# Ion Beam Mixed Oxidation protective coating on Zry-4 cladding

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## 1. Introduction

A method to prevent the hydrogen explosion has been explored. For this, two ways can be considered in general, that is, developing the new cladding material and oxidation protective coating. In this work, the oxidation protective coating was studied. SiC was selected as the oxidation protective coating material since SiC is hardly oxidized and one of the accepted nuclear materials, and has been investigated for use as a replacement for Zircaloy cladding in light water reactor [1]. However, the large difference in thermal expansion coefficients between the two materials and thermodynamic incompatibility (i.e., lacking chemical reaction) often lead to the bonding failure at the elevated temperature. This work was primarily focused on finding a way to adhere the SiC coating layer to the Zry-4 substrate at the elevated temperature. Ion Beam Mixing (IBM) was employed to enhance the adhesion of SiC on Zry-4. The ion mixing can be used as a tool to fasten a thin ceramic material to a metallic substrate [2, 3]. One of the merits of the ion beam mixing is that the surface pretreatment is not imperative for the metallic substrate as in conventional diffusion bonding, because a forceful intermixing by the energetic ions mitigates the effect of the initial surface conditions.

However, the cracks can be formed in the well adhered SiC layer due to the difference in the thermal expansion coefficients. The crack lines would be the main oxidation place; therefore, the crack healing method was explored and is reported in this paper.

## 2. Methods and Results

### *2.1 Coating and ion beam mixing (IBM) apparatus*

SiC was used as a coating material on Zry-4. SiC is one of the accepted nuclear materials and has been investigated for use as a replacement for Zircaloy cladding in light water reactor [1]. A dense amorphous SiO2 layer that can be formed on the surface of SiC coatings at high pressure of oxygen gas does not react with SiC to form SiO(g) and Co(g) at the normal condition and accidental condition because critical temperatures of stability are 829℃ for SiC and 1460℃ for SiO2 at normal operation conditions [4]. As in the case of Fukushima accident, the accidental condition indicates temperatures reaching 1400℃ in the atmosphere with high partial pressure of oxygen/water. Electron beam evaporation method with peak power ratings 10 kV and 500 mA was employed for coating. An ion implantation setup was with peak voltage of 120 kV and current of 15 mA. The whole system operates in high vacuum created by a turbo-molecular pump combined with a mechanical pump; the coating and the ion beam bombardment were done in the same vacuum chamber

### *2.2 Surface morphological change at the elevated temperature*

When IBM was not conducted, the deposited films were often easily delaminated at the elevated temperature as shown in Fig. 1a. The extent of the coating detachment would be dependent on the surface condition prior to the film deposition, since unwanted surface contaminants can exist although a necessary surface pretreatment was conducted. Although the film was peeled-off, interestingly in some cases, the deposited SiC onto the Zry-4 substrate remains at grain boundaries of the substrate (Fig. 1b).

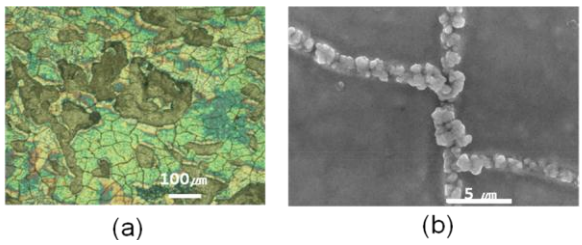


Fig. 1. The deposited films without ion beam mixing were often easily delaminated at the elevated temperature (a). Although the film was peeled-off, in some cases, the deposited SiC on Zry-4 substrate remains at grain boundaries of the substrate (b).

The Fig. 2 shows OM (Fig. 2a) and FE-SEM (Fig. 2b) micrographs of the film morphologies of SiC film-Zry-4 system as a function of temperature. In spite of about five times higher thermal expansion coefficient of Zry-4 than SiC at ~ 1000℃ the film did not peel-off at above 900 ℃, confirming the enhanced adhesion by ion beam mixing. Instead, the SiC film was cracked. The crack forms along the grain boundaries of the Zry-4 substrate. The grain boundaries on the surface of Zry-4 substrate seem to have been developed by a thermal etching, since the substrate surface was only polished before the film deposition. So, initially there should have been no grain boundary developed on the surface. The ion mixing seems to play a role in fastening a thin SiC layer to Zry-4 substrate until the interfacial reaction takes place as increasing the temperature. The interfacial reaction produces the intermediate compounds, which acts as a buffer layer. Certainly, this not only mitigates the differences in the thermo-mechanical properties between SiC layer and Zry-4 substrate but also stands for a strong bonding of the coated layer. Although the strong adhesion is achieved, there still remains a problem of the film crack caused by the lower thermal expansion coefficients of the ceramics than metals because the crack lines are wide enough to be oxidized preferentially.

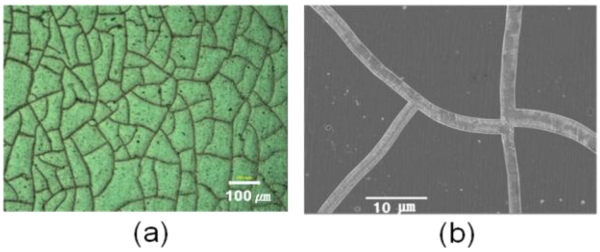


Fig. 2. In spite of about five times higher thermal expansion coefficient of Zry-4 than SiC at ~ 1000 ℃, the film did not peel-off at above 900 ℃, confirming the enhanced adhesion by ion beam mixing. Instead, the SiC film was cracked along the grain boundaries of the Zry-4 substrate.

### *2.3 Crack healing by multiple ion beam mixed coating*

Fig. 3a shows the higher magnification FE-SEM micrograph of crack lines of ion beam mixed SiC film on Zry-4 substrate after annealing at 900℃. Without covering the crack lines, the oxidation will take place primarily along the crack lines because Zry-4 is more prone to the oxidation due to its metallic nature than SiC. Therefore, the crack healing is needed to enhance the oxidation protectiveness of Zry-4. The crack formation is inevitable regardless of the film thickness; therefore, we devised a multiple ion beam mixed coating with a thinner layer. Repeating the thinner layer coating would be more effective than a single thicker coating.

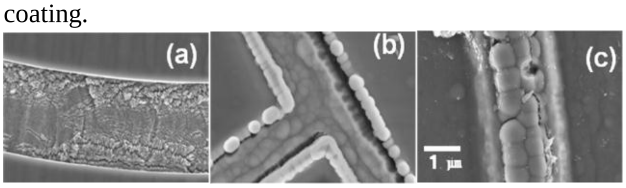


Fig. 3. After the first ion beam mixed coating/annealing process was finished, the crack lines are vivid (a). As repeating the process, the crack lines are gradually covered: The three times processed film making the total film thickness to 3 ㎛ (c) covers the crack line better than the twice processed (b).

In this work, we used 1 ㎛ thick SiC coating at each process. As can be seen in Fig. 3b and 3c, we see clearly that the three times coating making the film thickness to 3 ㎛ (Fig. 3c) covers the crack line more than the twice coating (Fig. 3b). However, during the accidental condition, there is no way to heal the crack. We suggest an artificial crack formation with surface heating and then coating repeatedly. The coating layer thickness of one process and the process repetition times should be further developed. Care is needed in selecting a surface heating method to make the cracks artificially. Considering the technical feasibility, we have employed the halogen lamp for the surface heating rather than laser surface heating. The duration to reach 1000℃ was about 10 min in this work. We are sure this does not affect the bulk properties of Zry-4.

## 3. Conclusions

Without IBM, the deposited SiC film is easily peeled-off at the elevated temperature. In spite of about five times higher thermal expansion coefficient of Zry-4 than SiC at ~ 1000 ℃ the film did not peel-off at above 900 ℃, confirming the excellent adhesion by ion beam mixing. Instead, the SiC film was cracked.

In order to cover the crack lines, the process of the ion beam mixed 1 ㎛ thick coating/annealing was repeated. When the ion beam mixed coating process was repeated three times making the film thickness to 3 ㎛, the crack line was well covered. In this work, an artificial crack formation with surface heating and then the repeated coating are suggested to enhance the anti-oxidation capability of the Zry-4 cladding tube.

## REFERENCES

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