Comparison of passivation behavior of SS316L with that of SS304 in tritiated water solution

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ABSTRACT

The effects of tritium on the passivation behavior and passive layer formed in tritiated water circumstance for SS316L were investigated by means of an anodic polarization measurement technique and X-ray photoelectron spectroscopy, respectively. The results were compared with those for SS304, since it was predicted from a model of the tritium effects on corrosion suggested in the previous studies that SS316L would be less affective to tritiated water circumstance than SS304. As the results, the passivation inhibition effect of tritium could not be observed for SS316L, while it was observed for SS304 and the other researched materials so far, as predicted. However, the thickness of the passive layer and the boundary between the passive layer and bulk of SS316L were found affected by tritium; thickened and gradated, respectively. From these results, it was concluded that SS316L would be more sustainable in tritiated water circumstance than SS304, although the corrosion of SS316L would be more or less enhanced in tritiated water circumstance.

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1. Introduction

In fusion reactors, much more tritium than ever before will be used, generated and processed, i.e. even an experimental reactor of ITER requires 15–18 kg of tritium as a total amount [1]. Therefore, it is necessary to consider the tritium safety much more than ever before. Since metal has little radiation susceptibility in general and tritiated water has been thought to be rather stable, the studies about the durability of metal materials in tritiated water has been regarded as less serious. On the other hand, some radiochemical effects, such as enhancement of corrosion, production of unexpected corrosion products, and so on, have been predicted to be induced in tritiated water since the water circumstances would be changed by tritiation of water due to radioysis of water, generation of 3He and hydrated electron, and so on. Indeed, it was reported so far that pH was changed in tritiated water [2–4]. From this viewpoint some studies about the corrosion behavior of tritiated water has been reported [5]. However, it is thought to be insufficient to understand the corrosion behavior of metal materials in tritiated water, since the reports seem not to be systematic but sporadic.

In the previous studies, the effects of tritium on passivation behavior of SS304 in 1 N sulfuric acid solution were studied by means of an anodic polarization method, one of the electrochemical techniques. As the results, it was indicated that there would be passivation inhibitory effect in tritiated water, resulting in the enhancement of corrosion. Additionally, the changes of open-circuit potential over time after cathodic treatment were measured to observe the self-passivation behavior of SS304. As the results, there found to be two steps of passivation and tritium affected both steps [6–8]. Additionally, the anodic polarization behavior of both chromium and F82H steel were measured with changing tritium and dissolved oxygen concentrations as in the above studies in 0.01 N sulfuric acid and 1 N sodium sulfate solutions, respectively. The results indicated that the passivation inhibitory effect of tritium was also observed for both samples [9,10]. In the present study, the passivation behavior of SS316L was studied in tritiated solution by means of an anodic polarization method and compared with SS304.

2. Model

A model of the passivation behavior of SS304 and the effect of tritium on it is described in Fig. 1, which is based on the previous experimental results [6–8]. In this model, the passivation of SS304 consists of two steps and concerns three (pseudo-)equilibriums named pre-passive, primary-passive and fully-passive states. At the
Table 1

<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>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS316L</td>
<td>≦0.030</td>
<td>≦1.00</td>
<td>≦2.00</td>
<td>≦0.045</td>
<td>≦0.030</td>
<td>12−15</td>
<td>16−18</td>
<td>2−3</td>
</tr>
<tr>
<td>SS304</td>
<td>≦0.08</td>
<td>≦1.00</td>
<td>≦2.00</td>
<td>≦0.045</td>
<td>≦0.030</td>
<td>8−10.5</td>
<td>18−20</td>
<td>—</td>
</tr>
</tbody>
</table>

manufactured by Solartron Analytical of AMETEK Inc. was employed as the equipment for electrochemical experiments.

The anodic polarization measurements were performed as following sequences; (i) polish the surface of sample electrode, (ii) set the electrochemical cell described above with 11 cm$^3$ of electrolyte of 1 N sulfuric acid solution, (iii) flow the purge gas for 60 min. to remove the dissolved gases derived from air and to equilibrate dissolved oxygen with purge gas. (iv) apply 0.9 V (SHE) for 10 min. called ‘cathodic treatment’ to remove oxide layers on surface, (v) keep open circuit for 1 h to observe the self-passivation, and (vi) sweep the potential from open circuit potential to 1.25 V (SHE) and sweep in the state of sample become trans-passive. It should be noted that no additional heat-treatments were applied onto the samples since the PEEK resin as insulator cannot be heated approximately 600 K and higher, and the surface passive layer was electrically removed as experimental pre-treatment.

The dependence of the anodic polarization behavior of SS316L on tritium concentration, $[T]$, and $[DO]$ were measured. In the present experiments, the range of $[DO]$ was from approximately 0 ($<10^{-3}$) to 43 g-O$_2$ m$^{-3}$ and the range of $[T]$ was from $<0.5$ Bq cm$^{-3}$ (without additional tritium) to 10 MBq cm$^{-3}$. Hereafter, the conditions with and without tritium are called ‘Hot’ and ‘Cold’, respectively. It should be noted that dissolved oxygen enhance the generation of highly oxidative radiolysis products which would be the key substances of the passivation inhibitory effect of tritium as indicated in Model section, although it generally works as a help of the passivation of stainless steels. The anodic polarization measurements were performed in the same manner as the above experiment.

Additionally, the passive layers for SS316L and SS304 were analyzed by means of X-ray photoelectron spectroscopy (XPS). The XPS apparatus used in the present study is VersaProbell design and fabricated by ULVAC-PHI Inc. For this measurement, the self-passivation treatments for them were performed with dissolved oxygen condition. The other conditions were the same as the anodic polarization measurements except for open circuit time (sequence (v)), which was changed from 1 to 4 hours. After the anodic polarization treatment, the samples were rinsed in ultrapure water to be detritiated and to remove surface sulfuric acid and dried in vacuum.

4. Results and discussion

The anodic polarization curves of SS316L obtained under Cold and Hot, with and without dissolved oxygen conditions as shown in Fig. 2. It is indicated that a passivation peak is observed in DO-removed for both of Cold and Hot conditions as in the previous studies. On the other hand in the solution with dissolved oxygen, the self-passivation due to dissolved oxygen is observed for both of Cold and Hot conditions and no obvious tritium effects could be observed such as passivation inhibitory effects. As a comparison, the anodic polarization curves for SS304 obtained under similar experimental condition except for $[T]$ (10 and 230 MBq cm$^{-3}$ for SS316L and SS304, respectively) of the present study is shown in Fig. 3, where obvious tritium effects can be seen; passivation inhibitory effect [6]. It should be noted that the passivation inhibitory effect could be observed in the solution with not only 230 MBq cm$^{-3}$ but also rather lower [T]. It is clarified from these

Fig. 1. A model of passivation mechanism of SS304 and assumed effects on it.

3. Materials and methods

Stainless steels of SS316L and SS304 used in the present study are fabricated so as to accord the Japan Industrial Standard (JIS G 4305) of which composition ratio is listed in Table 1 [12]. A cylindrical electrode sample made of SS316L used in the present study was 3 mm in diameter covered by poly-ether-ether-ketone (PEEK) resin except for the electrode surface (detail of this electrode and electrochemical cell can be found in [6]). To avoid the air contamination and for the radiological safety, the air-tight electrochemical cell purchased from ALS Co., Ltd. was used. The counter electrode was sheathed to prevent from the dispersion of O$_2$ generated during cathodic treatments. The model 1287 potentiostat/galvanostat

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results that the passivation of SS316L would be less affected in tritiated water than that of SS304.

The results of depth measurements of passive layers for SS316L and SS304 are shown in Figs. 4 and 5, respectively. For SS316L, the passive layer formed in Hot condition becomes thicker than that in Cold condition. Additionally, the interface between the passive layer and the bulk of SS316L formed in Hot condition looks less clear than that in Cold condition. However, no significant difference in the chemical composition of passive layer of SS316L could be observed. These results would be induced by pitting corrosion due to local further oxidation of Cr in passive layer, which would be induced by highly oxidative radiolysis products such as hydroxyl radicals, superoxide radicals and so on. Indeed, it was reported that pitting corrosion of SS316 could be observed in high concentration tritiated water [3,4]. Similar results as the effects of tritium could be observed for SS304.

It is suggested that the difference of the effects of tritium on the passivation between SS316L and SS304 would be mainly induced by Mo additive. Elution of chromium in passive and passivating layer by further oxidation induced by highly oxidative radiolysis products is predicted as a key reaction of passivation inhibitory effect as described in the above model. It has been reported for SS316L that Cr-based passive layer would be protected by Mo in Cr-corrosive circumstance [11]. As the result, SS316L is passivated with the help of dissolved oxygen whether the solution is tritiated or not, while the passivation of SS304 is inhibited in tritiated water solution with dissolved oxygen which help the generation of highly oxidative radiolysis products. Therefore, it could be concluded that SS316L would be less susceptible to tritiated water circumstance than SS304 as predicted, although the corrosion of SS316L would be more or less enhanced in tritiated water circumstance. Additionally, it is indicated that the additives which enhance the protection against the corrosion in Cr-corrosive circumstances would be effective on the anticorrosion in tritiated water circumstances, which may lead and help the development of future fusion materials.

5. Summary

The effects of tritium on the passivation behavior and the passive layer formed in the tritiated water circumstance for SS316L were investigated by anodic polarization measurements and XPS, respectively, and compared with those for SS304. The experimental results can be summarized as followings;

(1) Passivation inhibitory effect induced by tritium could not be observed for SS316L, while they were observed for SS304 and the others researched materials, so far.
(2) The thickness of the passive layer and the boundary between the passive layer and the bulk of SS316L were affected in tritiated water circumstance as becoming thicker and ambiguous, respectively. These results would be induced by pitting corrosion due to local further oxidation of Cr in passive
layer induced by highly oxidative radiolysis products such as hydroxyl radicals, superoxide radicals and so on.

From these results, it was concluded that SS316L would be more sustainable against tritiated water circumstance than SS304 as predicted from the model, although the corrosion of SS316L would be more or less enhanced in tritiated water circumstance.

References