Process heat exchanger for SO₃ decomposer fabricated with Ni-based alloys surface-modified by SiC film deposition and N ion beam bombardment

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1. Introduction

In the iodine-sulfur (IS) cycle [1] for the hydrogen production using the high temperature gas-cooled reactor (HTGR), one of the important components is the SO_3 decomposer which generates SO_2 and SO_3 gases under high temperature conditions [1]. Since this environment is extremely corrosive, the materials used for the decomposer should meet excellent mechanical properties at the elevated temperature as well as high corrosion resistance in SO_2/SO_3 atmospheres. In general, ceramics are protective against the corrosion, but metals exhibit limited corrosion resistance. In this work, the ceramic coating on the metallic substrate was studied. We selected SiC as coating materials and Ni-based alloys as the substrate materials. Since the adhesion between the coated layer and the substrate is most crucial in this application, we attempted to develop Ion Beam Mixing (IBM) [2-5] technique to produce a highly adherent coated layer.

For the fabrication of process heat exchange for SO_3 decomposer, the diffusion bonding at ~900°C is employed because this temperature does not affect the mechanical properties of materials.

2. Experiments and results

2.1. Sample preparation

Samples from Hastelloy-X polished on all surfaces to have the surface-roughness (*Ra*) less than 0.05 μm were ultrasonically cleaned in acetone to degrease the surfaces and then the surfaces of the samples were Ar-ion-bombarded to eliminate the surface contaminants before film deposition. The electron beam evaporative method was employed for the SiC film deposition. A ~50 nm thick SiC film was deposited on the samples and then N ions with an ion dose of about 1×10^{17} cm^{-2} were bombarded onto the film surface with an energy of 100 keV and 150 keV. A schematic of the coating and ion beam bombardment is shown in Fig.1. After depositing the film, the substrate holder was tilted by 90˚ in order to be bombarded by ions. Then, the substrate was re-tilted for the additional coating to 500nm thick.

For the development of the diffusion bonding process, mechanical clamping and heat-induced stressing method was employed.

2.2. Electrolytic etching with 10% oxalic acid

Electrolytic etching in 10% oxalic acid was performed on the partly coated samples with applying 4 V and 0.4 A until the grain boundaries on the uncoated
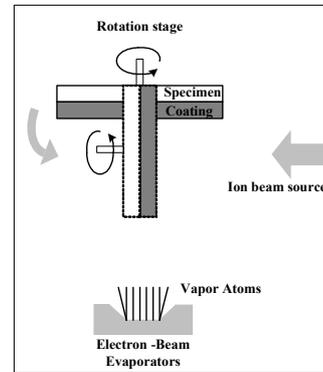

Fig. 1. Schematic of the coating and ion beam mixing process.

surface were observed. Then, optical microscopy was used to observe the morphology of the corroded and etched surfaces. Figure 2-a and -b shows the optical microscopic observation of the surfaces etched electrolytically.
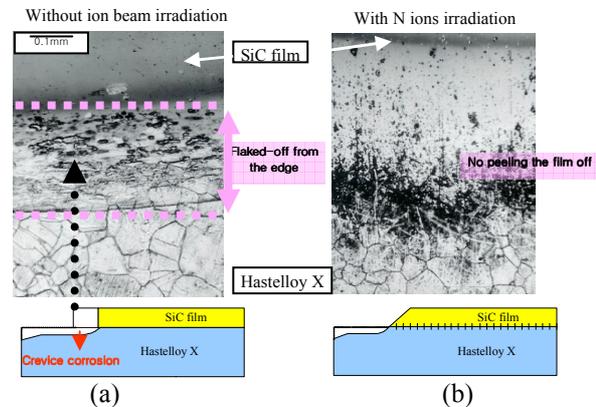

Fig.2. The optical-microscopic observation of the surfaces etched electrolytically.

The depth of the surface erosion was about 35 μm as estimated with optical microscopy by measuring the moving distance of the lens during focusing the image. The sample without the ion bombardment shows flakes at the edge of the film (Fig. 2a) after electrolytic etching, implying that the corrosion initiates from the uncoated substrate to the film and then penetrates underneath the film. As the erosion propagates, the film is flaked-off from the edge. However, such corrosion is not found in the ion-bombarded sample after etching in the same conditions (Fig. 2b). This means that the substrate under the film was reinforced to be corrosion-protective by ion beam mixing.

2.3 AES elemental mapping

Elemental distributions at the interface after and before the ion beam bombardment were investigated with Auger mapping technique. Figure 3 shows Si mapping acquired by AES at the interface between the SiC film and the Hastelloy X substrate before (Fig. 3a) and after (Fig. 3b) ion beam bombardment. White areas in each mapping denote distribution of Si element and dark area represents no existence of Si, that is, Hastelloy-X area. The existence of Si stands for the existence of SiC. The difference of Si distributions before and after IBM at the interfaces is clearly seen.
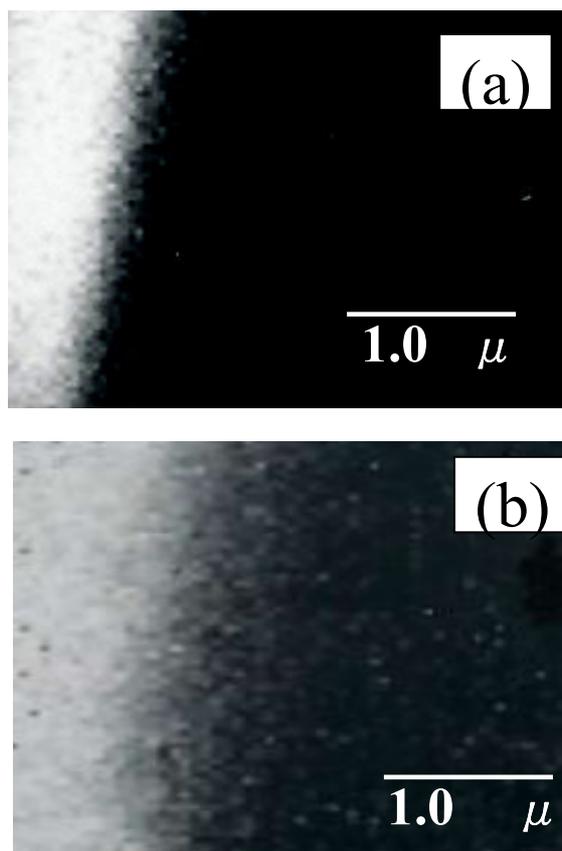
(a)

1.0 μ

(b)

1.0 μ

Figure 3. Si mapping acquired by AES at the interface between SiC film and Hastelloy X substrate: before (a) and after (b) 100keV ion beam bombardment.

Clearly, the intermixing took place at the interface. That is, the mixing results from the recoil implantation of the film atoms during ion beam bombardment. However, our previous works suggest the ion energy should be properly chosen depending on the film thickness, because the stopping range of ions is a function of the ion energy. In this sample AES depth profiling shows that the ion energy of 150 keV is too high to mix the interface, that is, most ions stop in the substrate region rather than at the film/substrate interface.

2.4. Diffusion bonding

The stainless work-pieces were pressed with Inconel clamping jigs that have lower thermal expansion coefficient than the work-piece, followed by heating. During heating, very high stresses should be exerted to the interface of the work-pieces due to the constrained thermal expansion, resulting in the well adhesion due to the thermal diffusion. Figure 4 is an example of the diffusion bonded stainless steel work-piece; a part of the interface appears as a grain-boundary while some part is not adhered completely, but a prolonged heat treating time should result in a complete adhesion.
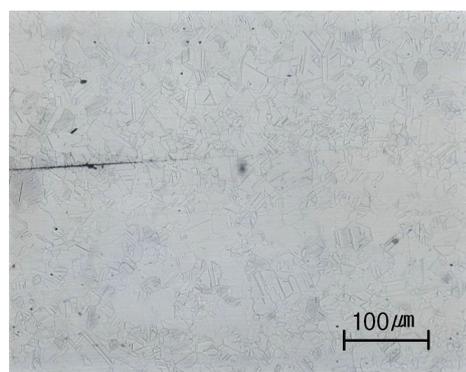
Figure 4. A cross sectional microstructure of the diffusion bonded stainless steel work-pieces at the interface.

3. Conclusions

The ion beam mixing of the ceramic thin film coated on metallic substrates presents feasibility in the development of sustainable materials at above $1173\,^{\circ}K$ in SO_3/SO_2 ambience. The mechanical clamping with heating, that is, the diffusion bonding, is good enough for the adhesion of the materials for the process heat exchanger, because the bonding occurs at $\sim 900\,^{\circ}C$.

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