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Enhanced oxidation resistance of SiC coating on Graphite by crack healing at the elevated temperature

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1. Introduction

During a long reactor shut down in VHTR, the supporting graphite components will be at high temperatures allowing the potential for significant oxidation with a corresponding loss of mechanical strength which may lead to a possible core collapse. An oxidation protective SiC coating on the graphite components could assist in slowing the oxidation down. However, the irradiation induced dimensional changes in the graphite (shrinkage followed by swelling) can occur, while the SiC CVD coating has been reported to swell even at a low dose neutron irradiation [1,2].

In this work, functionally gradient electron beam evaporative coating with an ion beam processing was firstly conducted and then SiC coating on the FG coating to the desired thickness is followed.

For the crack healing, both the repeated EB-PVD and CVD were performed. Oxidation and thermal cycling tests of the coated specimens were performed and reflected in the process development.

2. Methods and Results

2.1 Sample preparation

The nuclear grade graphite specimens (IG110, Toyo Tanso) were used for the substrate materials. The specimens are bar-shaped with ~7.20 mm in dia. X ~ 6.35 mm L adapted for the neutron irradiation test capsule.

Crucibles for e-beam evaporation were prepared with varied compositions of graphite and SiC such as G80/SiC20, G50/SiC50, G40/SiC60, G30/SiC70, G20/SiC80, G10/SiC90 and SiC100. The granules size of the graphite and SiC e-beam source materials was ~ 0.5 mm. The coating thickness for each composition was determined in consideration of the stresses' calculation in the total film thickness of ~ 30μm [8].

At the elevated temperature, the film cracks were formed even in this functionally gradient film. For the crack healing, additional SiC coating was performed by either repeating the EB-PVD or the chemical vapor deposition (CVD).

2.2 FE-SEM of the coated

As shown in Fig. 1a, the surface of the coating layer becomes much smoothened in nature. The film structure at the initial stage of coating shows somehow a dense columnar (Fig. 1b). The column structure could be strain tolerant against dimensional changes of the graphite and the SiC coated as a result of the neutron irradiation. However, if the inter-column width is larger, the graphite substrate may be more prone to oxidation. In this work, the samples were frequently re-positioned whenever compositions in the crucibles are changed during the coating. As a result, multiply stacked columnar growth of the film is shown (Fig. 1c).

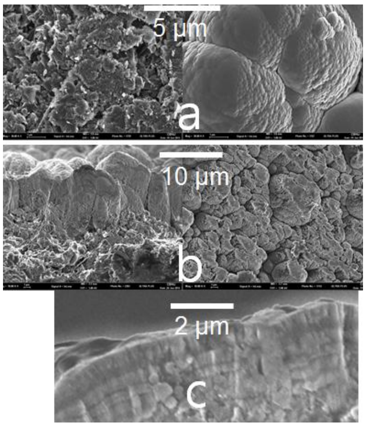


Fig. 1. As-received rough surface after SiC coating (a), the coating morphologies are the multiply stacked columnar growth (b - c).

2.3 Thermal cycling test

After 18 thermal cycles (1000 − 500 °C) in a vacuum, no coating delamination or crack formations at the interface owing to the difference in CTE between the film and substrate are observed, but the film is cracked (Fig. 2), ensuring a strong adhesion.

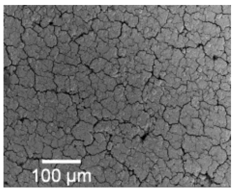
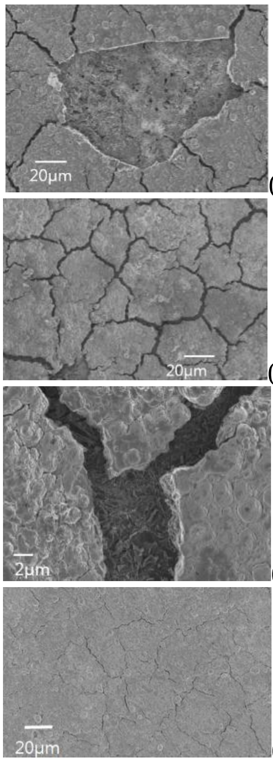


Fig. 2. After annealing at 1000 °, a film crack was formed rather than the delamination, suggesting a strong bonding.

2.4 Crack healing by EB-PVD

A vigorous oxidation took place when heated in air above 900℃, only leaving the SiC cask. In order to identify the causes of the vigorous oxidation, the coated sample was heated in vacuum and observed the surface morphology.

A few film spallation and lots of cracks were found (Fig. 3). These could be due to the difference in the thermal expansion coefficients between the graphite and SiC film. Then, the crack healing was our next task for slowing the oxidation down. We have repeated the EB-PVD with ion beam bombardment to fill the crack lines. The cracks and/or spallations could be considerably covered by the repeated EB-PVD shown in Fig 3d. The spallation with larger area could be covered more easily than the crack lines.



(a) (b) (c) (d)

Fig. 3. HR- SEM observation :The oxidation may have taken place through the defects such as spallations (a) and the crack lines (b,c) during heating. Repeating the EB-PVD could reduce the width of crack lines (d).

After EB-PVD crack healing, the oxidation test showed the weight reduction rate became less, but not so considerably (Fig. 4).

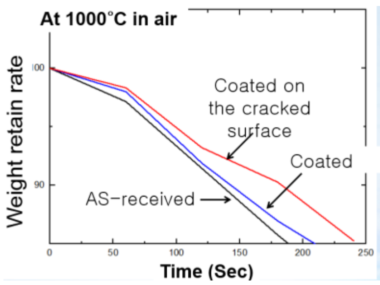
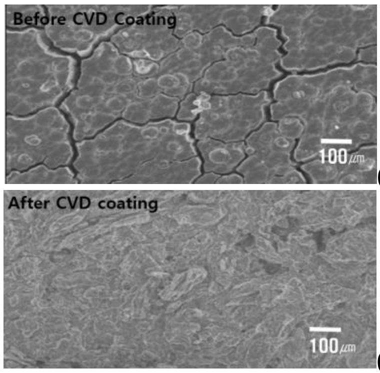


Fig. 4. Oxidation test after crack healing by EB-PVD with ion beam bombardment.

2.5 CVD coating

Next, we have tried with the chemical vapor techniques for the crack healing. The crack line filling capability for high density and high aspect ratio is generally believed to be better with CVD than with PVD because PVD is near line-of-sight nature and requires no substrate heating resulting in a poor filling capability, while CVD needs a substrate heating to promote the deposition reaction producing a better crack line filling for high density and high aspect ratio [9]. However, since the coated SiC with CVD tends to swell upon the neutron irradiation (Snead, et. al., 2007), CVD SiC coating alone on the graphite substrate should not be of the choice.



(a) (b)

Fig. 5. SEM micrographs of SiC coating surfaces by CVD shows crystals having well developed facets and grain boundarie (a) and the crack lines are almost completely filled (b).

Subsequently, we have conducted the oxidation of the crack healed specimen. As shown in Fig. 5, it took ~ 34 minutes for the 20% weight loss in oxidation test as a result of an annealing at 900℃, although it took about 4~5 minutes for the EB-PVD coated, exhibiting ~8 times increase in the same weight reduction at 900℃ in this experimental set-up.

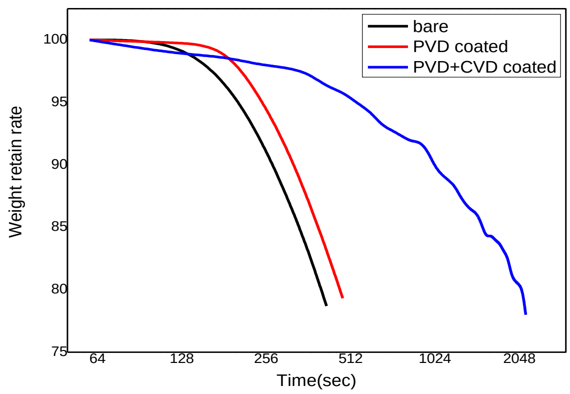


Fig.5. Coating by CVD on the cracked PVD sample increased the oxidation time for 20% weight reduction by ~ 4 times.

Judging from figures 4 - 5, the more effective way for the crack healing would be the CVD rather than the EB-PVD.

3. Conclusions

In this work, efforts have been paid to heal the cracks in the SiC coated layer on graphite with both EB-PVD and CVD. CVD seems to be more appropriate coating method for crack healing probably due to its excellent crack-line filling capability for high density and high aspect ratio. It took ~ 34 minutes for the 20% weight loss in oxidation test as a result of an annealing at 900℃, while it took about 4~5 minutes for the EB-PVD coated, resulting in ~8 times increase in the same weight reduction at 900℃ in this experimental set-up.

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