

Effects of ion beam mixing of silicon carbide film deposited onto metallic materials for application to nuclear hydrogen production

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Abstract

The effects of ion beam mixing of the SiC film coated on metallic substrates were studied, aiming at developing highly sustainable materials at above 1173 K in SO₃/SO₂ ambience. Firstly, ~50 nm thick SiC films were deposited by e-beam evaporative method on stainless 316 L, Inconel 800H, Inconel 690, and Hastelloy-X substrates, followed by the 100 keV (Ar and N) ions bombardment to mix the interfacial region. After ion beam mixing, additional ~500 nm thick SiC film was deposited onto the ion bombarded SiC film. Samples with and without ion beam mixing were immersed in 50% H₂SO₄ solution for 1 h with heating the solution up at 573 K. The film in the as-deposited sample was completely removed during the immersion, while the ion beam mixed sample exhibited no detachment of the deposited film. The corrosion of non-ion beam-mixed sample initiated from non-deposited metallic surface and then propagated to the film deposited region, flaking-off the film from the edge. The interface formed by ion beam mixing seems to be protective against the corrosion. The SiC film/metallic substrates were heated up to 1223 K. The film deposited on the stainless steel substrate was completely peeled off, while the films deposited on Ni-based alloys all sustained. This is due to the difference of thermal stresses between the film and substrate materials. The best materials combination in our experimental scheme is the SiC film and the Hastelloy-X, because their thermal properties are more similar than for the other materials combinations.

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1. Introduction

Recently, the global warming by the so-called green house effect resulted from carbon dioxide emission has become a serious environmental problem and, for this reason, hydrogen energy system

has acquired a great interest. Various R&D activities to meet the potential hydrogen demand are being conducted, mainly focusing on effective ways to produce hydrogen [1,2]. Nuclear energy is being considered as a promising candidate for the primary energy source, because it supplies a stable energy and is environmentally harmless. High temperature gas-cooled reactor (HTGR) has been considered to be quite suitable for hydrogen production [3] because of its high safety level and ability to supply heat of very high temperature up to 1223 K.

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Research work on the thermo-chemical hydrogen production has been conducted along with the R&D on HTGR by employing an iodine–sulfur (IS) cycle [2]. One of the important components in this system is the sulfuric acid (H_2SO_4) decomposer which generates SO_2 and SO_3 gases through evaporating the sulfuric acid under high temperature conditions [2]. 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. SiC was selected as coating materials and stainless steels and Ni-based alloys as the substrate materials. SiC coating is known to improve the lifetime or the performance of metallic substrates when exposed to aggressive environments [4]. The high resistance of SiC to the corrosion could be due to the very strong covalent bonding between silicon and carbon and its tetrahedral coordination [5]. Since the adhesion between the coated layer and the substrate is most crucial in this application, development of ion beam mixing (IBM) [6–9] technique to produce a highly adherent coated layer was attempted.

Ion beam induced mixing results from the recoil collisions of energetic ions with film atoms. IBM leads to the modifications of various properties at the film/substrate interface. These include intermixing [6,7], enhanced inter-diffusivity [8], relieving stresses in the film [9], generation of new alloy layers [10], etc. All these modifications are determined as functions of mass of the incident ion, irradiation temperature, and ion dose and are helpful for high sustainability of the coating layers in corrosive environment at high temperature.

2. Experimental

Samples chosen from SUS304, SUS316L, Alloy 800H, Alloy 690 and Hastelloy-X were cut to be 20 mm (W) \times 20 mm (L) \times 5 mm (T) and were then polished on all surfaces to have the surface-roughness (R_a) less than 0.05 μm . Samples were ultrasonically cleaned in acetone to degrease the surfaces and then the surfaces of the samples were bombarded with low energy (500 eV) Ar ions to clean the unwanted surface contaminants before film deposition. The electron beam evaporative method

was employed for the SiC film deposition. An electric power of 10 kW was applied to the electron gun to evaporate the bulk SiC. During the film deposition, the vacuum pressure was $\sim 2.5 \times 10^{-3}$ Pa. A ~ 50 nm thick SiC film was deposited on the samples and then the Ar and 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. The vacuum pressure during the ion beam irradiation was $\sim 1.3 \times 10^{-3}$ Pa. A schematic of the coating and ion beam bombardment is shown in Fig. 1. In the coating and ion beam irradiation system, the sample holder is located at ~ 600 mm distance above the evaporating source. After depositing the film, the substrate holder was tilted by 90° in order to be bombarded by ions. Then, the substrate was retitled to the original position for the additional coating. For the corrosion test, N ions were bombarded, and for investigation of elemental distribution at the film/substrate interface, Ar ions were bombarded. After ion beam bombardment, an additional ~ 500 nm thick SiC film was deposited onto the initial SiC film. For most samples the coating

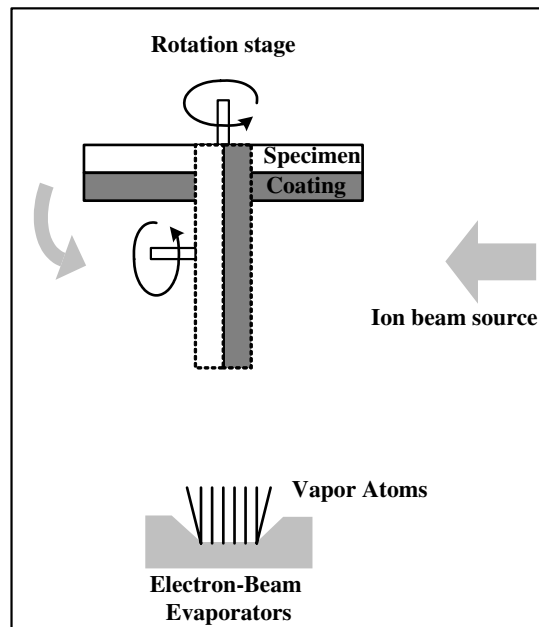


Fig. 1. A schematic of the film deposition and ions beam bombardment: the sample holder is located at about 600 mm distance above the evaporating source. After depositing the film, the holder is tilted by 90° in order to be bombarded by ions. Then, the substrate holder is retitled to the original position for the additional coating. The sample holder is rotatable for more uniform coating and irradiation.

was done on all six faces of the samples, however a few samples were only coated to 20 mm in diameter on one surface of the sample. The properties of the deposited SiC film were analyzed with Auger depth profiling. The samples coated on all the surfaces with and without N ion beam mixing were immersed in 50% H₂SO₄ solution for 1 h with heating the solution up at 273 K to determine if the coating and IBM improves the corrosion resistance. 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 surface were observed. Then, optical microscopy was used to observe the morphology of the corroded and etched surfaces. Elemental distributions at the interface after and before the ion beam bombardment were investigated with Auger mapping technique. Cross-sectional samples were prepared and the Si KLL peak was chosen for the mapping. Scanning Auger microprobe (SAM) Phi model 670 was employed for the mapping and the elemental depth profiling. Before data acquisition with SAM, the surface of the cross-sectioned sample was gently sputtered with 500 eV Ar ions for 30 s to eliminate the surface contaminants.

The as-deposited samples of SiC/Alloy690 and SiC/SUS316L were heated up to 1223 K for 3 h in air to see if the film is detached from the substrates due to the thermal strain.

3. Results and discussion

As verified with Auger depth profiling analysis of the as-deposited 50 nm thick SiC film deposited on Alloy 690, the surface of the SiC film is covered mostly with SiO₂, which seems to have been formed while taking the deposited sample out from the deposition chamber. The formation of SiO₂ on the surface of SiC in the service environment is inevitable, because the formation of SiO₂ is thermodynamically more stable than SiC [11]. However, the formation of SiO₂ on the surface of SiC does not seem to an adverse effect on the corrosion resistance, unless it is detached from the SiC layer.

Fig. 2 shows the surface morphologies of SiC/Alloy800H sample after exposing the samples to a 50% H₂SO₄ solution for 1 h at 573 K. The coating was performed for all six faces, but the ions were bombarded only onto one face. In Fig. 2(a) and (b), the differences of the color imply differences in thickness, because in the present experiment the deposition was done six times at changing the sample position. The surface bombarded with ions shows almost no film detachment (Fig. 2(a)), while the faces without ion bombardment are mostly denuded (Fig. 2(b)). Fig. 3(a) and (b) shows the optical microscopic observation of the surfaces etched electrolytically. The depth of the surface erosion was about 35 μm as estimated with optical

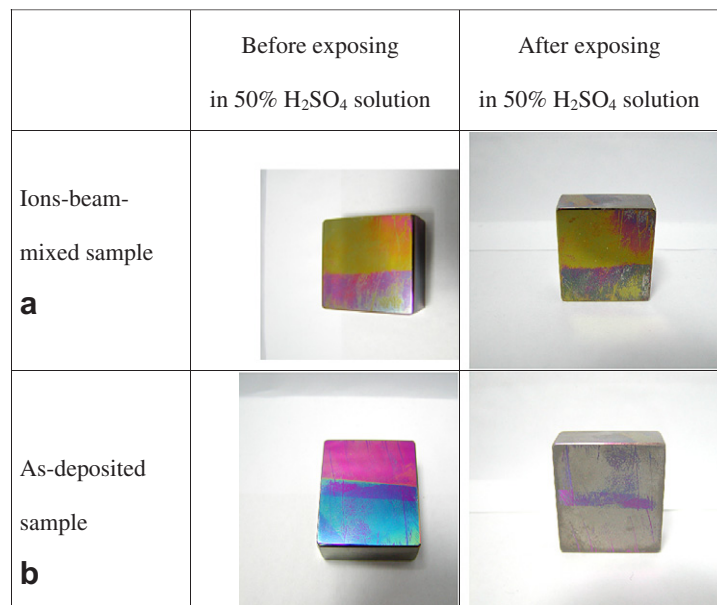


Fig. 2. The surface morphologies of SiC/Alloy800H sample before and after exposing the samples to 50% H₂SO₄ solution for 1 h at 573 K. The difference in the color is due to the differences in the film thickness.

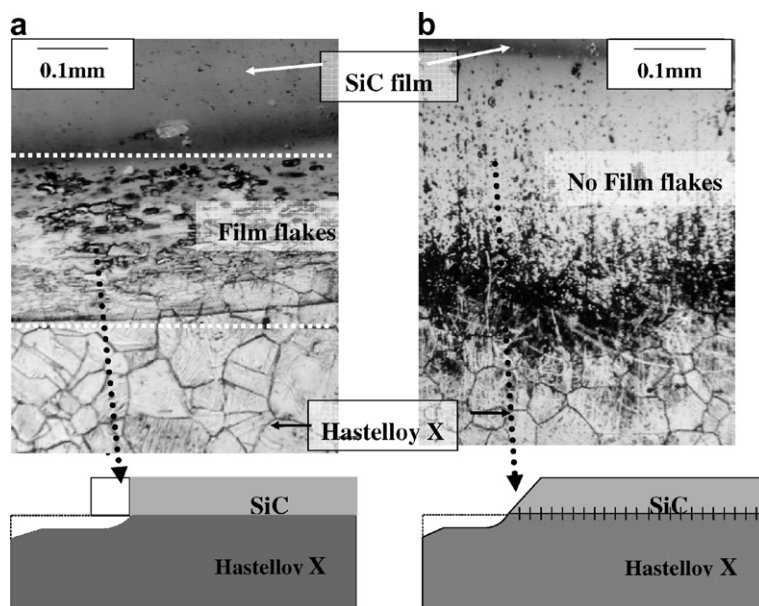


Fig. 3. The optical-microscopic observation of the surfaces etched electrolytically. The sample without the ion beam bombardment shows flakes at the edge of the film (a) after electrolytic etching. Such corrosion is not found in the ion beam bombarded sample after etching with the same condition (b).

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. 3(a)) 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. 3(b)). This means that the substrate under the film was reinforced to be corrosion-protective by ion beam mixing.

Fig. 4 shows Si mapping acquired by AES at the interface between the SiC film and the Hastelloy-X substrate before (Fig. 4(a)) and after (Fig. 4(b)) Ar 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. In fact, the existence of Si stands for the existence of SiC, because the recoil implantation should have occurred for both Si and C, although the recoil behaviors are different with each other. The differences of Si distributions at the interfaces can be clearly seen; that is, at the interface in the non-ion beam bombarded sample the black (Hastelloy-X substrate) and white (Si elements) areas are well separated (Fig. 4(a)) while white spots (Si elements) are

appreciably penetrated into Hastelloy-X substrate adjacent to the interface (Fig. 4(b)). It shows clearly how the intermixing took place at the interface. That is, the mixing results from the recoil implantation of the film atoms during ion beam bombardment.

Ion beam bombardment is known to be highly effective in improving wear and corrosion resistance of metals and is included in the major surface modification techniques along with coating technique [12,13]. Especially, N ion implantation is effective in the surface modification of the metallic materials, because metal nitrides can be easily formed even without post-implantation annealing [14]. As shown in Fig. 3, the uncoated surface implanted with nitrogen ions exhibits the well-developed grain boundaries, therefore it does not seem that the nitrogen ion implantation itself provides sufficient corrosion resistance, because transport of ions into matter (TRIM) [15] calculation suggests that the ion stopping range is about $0.2\ \mu\text{m}$ with $100\ \text{keV}\ \text{N}^+$ ion energy while the eroded depth by etching is about $35\ \mu\text{m}$. However, unlike the formation of the flakes from the edge of the as-deposited film as a result of electrolytic etching, the N ion-bombarded films do not show the film-flakes after the etching. This implies that the ion beam induced mixing at the interface between the SiC film and the metal

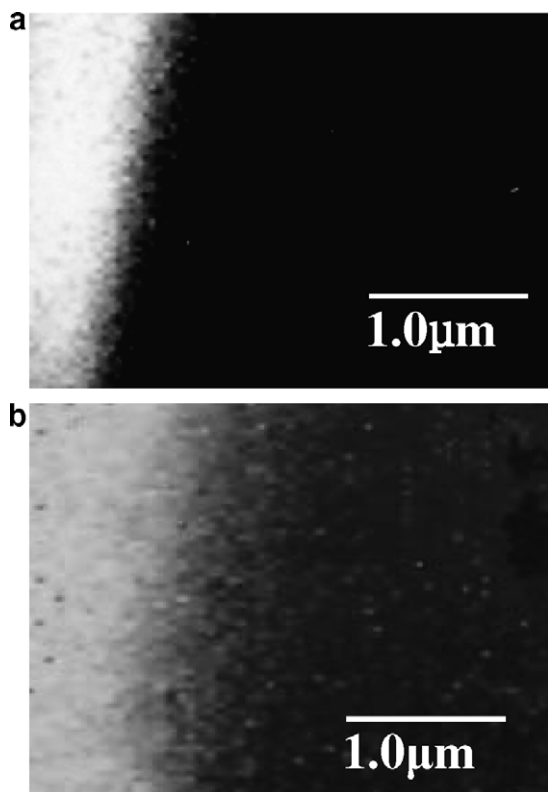


Fig. 4. Si mapping acquired by AES at the interface between SiC film and Hastelloy-X substrate: before (a) and after (b) Ar ion beam bombardment. White areas in each mapping denote distribution of Si element and dark area represents no existence of Si.

substrates intervenes in the propagation of the corrosion. The mixing has been explained in Fig. 4. The corrosion process in the 50% H_2SO_4 solution is believed to be similar to the electrolytic etching; probably, the imperfectly covered surfaces with SiC film corroded first, and then the corrosion propagates underneath the film, eventually flaking the film off. This is a kind of crevice type corrosion and is suggestive that the deposited film should be dense with high adhesion and very low microporosity.

Fig. 5(a)–(c) shows the surface morphologies after heating of the as-deposited SiC film/Alloy 690 (Fig. 5(a)), SiC film/Hastelloy-X (Fig. 5(b)), and SiC film/SUS316L (Fig. 5(c)) samples in air. The SiC film deposited on SUS316L is completely peeled-off (Fig. 5(c)), but the films deposited on Alloy 690 (Fig. 5(a)) and Hastelloy-X (Fig. 5(b)) all remained. However, the surface color changed to blue due to the oxidation of the film. The film removal after heating is attributed to the differences

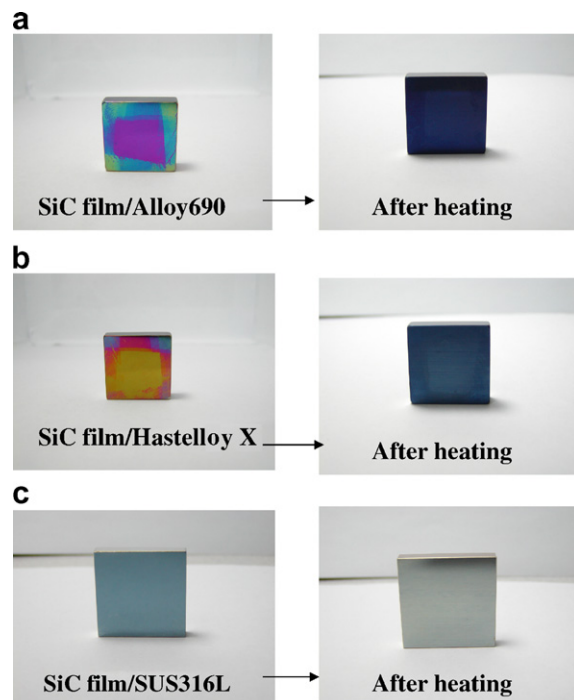


Fig. 5. The surface morphologies after heating the as-deposited SiC film/Alloy 690, SiC film/Hastelloy-X, and SiC film/SUS316L samples in air. The SiC film/SUS316L is completely peeled-off (c), but SiC films deposited on Alloy 690 (a) and Hastelloy-X (b) all remained. However, the surface color was changed to blue due to the oxidation of the film.

of thermal stresses applied on SiC film. The thermal stress is supposed to arise in the film as functions of the differences of the thermal expansion coefficients and the elastic modulus between SiC and the substrate materials. Since these values vary with the temperature, a quantitative analysis requires the determination of the thermal gradient first and then a calculation of the thermal stresses at the interfacial region.

In this work, SiC films deposited on stainless steels and several Ni-based alloys were investigated. In general, these substrate materials give excellent protection against corrosion, but these have been known to exhibit limited corrosion-resistances at above 1173 K in SO_2/SO_3 environment. The ceramic coating can thus be one of the possible techniques to solve these problems. However, SiC coating on stainless steels is not working while SiC coating on Ni-based alloys seems to work. As far as the coating is applied, it was not found any considerable difference among the Ni-based alloys used in this experiment and all of them seem to be useful in SO_2/SO_3 environment at above 1173 K.

However, the SiC film/Hastelloy-X is suggested more suitable, because their thermal properties are more similar with each other than the other materials combinations investigated in this experiment.

More stresses arise in the thicker film. When the thick coating is required, therefore, the process of the very thin film deposition and ion bombardment should be repeated to reduce the stresses exerting on the film/substrate interface at the elevated temperature. The ion bombardment also produces very dense film with very low microporosity.

4. Summary and conclusions

In this paper, a possibility of an ion beam mixing of the ceramic thin film coated on metallic substrates was demonstrated for developing sustainable materials at above 1173 K in SO₃/SO₂ ambience. A ~50 nm thick SiC film was deposited by the e-beam evaporative method on SUS 316L, Inconel 800 H, Inconel 690, and Hastelloy-X substrates, followed by the 100 keV (Ar and N) ions bombardment to mix the interfacial region. After ion beam bombardment, an additional ~500 nm thick SiC film was deposited onto the ion bombarded SiC film. As revealed by Auger elemental mapping of the cross-section of the SiC film/Hastelloy-X substrate, it is clear that Si atoms penetrate into the substrate materials due to the recoil implantation behavior by ion beam bombardment on the 50 nm thick SiC film. As exposed to an environment of 50% H₂SO₄ solution for 1 h at 573 K and, as proved by electrolytic etching, samples with ion beam mixing exhibited good corrosion resistance. On the other hand, the corrosion of non-ion beam-mixed sample was a crevice type in which the corrosion initiated from non-deposited metallic surface and then propagated underneath the deposited film, resulting in flaking-off the film from the edge.

When the SiC film/metallic substrates was heated up to 1223 K, the film deposited on the stainless steel substrate was completely peeled off, while the films deposited on Ni-based alloys were all sustained. This is due to the difference of thermal expansion coefficients and elastic modulus between the film and substrate materials. The best materials

combination in our experimental scheme is thus SiC film and Hastelloy-X, because their thermal properties are more similar than for the other materials combinations.

Acknowledgements

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