Study on fabrication and characterization of nano structured ZrO_2 thin films for cladding of advanced light water reactor

Seung Hyun Jee[a], Soo Ho Kim[a] and Young Soo Yoon[a,*]
Jong Hyuk Baek[b], Jun Hwan Kim[b]
[a] *Department of Advanced Material Engineering, Yonsei University, 134 Sinchon Dong, Seoul 120-749, Republic of Korea*
[b] *Recycled Fuel Development Division, Korea Atomic Energy Research Institute, P.O.Box 105, Yuseong, Daejeon, 305-600, Republic of Korea*
[*] *Corresponding author: yoonys@yonsei.ac.kr*

1. Introduction

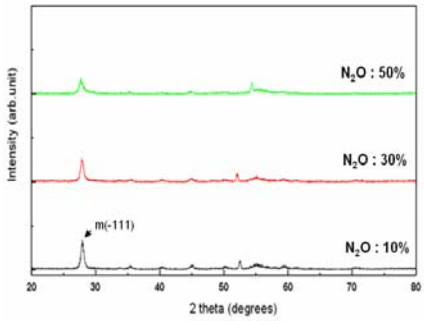
Recently, ZrO2 thin film has been considered as a protective layer for the Z-4 cladding material (Z-4) of a fuel assembly in a pressurized water reactor (PWR). [1] One of the major problems is the generation of surface oxidation of Z-4 during nuclear reactor operation at high temperature and pressure. This surface oxidation forms a ZrO2 thin layer, which is characterized by the presence of simultaneous monoclinic and tetragonal phases. Of these phases, the monoclinic phase could not prevent oxidation from occurring toward the center of Z-4 during nuclear reactor operation while the tetragonal phase was excellent for blocking further oxidation of the Z-4. These phenomena originated from lower oxygen diffusion coefficient of the tetragonal phase compared to that of the monoclinic phase. Therefore, the ZrO2 thin film grown on Z-4 should be in a tetragonal phase if the ZrO2 thin film is to be used as a protective layer of Z-4 [2,3].

2. Methods and Results

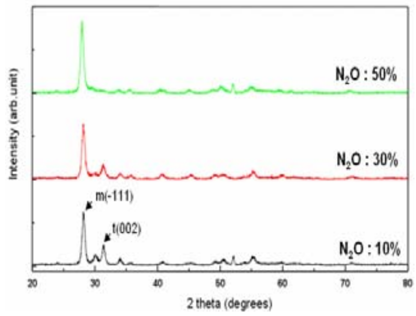
2.1 crystal structure and stoichiometry analysis

Zirconium-oxide (ZrO_2) thin films as protective layers were grown on a Z-4 as a substrate by RF reactive magnetron sputtering with N_2O gas at room temperature. To investigate the effect of plasma immersion on the structural and the corrosive properties of the as-grown ZrO_2 thin film, we immersed Z-4 in plasma during the deposition process. Generally, ZrO_2 presents three different crystallographic forms. ZrO_2 at room temperature has a monoclinic phase. Tetragonal and cubic phases also exist at high temperatures. X-ray diffraction (XRD) measurements showed that the as-grown ZrO_2 thin films immersed in plasma had cubic, well as monoclinic and tetragonal, phases whereas those immersed in the plasma had monoclinic and tetragonal phases only. The XRD patterns of samples 1 and 2 are shown in Fig. 2. In all samples, the as-grown ZrO_2 thin films showed crystalline phases. Sample 1 had monoclinic and tetragonal phases. The peaks at approximately 2θ=28°and 29°are attributed to the diffraction from the monoclinic (-111) plane and the tetragonal (-111) plane. On the other hand, sample 2 had the strong (220) ZrO_2 peak of the cubic phase. Fig. 2 shows the surface image of ZrO2 thin film by FESEM. The grain size was increased in plasma state.

To confirm the stoichiometry of the as-grown ZrO_2 thin films, we simulated the RBS spectrum shown in Fig.1 by using RUMP, which confirmed the composition of the as-grown film as $Zr_1O_{1.9}$ regardless of the deposition conditions. The RBS results show that plasma immersion does not influence the composition of the as-grown ZrO_2 thin film.

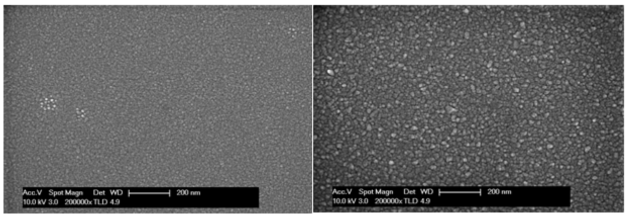


(a)



(b)

Fig. 1. X-ray diffraction results of ZrO2 thin film by Plasma immersing effect. (a) Out plasma state (b) In plasma state.

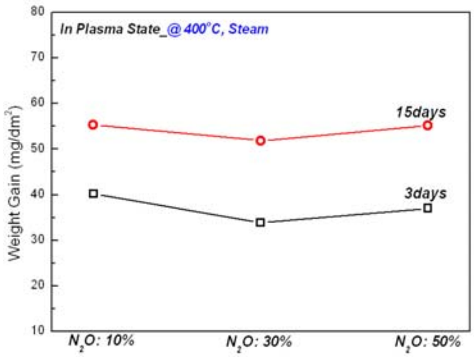


(a) (b)

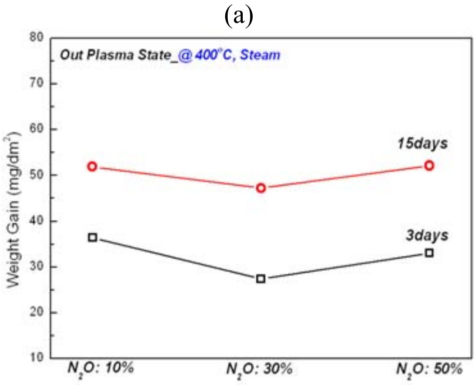
Fig. 2. Results of surface of ZrO_2 thin film by plasma immersing effect. (a) Out-plasma-state : N_2O 10% and (b) In-plasma-state : N_2O 10%.

2.2 Corrosion property analysis

The immersion in plasma increased in the weight gain of the Z-4 with the ZrO2 thin film, as shown in Fig. 4. The increase in the weight gain signifies a decrease in corrosion resistance. According to the XRD result, the mole fraction of the tetragonal phase in the ZrO2 thin film with in-plasma-state was higher than it was in ZrO2 thin film with out-plasma-state. This result shows well research reports showing that the corrosion resistance of the Z-4 is excellent when the mole ratio of the as tetragonal phase is high [4]. Therefore, this result indicates that the difference in weight gain or corrosion behavior may be related to the increased the tetragonal structure. Fig. 4 shows the real picture of ZrO2 thin film onto hemispherical surfaces.



(a)



(b)

Fig. 3. Results of corrosion chacteristic of ZrO_2 thin film by plasma immersing effect. (a) Out plasma state and (b) In plasma state.

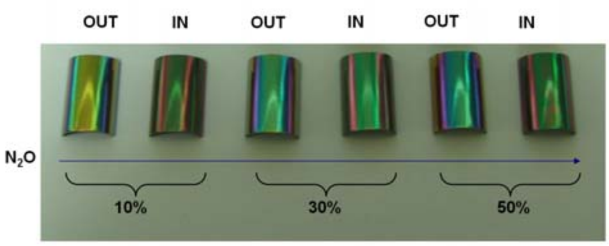


Fig. 4. Hemispherical zircaloy-4 cladding material deposited by ZrO_2.

3. Conclusions

The ZrO_2 thin films, as protective layers for Z-4, were grown by RF magnetron sputtering with N_2O gas. The XRD measurements showed existence of different crystalline phases, depending on the substrates location. The as-grown ZrO_2 thin film not immersed in plasma had monoclinic and tetragonal phases while the film immersed in plasma also had a cubic phase. As the RBS measurement showed, the stoichiometry of the as-grown films was $Zr_1O_{1.9}$, regardless of the deposition conditions. After corrosion tests for 30 h, the weight gain of the samples was larger in case of the samples that had been immersed in plasma. One of the reasons for the weight gain in the film is that the mole ratio of the tetragonal phase decreased. These results indicate that plasma immersion for growing ZrO_2 thin films when RF reactive magnetron sputtering induces the formation of the cubic crystalline phase and decreases the corrosive resistance of Z-4.

REFERENCES

[1] M. I. Maleto, L. I. Solovjeva, E. P. Turevskaya, K. A. Vorotilov and M. I. Yanovskaya, Thin Solid Films 249, 1 (1994).
[2] J. S. Kim, H. A. Marzouk and P. J. Reucroft, Thin Solid Films 254, 33 (1995).
[3] A. Feldman, X. Ying and E. N. Farabaugh, Appl. Opt. 28, 5229 (1989).
[4] Young Hwa Kim, Jong Hyuk Baek and Young Hwan Jeong. J. Kor. Inst. Met. Mater. 41, 916 (2003).