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Multi-layer Coating Study for Improved Barrier Property Under a Fuel-Clad Chemical Interaction

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1. Introduction

U-Zr metallic alloy including TRUs (transuranic elements) and REs (rare earth elements), and HT9 (Fe-12.0Cr-1.0Mo-0.6Ni-0.6Mn-0.52W-0.3V, etc. all values are wt.%) steel are promising candidates for fuel and cladding materials, respectively, in Sodium Fast Reactors (SFRs). It is the fuel and cladding of choice for several reasons such as excellent thermal and mechanical properties, proliferation resistance, and good compatibility with sodium coolant. SFRs are a type of Generation IV reactors and have been drawing attention due to its ability to recycle spent nuclear fuel attained by pyroprocessing. The most critical problem, however, using both U-Zr-TRUs fuel and HT9 cladding in SFRs is fuel-clad chemical interaction (FCCI). Elevated core temperatures (550─650 ^{o}C) and severe irradiation conditions initiate the FCCI decreasing the thickness of cladding, and hence, reduce the safety of reactor in various operational states.

The concept of coating chemically inert barriers on the inner surface of cladding has been well studied, and Cr coating layer has been an important metallic barrier candidate. Jun Hwan Kim et al. [1] and Seong Woo Yang et al. [2] performed the electrodeposition of Cr on HT9 disks and diffusion couple tests using U-10wt%Zr fuel. Electrodeposited Cr coating layer with a thickness of 20μm showed excellent barrier property at 740 and 800 ^{o}C for 48 h preventing FCCI. However, a penetration of U into the Cr coating layer was also observed. In our recent study, diffusion couple tests between Cr coated HT9 and Ce-Nd alloy disks at 650 ^{o}C revealed inter-diffusion areas. The Cr coating layer seemed insufficient to prevent FCCI at a temperature higher than eutectic temperature because massive liquid phase diffusion could occur. The eutectic temperature between U-Zr-TRUs-REs fuel and HT9 cladding is readily modified by Pu content in TRUs and can be decreased as low as 650 ^{o}C with relatively high Pu content near 5wt% in TRUs. The interfacial temperature between fuel and cladding could exceed this eutectic temperature in transient states such as transient overpower and control rod withdrawal conditions. Therefore, more reliable coating layer even at a temperature higher than the eutectic temperature is required to enhance the safety of SFRs.

The use of metal/ceramic multilayer coating can be a way to enhance the barrier performance of coating layer. The multilayer coating has been an important research subject during the last decade because of increasing number of applications demanding more diverse and higher properties that single coating layer cannot satisfy. It is well known that various mechanical properties such as hardness, toughness, wear, and modulus are dramatically increased by the multilayer coating [3]. In particular, some multilayer coatings have performed to enhance the corrosion resistance of substrate because an interdiffusion of corrosion elements was hindered by the multilayer [4]. Although this feature as a way of improving FCCI barrier performance is achievable using the multilayer coating, to the authors' knowledge, no reported literature exists for the use of multilayer coating in a nuclear cladding application.

In this work, a two-step process including electrodeposition and plasma nitriding was employed to fabricate Cr and CrN multi-layer coatings on HT9 disks, respectively, and compare their FCCI barrier properties with Cr coated HT9 disks. The two-step process is expected to have better applicability to the inner surface of cladding tubes than that of direct PVD deposition processes such as pulsed laser deposition for which high vacuum furnace and long deposition time are required. Recent diffusion couple tests with a misch metal composed of Ce and La showed that CrN layer with a 4.16 μm thickness deposited by radio frequency magnetron sputtering revealed good barrier performance at 933 K for 24 h; hence chromium nitride layer is obvious choice in our study. Plasma nitriding is a powerful surface modification technique and often applied to pre-deposited Cr layer to obtain chromium nitride layer on the surface and increase resistance to wear, corrosion, and fatigue [4-6]. In numerous research publications, the chromium nitride layer fabricated by plasma nitriding not only offered significant enhancement in diffusion barrier performance, but also provided a restoration of surface cracks in electrodeposited Cr layer [5]. Because the inter-diffusion of elements could occur through the microcracks, obtaining crack-free microstructure is critical for enhanced barrier property.

2. Experiments

Cr electrodeposition procedure on HT9 disks was described in detail in our recent publications [1, 2], and hence only a brief description is provided here. HT9 disks with 13 mm diameter and 5 mm thickness were cut from a HT9 ingot (Fe-12.0Cr-1.0Mo-0.6Ni-0.6Mn-0.52W-0.3V, etc. all values are wt.%). A face of each HT9 disk was mechanically polished with SiC abrasive paper, and 1 µm and 0.25 µm diamond paste successively. A thin electrical wire was attached on the rim of each polished HT9 disk using a spot welding. Pb-Sn alloy wire with a weight fraction of 9:1 was furled into a disk shape for use as an electrode. The electrolyte was prepared in a bicker by mixing distilled water, hexavalent chromium acid, and sulfuric acid with a weight ratio of 300: 100: 1. The HT9 disk and furled Pb-Sn wire were inserted into the prepared electrolyte and connected to a rectifier. The electrodeposition was performed then at 50 ^{o}C and 1.6 A/cm^2 for 70 mins. Magnetic bar was stirred at 150 rpm in the electrolyte during the electrodeposition.

After the electrodeposition procedure, plasma nitriding was performed on the pre-deposited Cr layer to coat CrN layer. Plasma nitriding equipment as shown in Fig. 1 consisting of RF power system, heater, and vacuum chamber was utilized for the plasma nitriding process. A RF generator was inserted in the chamber and was performed by a RF matching box and power supply. The specimen was fixed to the substrate panel of RF generator which was coiled around by a heating element to increase the temperature of specimen. A high level vacuum approximately 10^{-5} Pa was initially created in the chamber using a rotary and turbo pumps, and then, 10^{-2} Pa pressure was produced by injecting N_2+H_2 (60:40 in vol%) gas. 13.56 MHz RF frequency, the substrate dc bias voltage of -50 V, 180W RF power, and 630 ^{o}C specimen temperature were maintained during the plasma nitriding process. The processing temperature, 630 ^{o}C, could have influence on the mechanical property of HT9. Simply increasing RF power and plasma density may be better choices to decrease the mechanical property change. The nitriding time was various at 10 h and 20 h to investigate the influence of nitriding time on the element of coating layer.

The characterization of Cr/CrN coated HT9 disks consisted of microstructural analysis using Scanning Electron Microscopy (SEM) and determination of chemical compounds using XRD. The barrier property examination using a diffusion couple test with Ce-Nd alloy will be performed soon.

3. Results and discussion

As polished and Cr-coated HT9 disks are shown in Fig. 2 (a), while Cr and chromium nitride multilayer-coated HT9 disks using two-step process including electrodeposition and plasma nitriding are observed in Fig. 2 (b). The 10 and 20 h nitrided disks had two small marks in each surface as indicated. These marks came from the specimen holder fastening HT9 disks in the plasma nitriding equipment. Cr-coated HT9 disk had a bright gray color and this color was modified to a deep blue in the nitrided HT9 disks at 10 h. interestingly, another sky blue color was revealed in the surface of disk after 20 h nitriding. This difference in the surface color between 10 h and 20 h nitrided disks is due to the constituent in the coating layer as will be discussed in the next section. Cr- coated, and 10 h and 20 h nitrided HT9 disks for Cr/CrN multi-layer coating were cut and prepared for various characterization methods and the results are presented in the following.

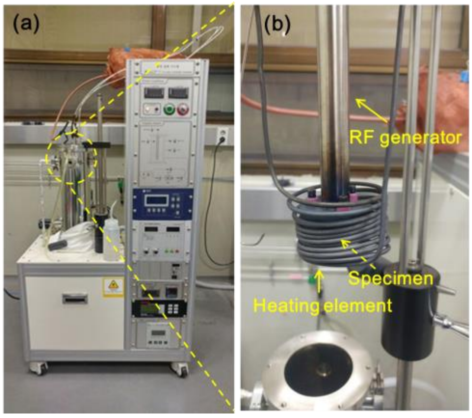

Fig. 1. (a) Plasma nitriding equipment and (b) configuration of chamber.

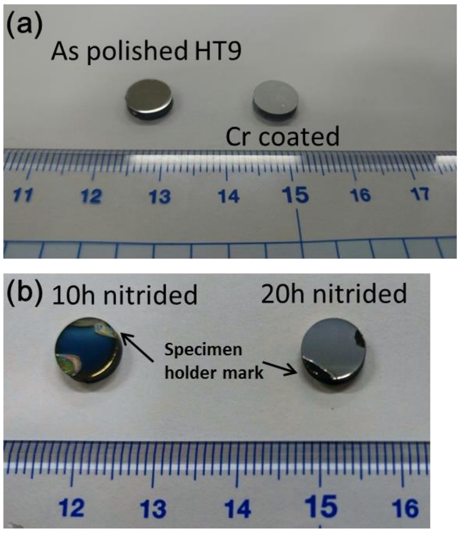

Fig. 2. (a) Untreated and Cr coated HT9 disks, and (b) 10 and 20 h nitrided disks after Cr electrodeposition.

3.1. X-ray diffraction

Fig. 3 shows the XRD patterns of the Cr-coated HT9 and specimens nitrided with 180W RF power and various nitriding times. The diffraction peak intensity of as-electrodeposited Cr layer was very weak indicating that most of the Cr layer was not crystallized. The intensity of Cr was increased by plasma nitriding with additional chromium nitride peaks. It is known that the amorphous Cr layer is crystalized during the nitriding process [5]. The Cr_2N phase was detected in the 10 h nitrided specimen, while the XRD pattern of 20 h nitrided specimen showed both CrN and Cr_2N peaks. It has been reported that Cr_2N phase is dominantly formed at a lower nitriding temperature than that of CrN phase, which is only produced at higher than 600 ^oC [7]. However, Cr_2N peak was detected after 10 h nitriding, even though the process temperature was 630 ^oC. The observed surface color difference (see Fig. 2) could be explained by the different coating materials on the surface. Even though material properties of Cr_2N and CrN are different from each other, both coated layers are expected to increase barrier property of Cr coating layer.

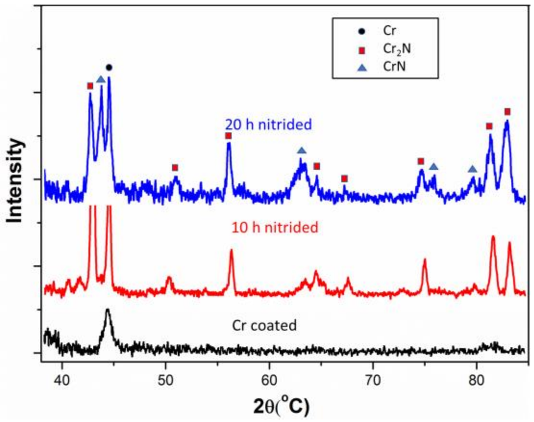

Fig. 3. Comparison of XRD spectra of Cr coated and two-step processed (Cr electrodeposition and plasma nitriding) HT9 disks.

3.2. Microstructure

Fig. 4 shows plain SEM images of as coated Cr, and 10 and 20 h plasma nitrided Cr layers on HT9 disks. The electrodeposition conditions for Cr coating such as electrolyte temperature, current density, and duration were identical for all specimens to investigate the influence of nitriding time on the microstructure. The plain view microstructure of as-coated Cr layer was dramatically changed by the plasma nitriding process. The crack-free Cr polyhedral grains were observed in as coated Cr layer while 10 and 20 h nitrided Cr layers had speculate grain structures. Small globular particles were also revealed in the specimen after nitriding as indicated in the figure. The number of these particles was increased with increasing the nitriding time from 10 to 20 h. When considering the XRD spectra of 10 and 20 h nitrided specimen, these particles seem to be related to CrN. EDS line scanning is necessary to verify the composition of these unknown particles.

4. Conclusions

A layer of Cr coating on the inner surface of HT9 cladding is a promising barrier to hinder fuel and cladding chemical interaction (FCCI) in sodum-coolded fast reactors (SFRs). However, single Cr barrier is not sufficient to prevent the inter-diffusion of spent fuel elements especially in transient overpower states of reactors. Therefore, Cr/CrN multi-barrier deposition was developed for sustainable FCCI hindrance. Cr_2N and CrN layers were successfully deposited on the pre-electrodeposited Cr barriers using plasma nitriding technique. XRD spectra of nitrided specimens revealed Cr_2N and Cr_2N+CrN elements in 10 and 20 h nitrided HT9 disks. Microstructure observation showed modified surface morphologies after plasma nitriding. Even though furthermore characterization including barrier property measurement using diffusion couple tests is necessary, this study demonstrates a promising method to enhance the barrier property of Cr coating layer and prevent FCCI in SFRs.

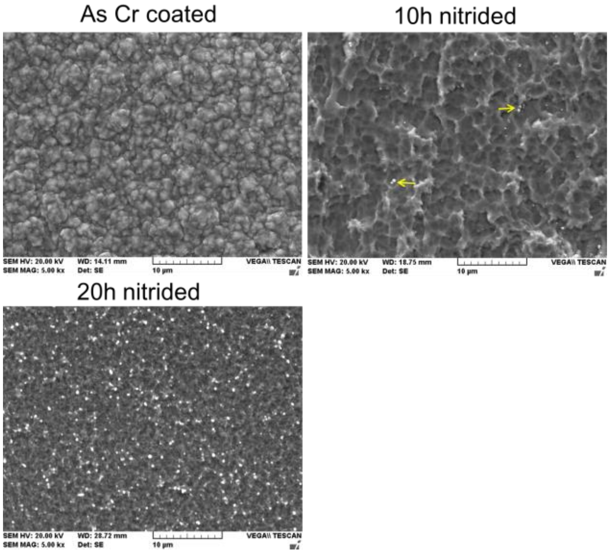

Fig. 4. Plane view microstructures of Cr coated and two-step processed (Cr electrodeposition and plasma nitriding) HT9 disks.

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