Corrosion Mitigation of Ferritic Steels in HF-Containing FLiNaK by Titanium Sacrificial Anodes

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Sacrificial anode methods are focused upon for suppression of the tritium fluoride corrosion of structural materials in molten salt blankets in fusion reactors. Stainless Steel 430 (SS430) is immersed into hydrogen fluoride (HF)-containing LiF-NaF-KF (FLiNaK) for 6 hours at 773 K with Ti. It has been found that (1) the presence of Ti suppresses the corrosion of SS430 by HF. Further, by the electrical connection between SS430 and Ti, (2) Ti can sufficiently lower the potential of SS430, (3) the weight loss of Ti increases, and (4) the grain boundary corrosion of SS430 by Cr dissolution is mitigated. The applicability of sacrificial anode methods to molten salt blankets has been established.

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1. Introduction

In the design of a helical fusion reactor, FFHR, better sustainable liquid blankets have been investigated [1]. Li-containing molten fluoride salts (FLiBe, FLiNaBe, FLiNaK, etc.) are stable in the air, and can be candidates for certain liquid coolants through the blanket.

In order to extend the lifespan of reactors, some corrosion experiments on structural materials in molten fluoride salts have been conducted [2]. In the blanket, tritium fluoride (TF) produced by high energy neutrons is a key issue because TF corrodes structural materials (M) in the following chemical reaction,

\[ \text{M} + z\text{TF} \rightleftharpoons \text{MF}_z + \frac{z}{2}\text{T}_2, \] (1)

where \( z \) is the valence of the structural metal ion. Redox control [3–6] and purification [7] have been methods for decreasing TF concentration in the molten fluoride salt.

In this experiment, sacrificial anode methods are focused upon. These methods can be readily used in the current blanket design. This is because only the metallic plates or blocks which have negative potential compared to structural materials and which are attached to the inner walls along flow paths are required. These plates or blocks serve as substitutes for the corrosion of the structural materials, and they are called “sacrificial anodes.”

Unfortunately, sacrificial anode methods have not yet been performed using molten fluoride salts, which are likely to be used in the blanket with dissolved TF. In this experiment, the applicability of sacrificial anode methods in FLiNaK containing hydrogen fluoride (HF), a simulant of TF, is investigated. The results of this study will also be useful for understanding methods of mixing Ti powder [6], which are based on similar thermochemical mechanisms.

2. Experimental

The apparatus for this experiment is modified from the apparatus for tests of the sacrificial effect of Ti powder mixed into FLiNaK on the suppression of the HF corrosion of ferritic steels [6]. Figure 1 shows the schematic diagram of the apparatus. Compared to the former apparatus, the gas injection tube is also insulated from the crucible by PTFE. The potential difference between the sample and Monel 400 can be measured.

Before each sample is immersed, 30 mL of FLiNaK (LiF-NaF-KF: 46.5-11.5-42.0 mol%, melting point 727 K) made from LiF, NaF, and KF powder (Kanto Chemical

Fig. 1 Schematic diagram of the apparatus. The potential of samples can be measured vs. the Monel 400 gas injection tube.
Table 1 Standard electrode potential ($E^\circ$) [9]. Ti can make fluoride complex ions. $E^\circ$ without any reference is calculated by the $E^\circ$ of other half-reactions.

| Half-reaction               | $E^\circ$ | Ref. |
|-----------------------------|-----------|------|
| Ti$^{2+} + 2e^- \rightleftharpoons Ti$ | -1.63     | [8]  |
| Ti$^{3+} + 3e^- \rightleftharpoons Ti$ | -1.208    | [8]  |
| [TiF$_4$]$^{2-} + 4e^- \rightleftharpoons Ti + 6F^-$ | -1.191    | [8]  |
| [TiF$_6$]$^{2-} + e^- \rightleftharpoons Ti$^{2+} + 6F^-$ | -1.137    | [8]  |
| Cr$^{2+} + 2e^- \rightleftharpoons Cr$ | -0.90     | [8]  |
| TiF$_4$ + 4e$^- \rightleftharpoons Ti + 4F^-$ | -0.89     | [8]  |
| [TiF$_6$]$^{2-} + 2e^- \rightleftharpoons Ti$^{4+} + 6F^-$ | -0.754    | [8]  |
| Fe$^{2+} + 2e^- \rightleftharpoons Fe$ | -0.44     | [8]  |
| Ti$^{3+} + e^- \rightleftharpoons Ti$^{2+}$ | -0.369    | [8]  |
| 2H$^+ + 2e^- \rightleftharpoons H_2$ | 0         | [8]  |

Co.), the purities of which are 98.0%, 99.0%, and 99.0%, respectively, is synthesized under the Ar atmosphere with 20 ppm or less of H$_2$O to reduce impurities.

Stainless steel 430 (SS430, Fe-17Cr), the Cr content of which is larger than that of structural materials such as RAFM steels, is used in this experiment in order to clearly observe the corrosion mitigated by sacrificial anode methods. This is because corrosion of steels in molten fluoride salts is mainly caused by depletion of Cr from the steels [8], i.e., a steel with large Cr content is easily corroded. A sample is 40 $\times$ 10 mm$^2$ of a rectangle cut out from a single SS430 plate containing 16 - 18 wt% of Cr (Nilaco Co.), the thickness of which is 0.30 mm.

Titanium (Ti) is used as the metal of the sacrificial anodes in this experiment. Table 1 shows standard electrode potential ($E^\circ$) [9], which means Ti has more negative potential than the ingredients of SS430 have. 40 $\times$ 10 mm$^2$ of a Ti rectangle is cut out from a single Ti plate (Nilaco Co.), the thickness and purity of which are 0.20 mm and 99.5%, respectively.

![Fig. 2 Three samples used in this experiment: (A) Only SS430 is used, (B) SS430 and Ti are insulated by Al$_2$O$_3$, and (C) SS430 and Ti are electrically connected.](image)

H$_2$ + NiF$_2$ $\rightarrow$ Ni + 2HF.  

(2)

The production rate of HF is calculated as 4 $\times$ 10$^{-7}$ mol/s, the value per unit volume of which is about 1,000 times higher than that of TF estimated in the FFHR blanket.

The immersion is maintained for 6 hours. After the immersion, the sample, the gas injection tube, and the thermocouple are pulled up, and the apparatus is cooled down to the room temperature in several hours. The sample is subjected to ultrasonic cleaning with ion exchanged water for 30 minutes after having been removed from the apparatus.

A part of the sample immersed into the FLiNaK is cut out, and its weight ($M_1$ [g]) and side lengths of the rectangle ($a_1$, $b_1$ [mm]) are measured. The corrosion weight loss of the sample ($W$ [mg/cm$^2$]) is derived by the following equation,

$$W = \frac{M_0 a_0 b_0}{2a_1 b_1} - M_1 \times 10^5.$$  

(3)

Note that the area of the sample is regarded as only its front and back rectangles, ignoring its side faces. The corrosion rate of the sample ($v$ [mm/year]) is calculated from the following equation, assuming entire surface corrosion,

$$v = \frac{24 \times 365 \times W}{6.0 \times \rho} \times 10^{-2},$$  

(4)

where the density ($\rho$ [g/cm$^3$]) is set to 7.7 for SS430 and 4.5 for Ti.

Some surfaces of the samples are observed by Scanning Electronscope Microscopy (SEM; 3,000x, 10,000x or 30,000x magnification) and analyzed by Energy Dispersive X-ray spectrometry (EDX).
3. Results and Discussion

Figure 3 shows the weight loss and rates of the corrosion of SS430. The left Y-axis is the corrosion weight loss obtained from Eq. (3), and the right Y-axis is the corrosion rates obtained from Eq. (4). The weight loss of (A) is the same in the Ref. [6]. The weight loss of (B) and (C) decreases compared to (A). It has been found that the corrosion of SS430 by HF can be suppressed by the presence of Ti. One of the possible reasons is the faster corrosion rates of Ti than SS430.

Figure 4 shows the weight loss and rates of the corrosion of Ti. The Y-axes are the same as in Fig. 3. The weight loss of (C) increases compared to (B). Because the corrosion rate of (C) differs from that of (B), the diffusion of HF is not rate-determining. It is considered that reactions on Ti surfaces are rate-determining in this experiment by the following reason. Table 2 shows the measured potential and overvoltage of SS430 or Ti with respect to Monel 400 after the HF injection. The electric potential of both SS430 and Ti is changed by the electric connection, leading to overvoltage. The relationship between dissolution rates and overvoltage can be described as the following Butler-Volmer equation,

\[
i = i_0 \left( e^{\eta \pi - \eta \pi} - e^{\eta \pi - \eta \pi} \right),
\]

where \(i\) is the current density for metal dissolution (the values are positive when metal dissolves), \(i_0\) is exchange current density, \(\eta\) is overpotential, and \(B_A\) and \(B_C\) are constant. According to Table 2 and Eq. (5), the following can be predicted. In the case of SS430, the overvoltage is sufficiently negative so that the reduction rate (second term) is faster than the dissolution rate (first term), leading to the mitigation of the corrosion. Likewise, in the case of Ti, the overvoltage is positive so that the dissolution rate is faster, leading to the acceleration of the corrosion.

Figure 5 shows surface images of each sample and a cross sectional image of (C). In (A), surfaces are completely peeled off compared to surfaces of (Z). According to EDX, the ratio of Fe and Cr content of (A) is constant in grains and grain boundaries, and the ratio is 17 wt% Cr equal to the ratio of SS430 before the immersion. In addition, the corrosion products of (A) consist of Fe, Cr, and F (possible compounds are FeF2 or CrF2). It is considered that the entire surface corrosion by HF occurs on surfaces of (A), so that the rate of its corrosion is faster than that of sensitization around grain boundaries. On surfaces of (B), grain boundaries are selectively corroded. According to EDX, the proportion of Cr increases around grain boundaries compared to the inside of grains. The Cr content in grains decreases to 11 wt%. It is considered that Cr is selectively diffused into grain boundaries, sensitization occurs, and the grain boundaries are corroded. Other results also show that corrosion rates in molten fluoride salts tend to increase as Cr content increases [10]. One of the possible mechanisms is the formation of local cells between Fe rich layers and Cr rich layers [7, 8, 11]. On surfaces of (C), grain boundaries are not selectively corroded, and the surfaces are close to surfaces of (Z). According to EDX, the ratio of Fe and Cr content of (C) was 16 wt% in both grain boundaries and the inside of grains. It has been found that the grain boundary corrosion of SS430 can be suppressed by the electrical connection with Ti.

|          | B     | C     | Overpotential |
|----------|-------|-------|---------------|
| SS430    | -0.27 V | -1.90 V | -0.82 V |
| Ti       | -1.19 V | -1.09 V | +0.10 V |

Table 2 Measured potential for each sample vs. Monel 400. Electrical connection provides overpotential.
From the above, it has been found that the simultaneous immersion of SS430 and electrically connected Ti sacrificial anodes can mitigate both the entire surface corrosion of SS430 by HF and the grain boundary corrosion of SS430 by Cr dissolution.

Ti precipitates are found on a part of the surfaces of (C), the size of which is about 1 μm in width and about 1 μm of height by the cross-sectional EDX. The EDX analysis of cross sections of (B) shows that no Ti precipitate are found on its surfaces. In other words, Ti precipitates are observed only when SS430 and Ti are electrically connected each other. In this experiment, Ti is in the form of plate, and the following can be explained. Metal Ti is oxidized to Ti ions and dissolved into FLiNaK, and thereafter, the Ti ions are reduced to metal Ti on the surface of SS430. Judging from the standard electrode potential on Table 1, possible reactions on Ti surfaces are as follows,

\[
\begin{align*}
\text{Ti} & \rightarrow \text{Ti}^{3+} + 3e^{-}, \\
\text{Ti}^{3+} + 6\text{F}^{-} & \rightarrow [\text{TiF}_6]^{2-} + e^{-}, \\
2\text{H}^{+} + 2e^{-} & \rightarrow \text{H}_2.
\end{align*}
\]  

(6)

And those on SS430 surfaces are as follows,

\[
\begin{align*}
[\text{TiF}_6]^{2-} + 4e^{-} & \rightarrow \text{Ti} + 6\text{F}^{-}, \\
2\text{H}^{+} + 2e^{-} & \rightarrow \text{H}_2.
\end{align*}
\]  

(7)

These Ti impurities may affect the properties of molten fluoride salts. Further investigation of continuous recovery methods from TiF₆⁻ to Ti (e.g., the opposite of Eq. (6) or (7)) is important.

4. Conclusions

In order to establish the applicability of sacrificial anode methods to molten salt blankets, corrosion experiments are conducted to immerse a structural material (SS430) electrically connected with Ti for 6 hours in HF-containing FLiNaK. The following are our findings.

(1) The presence of Ti can suppress the corrosion of SS430 by HF.

By the electrical connection between SS430 and Ti,

(2) Ti can sufficiently lower the potential of SS430,

(3) the weight loss of Ti increases, and

(4) the grain boundary corrosion of SS430 by Cr dissolution is mitigated.

The corrosion of SS430 by HF and the grain boundary corrosion of SS430 by Cr dissolution are simultaneously mitigated by Ti sacrificial anodes. The applicability of sacrificial anode methods to molten salt blankets has been established.

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