Electroplating of Erbium on Steel Surface in $ErCl_3$ Doped LiCl-KCl[*]

Masatoshi KONDO, Teruya TANAKA[1], Takeo MUROGA[1], Hiroyuki TSUJIMURA[2] and Yasuhiko ITO[3]

Tokai University, 4-1-1 Kitakaname, Hiratuka 259-1292, Japan
[1]*National Institute for Fusion Science, 322-6 Oroshi-cho, Toki 509-5292, Japan*
[2]*I' MSEP Co.LTD, D-egg, No1, kodo, Jinzodani, Kyotanabe, Kyoto 610-0332, Japan*
[3]*Doshisha University, Tatara, Miyakodani, Kyotanabe, Kyoto 610-0321, Japan*

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The electroplating of Er metal on the reduced activation ferritic martensitic steel, JLF-1 (Fe-9Cr-2W-0.1C), in a molten salt was studied. The specimen was immersed in the molten $ErCl_3$ doped LiCl-KCl electrolyte. The electroplating was carried out by a constant potential electrolysis method and a pulsed current electrolysis method. It was found that the Er metal was deposited on the specimen surface due to the electrochemical reaction.

Keywords: blanket, coating, tritium permeation barrier, electrical insulation layer, electroplating

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1. Introduction

Liquid metals lithium (Li) and lead lithium (Pb-17Li) are considered as a coolant and a tritium breeder for the blanket systems of fusion reactors [1]. The functional layers such as a tritium permeation barrier and an electrical insulation layer coated on the structural materials of the blanket systems are the essential ones for the liquid breeder blankets [2].

One of the candidates of the functional layers is an erbium oxide (Er_2O_3) layer. The chemical stability of the oxide was extremely high [3], and the high chemical stability can allow a long-term application in reductive liquid breeders. Reduced activation ferritic martensitic (RAFM) steels are the prime candidate for the structural materials of fusion blanket systems. Therefore, the layer is expected to be fabricated on the surface of the RAFM steel. Then, the methodology of the oxide layer fabrication on the steel surface has been studied.

The hydrogen permeation of the Er_2O_3 layer and the compatibility with a liquid metal Li have been investigated [4, 5]. An important issue for the functional layers is an improvement of adhesion at the interface between the oxide layer and the substrate. The thermal stress was induced on the surface layer by the difference of the thermal expansion ratio between the oxide layer and the substrate, when the temperature increased or decreased. The stress concentrated at the interface between the layer and the substrate. Then, the interface was destroyed, and the exfoliation of the layer from the substrate was promoted [6]. It is well known that the formation of the layer with a composition gradient is effective for the relaxation of the stress concentration [7]. The relaxation is obtained when the composition gradient exists at the oxide layer/substrate interface.

The Er_2O_3 layer, which works as the functional layer, can be made by the oxidation of Er metal, which was plated on the steel surface. Then, the oxidation makes a composition gradient in the layer due to an inner diffusion of oxygen into the metal matrix. The oxidation characteristic of the Er metal in a liquid Li was already investigated [8]. The Er_2O_3 layer was formed on the Er metal in an oxygen doped Li, though some cracks and an exfoliation of the layer were detected. The steel surface plated with the Er metal can work as self-healing layer by an in-situ oxidation even if some parts of the oxide layer were cracked and exfoliated from the metal layer in the liquid Li [9].

The plating method of the Er metal plating on the structural materials is not made clear so far. The plating technology for the Er metal, which is easily oxidized due to the extremely high affinity with the oxygen, is not established so far. The purpose of the present study is to make clear the feasibility of the Er metal plating on the steel surface by an electroplating method.

2. Experimental Procedure

The electroplating tests were performed using the specimen of reduced activation ferritic martensitic steel, JLF-1 (JOYO-HEAT) [10]. The chemical composition was Fe-9Cr-2W-0.1C. The specimen was rectangular plate, and the size was 10 mm × 15 mm × 2 mm. The specimen after the machining was used for the tests without a surface polishing.

Figure 1 shows the experimental apparatus used in the

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author's e-mail: kondo.masatoshi@tokai-u.jp

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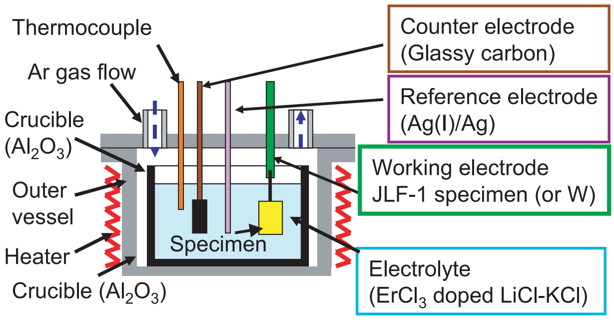

Fig. 1 Experimental apparatus.

Table 1 Test conditions.

Temperature	450ºC
Electrolyte	$ErCl_3$ doped LiCl-KCl (59:41) 400 g (= 235 cc) $ErCl_3$: 0.3 mol%
Constant potential electrolysis	0.2 V(vs. Li^+/Li) Experimental duration : 1.5 hours
Pulsed current Electrolysis	- 115 mA for 0.1s + 0 mA for 0.4 s Experimental duration : 3 hours

present study. The electroplating with Er metal on the specimen surface was performed in the molten salt $ErCl_3$ doped LiCl-KCl (59 : 41) electrolyte. The inventory of the molten salt was 400 g (235 cc). $ErCl_3$ was doped in the molten salt with the concentration of 0.3 mol%. A specimen was mounted on the working electrode. The material of the counter electrode was glassy carbon and that of the reference electrode was Ag(I)/Ag. The Ar gas was used as a cover gas in the apparatus.

Table 1 presents the test conditions. The test temperature was 450°C. Before, the electroplating tests using the specimen of JLF-1 steel, a cyclic voltammogram was measured using the working electrode of tungsten (W) to investigate the electrodeposition of Er on the electrode surface in the electrolyte. Here, the W electrode was used to obtain a clear current peak of the cyclic voltammogram, because the W electrode is chemically inactive in the molten salt in the potential region of the experiment. The scan rates were 50, 100 and 200 mV/sec.

The electroplating tests for the JLF-1 steel were performed by a constant potential electrolysis method and a pulsed current electrolysis method. It is known that the current density obtained in the electrodeposition process by the pulsed current electrolysis method is higher than that by constant potential electrolysis method. After the plating, the specimen was taken out from the molten salt. Then, the specimen was rinsed in water, and LiCl-KCl adhered on the specimen surface was removed. The specimen surface was observed and analyzed using SEM and XRD.

3. Results and Discussion

3.1 Cyclic voltammogram

Figure 2 shows the measurement result of cyclic voltammogram. The result indicated that an anodic current peak appeared at the potential of 0.57 V and a cathodic current peak appeared at the potential of 0.37 V (vs. Li^+/Li), respectively. The former peak was due to the anodic dissolution of Er metal according to the reaction,

$$Er \rightarrow Er^{3+} + 3e^-, \quad (1)$$

and the latter peak was due to the formation of the Er metal on the W electrode according to the reaction,

$$Er^{3+} + 3e^- \rightarrow Er. \quad (2)$$

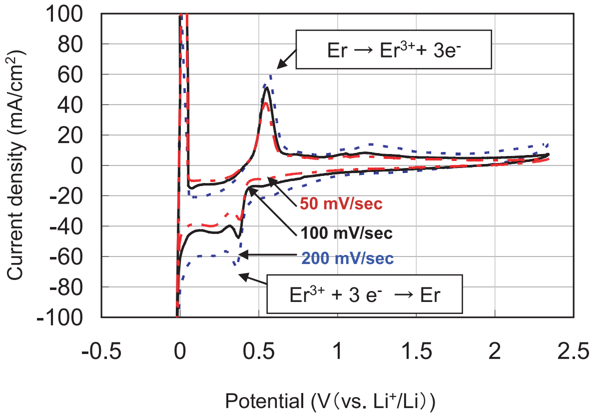

Fig. 2 Cyclic voltammogram of Er deposition in $ErCl_3$ doped LiCl-KCl (59 : 41) (Working electrode: W).

The current density at the peaks in Fig. 2 was in proportion to square root of the scan rate. The absolute value of the anodic peak current was almost the same to that of the cathodic peak current. Therefore, it was found that the electrodeposition of Er was reversible reaction and the activation reaction was sufficiently rapid.

3.2 Electroplating of JLF-1 steel by constant potential electrolysis and pulsed current electrolysis

The result of visual inspection on the specimen electroplated by the constant potential electrolysis method indicated that the specimen surface had a metallic luster as shown in Fig. 3 (a). The result of SEM observation indicated that Er metal was deposited as small particles on the surface. However, the specimen surface was not fully covered by the Er metal. The result of XRD analysis (Fig. 4) indicated the presence of the Er metal and the Er oxide (Er_2O_3) on the specimen surface. The peak in the XRD pattern, which indicates the presence of the Er metal and Er_2O_3, was weak because the quantity of the depositions on the specimen surface was small. The Er metal might be partially oxidized during the electroplating process in the molten salt bath due to the reaction with dissolved oxygen and/or water in the molten salt.

In the specimen tested with the pulsed current electrolysis method, the specimen surface was fully covered with the depositions as shown in Fig. 3 (b). The quantity of the

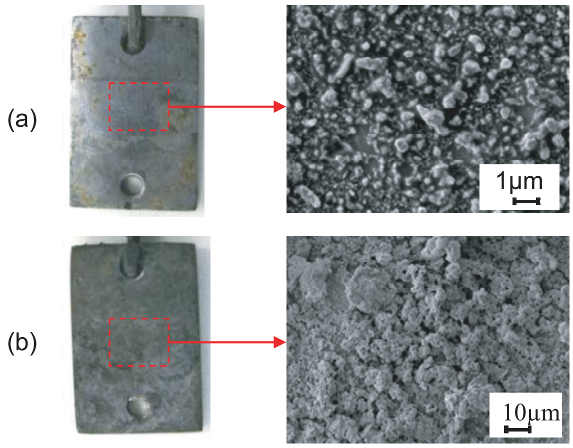

Fig. 3 Photograph of specimen surface and SEM micrograph of JLF-1 specimen after electroplating, (a) constant potential electrolysis, (b) pulsed current electrolysis.

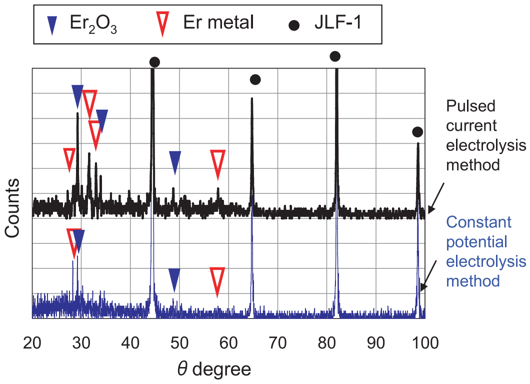

Fig. 4 XRD analysis for JLF-1 specimen after electroplating.

depositions by the pulsed current electrolysis method was much larger than that by the constant potential electrolysis method. The results of XRD analysis clearly indicated the presence of the Er metal and the Er_2O_3.

The quantity of the depositions by the pulsed current electrolysis method was much larger than that by the constant potential electrolysis method. The long duration period might not influence on the large deposition, because the duration for the electrolysis in the pulsed current electrolysis method was 36 min when the interval was removed from the total duration of 3 hr (Table 1). The duration for the electrolysis in the constant potential electrolysis was 1.5 hr. The time for the deposition in the pulsed current electrolysis method was shorter than that for the constant potential electrolysis method. The main reason of the large deposition is the large current density in the pulsed current electrolysis.

When the surface of the Er metal layer is oxidized in a liquid Li, the Er oxide (Er_2O_3) can be formed on the surface [3]. The thickness of the oxide layer can be larger by the growth. Then, the Er_2O_3 layer can be cracked and exfoliated by the internal stress which is generated in the layer due to the growth of the layer. If the oxide layer is partially exfoliated from the substrate, the fresh surface of the Er metal appears and must be oxidized as the same as the initial oxidation. The substrate newly oxidized must work as the tritium permeation barrier and the electrical insulation layer. The thickness of the exfoliated oxide layer must be much thinner than that of Er metal layer plated on the substrate. Therefore, the oxide layer, which works as the functional layer, can be self-healed several times. The mechanism is the same to that of the in-situ formation of the protective oxide layer in the liquid metals of Pb and Pb-Bi [9].

4. Conclusion

Major conclusions are follows;

1. Cyclic voltammogram for the electro deposition of Er metal in the molten salt ErCl3 doped LiCl-KCl electrolyte was obtained. The cyclic voltammogram indicated the Er metal was deposited by a cathodic reaction.
2. The specimens of JLF-1(Fe-9Cr-2W-0.1C) were immersed in the molten salt. Then, electro deposition on the specimen surface was performed both by the constant potential electrolysis method and the pulsed current electrolysis method. The Er metal was deposited on the specimen surface due to the electrode reaction with both methods.

[1] S. Malang, A.R. Raffray and N.B. Morley, Fusion Eng. Des. **84**, 2145 (2009).
[2] T. Muroga and B.A. Pint, Fusion Eng. Des. **85**, 1301 (2010).
[3] M. Nagura, M. Kondo, A. Suzuki, T. Muroga and T. Terai, Fusion Eng. Des. **84**, 630 (2009).
[4] D. Zhang, M. Kondo, T. Teruya, T. Muroga and T. Valentyn, Fusion Eng. Des. **86**, 2508 (2011).
[5] M. Kondo, T. Watanabe, T. Tanaka, D. Zhang and A. Sagara, Plasma Fusion Res. **6**, 2405117 (2011).
[6] M. Kondo, M. Takahashi, T. Tanaka, V. Tsisar and T. Muroga, Fusion Eng. Des. in press.
[7] R. Watanabe, Functionally Gradient Materials (Kogyo Chosakai Publishing Co., Ltd., 1993), Printed in Japan.
[8] M. Nagura, A. Suzuki and T. Terai, Fusion Eng. Des. **86**, 2670 (2011).
[9] M. Kondo, M. Takahashi, N. Sawada and K. Hata, J. Nucl. Sci. Technol. **43**, 107 (2005).
[10] H. Ono, R. Kasada and A. Kimura, J. Nucl. Mater. **329**-**333**, 1117 (2004).