Ion Beam Bombarded SiC Coating on Hastelloy X for Nuclear Hydrogen Production System

Jae-Won Park[a*], Zuhair S Khan[b], Hyung-Jin Kim[a] and Yongwan Kim[a]
[a] *Korea Atomic Energy Research Institute, 150 Dukjin-Dong, Yusung-Gu, Daejeon, South Korea.*
[b] *Department of Physics, COMSATS Institute of Information Technology, 30 H-8/1, Islamabad, Pakistan.*
[*] *Corresponding author :pjw@kaeri.re.kr*

1. Introduction

The process heat exchanger (PHE) in the IS cycle of the nuclear hydrogen production system is composed of He gas channels and decomposed sulfuric acid ($SO_2/SO_3/H_2O$) gas channels [1]. The materials for the PHE require excellent mechanical properties at an elevated temperature as well as a high corrosion resistance in SO_2/SO_3 environment. In this work, a surface modification of Hastelloy X using a SiC has been studied. The SiC coating is known to improve the lifetime or the performance of metallic substrates when exposed to an aggressive environment [2].The SiC coated layer exhibits a poor adhesion with Hastelloy X due to a big difference in their coefficients of thermal expansion. we have developed an ion beam mixing (IBM) [3 – 4] technique to produce a highly adherent coated layer and to reinforce the base materials and an ion beam hammering(IBH) onto the final SiC coating layer to surmount the vacuum sublimation.

2. Methods and Results

2.1 Experimental procedure

SiC films were deposited with an electron beam evaporative method on Hastelloy X sheets (~ 15x15x0.5mm) surface-polished up to 0.05 μm. Prior to a SiC deposition, a sputter cleaning of the sample was carried out for 10 minutes with a N ion energy of ~10 keV and current of 0.5 Ampere. Then, the electron beam evaporation of the SiC was performed up to 50 nm thick, followed by a nitrogen ion beam mixing at 70keV with a dose of ~ $5x10^{16}/cm^2$. The work chamber vacuum pressure during sputtering and evaporation were $5.0x10^{-5}$Torr and $1.0x10^{-5}$ Torr, respectively. A further SiC evaporative deposition up to totally 2 μm was then conducted with a deposition rate of ~3 Å/s produced by an electron beam current of ~0.15 A. The substrate temperature during the e-beam evaporative deposition was ~150℃. And then, the N ions bombardment onto the deposited film was done at 70 keV with a dose of ~ $5x10^{16}/cm^2$. The e-beam evaporative deposition device used in this work is equipped with a 100 keV ion implanter, aiming the coating and ion beam bombardment to be performed in the same vacuum work chamber. During the deposition process the thickness of the deposited film was monitored in-situ by a gold plated quartz crystal, followed by an actual measurement with the cross sectional SEM observation.

The surface was characterized with Auger electron spectroscopy Phi Model SAM670).

Surface morphology of a SiC film on Hastelloy X prepared in this work was observed with SEM before and after immersing in 98% H_2SO_4 for 25 hrs at ~300℃.

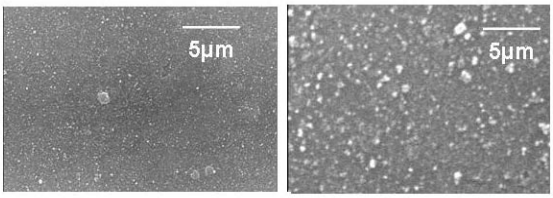
The samples were placed in an alumina boat and annealed in a quartz tube vacuum furnace with a heating rate of ~7.5□/min at 950℃ for 2 hrs. The work chamber vacuum pressure was ~1.5 $x10^{-5}$ Torr. X-ray diffraction(XRD) was then performed to see any new phase formation between the film and the substrate. XRD was conducted with a Rigaku Geiger count diffract meter.The samples were weighed with a micro balance of a readability of 0.01mg (a repeatability of 0.02mg) to determine the resultant sublimation rate.

2.2 RESULTS AND DISCUSSION

The surface of the film is covered with thick oxide layers and the oxides are proved to be silicon oxides [8].

2.2.1 Morphology of the surfaces after immersing in 98% H_2SO_4

Fig. 1 is the surface morphologies observed with SEM of a SiC film on Hastelloy X prepared in this work before and after immersing in 98% H_2SO_4 for 25 hrs at 300℃. The SiC film looks amorphous embedded with small coalescent particles. After corrosion, no etch pit is found on the surface, implying that the deposited film does not contain significant defects such as micro-pipes, voids, inclusions, etc. However, the small particles become larger (fig. 1b), implying that the SiC particles embedded in the amorphous SiC film grow as heating. We found the amorphous transform mostly to the crystalline at the temperature of 700-800℃.



(a) (b)

Fig 1. The SEM surface morphologies SEM before (a) and after (b) immersing in 98% H_2SO_4

2.2.2 X-ray diffraction

As shown in fig. 2, the Hastelly X FCC peaks and SiC FCC peaks were identified. The lattice parameters

estimated as 3.66Å(Hastelloy X) and 4.4Å(SiC) are well consistent with the lattice parameters of the standard samples. Some of the peaks seem to come from SiO_2 formed on the surface of the deposited film. However, there are many unidentified peaks as arrow-marked, which seem to stand for the compounds formed among Ni, Cr, Si, C and/or O. Once the reaction takes place, new phases are developed at the interface under the consumption of the film and the substrate materials. The new phases have not been identified clearly yet, but it seems most of them should be Ni-Si compounds because Ni is very reactive with SiC [6, 7]. The further reaction may be governed by the thermal diffusion between the film and the substrate.

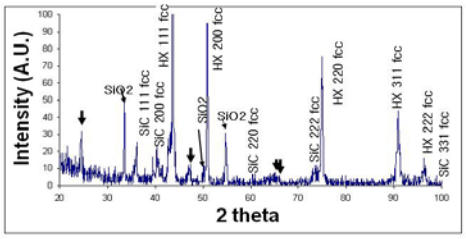
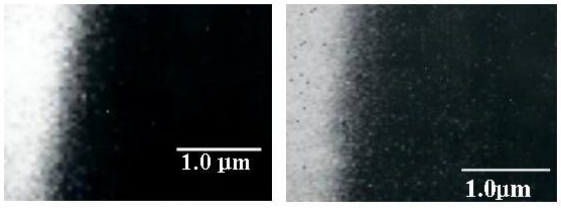


Fig. 2. X-ray diffraction pattern

2.2.3 Auger elemental mapping at the interface

Figure 3 shows the Auger elemental mapping from the coated layers to the base materials before (Fig. 3a) and after (Fig. 3b) an ion beam bombardment. It shows clearly how an intermixing took place at the interface. TRIM software [8] suggests that 100 keV N ions stop mostly at about 70nm in depth from the surface of a 50nm thick SiC film/Hastelloy-X substrate. This means that 100 keV N ions pass over the coating layer and stop mostly in the substrate area. Therefore, a N ions bombardment should produce not only a mixing of the film with the substrate at the interface but also a reinforcement of the substrate.



(a) (b)

Fig. 3. Auger elemental mappings.

2.2.4 Ion beam hammering (IBH) to suppress the sublimation during a vacuum annealing

As determined by the weight changes, the surface areas of the sample, and the SiC film thickness, the density of the SiC films in this work was about 1.92 g/cm^3 that is about 40% lower than that of the bulk SiC (3.217 g/cm^3) [9]. The SiC film in the sample without IBH is mostly sublimed to coat onto the adjacent surfaces during an annealing at a temperature of 950℃ in a vacuum of $1.5x10^{-5}$ torr. However, an ion-beam bombardment on the deposited SiC film did not reveal a deposition onto the adjacent surfaces while annealing it at 950℃.

Table 1. Weight variations before and after an annealing in a vacuum

	Before-coating (mg)	After-coating (mg)	After vacuum-Annealing at 950℃ for 2hrs (mg)	SiC film Thick. change
IBH 1	920.72	921.58	921.22	– 0.4μm
IBH 2	920.87	921.73	921.46	– 0.3μm

3. Conclusions

The IBM SiC protective coating on Hastelloy X can be sustained at the elevated temperature. IBM plays a role of fastening the SiC film on the Hastelloy X substrate until the interfacial reaction takes place as heating. Once the reaction takes place, new phases are developed at the interface under the consumption of the film and the substrate materials and act as buffer layers.

A SiC film deposited by an electron beam evaporation is sublime during an annealing in a vacuum. However, an ion-beam bombardment on the deposited SiC film is likely to densify and strengthen the film, producing a sublimation barrier. The resultant film exhibits a high corrosion resistance behavior.

REFERENCES

[1] H. Ota, S. Kubo, M. Hodotsuka, T. Inatomi, M. Kobayashi, A. Terada, S. Kasahara, R. Hino, K. Ogura, S. Maruyama, Proc. 13th International Conference on Nuclear Engineering, Beijing, China, May 16-20, 2005, ICONE-13-50494

[2] J.-P. Riviere, J. Delafond, P. Misaelides, F. Noli, Surf. Coat. Technol. 100-101 (1998) 243

[3] R. Nakatani, R. Taniguchi, Y. Chimi, N. Ishikawa, M. Fukuzumi, Y. Kato, H. Tsuchida, N. Matsunami, A. Iwase, Nucl. Inst. Meth. B 230 (2005) 234

[4] Wolfgang Bolse, Mat. Sci. Eng. A253 (1998) 194

[5]. Jae-Won Park, Youngjin Chun, Jonghwa Chang, Journal of Nuclear Materials, Volume 362 (2007) 268-273

[6] B. Peez, G. Radnoczi, C. Brylinski, C. Arnodo, O. Noblanc, Diamond and Related Materials 6(1997)1428-1431

[7] C. S. Pai, C. M. Hanson, S. S. Lau, J. Appl. Phys. 57 (1985) 618

[8] J. F. Ziegler, J. P. Biersack, U. Littmark, "The Stopping Range of Ion in Solids", Pergamon Press, New York, (1985)

[9] CRC hand book of chemistry and physics, CRC press Inc. , 1988, B-60, ISBN 0-8493-0740-6