38CS and Steel A after the immersion tests for 7 days in the deionized water are shown in Fig. 10. Many bright spots were observed on the surface of steel matrixes of K-M38CS and Steel A. The spots were thought to be Fe oxides according to the previous study. Whereas the inclusion in K-M38CS did not dissolve, the inclusion in Steel A dissolved partially during the 7-day immersion in the deionized water. The EDS maps show that Ti-containing and Cr-containing oxides were formed on the inclusions in K-M38CS and Steel A, respectively. These results suggest that the high corrosion resistance of K-M38CS in pure water is attributed to the formation of TiO2 on Ti4C2S2 inclusions, and that the selective dissolution of Mn and the composition change to Cr2O3 proceeded on (Mn,Cr)S inclusions in Steel A as expected in accordance with the thermodynamic...
discussion. In addition, it is suggested that when (Mn,Cr)S inclusion is covered with a Cr$_2$O$_3$ film, the dissolution of the inclusion is suppressed, as indicated by the plateau region in the Mn concentration vs. time curve in Fig. 3(c).

In summary, K-M38CS has high corrosion resistance under the free immersion condition in pure water because of TiO$_2$ formation on the surface of Ti$_4$C$_2$S$_2$ inclusions. Besides this, K-M38CS has high electrochemical stability at high potentials comparable to that of K-M38, which is a conventional soft-magnetic stainless steel with high corrosion resistance. This is evidence that K-M38CS will not have a detrimental effect on the quality of pure water and is a promising material for use in the magnetic core of solenoid valves for pure water flow systems.

4. Conclusions

Immersion corrosion tests in deionized water and anodic polarization measurements in neutral Na$_2$SO$_4$ solution were carried out to clarify the influence of Ti$_4$C$_2$S$_2$ and (Mn,Cr)S inclusions on the corrosion resistance of free-cutting soft-magnetic stainless steels in pure water. The following conclusions are drawn:

(1) In the immersion corrosion tests in deionized water at 353 K, the negligible dissolution of metallic ions from the soft-magnetic stainless steel with Ti$_4$C$_2$S$_2$ inclusions is evidence of their high corrosion resistance. On the other hand, (Mn,Cr)S inclusions in steel suffered from the selective dissolution of Mn, followed by the pure water pollution.
The anodic polarization curve of the soft-magnetic stainless steel with Ti$_4$C$_2$S$_2$ inclusions exhibits a passivity region, typical of 18-Cr stainless steels, in 0.1 M Na$_2$SO$_4$. That of the steel with (Mn,Cr)S inclusions shows an increase in anodic current at potentials above 0.2 V due to the anodic dissolution of the MnS inclusions.

TiO$_2$, Mn$^{2+}$, and Cr$_2$O$_3$ are found to be thermodynamically stable species in pure water for Ti$_4$C$_2$S$_2$, MnS, and CrS inclusions respectively. This explains the high corrosion resistance of Ti$_4$C$_2$S$_2$ inclusions and the selective dissolution of Mn from (Mn,Cr)S inclusions in pure water.

REFERENCES