Effect of Zr-O-N thin film deposited by metalorganic chemical vapor deposition as a FCCI barrier layer for U-Zr-X metal fuel

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1. Introduction

The unique properties of metal fuel, such as high thermal conductivity, proliferation resistance, ease of fabrication, and a good compatibility for sodium have stimulated research in Sodium-cooled Fast Reactor (SFR) for burning the long-lived fission products. Among various metal fuels, U-Pu alloy exhibits high solidus temperature by adding Zr with content of 10~20 %. It is, however, very hard to use U-Pu-Zr metal fuel directly since actinide elements have a fuel-clad chemical reaction (FCCI) or eutectic reaction with stainless steel based cladding material even at just above 650°C. Recently, ferritic martensitic steels (FMS) have been studied for cladding materials of SFR fuel due to their superior performance during irradiation. It was reported [1,2,3] that a Zr sheath on U-Pu-Zr fuel rod is very effective to mimitigate clad-fuel interaction because the Zr sheath acts as a diffusion barrier. In this study, Zr-O-N thin films with different nitrogen contents were deposited on a inner surface of tube type metal clad by a metalorganic chemical vapor deposition (MOCVD) not only to reveal the nitrogen effects but also to propose the possibility of many other metal candidates as the barrier materials when nitride form thin film of those materials can be deposited onto the inner surface of the clad, even below µm level.

2. Methods and Results

2-1 Deposition of ZON thin films

It is very important to select optimal chemical precursors as the metalorganic (MO) source. Among many different type of MO sources with Zr, Tetrakis (Ethylmethylamino) Zr ($Zr(N(C_2H_5)(CH_3))_4$ with a purity of 99.99%was selected since it did not show any homogeneous reactions during deposition process. ZON thin films with various nitrogen contents (We'll reveal the composition at the result) were deposited onto surface of HT9 (Fe-12Cr-1.0Mo-0.6Ni-0.6Mn-0.52W-0.3V-etc. all values are wt%) with tube shape simulating FMS cladding by a horizontal type MOCVD. After HT9 was cleaned to remove any chemical and particle contaminations on HT9 clad, it was mounted onto a quartz susceptor.

2-2 Characteristics of ZON thin films

Scanning electron microscopy (SEM) and wide angle X-ray diffraction (XRD) measurements were carried out to identify the microstructure and crystalline properties, respectively. A depth profile of auger electron spectroscopy (AES) was conducted to detect and chemically identify the elements in the as deposited thin films quantitatively. Qualitative composition of the as deposited thin films was revealed by Rutherford backscattering spectrometry (RBS).

2-3 Preparation of metal fuel

Both uranium-zirconium alloy (U- Zr of 10 wt% ; U-10Zr) was used as a metallic fuel. A rod type of this metallic fuel was fabricated from uranium and zirconium lumps by an induction melting. Fuel rod was furnace-cooled after a melting in zirconia crucibles.

2-4 Diffusion couple test

A couple test, as shown in figure 1, was conducted to investigate function of the as deposited ZON thin films as the barrier layer to prevent FCCI. The temperature of the vacuum furnace was kept in 800 °C for 25 hours. There are two reasons why higher temperature than the normal operation temperature for metal fuel including metal Pu (For example, sodium cooled fast reactor is operated at 650 °C) is used in this study. The first is to evaluate the barrier performance in a short time or acceleration test and the second is to compensate for the missing Pu which can lowers the eutectic temperature between U-Zr-Pu metal fuel and Cladding compared to that between the binary fuel, U-Zr, and cladding.

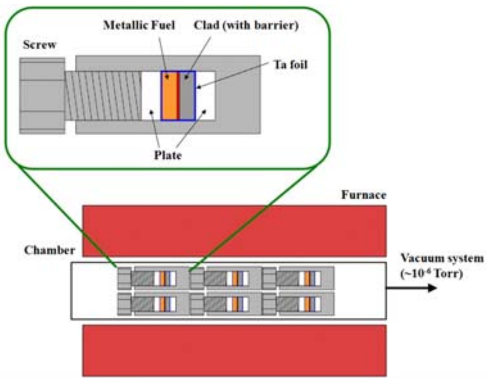

Fig. 1. Schematic illustration of diffusion couple test between metallic fuel and clad

2-5 Results

X-ray diffraction(XRD) patterns indicated that an amorphous structure of the ZON thin film deposited onto the inner surface of the HT 9 clad material.

Figure 2 shows cross-sectional view of the as deposited thin films. The thickness is depending on the hydrogen flow rate or sample (a) with hydrogen flow rate of 30 sccm and (b) with 50 sccm showed 650 nm and 600 nm, respectively. Nevertheless, the grain shapes are almost same to each other. In addition, no chemical reactions or interdiffusion phenomena were found at the interface between the as deposited thin film and the inner surface of the HT 9 clad.

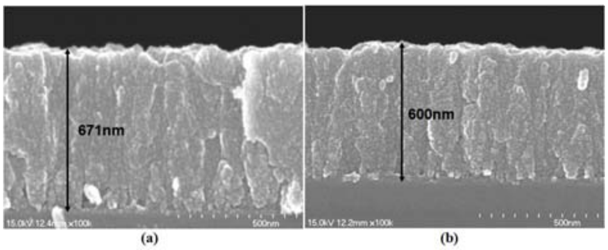

Fig. 2. cross-sectional view of as deposited ZON thin films with hydrogen flow rate of (a) 30 sccm and (b) with 50 sccm.

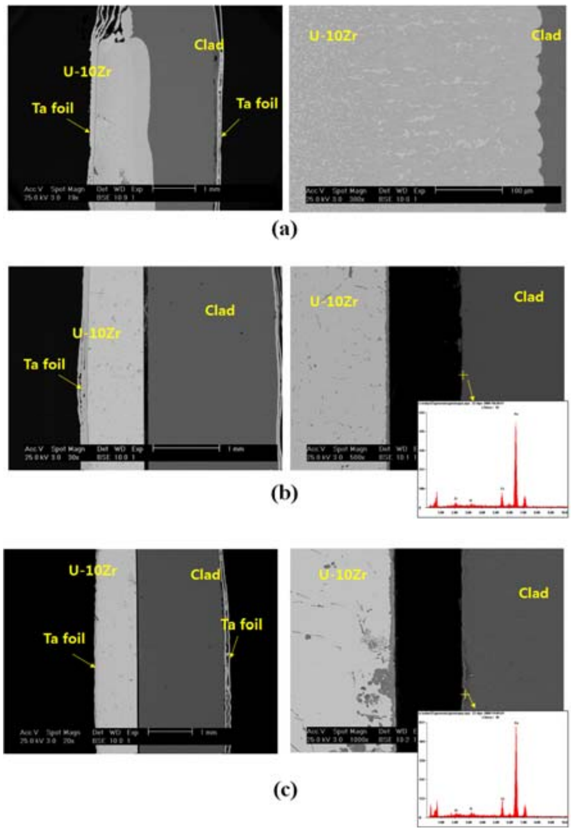

Fig. 3. Low magnitude cross-section SEM results of interface structures of the specimens after the diffusion couple test (a) without diffusion barrier and ZON film with hydrogen flow rate of (b) 30 sccm and (c) with 50 sccm.

The low magnitude cross-section SEM results of interface structures of the specimens after the diffusion couple test at 800°C for 25 hours were shown in figure 3. A chemical reaction was found massively in the sample without the diffusion barrier as shown in figure 7 (a). A little interdiffusion was found in the sample (b) as shown the figure 3. Besides, in figure 3 (b), a little Uranium was also observed at the interface (cross expression in figure 3 (c)) between ZON thin film and cladding material by EDS spectrum. The HT 9 clad and alloy fuel diffused toward the fuel and the clad, respectively, resulting in formation of a chemical reaction interface area which is one of the typical shapes for the interface melt reaction. That is, the eutectic reaction was occurred in the sample (b), which means the as deposited ZON thin film could not prevent interdiffusion or eutectic reaction between the HT 9 clad and the alloy fuel.

In the case of sample (a), No visible interdiffusion at the interface was observed between the HT 9 and the U-10Zr. Besides, in figure 3 (a), little Uranium was observed at the interface (cross expression in figure 3 (b)) between ZON thin film and cladding material by EDS spectrum. Even though it is hard to explain why the alloyU-10Zr fuel and the HT 9 clad were found to be detached from each other, it can be speculated that the ZON thin film might be removed by a cutting process for preparing the cross-section view SEM sample due to mechanical force of the cutting wheel. This phenomenon is originated from no chemical reactions between the alloy fuel and the ZON thin film as well as the HT 9 clad and the ZON thin film.

This result suggested that nitride form of ZON thin film, even with the thickness below μm level, has very high possibility as an effective barrier against FCCI.

3. Conclusions

The prevention in the interdiffusion or eutectic reaction between the U-10Zr alloy fuel with the HT 9 clad was shown for the HT 9 clad with the ZON thin film. ZON thin films were deposited by MOCVD with MO source, such as Tetrakis (Ethylmethylamino) $Zr(Zr(N(C_2H_5)(CH_3))_4$ for the diffusion barrier. In case of the sample at the interface with ZON thin film, interdiffusion at the interface was not observed between the HT 9 clad and the U-10Zr fuel. Based on RBS, We confirmed that ZON thin film with high nitrogen content could prevent the FCCI between the HT 9 clad and the U-10Zr fuel.

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