Preliminary Study on Electrochemical Corrosion Behavior of F82H Steel

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A study on the corrosion behavior of F82H steel and the effects of tritium on it using the electrochemical techniques of Tafel extrapolation and anodic polarization has just been started and the preliminary results without the use of tritiated water were introduced in the present report. Using Tafel extrapolation, the corrosion rate of F82H steel in 5w% H_2SO_4/H_2O could be estimated as approximately 2 cm year^{-1}, which was approximately 2 orders of magnitude larger than that of SUS 304. In anodic polarization curve, the regions of passivation, passive layer sustention and transpassivation could be observed under the same circumstance as Tafel extrapolation experiment and the quantum of electricity for F82H steel to passivate was approximately 100 C cm^{-2}, which was approximately 3 orders of magnitude larger than that of SUS304. Therefore it was expected that the corrosion rate of F82H steel could far higher than that of SUS304, even though only a preliminary experiments under the highly corrosive circumstance has been performed.

Keywords: tritium, radiochemistry, electrochemistry, corrosion

I. Introduction

In fusion reactors, much more tritium than ever before will be used, generated and processed. Therefore, the establishment of the tritium confinement technique is one of the most important issues to realize fusion reactors, and wide-ranging studies have been performed to understand the behavior of tritium, especially in functional materials for fusion reactors. In almost all of these studies, however, tritium was treated only as one of hydrogen isotopes, although some radiochemical effects on the materials should be also taken into consideration, especially on the boundary between a material and tritiated water [1]. The effects of tritiated water on the materials have not been well-understood, while in some facilities, the inner surface of piping or vessel which had contact with tritiated water corroded more than expected, indicating that change in water condition and/or local equilibrium collapse could be induced by tritiated water. Indeed, it has been reported that pH changes in highly concentrated tritiated water [1]. Therefore in tritiated water, such exotic corrosion behavior due to tritium and/or radiolysis products are expected as enhancement of corrosion, distraction of passive layer, local corrosion including pitting corrosion, and so on.

On the other hand, F82H steel, one of the reduced activation ferritic/martensitic steels was developed as one of the most promising candidate structural materials for fusion reactor, and therefore, will be used for the structural material of water cooled solid breeder (WCSB) test blanket module (TBM) for ITER [2-6]. It is imperative to clarify the effects of tritiated water on corrosion of F82H steel, since the data on F82H steel is limited and rupture of WCSB TBM will bring not only destruction of tritium confinement but also serious accidents such as explosion due to hydrogen generated by the reaction between neutron multiplier of beryllium

and cooling water.

Therefore, the study on the effects of tritium on the corrosion behavior of F82H steel has just been started using electrochemical technique. In this report, preliminary study about the electrochemical corrosion behavior of F82H steel in corrosive water circumstance is introduced.

II. Theory

In the present study, two electrochemical experiments of Tafel extrapolation and anode polarization were employed to obtain the corrosion current which derives the corrosion rate, and to observe the passivation behavior, respectively.

II. A. Tafel extrapolation [7]

It is well known that the electrochemistry of corroding metals involves two or more half cell reactions as followings;

$$M \rightarrow M^{n+} + ne^- \quad (1)$$
$$2H^+ + 2e^- \rightarrow H_2, \quad (2)$$
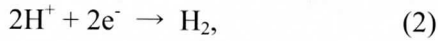
where n means the valence number of half cell reaction, and M is metal or corroding material. These half cell reactions are expected as the most probable electrochemical reactions on the sample surface in the present experiment. Since the main constituent elements of the samples of the present study were Fe, Cr and Ni, M was each of them and n could be assumed as 2. For the dissolution of M of F82H steel in acid solutions, the anodic rate (indicating the corrosion of the sample) and the cathodic rate (indicating the generation of H_2) should be the same at the equilibrium potential. Therefore, corrosion current, I_{corr}, resulting in corrosion rate, could be estimated at equilibrium potential (the same as corrosion potential, E_{corr}) by applying Butler-Volmer equation as following;

$$I = I_{corr}\left\{ e^{\frac{\alpha n F \eta}{RT}} - e^{-\frac{(1-\alpha)nF\eta}{RT}} \right\} \quad (3)$$

where I, α, F, R and T mean the current, the transfer coefficient (usually 0.5), Faraday constant, gas constant and absolute temperature, respectively. η is called overpotential that can expressed as following;

$$\eta = E - E_{corr} \quad (4)$$

where E means applied potential. When the rate of either reaction is negligible, Eq. (4) gives:

$$E = a + b \log I \quad (5)$$

where a and b are constants. This equation is called Tafel's law, and the basis of the Tafel extrapolation is to extrapolate Eq. (5) toward E_{corr} so as to obtain I_{corr}. The intersection point of Eq. (5) for both cathodic and anodic reactions should be theoretically on the E_{corr}. The corrosion rate could be estimated using I_{corr}.

II. B. Anodic polarization

It is well known that the anodic polarization is one of the best methods to elucidate such electrochemical behavior as dissolution, passivation and transpassivation [8,9]. In an anodic polarization experiment, the applied potential was swept from equilibrium potential (usually E_{corr}) toward anodic side up to transpassivation region with a certain sweep rate. An anodic polarization spectrum for a stainless steel or the other passivating metal under 5wt.% sulfuric acid solution usually consists of three parts; (i) passivating region, (ii) passive layer sustention region and (iii) transpassivation region. If the passivation is affected by tritium, it will appear in the passivating region, and if the passive layer is affected, it will be observed in the passive layer sustention region.

III. Experimental

III. A. Sample preparation

The materials used in the present study were a disc of F82H steel with 8 mm in diameter and a sheet of SUS304 with its size of 10×10 mm^2 as a reference. Both of samples were insulated using epoxy resin except for measurement surface, polished using 1 μm alumina polisher and ultrasonically cleaned in pure water for 30 min sequentially.

III. B. Experimental procedure

The sample was set in the cell for electrochemical measurement as working electrode with the other accessories of counter electrode, reference electrode, and gas purge lines as indicated in Fig. 1. The solvent of 5w% H_2SO_4 aqueous solution was poured to soak the electrodes. After the cell was made airtight, Ar gas was purged for 1 h to remove the dissolved oxygen. Cathode treatment at 0.7 V vs. reference electrode was performed for 20 min and thereafter the electric circuit was kept opened for 40 min to reach equilibrium potential (corrosion potential). Two types of electrochemical measurements were performed: one is Tafel sweeping from corrosion potential to ± 0.2 V with the sweeping rate of 1 mV s^{-1} to obtain the corrosion rate and the other is anodic
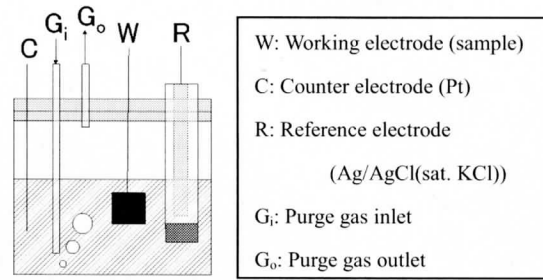

Fig. 1 Conceptual diagram of electrochemical experimental set-up.

polarization from corrosion potential up to 2.0 V with the sweeping rate of 0.33 mV s^{-1} to understand the passivation behavior.

IV. Results

IV. A. Tafel extrapolation

In the spectra for Tafel sweeping of both samples, the linear regions of both cathodic and anodic sides were extrapolated. From the intersection of both extrapolated lines, the corrosion rate could be derived as shown in Fig. 2, where two results for both experiments were plotted to obtain the deviation. The corrosion rate of F82H steel and SUS304 in 5w% H_2SO_4 aqueous solution were estimated as 9.1 ± 0.2 and 0.038 ± 0.003 cm year^{-1}, respectively, indicating that the corrosion rate of F82H steel was approximately 2 orders of magnitude larger than that of SUS304.
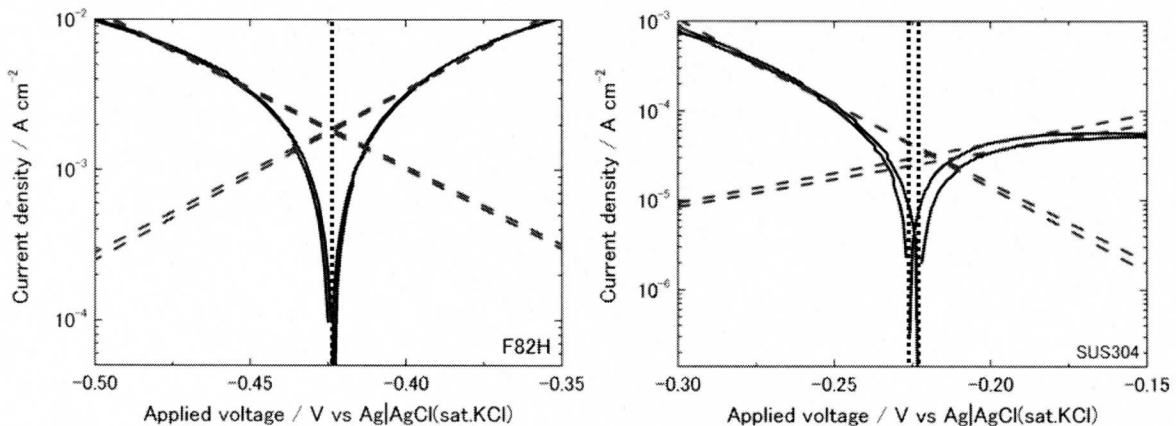

Fig. 2 Tafel extrapolation views for F82H steel and SUS304. Solid curves, dotted lines and broken lines mean experimental results, E_{corr} and Tafel extrapolation, respectively.
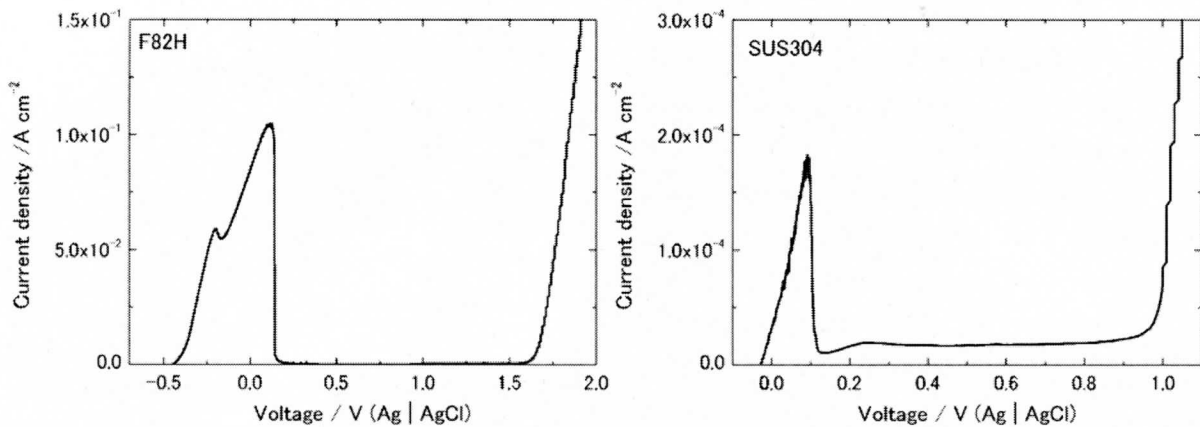
Fig. 3 Anodic polarization curves for F82H steel and SUS304.

IV. B. Anodic polarization

The spectra of anodic polarization measurements of F82H steel and SUS304 are shown in Fig. 3. In this figure, both spectra could be consist of three regions as the same as an usual stainless steel: (i) passivation (or active) region where peaks of current density were observed in lower applied potential region, (ii) passive layer sustention (or simply, passive) region where low and approximately constant current density was observed in the applied potential region between (i) and (iii), and (iii) transpassive region where sharp increase of current density was observed in higher applied potential region, and the other is passive region where small and steady current density could be observed between passivation and transpassive region. The quantum of electricity to passivate F82H steel and SUS304 were approximately 100 C cm^{-2} and 0.04 C cm^{-2}, respectively. These results indicate that F82H steel would be reluctant to passivate, if compared with SUS304 stainless steel.

V. Sammary

In the present study, the corrosion behavior of F82H steel and SUS304 as a reference in highly corrosive circumstance of 5w% H_2SO_4/H_2O were observed by means of the electrochemical techniques of Tafel extrapolation and anodic polarization, as pre-experiments to investigate the effects of tritium on the corrosion of F82H steel. As the results, the corrosion rates of F82H steel and SUS304 stainless steel were estimated as 9.1 ± 0.2 and 0.038 ± 0.003 cm year^{-1}, respectively. From the deviation, it was expected that Tafel extrapolation method would be able to apply the experiments to see the effects of tritiated water on corrosion rate. On the other hand of anodic polarization measurement, three regions (passivation, passive and transpassive regions) could be observed in both samples of F82H steel and SUS304 stainless steel. Therefore, it was expected that the effects of tritiated water on passivation and/or passive layer could be observed.

VI. Future work

Before the experiments in tritiated water, pH dependence experiments, especially in less corrosive circumstance than the present study, and dissolved oxygen concentration dependence to understand its effects on passivation and passive layer will be performed. Thereafter, the experiments in tritiated water will be performed to investigate the effects of tritium on the corrosion behavior of F82H steel.

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