Preparation and Analysis of Thick Simulated Crud Films on Fuel Cladding Tube through Electrodeposition Method

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Keywords : Crud, CILC, Fuel Cladding, Electrodeposition, Primary System

1. Introduction

Fuel cladding in pressurized water reactor(PWR) are mostly made of zirconium alloys. During operation, fuel cladding are immersed in the high-temperature and high-pressure primary water [1]. To ensure the fuel integrity, the thickness of fuel cladding oxide layer are generally limited to less than 100 ㎛ during three-cycle operation.

Employing recently the economic operation strategies such as power uprate, high burnup and long-term operation [2,3] in PWR power plant, led to accelerating the oxidation of fuel cladding and the deposit of corrosion product on it [4], which is called as 'crud'. Crud is known to be mainly composed of oxides including Ni, Fe, Zr, and B elements, such as nickel ferrite ($Ni_xFe_{3-x}O_4$), nickel oxide (NiO), zirconium oxide (ZrO_2), bonaccordite (Ni_2FeBO_5), and magnetite (Fe_3O_4), etc [5,6,7]. The morphology of crud has been found in polyhydral and needle-like shapes, and mostly porous structure due to sub-cooled nucleate boiling (SNB) in clad/coolant interface. In addition, heavy deposition of crud has often caused various problems of fuel such as Crud-Induced Power Shift (CIPS) or Crud-Induced Localized Corrosion (CILC). CILC occurs when heat transfer from the surface of cladding to the coolant are obstructed by the thick crud over 100 ㎛ due to its higher thermal resistance, resulting the acceleration of fuel cladding corrosion [8]. However, the acceleration of fuel cladding corrosion has rarely been studied due to its high radioactivity. Furthermore, the thick deposition of simulated crud film on fuel cladding is very difficult through previous deposition process using simulated primary water loop and physical vapor deposition system.

In this work, the thickness of magnetite film as an representative crud content is deposited up to 300 ㎛on zirconium alloy cladding tube using electrodeposition method. The thickness and morphology of crud layer can be easily controlled in various conditions. The simulated Fe3O4 crud films coated by using electrodeposited have been analyzed by using SEM-EDS, FIB-SEM, optical surface profiler, etc.

2. Experiment Methods

2.1 Preparation of Fuel cladding specimen

Zirconium base alloy tube, which has the same properties with Zirlo™, the commercial fuel cladding tube, with one end laser welded with zirconium plug was used as a test specimen having the characteristics as summarized in table 1. The dimension of the test tube for both analysis and experiment was an outer diameter (OD) of 9.5 mm and inner diameter (ID) of 8.3. Each four specimens for analysis and CILC test were prepared in the length of 300 mm and 550 mm, respectively.

Table 1. Chemical composition and mechanical properties of Zr alloy cladding tube

Chemical composition (wt%)				
Sn	Fe	O	Nb	Zr
1.0	0.1	0.12	1.0	Bal.

Mechanical properties (at RT)		
YS (MPa)	UTS (MPa)	Elong. (%)
612.5	819.2	15.8

2.2 Electrodeposition of magnetite on cladding

Fig. 1 shows a schematic of the magnetite electrodeposition system used in this study. The electrodeposition was carried out in a three-electrode cell. Saturated calomel electride (SCE) and graphite rod were used as a reference electrode (RE) and counter electrode (CE), respectively. The source solution for electrodeposition was prepared by dissolving 2M NaOH, 0.043M Fe2(SO4)3, 0.1M triethanolamine into the deionized (DI) water.

The electrodeposition of magnetite film was carried out in a source solution with applying the potential of -1.0V at 80 °C without stirring. Fig. 2 displays the average thickness of magnetite film electrodeposited with increasing the deposition time. Finally, specimens with crud layers of 100 ㎛ and 300 ㎛ thickness were prepared to evaluate the corrosion characteristics of the fuel cladding. The solution was replaced every 12 hours to maintain the concentration of source solution. To obtain a homogenous magnetite film, zirconium alloy substrate as a working electrode (WE) was located in the middle between two counter electrodes.

The electrodeposited specimens were analyzed by using scanning electron microscopy (SEM), X-ray diffractometer (XRD) and optical surface profiler to investigate the characteristic of magnetite film.

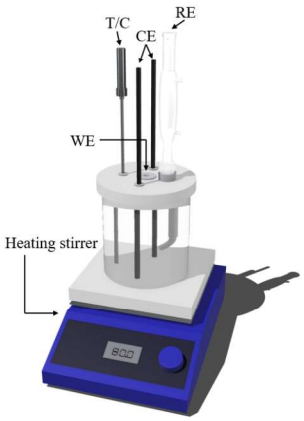


Fig. 1. Schematic of magnetite electrodeposition system.

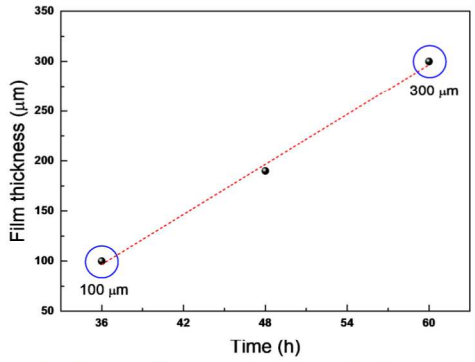
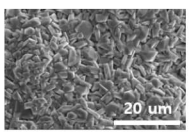
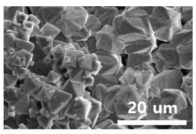
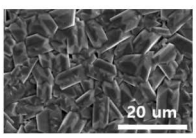


Fig. 2. Thickness of magnetite film with increasing electrodeposition time.

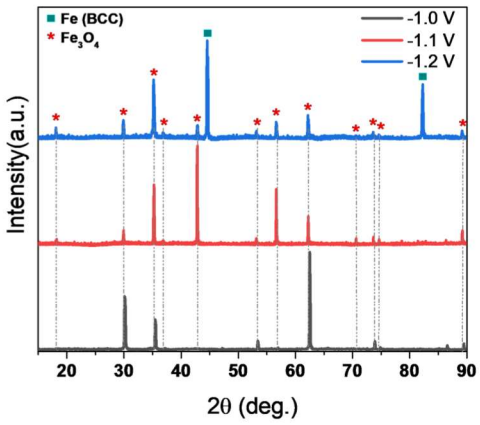
3. Results and Discussions

3.1 Analysis of electrodeposited magnetite film

Prior to sample preparation, an linear sweep has been undergone to decide an appropriate potential for magnetite film formation on zirconium alloy fuel cladding. Fig. 3(a) shows the comparison data on surface morphology of magnetite film deposited at three different potentials of -.10, -1.1, and -1.2V, respectively.

Potential (V)	Picture	SEM image
-1.0		
-1.1		
-1.2		

(a)

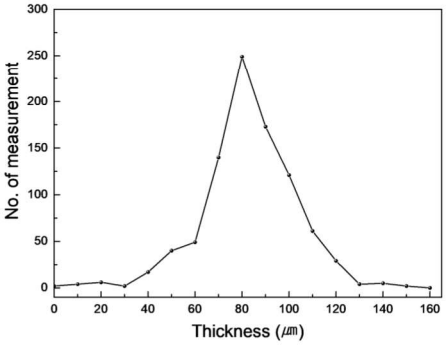


(b)

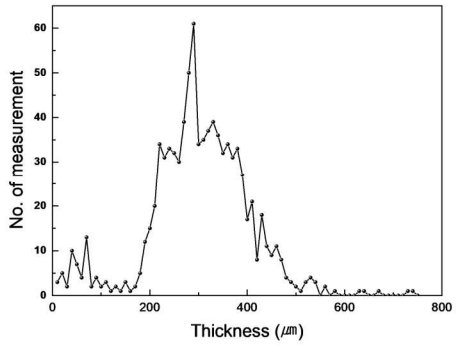
Fig. 3. (a) Morphology, (b) XRD - Phase analysis for different deposition potential.

All electrodeposited films were analyzed by Fe_3O_4 (magnetite) as shown in XRD patterns of Fig. 3(b). However, the metallic iron phase was investigated in the specimen electrodeposited at -1.2 V. Therefore, it is considered that the most suitable deposition potential of magnetite film is -1.0 V from these data.

Fig. 4 presents the spatial thickness data measured from magnetite-deposited fuel cladding using optical surface profiler. The thickness of specimen deposited for 36 hours was measured in the range of 0- 150 ㎛ and average thickness was 82.9 ㎛. In addition, the thickness of specimen deposited for 60 hours was measured in the range of 10-740 ㎛ and average thickness is 302.5 ㎛.



(a)



(b)

Fig. 4. Thickness measurement data of (a) the 36h-deposited specimen, (b) 60h-deposited specimen measured by optical surface profiler.

4. Conclusion

We successfully simulated thick magnetite crud film through electrochemical deposition method in this work.

(1) The thickness of magnetite film can be easily controlled by increasing the deposition time.
(2) The optimum potential for depositing magnetite film is -1.0 V at 80°C and the XRD patterns of electrodeposited film is corresponded with the characteristic peaks of magnetite referred to JCPDS No. 88-0380.

Therefore, it is predicted that this crud simulation method will be used to understand the accelerated corrosion of fuel cladding with thick crud film.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation (NRF) grant funded by the Korean government (Grant No. RS-2022-00143316).

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