FCCI Barrier Performance of a Nitrided Cr Plating Layer

Ho Jin Ryu*, Seong Woo Yang, Jun Hwan Kim, Jin Sik Cheon, Byoung Oon Lee, Chan Bock Lee
Recycled Fuel Development Division, Korea Atomic Energy Research Institute, Yuseong, Daejeon, 305-353
**Corresponding author: hjryu@kaeri.re.kr*

1. Introduction

Metallic fuel for a sodium-cooled fast reactor (SFR) has many advantages such as a good thermal conductivity, high neutron economy, inherent passive safety and compatibility with sodium. However, fuel cladding chemical interaction (FCCI) is one of the factors limiting the performance of metallic fuel. In order to avoid eutectic melting from FCCI, the maximum fuel-cladding interface temperature should be kept lower than the eutectic melting temperatures around 725°C for U-Zr fuel and 650°C for U-Pu-Zr fuel. Insertion of diffusion barrier layers onto cladding inner wall has been proposed in order to retard FCCI[1]. Recent preliminary screening tests showed that V and Cr have good diffusion barrier performance when compared with other candidate materials such as Zr, Ti, and Nb[2]. Electroplating of Cr on the inner wall of a cladding was carried out by Yang et al.[3]. Cr layers of 20 μm in thickness were electroplated on ferritic/martensitic steel (FMS) and their diffusion barrier performance was evaluated by diffusion couple tests between a metallic fuel and FMS. When the diffusion couple tests using Cr-plated FMS were conducted at temperature of 700, 740, and 800°C and compared with diffusion couple tests without a Cr-plated layer, plated Cr layer retard a eutectic melting between U-Zr and FMS effectively up to 800°C for 25 h. However, a penetration of U along the cracks in the Cr layer was observed. The penetration of U through the Cr layer should be avoided in order to minimize cladding wastage.

In this study, Cr plating layers on FMS disks were nitride in order to inhibit the U penetration through the cracks in the Cr plating layer. FCCI barrier performance of nitrided Cr plating layer was evaluated by diffusion couple tests between U-Zr or U-Zr-Ce and Cr plated T91 cladding steels.

2. Experimental Procedures

U-10wt%Zr and U-10wt%Zr-6wt%Ce were used as fuel materials. They were fabricated by an induction melting and low pressure gravity casting by using elemental lumps of U, Zr and Ce. Each rod with a diameter of 10 mm was cut into a disk with 1 mm in thickness. T91 (Fe-9Cr-1Mo-0.2V-0.1C-0.45Mn-0.4Si-0.08Nb-0.05N) disks were used as a FMS cladding material. Their diameter and thickness were 8 and 1.5 mm, respectively. Cr was electroplated on the polished surface of T91 in a bath containing 250 g/*l* of chromic acid and 2.5 g/*l* of sulfuric acid. Cr plated T91 disks were nitride at 750°C for 3 hours in a flowing ammonia (NH_3) atmosphere. The surface structure of nitride layer was measured by X-ray diffraction(XRD). The fuel/cladding diffusion couples were heat-treated at temperature of 700°C for 96 hours and 800°C for 25 hours in a vacuum tube furnace, where the vacuum level was $5x10^{-3}$ torr. The cross-sectional microstructures of the diffusion couple were characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

Crystalline structure of Cr is bcc (a=2.884 Å), Cr_2N is hcp (a=4.811Å, c=4.484 Å) and CrN is fcc (a=4.140 Å). Fig. 1 is XRD patterns of nitrided surface of Cr plating showing diffraction peaks mainly for Cr_2N and a few peaks for CrN phase. It is reported that a mixture of Cr and Cr_2N is formed between 600 and 700°C and two-phase structure of CrN and Cr_2N is formed between 700 and 1100°C[4]. After gas nitriding at 750°C in this study, Cr_2N and CrN seem to be the main phases according to XRD patterns. EDS analyses on nitrided layer showed that a nitrided layer has a composition closer to Cr_2N than CrN. It was difficult to measure nitrogen content in the remaining Cr plating layer by EDS analyses, but nitrogen can be dissolved into the Cr plating layer. Volume expansion for a conversion from Cr to Cr_2N is 250% and for Cr to CrN is 150%[4]. Compressive stress is applied to remaining Cr matrix after nitriding of Cr plating and it will make diffusion through the layer more difficult. In addition, cracks in a Cr plating layer can be removed by the conversion of its surface layer to chromium nitrides because surface diffusion of nitrogen is activated along cracks. Therefore, diffusion barrier performance of the Cr plating layer can be improved by a gas nitriding treatment. A gas nitriding temperature higher than 780°C is not recommended because a tempering temperature for FMS is usually around 780°C.

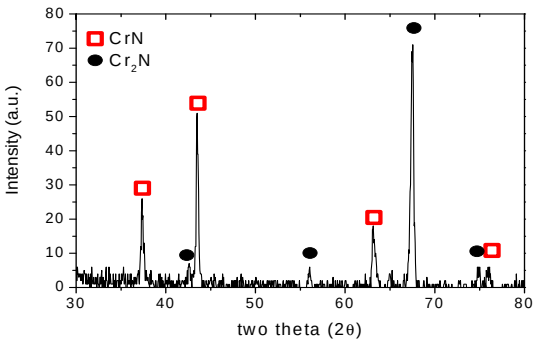
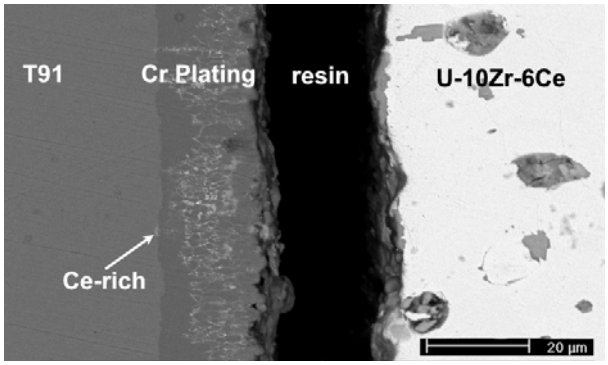
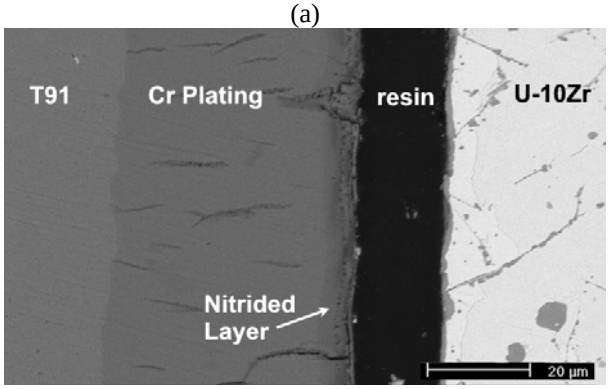


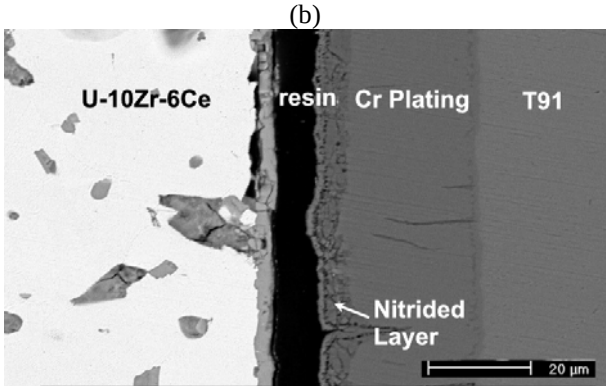
Fig. 1. XRD patterns of a nitrided Cr plating layer.



(a)



(b)



(c)

Fig. 2. Back-scattered electron images of diffusion couple samples tested at 800°C for 25 h; (a) U-10Zr-6Ce vs. Cr plated T91, (b) U-10Zr vs. Cr plated T91 after nitriding, (c) U-10Zr-6Ce vs. Cr plated T91 after nitriding.

Fig. 2 shows cross-sectional micrographs of diffusion couples annealed at 800°C for 25 h. Although the maximum fuel cladding interface temperature is about 600-650°C for SFR fuel, diffusion couple tests at 800°C were carried out in order to simulate transient conditions. When a diffusion couple of U-10Zr-6Ce vs. Cr plated T91 was tested (Fig. 2a), no eutectic melting was observed after annealing at 800°C. But uranium-rich phase was found along the cracks of Cr plating and Ce-rich phase was penetrating through the cracks and reached a T91 cladding surface. It seems that the addition of rare earth elements enhances the interdiffusion of uranium through the crack surfaces. It is necessary to reduce the cracks which can be fast diffusion paths for uranium, plutonium, minor actinides or rate earth elements. When the Cr plating layers were nitrided by ammonia gas treatment at 750°C for 3 hours, the penetration of uranium or cerium was not observed after diffusion couple tests at 700 or 800°C(Fig. 2b, 2c). In addition to changes in chemical affinity by nitriding, compressive stress by volume expansion, and crack closure after nitriding may be the reasons for the reduction of uranium and cerium penetration through the Cr plating layers. Considering the large thermal expansion mismatch between chromium nitrides and FMS, surface nitriding of Cr-plated FMS is an adequate multilayer formation for FCCI barrier coatings on FMS cladding inner wall. In future, gas nitriding condition should be optimized in order to minimize detrimental effects on the mechanical properties of FMS cladding. Plasma or ion-beam assisted nitriding processes can be applied to enhance the nitriding efficiency of Cr plating layers on FMS cladding.

4. Conclusions

Although Cr plating exhibited good FCCI barrier performance against U-Zr fuel, U and Ce penetration was observed extensively in a diffusion couple of U-Zr-Ce and Cr-plated T91. When the Cr-plating layer on T91 was nitrided under an ammonia stream, the U or Ce penetration was not found after diffusion couple tests at 700°C for 96 hours and 800°C for 25 hours. Gas nitrided Cr-plating layers showed excellent FCCI barrier performance especially against rare earth elements containing metallic fuel.

ACKNOWLEDGMENTS

This study was supported by the National Nuclear R&D Program of the Ministry of Education, Science and Technology (MEST) of Korea.

REFERENCES

[1] D. D. Keiser, Jr and J. I. Cole, An Evaluation of Potential Liner Materials for Eliminating FCCI in Irradiated Metallic Nuclear Fuel Elements, Global 2007, Sep.9-13, 2007, Boise, USA.

[2] H. J. Ryu, B. O. Lee, S. J. Oh, J. H. Kim, and C. B. Lee, Performance of FCCI Barrier Foils for U-Zr-X Metallic Fuel, *Journal of Nuclear Materials*, Vol.392, p.206, 2009.

[3] S.W. Yang, H.J. Ryu, J.H. Kim, B.O. Lee, C.B.Lee, Performance of electroplated Cr as a FCCI barrier material for a sodium-cooled fast reactor (SFR) cladding, *KNS Spring Meeting*, May 22, 2009, Jeju, Korea.

[4] J. G. Buijnsters, P. Shankar, J. Sietsma, J. J. ter Meulen , Gas nitriding of chromium in NH_3–H_2 atmosphere, *Materials Science and Engineering A*, Vol.341, p.289, 2003.