

Characterization of ceramic coatings of melting crucible for metal fuel

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1. Introduction

Traditionally, graphite has been the base material for a lot of crucible work, and metallic nuclear fuels, such as the U – Zr/U-TRU-Zr alloy system used in or proposed for sodium cooled fast reactors (SFR), have been melted and cast in graphite crucibles. However, owing to the high chemical reactivity of uranium, a slurry-coated graphite crucible or slurry-coated quartz mold has been used to prevent contact with the uranium [1]. In this research, SiC, ZrC, ZrO₂, Y₂O₃, and Y₂O₃ st. ZrO₂ were selected through a literature search as promising candidate coating materials to prevent the chemical reactions and the formation of the reaction phases [2-3]. These materials have been used as coatings in thermal barrier, high-reflectivity, and electronic device applications [4-8]. Niobium was also selected as a substrate because of its refractory nature, because the coefficient of thermal expansion (CTE) is similar to many of the candidate materials.

The microstructure of the coated materials was characterized and thermal cycling tests were performed to investigate the effect of repeated heating and cooling on the contact state of the interface between the coating layer and substrates. Interaction studies were also carried out at an elevated temperature in U-Zr-Ce fuel melt to investigate the refractory of the coating materials.

2. Experimental Procedure

The material used for the substrates were 99.8% pure niobium and graphite materials. SiC, ZrC, ZrO₂, Y₂O₃, and Y₂O₃ st. ZrO₂ were coated onto niobium and graphite discs and rods by vacuum plasma spraying (VPS) and chemical vapor reaction (CVR). The plasma generator used argon and hydrogen as plasma-forming gases and the thickness of the coatings on the substrate was controlled by the number of coating layers to a substrate. Thermal cycling test consisting of heating of the specimens to 1450°C at a rate of 20°C/min and holding at a temperature for 30 min, followed by furnace cooling to near-room temperature. Coating/melt interaction studies were performed by immersing the coated rods in U-10wt.%Zr-5wt.%Ce alloy melt contained in an inductively heated Y₂O₃-slurry coated graphite crucible under a vacuum. To provide comparable results, SiC, ZrO₂, Y₂O₃, and Y₂O₃ st. ZrO₂

coated rods were performed together in the same sample holder. Cross-sectional morphology and the reaction layer of the degraded coatings were observed using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

The interface between the coating layer and substrate showed an excellent contact state except the Y₂O₃ slurry coating on the graphite substrate, which had bigger pores compared to other coatings. The porosity or porosity distribution in the coatings showed no significant difference. After 5 thermal cycles at 1450 °C, cross-sectional SEM micrographs of the graphite disc showed several large vertical cracks propagating through the pores. These cracks seemed to originate from the pores on the surface of the boundary. Netlike micro-crack zones were also observed in the coating layers of niobium substrate during a thermal shock; however, the cracks were not yet interconnected.

After the immersion experiment, significant degradations occurred on a graphite rod. The coatings and graphite substrates dissolved through a reaction with a U-Zr-Ce fuel melt. Fig. 1 shows the cross-sectional view of the remaining graphite rods which were immersed in U-Zr-Ce melt at 1600°C for 10 min. The morphologies of the reaction layer in the ZrC and ZrO₂ coated niobium substrates were similar, showing a smooth and round interface boundary developed as the coated rod reacted with the melt. The reaction layers consisted of a lot of coarse particles, which had Ce levels of about 75wt.%. Fig. 2(b) shows the outer reaction band of a ZrO₂ coated rod separated from the inner reaction band and much more precipitations existed at the interface boundary, hinting at differences in the coefficients of thermal expansion, and were broken away. On the other hand, the plasma-sprayed Y₂O₃ coating layer on niobium substrate was free from dissolution, and no penetration of U, Zr, and Ce elements into the coating layer occurred, and no reaction layer was observed in spite of the lower melting temperature. The morphology and thickness of the Y₂O₃ coating layer (Fig. 2(c)) was similar to before the experiment. In the standpoint of thermodynamics [9], since yttrium does not have any eutectic or eutectoid reactions with uranium in the phase diagram [4,10] it is thought that Y₂O₃ is more stable from equilibrium

thermodynamics than ZrC or ZrO₂, which have an eutectic reaction with molten melt at lower temperature.

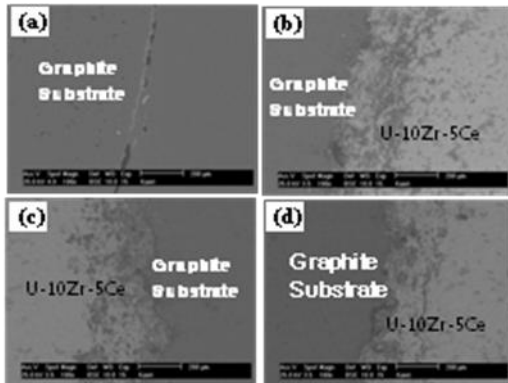


Fig. 1. Cross-sectional BSE micrographs showing the interface between U-10wt.%Zr-5wt.%Ce and coated graphite rod after dipping at 1600°C for 10 min: (a) SiC, (b) ZrO₂, and (c) Y₂O₃, and (d) Y₂O₃ st. ZrO₂

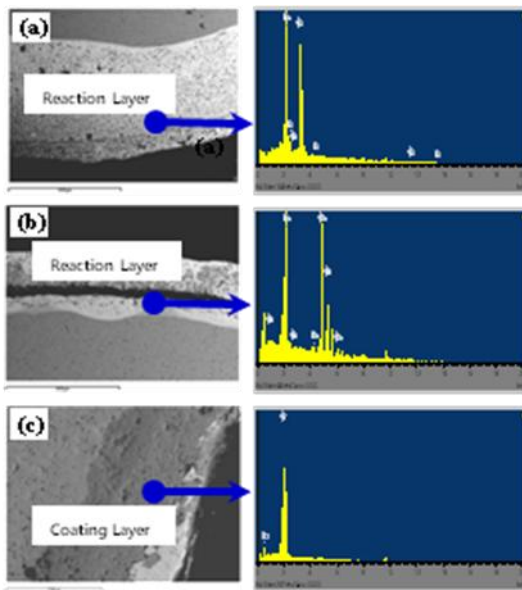


Fig. 2. Cross-sectional BSE micrographs showing the interface between U-10wt.%Zr-5wt.%Ce and coated niobium rod after dipping at 1600°C for 10 min (left) and EDX spectra (right): (a) ZrC, (b) ZrO₂, and (c) Y₂O₃

4. Conclusion

Candidate coating materials, such as SiC, ZrO₂, Y₂O₃, and Y₂O₃ st. ZrO₂ for nuclear fuel crucibles were coated onto niobium and graphite substrates. The microstructure of coating layers and thermal cycling behavior were characterized, and the U-Zr-Ce melt interaction studies carried out. The consolidations of the coated samples were generally good except slurry coated Y₂O₃ on graphite substrate. Thermal cycling

tests showed that the plasma-sprayed Y₂O₃ coating on niobium substrate had better cycling characteristics with few interconnected cracks compared to other coatings. In the interaction studies by U-Zr-Ce melt dipping tests, the ceramic coatings on the graphite substrate showed significant reaction with fuel melt, but the Y₂O₃ coating on the niobium substrate was free from dissolution and no reaction layer was observed. Y₂O₃ coating on niobium substrate exhibited the most promising performance.

5. Acknowledges

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6. References

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