

# THE FABRICATION OF A PROCESS HEAT EXCHANGER FOR A SO<sub>3</sub> DECOMPOSER USING SURFACE-MODIFIED HASTELLOY X MATERIALS

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This study investigates the surface modification of a Hastelloy X plate and diffusion bonding in the assembly of surface modified plates. These types of plates are involved in the key processes in the fabrication of a process heat exchanger (PHE) for a SO<sub>3</sub> decomposer. Strong adhesion of a SiC film deposited onto Hastelloy X can be achieved by a thin SiC film deposition and a subsequent N ion beam bombardment followed by an additional deposition of a thicker film that prevents the Hastelloy X surface from becoming exposed to a corrosive environment through the pores. This process not only produces higher corrosion resistance as proved by electrolytic etching but also exhibits higher endurance against thermal stress above 900 °C.

A process for a good bonding between Hastelloy X sheets, which is essential for a good heat exchanger, was developed by diffusion bonding. The diffusion bonding was done by mechanically clamping the sheets under a heat treatment at 900 °C. When the clamping jig consisted of materials with a thermal expansion coefficient that was equal to or less than that of the Hastelloy X, sound bonding was achieved.

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**KEYWORDS :** Nuclear Hydrogen Production, Coating, Ion Beam Mixing, Corrosion, Auger Electron Spectroscopy

## 1. INTRODUCTION

Hydrogen energy systems are considered to be a future energy source and a potential solution for environmental problems that include what is known as the green house effect caused by CO<sub>2</sub> gas emissions [1]. A high-temperature gas-cooled reactor (HTGR) is considered as suitable for hydrogen production due to its high safety level and ability to supply heat of a very high temperature up to 950 °C [2]. R&D concerning thermo-chemical hydrogen production has been conducted along with the R&D on a HTGR by employing an iodine-sulfur (IS) cycle. One of the important components in the IS cycle is a process heat exchanger for a SO<sub>3</sub> decomposer which generates SO<sub>2</sub> and SO<sub>3</sub> gases under high-temperature conditions [3]. The PHE is composed of helium gas channels and sulfuric oxides gas channels. The fabrication of the PHE outlined in this work consists of the shaping of surface-polished sheets to the PHE, surface modification of a Hastelloy X sheet, diffusion bonding of the sheets, and laser or electron beam welding of the ancillary parts. In this work, surface modification of Hastelloy X and diffusion bonding as the key processes in the fabrication of PHE were studied.

The materials used for the SO<sub>3</sub> decomposer require excellent mechanical properties at an elevated temperature as well as a high corrosion resistance in a SO<sub>2</sub>/SO<sub>3</sub> environment. Thus far, no metallic materials have proven to be useful in such an environment. In this work, a surface modification technique is studied.

The surface modification method consists of SiC coating and ion beam mixing. Coating with SiC is known to increase the lifetime or improve the performance of metallic substrates when exposed to an aggressive environment [4]. In addition to its tetrahedral coordination, the high resistance of SiC to corrosion is likely due to the very strong covalent bonding between silicon and carbon [5]. Hastelloy X was selected as a metallic substrate because the thermal expansion coefficient of Hastelloy X ( $16.6 \times 10^{-6}$  at 980 °C) is closer to that of SiC ( $5.0 \times 10^{-6}$  at 1000 °C) compared to most other metals including Ni-based alloys (i.e., CTE of Alloy690 and Alloy800H, at  $17.01 \times 10^{-6}$  at 900 °C and  $18.0 \times 10^{-6}$  at 800 °C, respectively). Moreover, its corrosion resistance in SO<sub>3</sub>/SO<sub>2</sub> gases is known to be better than most other metallic materials.

Often a ceramic-coated layer does not show the advantages of a good resistance against thermal stress at an elevated

temperature along with corrosion resistance over uncoated materials due to delamination. Thus, an additional treatment of the base materials before or after the coating process is necessary. In this work, an Ion Beam Mixing (IBM) [6 – 9] technique that produces a highly adherent coated layer and reinforces the base materials was developed. Ion-beam-induced mixing results from the recoil collisions of the energetic ions in the material with the atoms of the film. IBM leads to the modification of various properties at the film/substrate interface. These include intermixing [6], enhanced inter-diffusivity [7], relieving of the stresses in the film [8], and the generation of new alloy layers [9]. All of these modifications are known functions of the mass of the incident ion, the irradiation temperature, and the ion dose. They are helpful for the high sustainability of the coating layers in a corrosive environment at a high temperature. The ideal condition is one in which the highest ion stopping range forms around the film/substrate interface. Ion implantation into the base materials also increases the corrosion resistance of the base materials in some way and provides the base materials with high strength and hardness near the film/substrate interface.

As a method of assembling surface-modified plates to build a heat exchanger, a diffusion bonding method is developed in this study because undesirable effects such as metallurgical reactions and the distortion of materials must be minimized. For good contact between workpieces during the application of heat for the diffusion, mechanical clamping is employed in this work.

## 2. EXPERIMENTAL

### 2.1 Ion Beam Mixing of a SiC Film Deposited onto Hastelloy X and Characterizations

Hastelloy X samples cut to 20 mm (W) x 20 mm (L)

x 5 mm (T) were polished on all surfaces until they had a surface roughness (*Ra*) that was less than 0.05 μm. Samples were ultrasonically cleaned in acetone to degrease the surfaces and the surfaces of the samples were then bombarded with low energy (500 eV) N ions to clean away unwanted surface contaminants before the film deposition.

An electron beam evaporative method was employed for the SiC film deposition. Electric power of 1.4 kW was applied to the electron gun to evaporate the bulk SiC. During the film deposition process, the vacuum pressure was ~ 6.0 x 10<sup>-6</sup> Torr. A SiC film of a thickness of approximately 50 nm was initially deposited onto the samples and 100 keV N ions were then bombarded onto the film surface with an ion dose of approximately 1x10<sup>17</sup> cm<sup>-2</sup>. The vacuum pressure during the ion beam irradiation procedure was ~5.0 x 10<sup>-5</sup> Torr. A schematic of the coating and the ion beam bombardment is shown in Fig.1. After ion beam mixing, an additional SiC film at a thickness of 500 nm was deposited over the initial SiC film. The samples were partly coated to compare the coated and uncoated conditions.

Electrolytic etching in 10 % oxalic acid was performed on the partly coated samples by applying 4 V and 0.4 A until the grain boundaries on the uncoated surface were observed. Optical microscopy was then utilized to observe the morphology of the corroded and etched surfaces.

Elemental distributions at the film/substrate interface before and after ion beam bombardment were investigated with a Scanning Auger Microprobe (SAM) (Phi model 670).

### 2.2 A Study on a Diffusion Bonding of Hastelloy X

The Hastelloy X workpieces were clamped mechanically with jigs made of Hastelloy X and alumina. This was followed by heating at 900 °C in a vacuum for two hours. The workpieces were tightly bound to the jig securely with screw clamps when the Hastelloy X jig was used

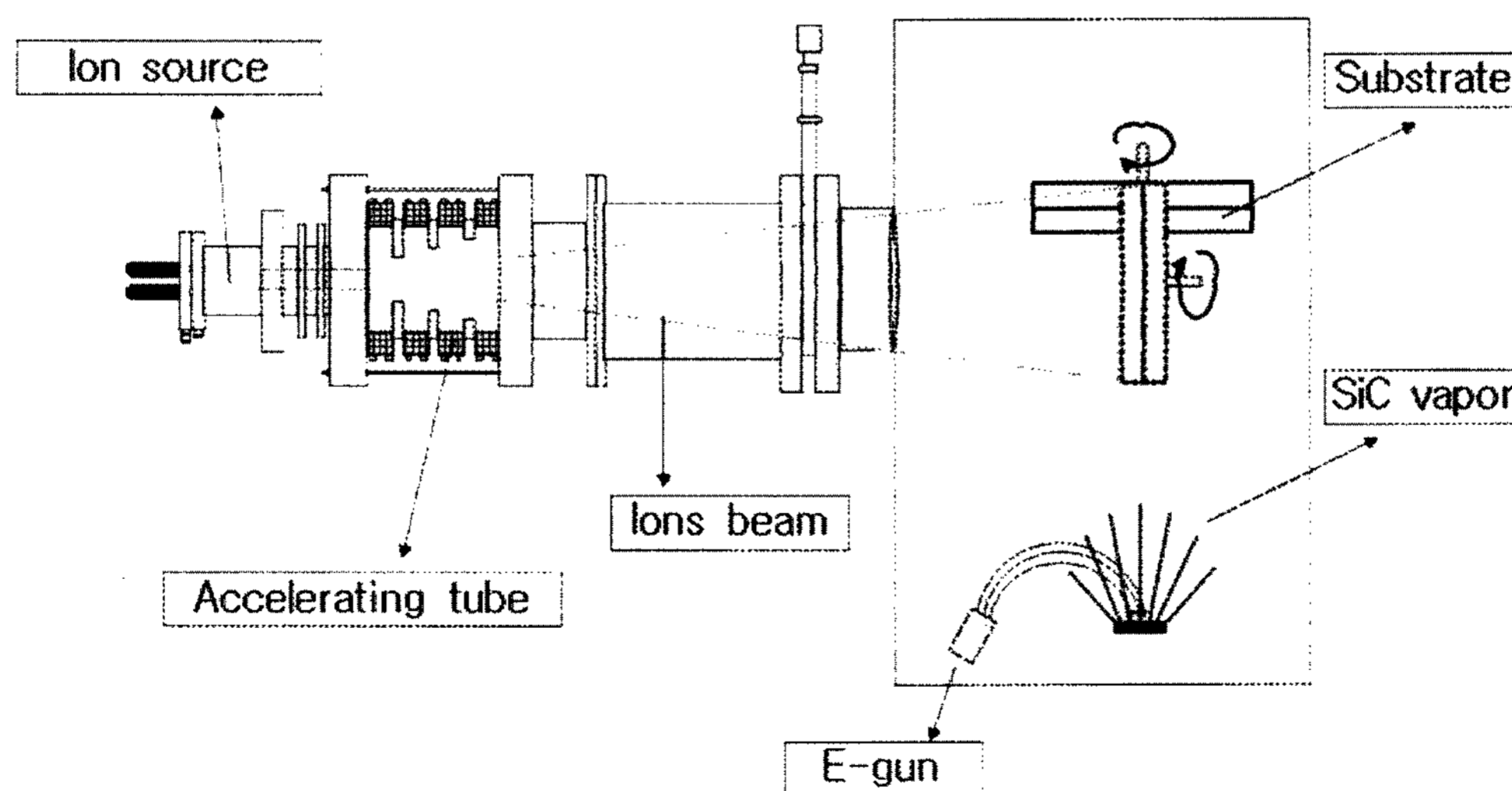


Fig. 1. Schematic Illustration of the Coating and Ion Beam Mixing Apparatus

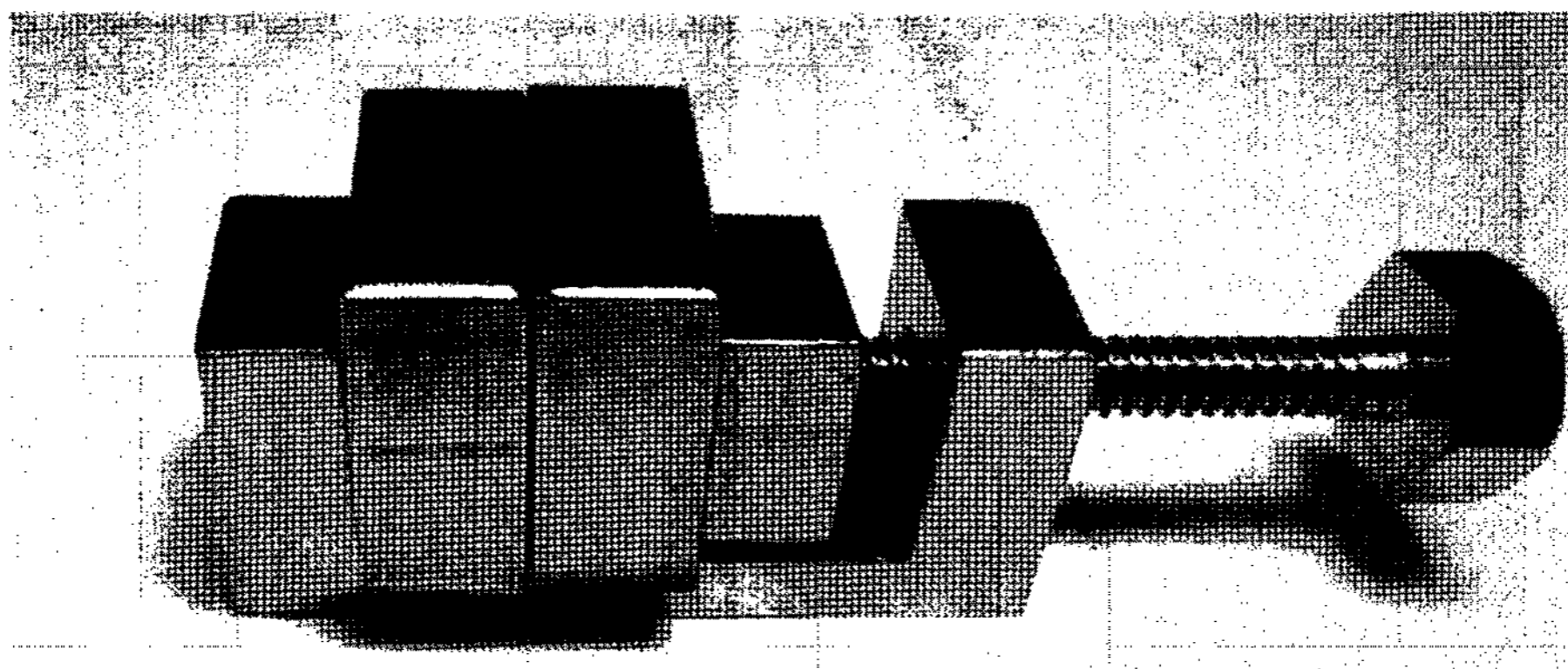


Fig. 2. Hastelloy X Clamping Jig used in This Work

(Fig. 2), whereas the contact pressure was moderately controlled when the alumina jig was used.

### 3. RESULTS AND DISCUSSION

#### 3.1 Corrosion Resistance Investigated by Electrolytic Etching

Fig. 3 shows the optical microscopic image of the surfaces after they were etched electrolytically. The depth of the erosion of the uncoated part of the sample was approximately 35  $\mu\text{m}$ , as estimated by measuring the moving distance of the lens while focusing the image. The sample that did not undergo ion bombardment shows flakes at the edge of the film (Fig. 3a) 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 flakes off from the edge. However, such corrosion is not found in the ion-bombarded sample after etching under identical conditions (Fig. 3b). This demonstrates that the substrate under the film was reinforced by the ion beam mixing process to protect against corrosion.

Fig. 4 shows the Auger elemental mapping from the coated layers to the base materials before (Fig. 4a) and after (Fig. 4b) ion beam bombardment. The figures clearly show how the intermixing took place at the interface. This mixing can be attributed to the recoil implantation of the film atoms during ion beam bombardment. TRIM software [10] suggests that 100 keV N ions essentially stop at a depth that is approximately 70 nm from the surface of a 50 nm thick SiC film/Hastelloy X substrate. This implies that 100 keV N ions pass over the coating layer and mostly stop in the substrate area. Therefore, bombardment with N ions should lead not only to the mixing of the film with the substrate at the interface but also the reinforcement of the substrate. The IBM process should enhance the adhesion of the deposited film and the implantation of N ions

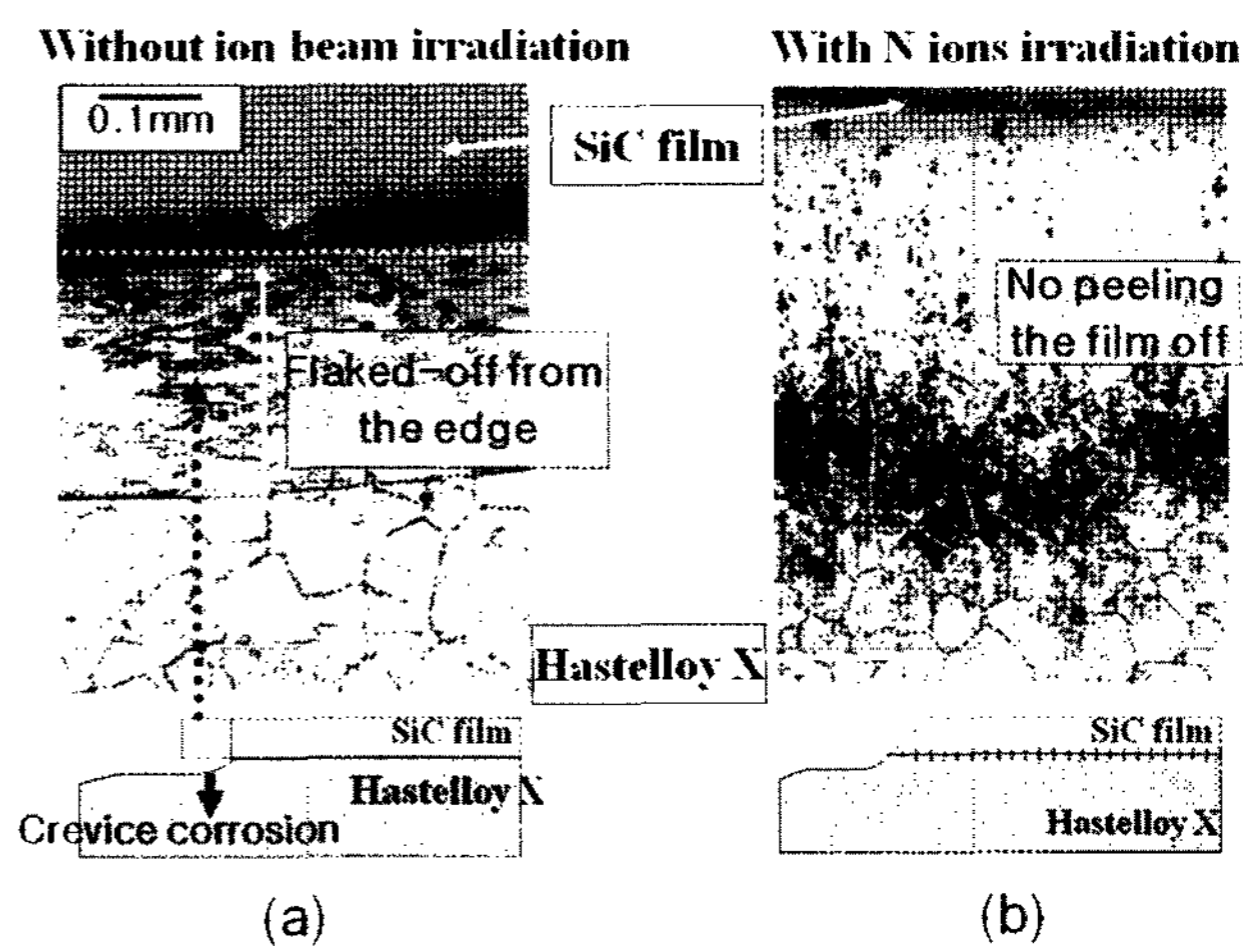


Fig. 3. The Optical Microscopic Observation of the Surfaces Etched Electrolytically: As-Deposited (a) and Ion Beam Mixed (b) Samples

should reinforce the base materials by forming nitrides that increase the hardness as well as the corrosion resistance of the Hastelloy X underneath the film. The increased hardness of the base materials plays the role of a load support for the coated layer, which should be another factor that increases the quality of the adhesion.

Ion implantation is known to be highly effective in improving the wear and corrosion resistance of metals; it is included among the major surface modification techniques together with coating techniques [11-12]. In particular, N ion implantation is effective for the surface modification of metallic materials, as metal nitrides can be formed easily without post-implantation annealing [13]. As shown in Fig. 3a, an uncoated surface implanted with nitrogen ions exhibits well-developed grain boundaries; therefore, it does not appear that nitrogen ion implantation itself provides sufficient corrosion resistance. However, unlike the case

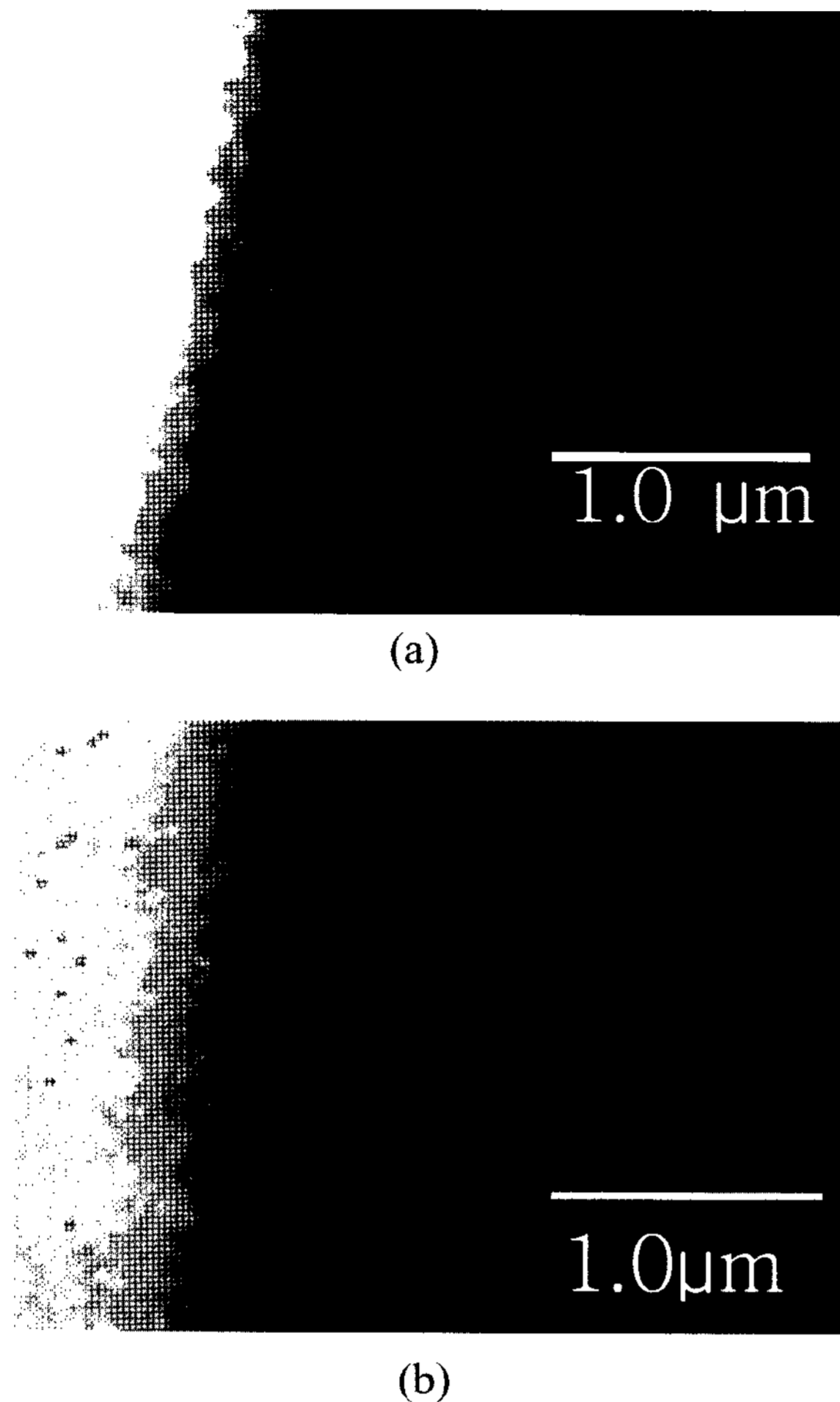


Fig. 4. Auger Si Mapping at the Interface between the SiC Film and the Hastelloy X Substrate Before (a) and After (b) Ar Ion Beam Bombardment

involving the formation of flakes from the edge of the as-deposited film after electrolytic etching, the N ion-bombarded films do not show film flakes after etching. This implies that the ion beam induced mixing at the interface between the SiC film and the metal substrates and that the mixing intervenes in the propagation of corrosion. This is a type of crevice corrosion; it is suggested that the deposited film should be dense with high adhesion and very low microporosity. In this work, the adhesion between the SiC film and Hastelloy X substrate appears to be enhanced due to both mechanical locking at the atomic scale at the interface and by interfacial reactions that possibly form Si-C-Ni compounds. The other benefit obtained through IBM may be the implantation into the substrate of some N ions that did not experience a collision with the Si and C atoms in the coated layer. This can reinforce the substrate by forming nitrides in the substrate and thus should reduce the roughness of the interface.

In this work, SiC films deposited on Hastelloy X were

investigated. In general, Ni-based alloys including Hastelloy X provide excellent protection against corrosion, but these materials have been known to exhibit limited corrosion resistance at temperatures greater than 900 °C in a SO<sub>2</sub>/SO<sub>3</sub> environment. A ceramic coating is one possible technique that solves these problems. However, more stress arises in a thicker film. When a thicker coating is required, therefore, the process of a very thin film deposition and ion bombardment should be repeated to reduce the stress that is exerted on the film/substrate interface at an elevated temperature. This will lead to no adverse effect, as the ion bombardment also produces a very dense film with very low micro-porosity. In order to achieve interfacial mixing to enhance the adhesion with N ion implantation into the substrate materials and the production of a very dense film with low micro-porosities, the ion energy should be selected carefully in relation to the deposited film thickness.

### 3.2 Thermal Stability of SiC Film Deposited onto Hastelloy X

Samples with and without IBM were heated to 900 °C. Neither sample showed peeling of the film, but the sample with IBM exhibited less surface damage compared to the sample without IBM (Fig. 5). The edge of the coated area was spread over the uncoated area due to the ion bombardment process. The existence of less damage is attributed to the mixed interface and the reinforcement of the base materials under the film by the implantation of N ions. The color change of the Hastelloy X surface was likely caused by oxidation during the heating process.

SiC coating layers without IBM often show film detachment even at room temperature when the substrate surface prior to the deposition was not carefully cleaning. Occasionally, the film peels off directly after the deposition process as the film thickness increases.

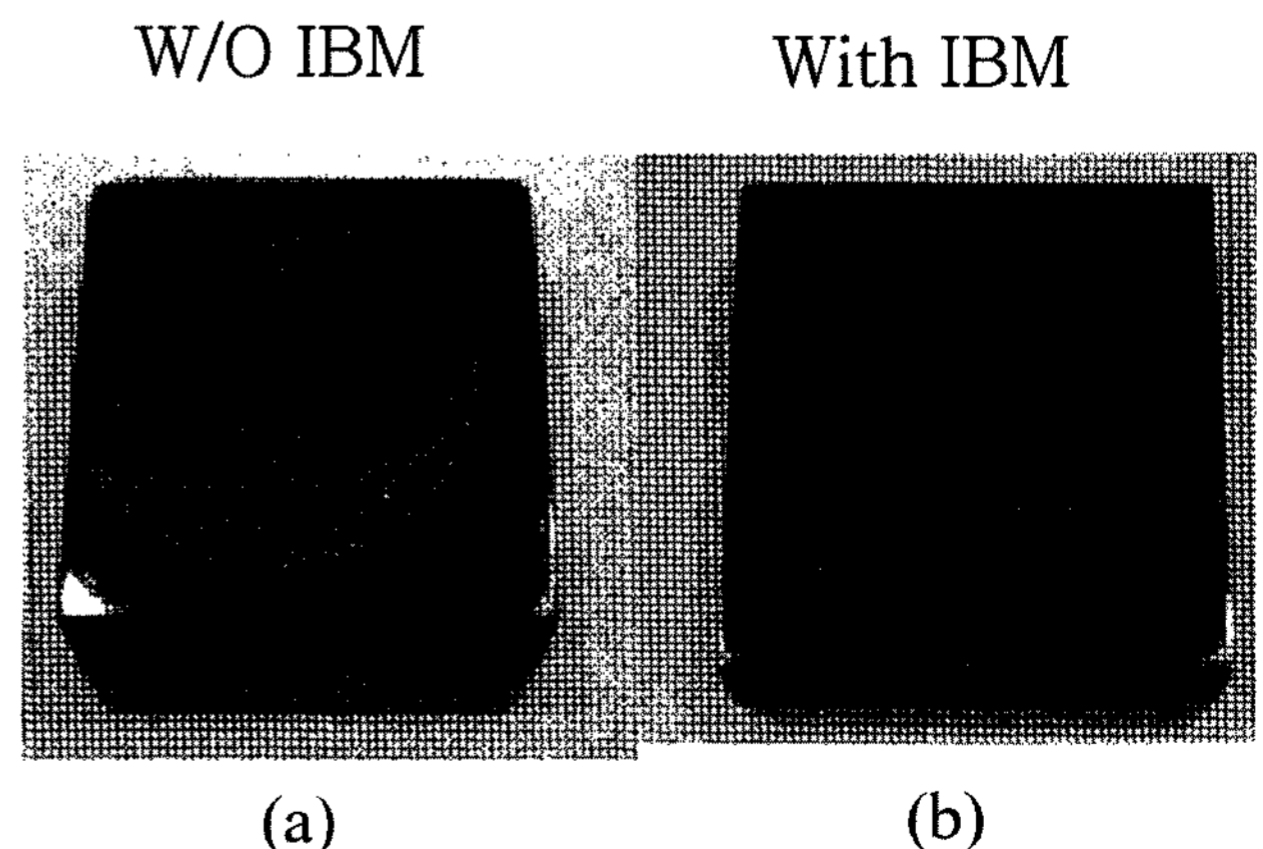


Fig. 5. The Coated Samples with and Without IBM Heated up to 900 °C: A Coating Layer with Less Damage on the Sample with IBM

It was felt that manner in which the SiC film on the Hastelloy X is sustained at above 900 °C should be ascertained. Recent work by the authors suggests that an interfacial reaction may take place between the SiC and Hastelloy X (Ni-based alloy) at an elevated temperature which leads to the production of a functionally-degraded layer at the interface as the temperature increases. The details of this work will be published elsewhere.

The samples shown in Fig. 5 were electrolytically etched. The delaminated area in the sample without IBM showed a well-developed microstructure (Fig. 6), but the IBM-treated sample did not show any microstructure in the damaged area (Fig. 7). In Figs. 6 and 7, the differences are shown clearly; that is, the coated layer in the sample without IBM does not adhere well to the Hastelloy X substrate while the coated layer in the sample with IBM exhibits a good adherence onto the substrate. The ion beam mixing process, even in the range of a few tens of nanometers at the interface, does have an effect on the corrosion resistance properties at elevated temperatures.

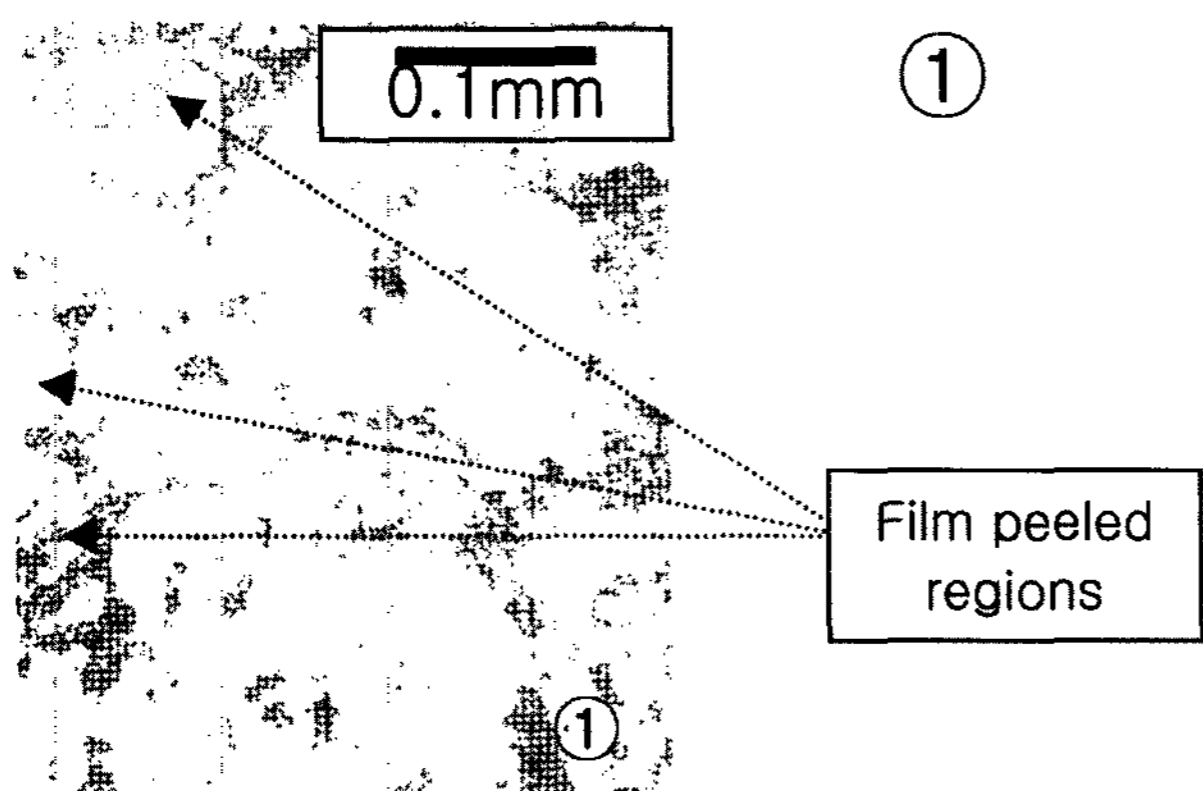


Fig. 6. Optical Microscopic Image After Electrolytic Etching on the Peeled Region of the Film of the SiC/Hastelloy X Sample Without IBM After Heating to 900 °C

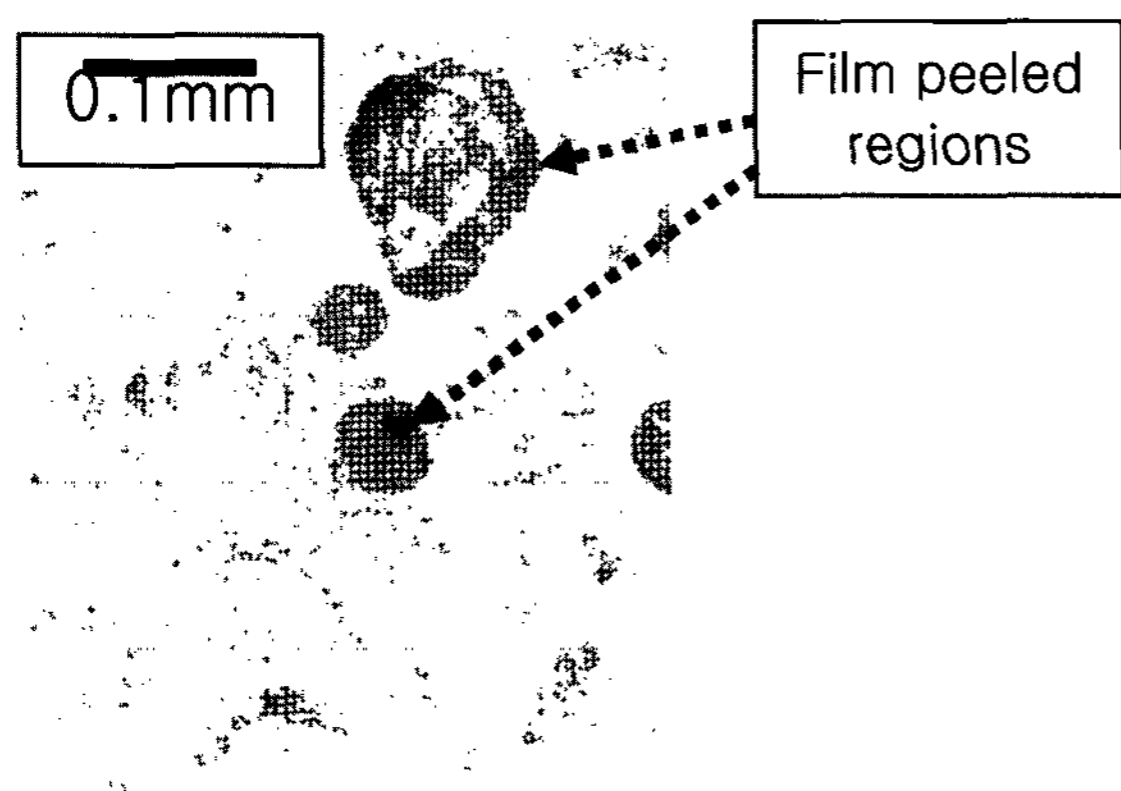


Fig. 7. Optical Microscopic Image After Electrolytic Etching on the Peeled Region of the Film of the SiC/Hastelloy X Sample with IBM After Heating to 900 °C

### 3.3 Diffusion Bonding Between Hastelloy X Sheets

In order to be used in a SO<sub>3</sub> decomposer, a process heat exchanger must be free from undesirable effects such as metallurgical reactions and materials distortion as it is fabricated. Diffusion bonding is considered as one method that meets such requirements. Successful diffusion bonding requires good contact between the workpieces followed by atomic transport across the interface by heat. Once good contact between two workpieces is achieved, the diffusion is merely a function of the heating temperature and time. Fig. 8 shows an example of the diffusion-bonded Hastelloy X workpiece obtained in this work. When an alumina jig was used to clamp the Hastelloy X workpieces, the bonded interface appears to be successful. However, the jig was easily broken due to the thermal stress during the heating step. When a Hastelloy X jig was used, unlike the alumina jig the workpieces were tightly clamped because a difference in the thermal expansion coefficient between the workpieces and the jig did not occur. Eventually, in this work, the bond between the workpieces was successful with both the alumina jig and the Hastelloy X jig. More care, however, was needed when the alumina jig was used. This work suggests that a better clamping jig material may be a material such as MAXTHAL (for example, Ti<sub>3</sub>SiC<sub>2</sub>) which has mechanical properties that are between those of Hastelloy X and alumina. The heating can be conducted either in air or in a vacuum. However, a vacuum condition may be better because oxides should not be formed on the contact surfaces during the heating process.

In a practical application, the coating process should be carefully controlled for diffusion bonding. Fig. 9 shows a conceptual drawing of the process heat exchanger under consideration here. The coating thickness diminishes

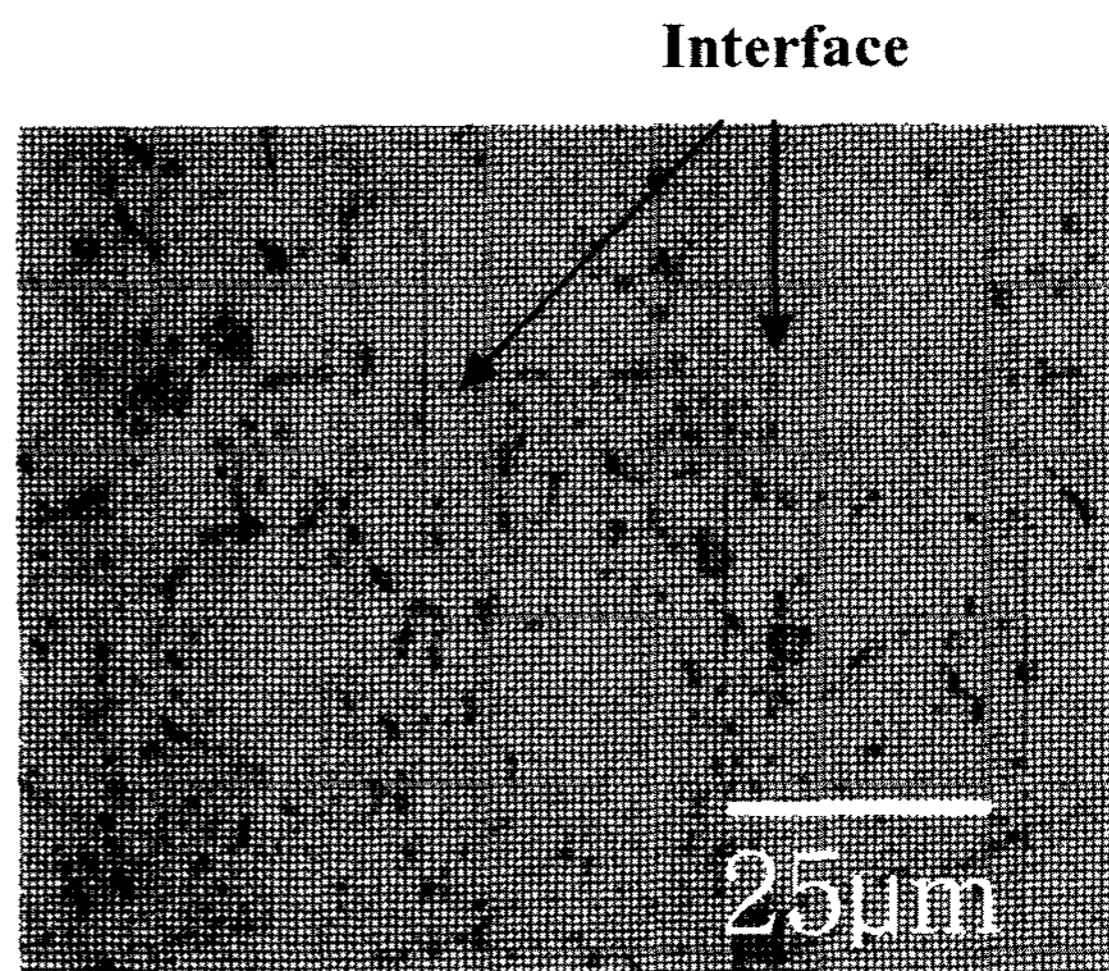


Fig. 8. Diffusion Bonded Hastelloy X by Mechanical Clamping and Heating at 900°C for Two Hours

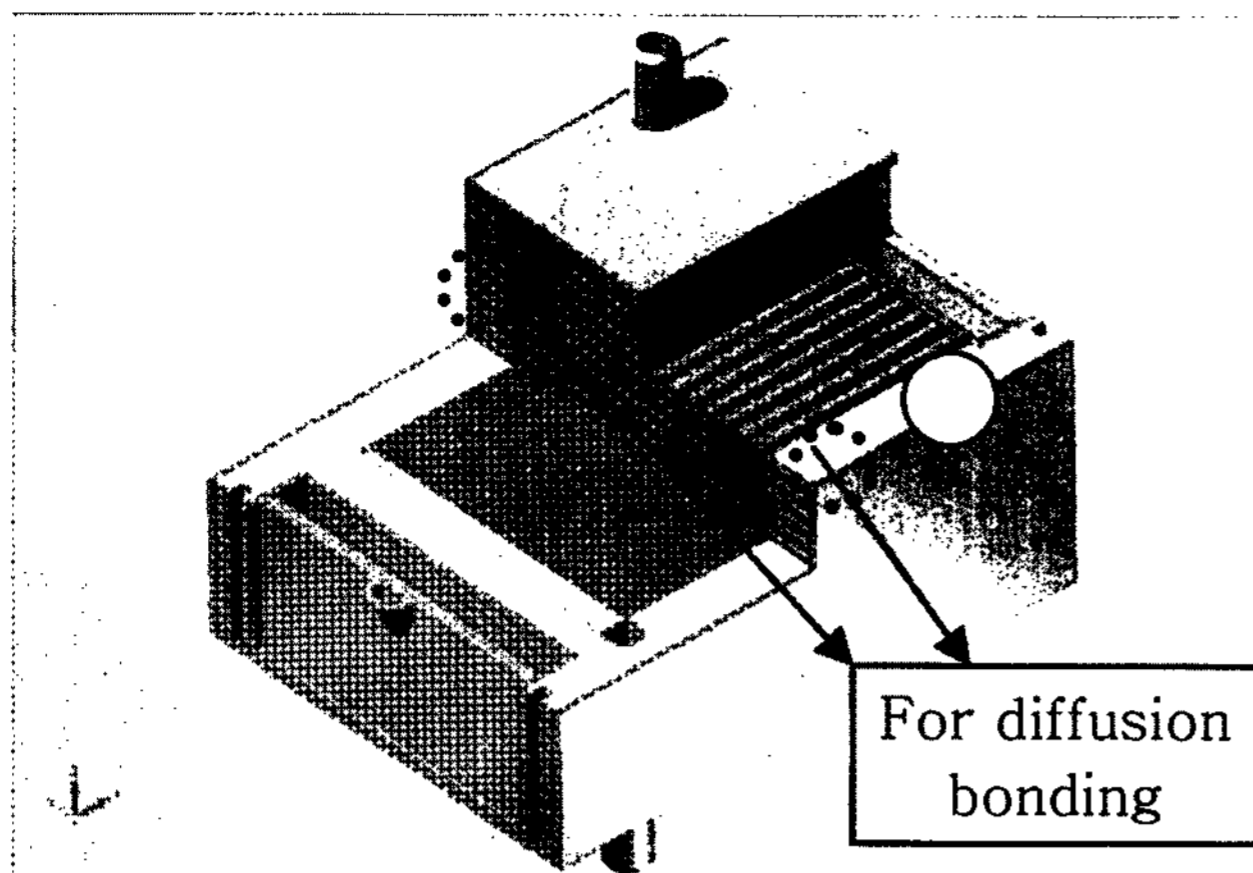


Fig. 9. A Conceptual Drawing of a PHE Showing the Area for Diffusion Bonding

along the outer area of each sheet, resulting in only a slight SiC layer on the area for the diffusion bonding.

Further experiments in an actual environment are necessary to verify the effects of the IBM surface modification.

#### 4. SUMMARY AND CONCLUSIONS

The possibility of an anti-corrosion surface modification process involving a ceramic film coated onto Hastelloy X at an elevated temperature was demonstrated by utilizing an ion beam mixing technique to develop sustainable materials at temperatures greater than 900 °C in a SO<sub>3</sub>/SO<sub>2</sub> ambience. A SiC film with a thickness of approximately 50 nm was deposited in an e-beam evaporative method on a Hastelloy X substrate. This step was followed by bombarding 100 keV N ions to mix the interfacial region. After the ion beam bombardment, an additional ~500 nm thick SiC film was deposited onto the ion bombarded SiC film. As revealed by Auger elemental mapping, the Si atoms penetrated into the Hastelloy X substrate due to recoil implantation. As shown via electrolytic etching, samples with ion beam mixing exhibited good corrosion resistance and sufficient endurance against thermal stress above 900 °C. On the other hand, the non-ion-beam-mixed sample exhibited crevice-type corrosion in which the corrosion initiated from a non-deposited metallic surface and then propagated underneath the deposited film, resulting in the flaking off of the film from the edge.

The diffusion bonding attempted in this work by mechanical clamping under heating at 900 °C demonstrates

a feasible means of fabricating a process heat exchanger for a SO<sub>3</sub> decomposer with surface-modified Hastelloy X plates. It is suggested that the clamping jig for the assembly of the plates into a PHE should be made of materials with a thermal expansion coefficient that is equal to or less than the coefficient of Hastelloy X, as the jig should act as a constraint against the expansion of the workpieces while they are heated for diffusion bonding.

#### ACKNOWLEDGMENTS

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