DOI: 10.15669/pnst.5.192

Progress in Nuclear Science and Technology
Volume 5 (2018) pp. 192-195

ARTICLE

Interaction studies between U-Zr alloy system and ceramic plasma-spray coated layer at elevated temperature

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Refractory coatings were applied to niobium and graphite substrates by vacuum plasma-spray (VPS) coating method. Melt dipping tests conducted were the coated rods lowered into U-10wt.%Zr melt at elevated temperature, and withdrawn and cooled outside the crucible in the inert atmosphere of the induction furnace. Melt dipping tests of the coated Nb rods indicated that plasma-sprayed TiC, TaC, and Y_2O_3 coating doesn't form significant reaction layer between fuel melt and coating layer. In order to develop the VPS coating method for re-usable crucible of metal fuel slugs to be overcome the issue of thermal expansion mismatch between coating material and crucible, Various combinations of VPS coated specimens were applied to investigate the bonding effect on the crucible substrate and the interaction of metal fuel with the VPS coated crucible substrate. It is observed that most coating methods maintained sound coating state in U-10wt.%Zr melt. All coated rods showed no reaction with the melt and also maintained the integrity of the coating layers even after three cycles. Thus, the ceramic plasma-spray coatings are thought to be promising candidate coating methods for a reusable crucible to fabricate metal fuel slugs.

Keywords: U-Zr alloy; SFR; metal fuel; uranium; injection casting; plasma-spray coating; melting crucible; interaction

1. Introduction

A sodium-cooled fast reactor (SFR) is being developed in combination with the pyro-electrochemical processing of spent fuel at KAERI [1-3]. U-Zr and U-TRU-Zr metal fuels have been considered as the driver fuels for SFR in Korea [4-5]. The spent nuclear fuel that is produced at an LWR can be used at an SFR. Existing uranium utilization rate in LWR is slightly within 8%, but can be improved to more than 90% when using an SFR system [6-8]. Therefore, SFRs are expected to resolve the issue of nuclear spent fuel problems, which include radioactive waste repository [9-11].

Metal fuel slugs with a driver fuel assembly have been generally fabricated by the injection casting of fuel alloys under a vacuum state [12-15]. Zirconium was added to increase the melting point of the nuclear fuel slug and thereby maintain stability at high temperature. Traditionally to prevent melt/material interactions metal fuels, such as the U-Zr/U-TRU-Zr fuels for the SFR, have been melted and cast in slurry-coated graphite crucibles and slurry-coated quartz molds [16-18]. Application of these coatings in a hot cell environment is labor-intensive and operator-dependent, and can introduce additional waste streams. Also, coating reaction and porous coatings can be a source of melt contamination and fuel losses, respectively.

Reducing these interactions will result in a fuel loss reduction. As part of this effort a coating technology for the crucibles will be developed in order to develop a re-usable crucible. The coating must possess excellent compatibility between the fuel melt and coating layer, and have good thermal cycling characteristics. Application of a permanent coating will reduce fuel loss through coating infiltration, contamination of the melt with coating materials and/or crucible materials, and casting preparation time. The refractory coating must have excellent compatibility between the U-Zr/U-TRU-Zr melt and the crucible material, withstand multiple thermal cycles, and have good substrate adhesion.

In this study, refractory coatings were applied to melting crucible substrates by plasma-spray coating method. Melt dipping tests conducted were the coated rods lowered into U-10wt.%Zr melt at elevated temperature, and withdrawn and cooled outside the crucible in the inert atmosphere of the induction furnace.

The ceramic coating materials showed separations in the coating interface between the substrate and coating layer, or between the coating layer and fuel melt after

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the dipping test. To develop a re-usable meting crucible, the issue of a thermal expansion mismatch between the coatings and crucibles must be overcome. Various combinations of coating conditions such as the coating thickness and multi-layer coating methods including bond coating materials with substrate materials were investigated to find the bonding effect on the substrate and the interaction of metal fuel with a plasma-spray coated crucible substrate.

2. Experimental procedure

The substrate was 99.8% pure niobium and graphite materials with a diameter of 10 mm. SiC was coated about 3 μm in thickness with chemical vapor reaction method on graphite substrate at high temperature. A plasma spray method was used to apply an approximately 100 μm thick coating to niobium/graphite rods of 10 mm in diameter. HfC, TaC, TiC, ZrC, and Y_2O_3, Y_2O_3 st. ZrO_2 powders, ranging from 10μm to 45μm in size, were plasma-sprayed under a protective atmosphere onto the substrates, including multi-layer coatings. 2 kinds of coating methods such as Y_2O_3(150 μm) and TaC(50μm)-Y_2O_3(100μm) have been selected as promising coating candidate materials. The thickness of the coatings on the substrate was controlled by the number of coating layers to the substrate, with a torch input power of about 15 kW, and a plasma gas of argon and helium.

A rough surface finish was provided to enhance the adhesion of the coating layer by grit blasting the niobium and the graphite substrates with alumina after which it was cleaned using a standard ultrasonicator. Approximately 100μm thick coatings were deposited by controlling the number of the coating layers, with a torch input power of about 15 kW, an arc current of about 750 amperes, and a plasma gas of an argon and helium mixture. Dip tests conducted were the samples lowered into the melt at 1600°C, that is, casting temperature of U–10wt.%Zr alloy system fuel slugs, and withdrawn and cooled outside the crucible in the inert atmosphere of the induction furnace. The coating microstructure before and after testing was characterized using a scanning electron microscope (SEM). The chemical compositions of the coated specimens were measured by energy-dispersive spectroscope (EDS).

3. Results and discussion

After exposure to the U-10wt.%Zr melt of the coated Nb rods at 1600°C for 5min, and cooling in separated state from the melt, the HfC coated rod showed significant penetrations of U-10wt.%Zr melt into HfC coating layer with the thickness of about 30 μm, as shown in **Figure 1(a)**. No reaction layer formation or no penetration of U-Zr melt into the coating, in **Figure 1(b)**, was observed in the TaC coating layer. The TiC coated rod showed a little reaction of U-Zr melt between TiC coating layer and U-Zr alloy after exposure to the melt, as shown in **Figure 1(c)**. **Figure 1(d)** showed the discrete ZrC coating layer completely disappeared due to the eutectic reaction in U-Zr melt with the coating layer. No reaction layer formation or no penetration of U-Zr melt into the Y_2O_3 coating, in **Figure 1(e)**, was observed in the Y_2O_3 coating layer, since Y_2O_3 is more stable from equilibrium thermodynamics than the other ceramic crucible materials. The Y_2O_3 st. ZrO_2 coated Nb rod showed a discrete coating interface between Y_2O_3 st. ZrO_2 coating layer and U-Zr alloy layer, but significant penetrations of U-Zr melt between Y_2O_3 st. ZrO_2 coating layer and U-Zr alloy with the thickness of about 70 μm did occur, as shown in **Figure 1(f)**.

After exposure to the U-10wt.%Zr melt of the coated Nb rods at 1600°C for 15min, and cooling in separated state from the melt, HfC, ZrC, and Y_2O_3 st. ZrO_2 coated rods were already greatly deteriorated, but, TiC, and Y_2O_3 coated rods still appeared sound. No reaction layer formation or no penetration of U-10wt.%Zr melt into the TaC coating layer. The TiC coated rod showed a little reaction of U-Zr melt between TiC coating layer and U-Zr alloy after exposure to the melt. No reaction layer formation or no penetration of U-Zr melt into the Y_2O_3 coating, was observed in the Y_2O_3 coating layer.

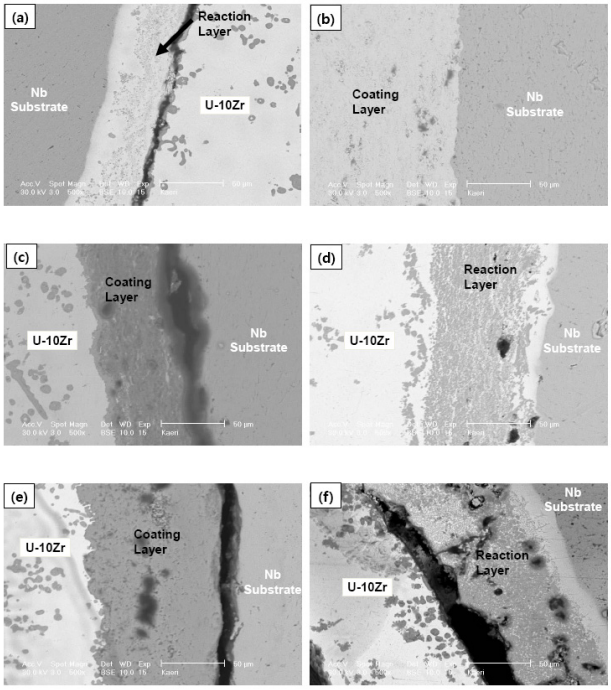

Figure 1. Cross-sectional BSE micrographs showing the interface between U-10wt.%Zr and ceramic plasma-sprayed layer on Nb substrate after dipping at 1600°C for 5min and cooling in separated state from the melt ; (a) HfC, (b) TaC, (c) TiC, (d) ZrC, (e) Y_2O_3, and (f) Y_2O_3 st. ZrO_2.

After exposure to the U-10wt.%Zr melt at 1600°C for 15min and cooling separated from the melt, the SiC formed a significant reaction layer between the U-10wt.%Zr melt and the coating layer, as shown in **Figure 2(a)**. The plasma-spraying Y_2O_3 st. ZrO_2 rod showed an indiscrete coating interface, and an extensive

interaction layer of about 100 μm in thickness formed by the penetration of U-Zr melt into the coating layer, as shown in **Figure 2(b)**. The multi-layer coated rod with the chemical vapor reaction of SiC and the plasma-spraying of Y_2O_3 showed little reaction layer formation with the Y_2O_3 coating, as shown in **Figure 2(c)**. Finally, in **Figure 2(d)~(e)**, no reaction layer formation or penetration of U-Zr melt into the coating was observed in the Y_2O_3 coating layer, since Y_2O_3 has thermodynamic stability with the U-Zr melt.

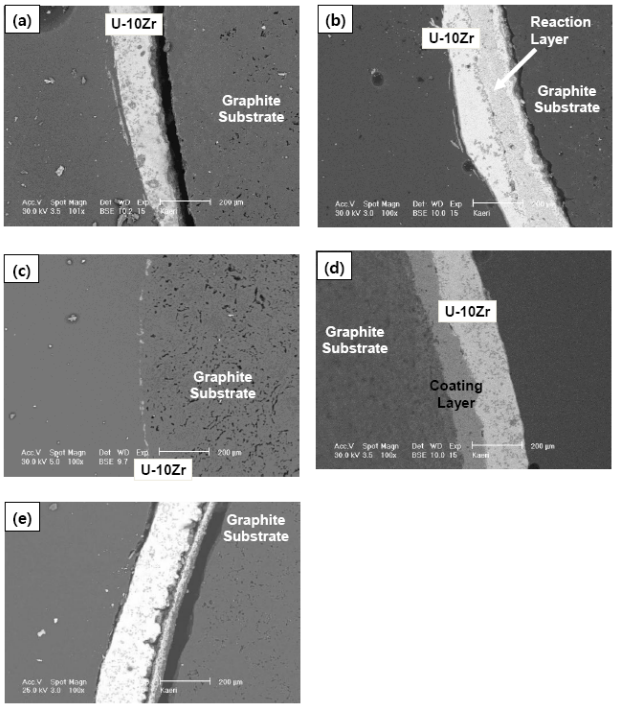

Figure 2. Cross-sectional BSE micrographs showing the interface between U-10wt.%Zr and ceramic coating layer on graphite substrate after dipping at 1600°C for 15min and cooling in separated state from the melt; (a) chemical-vapor-reacted SiC, (b) plasma-sprayed Y_2O_3 st. ZrO_2, (c) chemical-vapor-reacted SiC, and then plasma-sprayed Y_2O_3, (d) plasma-sprayed Y_2O_3, and (e) slurry-sprayed Y_2O_3.

Figure 3 shows BSE micrographs of the coated Nb rods after three cycles of exposure to the U-10wt.%Zr melt. The coated rods generally showed a good appearance after exposure to the melt. All coated rods showed no reaction with the melt and also maintained the integrity of the coating layers even after three cycles. Y_2O_3(150) VPS coated Nb substrate showed no significant penetrations of U-10Zr melt into the Y_2O_3 coating layer, as shown in Figure 3(a). The single layer of Y_2O_3 showed a strong resistance to the thermal shock and the expansion mismatch, and a strong resistance to the interaction with the U-10wt.%Zr melt. The coating rods having a double layer such as TaC(50)-Y_2O_3(100), Y_2O_3(50)-TaC(100) and Y_2O_3(50)-TiC(100) coated Nb substrates also showed no penetration of U-Zr melt into the coating layer, as shown in Figure 3(b), (c), and (d). No reaction with the U-Zr melt was verified in the case of TaC and TiC coating through an EDX analysis. The double layer coating of TaC-Y_2O_3 showed a sound state in the coating interfaces. The double layer coating of Y_2O_3(50)-TaC(100) and Y_2O_3(50)-TiC(100) showed a sound state, but a separation of the coating interface between the Y_2O_3 and TaC bonding layers. The triple layer coating such as Y_2O_3(100)-TaC(100)-Y_2O_3(100) and Y_2O_3(100)-TiC (100)-Y_2O_3(100) also showed no penetration of U-Zr melt into the Y_2O_3 coating layer, as shown in Figure 3(e) and (f). It was also found that the triple layers with Y_2O_3 as a bonding material separates

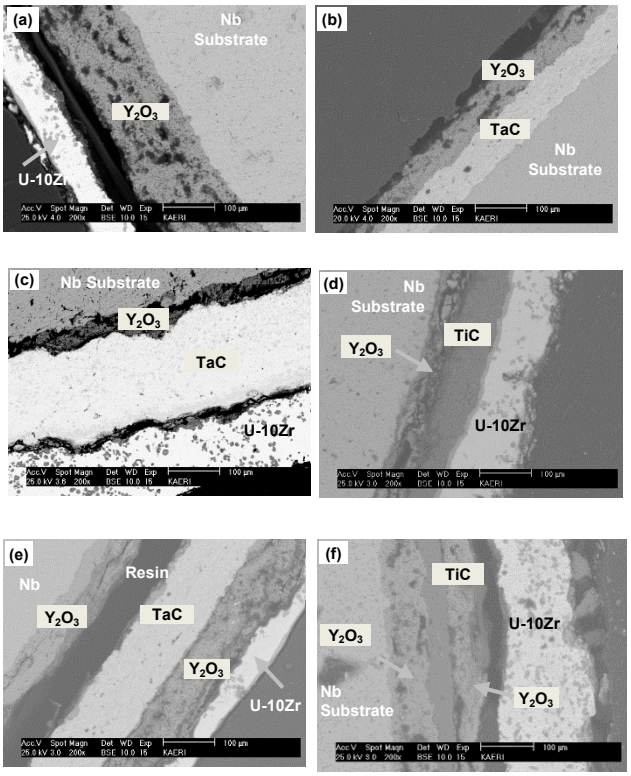

Figure 3. Cross-sectional back-scattered scanning electron (BSE) micrographs showing the interface between U-10wt.%Zr and coating layer after three cycles of dipping at 1600°C for 5 min: (a) Y_2O_3(150), (b) TaC(50)-Y_2O_3(100), (c) Y_2O_3(50)-TaC (100), (d) Y_2O_3(50)-TiC(100), (e) Y_2O_3(100)-TaC(100)-Y_2O_3(100), and (f) Y_2O_3(100)-TiC(100)-Y_2O_3(100).

easily from the substrate, indicating a similar result with the melt dipping of the single layer. Judging from these results, it can be considered that the intimate adhesion between Y_2O_3 bond layer and niobium substrate is a more important factor to determine the coating performance of the triple coating method.

4. Conclusion

To develop a re-usable meting crucible, plasma-sprayed coatings of high-temperature ceramic crucible materials were applied, and elevated temperature interaction studies were carried out between U-10wt.%Zr alloy system fuel and ceramic plasma-sprayed layer. The coated rods were dipped in U-Zr melt, and then characterized for interaction studies.

Melt dipping tests of the coated graphite rods indicated that plasma-sprayed Y_2O_3 coating don't form significant reaction layer between U-10wt.%Zr melt and coating layer. Melt dipping tests of the coated Nb rods showed that TiC, TaC, and Y_2O_3 coatings exhibited the promising performance among other ceramic coatings. All coated rods showed no reaction with the melt and also maintained the integrity of the coating layers even after three cycles. Thus, the ceramic plasma-spray coatings are thought to be promising candidate coating methods for a reusable melting crucible to fabricate metal fuel slugs for SFR.

Acknowledgements

This work has been carried out under the Nuclear Research and Development Program supported by the Ministry of Science and Technology in the Republic of Korea.

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