

Formation of functional layer structure by pre-oxidation process and in-situ evaluation of layer structure by EIS analysis

予備酸化処理による機能性被覆構造の形成と
電気化学測定法による構造のその場解析に関する研究

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核融合炉ブランケット用の機能性被覆を金属の予備酸化により形成させ、その電気化学的特性について電気化学インピーダンス(EIS)法を用いてその場分析を実施した。773Kの空気雰囲気下の予備酸化プロセスにより様々な金属表面に形成された酸化被膜について、高温条件時の電気化学特性の獲得に成功した。特に、金属ジルコニウム(Zr)の表面に形成された酸化皮膜が緻密な組織や高い電気抵抗率を有する事が明らかになった。

1. Background and purpose

The applications of functional materials such as an electrical insulator and a tritium diffusion barrier to fusion blanket systems are essential technology. Several oxides, such as ZrO_2 , Y_2O_3 , Al_2O_3 and Er_2O_3 , are thermodynamically stable, and the coating layers by these oxides have relatively good performance as a hydrogen permeation barrier [1, 2]. These functional layers can be formed by the oxidation of surfaces of Zr, Y, Al and Er metals, which are plated on the structural materials [3]. The Pilling- Bedworth (PB) ratio of ZrO_2 on Zr metal is 1.17 at 673K, and indicates the excellent protectiveness of the layers. However, these oxide layers cannot be formed as planned when the dissolution type corrosion [4] is initially caused on their surface in the liquid breeders. Then, a pre-oxidation treatment on the metals can improve the initial corrosion characteristics. The electrochemical impedance spectroscopy (EIS) must be a feasible technique to monitor the formation and the degradation of the functional layers in some liquid metals [5]. The EIS is a non-destructive way to figure out the change of the electrical properties and the thickness of the functional layer in liquid metals.

The purpose of the present study is to investigate the oxidation behaviors of Zr, Y and Er metals and the electrical characteristics of these oxide layers around the reactor operation temperature by EIS method.

2. Experimental conditions

2.1. Pre-oxidation treatment of specimens

The test materials were Zr, Y and Er metals. The specimens for the pre-oxidation tests are shown in Fig. 1 (a). The pre-oxidation tests were performed in an air atmosphere at 773K. The test times are 100, 250 and 500 hours. The weight changes of the pre-oxidized specimens were measured using an electro-reading balance with accuracy 0.1mg. The oxide layers formed on the specimen surfaces were analyzed by XRD. Their surfaces and cross sections were metallurgically

analyzed by EPMA.

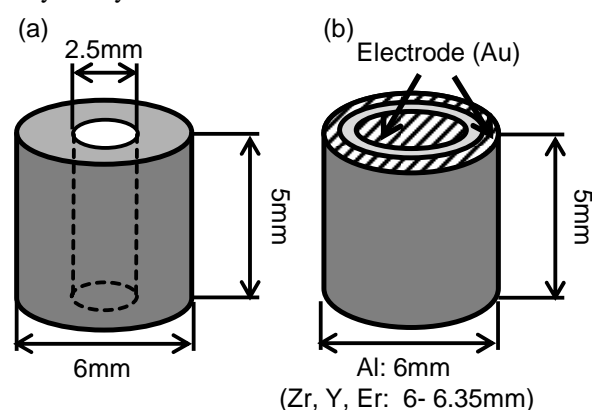


Fig. 1 Specimens (a) pre-oxidation test, (b) EIS measurement after pre-oxidation

2.2. EIS measurement

The specimen for the EIS analysis was oxidized at the same conditions with the pre-oxidation tests. Fig. 1 (b) shows the cylindrical type specimen for the EIS analysis. The electrode of Au was plated on the top of the specimen surface by a sputter coating. Figure 2 shows the schematic diagram of the test apparatus for the EIS analysis. The temperature of the test vessel was controlled by the heater and the thermocouple, which is placed at the bottom of the vessel. The test section was installed in the test vessel filled with Ar having the purity of 5N. Figure 2 (b) shows the detail structure of the test section. The EIS analysis was performed by VERSASTAT 3 manufactured by Princeton applied research. Three terminals i.e. a working electrode, a guard electrode and a reference electrode were used for the analysis. The counter electrode was connected to the bottom of the specimen, where the oxide layer was removed by a grinding in advances. The analysis was performed at the temperature up to 773K.

3. Experimental results and discussions

The oxide layers were formed on the specimen surfaces

of Zr and Y, and these layers were observed by EPMA and analyzed by EIS. The thickness of the layer formed on the specimen surface was evaluated from the results of EPMA cross sectional analysis and summarized in Table 1. The results indicated the variation of the layer thickness. The thickness of the oxide layer formed on the Er specimen could not be evaluated, since the most part of the specimen was oxidized and broken into the small pieces.

The results of EIS analysis on the oxide layers were summarized into the Nyquist plot, and the Nyquist plot obtained at 673K for the Zr specimen pre-oxidized at 773K for 250 hours is shown in Fig. 3 as an example. The plot in a semi-elliptical shape indicated the inhomogeneity of the layer structure such as a thickness variation and/or a porosity of the layer. This feature agreed with the thickness variation observed by EPMA analysis. The oxide layer was modeled as a parallel RC circuit with the elements of electrical resistance (R [Ω]) and capacitance (C [F]) as reported in detail in ref. [4]. These elements are expressed as

$$R = \frac{\rho d}{A} \quad (1),$$

$$C = \frac{\epsilon \epsilon_0 A}{d} \quad (2),$$

where ρ is the electrical resistivity [$\Omega \cdot m$] of the oxide layer, A is the surface area of the working electrode [m^2] and d is the thickness of the oxide layer [m], ϵ is the relative permittivity of the oxide layer and ϵ_0 is the permittivity of vacuum (i.e. 8.854×10^{-12} F/m). The electrical resistance of the oxide layer was estimated as app. $2.5 M\Omega$ from Fig. 3. The harmonic mean thickness of the oxide layer was evaluated as app. $3.3 \mu m$. Then, the electrical resistivity of the layer at 673K was obtained as $4.35 \times 10^6 \Omega m$ according to Eq. (1). This value was much larger than the literature value of $8 \times 10^3 \Omega m$ [6]. The relative permittivity was evaluated as 37.8 , and this value was close to the literature value of 35 ± 2 [7].

4. Conclusion

The experimental studies on the functional layer formation by pre-oxidation treatment and in-situ evaluation of the layer structure by the EIS were performed. The compact oxide layers were formed on the Zr and Y metals in air atmosphere at 773K. The EIS analysis on the Zr and Y specimens were performed. Their electrical properties around the reactor operation temperature were successfully obtained on-line by EIS analysis. The information on the geometrical features of the oxide layer such as the thickness and the variation of thickness could be obtained from EIS results.

Reference

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Table 1 Thickness of oxide layers formed at 773K evaluated from results of EPMA analysis

	Time [hour]	Thickness [μm]		
		Variation	Arithmetic mean	Harmonic mean
Zr	100	1.3-3.5	1.9	1.9
	250	2.0-4.8	3.5	3.3
	500	1.6-8.2	4.6	4.2
Y	100	3.2-15.8	9.8	8.0
	250	14.6-43.0	27.8	25.0
	500	17.1-55.1	35.1	32.3

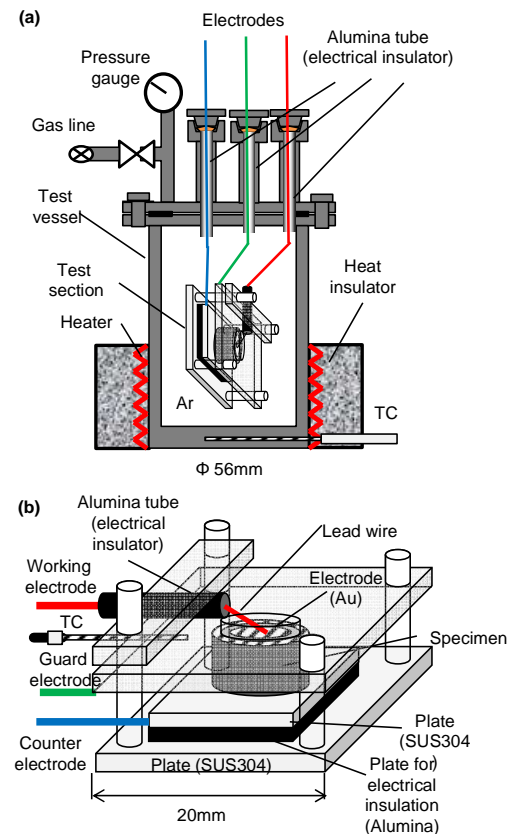


Fig. 2 (a) Test vessel for EIS analysis, (b) test section

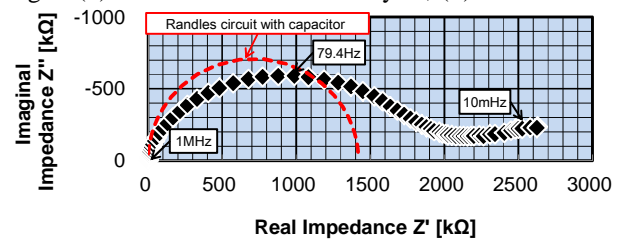


Fig. 3 Nyquist plot obtained at 673K with Zr specimen pre-oxidized at 773K