Microstructure change and deuterium permeation behavior of ceramic-metal multi-layer coatings after immersion in liquid lithium-lead alloy

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ABSTRACT

For the establishment of liquid tritium breeding concepts, static lithium-lead corrosion tests for single-layer erbium oxide coatings and erbium oxide-metal multi-layer coatings were carried out, followed by deuterium permeation measurements. Grain boundary corrosion of erbium oxide coatings was confirmed by the static immersion tests at 550 and 600 °C. An erbium oxide-iron two-layer coating sustained its structure after lithium-lead immersion at 600 °C for up to 3000 h. The results of gas-driven deuterium permeation measurements for multi-layer coatings immersed at 550 and 600 °C indicated that crystallization and grain growth of erbium oxide would sufficiently occur during the immersion at 600 °C, and then the sample showed lower permeabilities in the first measurements at lower temperature. On the other hand, permeation reduction factors of the sample immersed at 550 °C were estimated to be 100–200 in the temperature range of 400–550 °C. A corrosion layer formed on the coating surface might work as an additional diffusion barrier after the permeation test at 600 °C.

1. Introduction

Liquid tritium breeding materials have been proposed in ITER test blanket module and future fusion reactors due to its high thermal efficiency, tritium breeding ratio, etc. However, tritium permeation through metal structural materials will be a severe problem in the case of lithium-lead (Li-Pb) and molten salt blanket systems, and corrosion of metal pipework will also cause degradation of its mechanical properties. To solve these issues the development of a functional coating as a tritium permeation barrier with corrosion resistance is required. Up to today, ceramic coatings, mainly metal oxides, have been investigated as hydrogen isotope impermeable materials [1–5]. Our recent efforts were dedicated to erbium oxide (Er_2O_3)-coated reduced activation ferritic steels showing high permeation reduction factors (PRFs) [6]. On the other hand, compatibility with liquid breeders should be also ensured for practical applications. Corrosion studies on Er_2O_3 were primarily conducted with liquid Li under various conditions [7–11]. A few papers on Li-Pb compatibility of Er_2O_3 coatings were subsequently published [11,12]. In both cases, peeling of the coatings from the coating-substrate interface and chemical reactions such as formation of a ternary oxide ($LiErO_2$) and loss of Er would be the main causes of barrier deterioration. Meanwhile, our previous works showed that Er_2O_3-Fe two-layer coatings showed a deuterium permeability similar to that of single-layer Er_2O_3 coatings with a decrease of the corrosion rate because the outer Fe layer had a better Li-Pb compatibility [12,13]. That suggests that the multi-layer coating is promising for the application to the actual reactors, and then an improvement of PRF and compatibility is expected by further stratification and optimization of layer structures [14]. In this study, corrosion mechanism of the multi-layer coatings in liquid Li-Pb and deuterium permeation behavior for the immersed coatings have been investigated.

2. Experimental

2.1. Sample preparation

Steel plate substrates with a thickness of 0.5 mm were mirror finished by mechanical polishing. Er_2O_3 layers of 1–4 μm in thickness were fabricated by filtered vacuum arc deposition on the substrates as reported previously [15]. Er_2O_3-Fe two-layer coating samples were prepared with 10-μm-thick Fe foils covering the Er_2O_3-coated samples. For the preparation of an Er_2O_3-V-Er_2O_3-Fe four-layer coating, radio-frequency magnetron sputtering was also used to fabricate 1-μm-thick V and Fe metal layers.

Fig. 1. Conceptual diagram of Li-Pb immersion capsules.
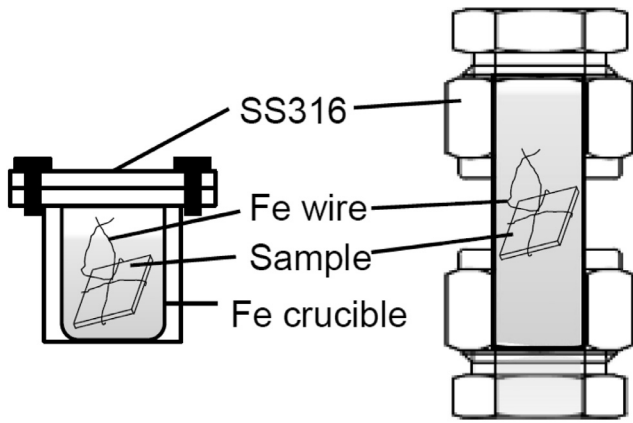
Capsule 1:

Li-Pb: 20–25 cc

Capsule 2:

Li-Pb: 35–38 cc

2.2. Static Li-Pb immersion test

Li-Pb eutectic alloy (atomic ratio of Li: Pb = 15.7:84.3) was synthesized with pure Li (purity: 99.9%) and Pb (99.999%) ingots in an argon glovebox. The Li-Pb and the coated samples were encapsulated into 316 type stainless steel capsules, and then the capsules were heated in an electric furnace. The conceptual diagram of immersion capsules is shown in Fig. 1, and the test parameters of Li-Pb immersion were listed in Table 1. In this study, crystallized Er_2O_3 coatings were applied to deuterium permeation tests to unify the microstructure of the coatings [16]. After the immersion tests, only Sample 4 was cleaned with liquid Li to remove adhered Li-Pb. Surface and cross-sectional observations were performed using a field-emission scanning electron microscope (FE-SEM, JSM-7100F, JEOL Ltd.) and a transmission electron microscope (TEM JEM-2800, JEOL Ltd.) located at National Institute for Fusion Science (NIFS). Crystal structure of immersed samples was analyzed by grazing incidence X-ray diffraction (GIXRD, RINT Ultima III, Rigaku Co.) with the fixed incident angle of 0.5°.

2.3. Deuterium permeation test

The back surface of the immersed samples were polished using abrasive papers, which was also conducted in our previous study [5]. The sample was mounted into a gas-driven deuterium permeation apparatus described in Ref. [15] with the coating surface facing to the upstream where deuterium was introduced to 10–80 kPa. Deuterium permeation experiments were performed in the temperature range of 400–650 °C. Permeated deuterium was detected by a quadrupole mass spectrometer at the downstream ($\sim 10^{-6}$ Pa). The permeation flux J at the steady-state is expressed by the following formula:

Fig. 2. Cross-sectional TEM images of Sample 1 after Li-Pb immersion.

$$J = P\frac{p^n}{d} \qquad (1)$$

where P is the deuterium permeability, p is the upstream pressure, and d is the thickness of the sample. The pressure exponent n which is obtained by pressure dependence indicates a rate-determining process of permeation. When n is 1.0, the permeation flux is limited by a
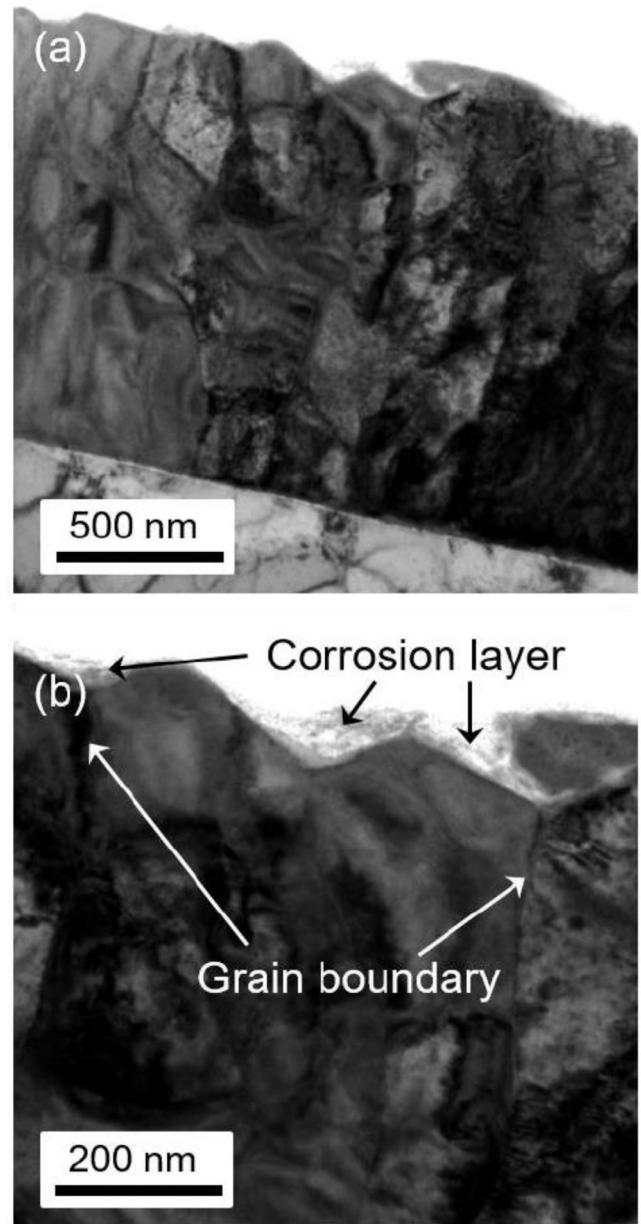
Table 1
Samples for Li-Pb immersion tests and immersion parameters.

Sample	Substrate	Coating / Thickness	Duration / h	Temperature / °C	Cleaning	Capsule
1	JLF-1	Er_2O_3 1.3 μm	400	550	Not conducted	1
2	F82H	Er_2O_3-Fe 3.6 + 10 μm	3000	600	Not conducted	2
3	SS316	Er_2O_3-Fe 2.8 + 10 μm	200	600	Not conducted	2
4	F82H	Er_2O_3-V-Er_2O_3-Fe 1.3 + 0.8 + 1.3 + 1 μm	1000	550	Liquid Li	2