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Application of high-temperature ceramic plasma-spray coatings for a reusable melting crucible

Ki-Hwan Kim [a,*], Jong Hwan Kim [a], Ki-Won Hong [b], Jeong-Yong Park [a], Chan-Bock Lee [a]

[a] *Next Generation Fuel Development, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea*
[b] *Materials Science & Engineering, Chungnam National University, Daehakro 99, Yuseong-gu, Daejeon 34134, Republic of Korea*

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ABSTRACT

Metallic fuels, such as the U-Zr alloy system for sodium-cooled fast reactor (SFR), are melted in a Y_2O_3 slurry-spray-coated graphite crucible in order to prevent melt/material interactions. Reactive and porous coatings such as the Y_2O_3 slurry-spray-coating are a source of melt contamination and fuel loss, respectively. Therefore, a dense plasma-spray coating of non-reactive materials is desirable for a reusable melting crucible. In this study, ceramic materials such as Y_2O_3 and 8 mol% Y_2O_3-st. ZrO_2, are selected as candidate protective coating materials for reusable crucibles for melting metallic fuel slugs. Studies are conducted to characterize the thermal cycling performance of the coatings, and the interactions between the U-10wt% Zr fuel and the coating layer on the substrates. The thermal cycling tests of the ceramic plasma-spray coatings exhibit good thermal cycling characteristics with few interconnected cracks. The Y_2O_3 plasma-spray coating does not form a significant reaction layer between the melt and the coating layer due to the thermodynamic stability of Y_2O_3. Hence, the Y_2O_3 plasma-spray coating exhibits the most promising performance among the ceramic coatings investigated, for use in reusable melting crucibles.

1. Introduction

A sodium-cooled fast reactor (SFR) is being developed in combination with the pyro-electrochemical processing of spent fuels at Korea Atomic Energy Research Institute (KAERI) [1–5]. This could resolve the problem of the accumulation of pressurized water reactor (PWR) spent fuels and increase the utilization of uranium resources, while maintaining higher resistance to proliferation [6–10]. U-Zr and U-TRU-RE-Zr metallic fuels have been selected as the driver fuels for SFR in Korea [11,12]. The metallic fuel slugs of the driver fuel assembly are fabricated through injection casting in a vacuum or in an inert atmosphere [13–19].

Metallic fuels such as the U-Zr alloy systems used for SFR, are melted in Y_2O_3 slurry-spray-coated graphite crucibles in order to prevent melt/material interactions [20–22]. However, the hot cell coating applications are labor-intensive and operator-dependent. Furthermore, reactive coatings and porous coatings can be a source of melt contamination and fuel loss, respectively. It is very difficult to reuse the slurry-spray-coated graphite crucibles due to the reactivity and porosity of the coating layers. Thus, a dense ceramic plasma-spray coating of non-reactive materials is desirable in order to realize reusable melting crucibles. The plasma-spray coating could enable a crucible with a denser coating layer compared with the more friable coating layer formed by the slurry-spray-coating. Furthermore, the penetration of the U-Zr melt through the protective layer is more difficult with a dense coating than with a porous coating. Plasma-spray and chemical vapor reaction (CVR) coatings can provide the crucible with a denser coating layer compared with the slurry-spray-coating. The plasma-spray coating is consolidated using the process of bonding particles and densification of materials through applying heat from plasma [23]. The plasma-spray coatings of refractory materials could be applied in order to realize reusable melting crucibles for metallic fuels.

In this study, plasma-spray and CVR coatings were applied and compared with a porous slurry-spray-coating in order to investigate the feasibility of reusing the crucibles in which the metallic fuel slugs were melted. Graphite, which is widely used as the conventional crucible material for uranium and uranium alloys, was selected as the crucible substrate here due to its refractory nature, and its excellent thermal shock resistance. Nb was also selected as a substrate due to its refractory nature and its coefficient of thermal expansion (CTE), which is similar to that of many candidate materials. High-temperature ceramic materials of Y_2O_3 (a coating material used for melting crucibles) and 8 mol% Y_2O_3-st. ZrO_2 (a coating material used for casting molds) were selected as the candidate coating materials. The CVR coating method of SiC was selected for bonding between the protective coating and substrate materials. Thermal cycling tests of the ceramic coatings were performed in order to investigate the reusability of the candidate coating materials

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[*] Corresponding author.
E-mail address: khkim2@kaeri.re.kr (K.-H. Kim).

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Table 1
Coating methods of ceramic materials on the graphite substrate.

No.	Coating powder	Coating method	Nominal thickness (μm)
1	Y_2O_3	Slurry-spray	60
2	Y_2O_3	Plasma-spray	100
3	8 mol% Y_2O_3-st. ZrO_2	Plasma-spray	100
4	SiC + Y_2O_3	CVR (SiC) + Plasma-spray (Y_2O_3)	100

[24,25]. Interaction studies between the U-Zr fuel and the ceramic layer were also conducted at elevated temperature.

2. Materials and methods

An atmospheric plasma-spray coating system with a torch input power of 20 kW was used to apply a 100 μm-thick coating on the substrate. The plasma-spray coating layers on the substrate were deposited while controlling the plasma-spray parameters with an arc current of 750 A, a gas flow rate of 35, and 5 standard liter/min for Ar and He, respectively, a stand-off distance of 100 mm, and five passes of plasma-spraying. The substrates were pure graphite and niobium in the form of discs and rods with diameters of 10 mm. SiC, which was used to bond the crucible substrate and protective coating layer, was coated onto the graphite substrate in a layer in 3 μm-thick using the CVR method at a high temperature. The SiC coating layer was formed via thermal decomposition of the SiO_2 powder on the graphite substrate. The SiO_2 powder as a precursor was heated to 2200 °C in the reaction furnace, which resulted in the decomposition of the Si and O element. The SiC coating layer was formed on the graphite surface of the graphite via penetration by the Si element.

Either the slurry-spray-spray coating or the plasma-spray coating method was used to apply a coating approximately 100 μm-thick on the substrate. The Y_2O_3 and 8 mol% Y_2O_3-st. ZrO_2 powders (ranging from 10 to 45 μm in size), were plasma-spray-coated onto the substrates [26]. A rough surface finish was provided in order to enhance the adhesion of the coating layer; this was achieved through grit blasting the substrate with alumina cleaning a standard ultrasonicator. The methods for coating the ceramic materials onto the graphite substrate are summarized in Table 1.

Thermal cycling test of the coated discs on the graphite substrate was conducted in a programmable vacuum furnace. The thermal cycle temperature and holding time were based on the melting and casting conditions of the U-10wt% Zr alloy fuel. The thermal cycle consisted of heating the specimens to 1450 °C at a rate of 20 °C/min and holding at that temperature for 30 min; followed by furnace cooling to near room temperature. Dip tests were conducted in which the coated rods were lowered into U-10wt% Zr alloy melt in a coated graphite crucible at 1600 °C; then, they were then withdrawn and cooled outside the crucible in a vacuum in the induction furnace. The coating microstructure before and after testing was characterized using scanning electron microscope (SEM). The chemical compositions of the coated specimens were measured using energy-dispersive spectroscope (EDS).

3. Results and discussion

The summarized results of the coating layers on the graphite substrate after the thermal cycling and melt dipping tests, are presented in Table 2. SEM micrographs of the ceramic-coated graphite discs depicting the coating layers are also presented in Fig. 1. The Y_2O_3 slurry-spray-coating layer had non-uniform thickness with an even contact surface with the substrate. Numerous pores were visible with a porosity of 18.4%, but there was good interface contact between the coating layer and the graphite substrate, as seen in Fig. 1-(a). The plasma-spray-coated Y_2O_3, the plasma-spray coated 8 mol% Y_2O_3-st. ZrO_2, the multiple layers of CVR-formed SiC and plasma-spray Y_2O_3 coating layers, as depicted in Fig. 1-(b) to (d), respectively, had a relatively uniform thickness despite an uneven contact surface with the substrate due to the grit blasting. The coating layers were also well consolidated with few pores with a porosity ranging from 3% to 5%, and good interface contact was exhibited between the coating layer and the graphite substrate. The porosity of the slurry-spray-coating was significantly higher than those of the plasma-spray coating due to the absence of consolidation at high temperature. The plasma-spray coating provided the melting crucible with a denser coating layer than the more friable coating layer formed by the slurry-spray-coating. The plasma-spray coatings were bonded via mechanical interlocking of the molten particles at the instant of impact on the graphite substrate, which led to an interdiffusion layer between the graphite substrate and the coating [23]. The powder densification involved in-flight melting of the material in particulate form, followed by gradual cooling and freezing at the graphite substrate. It was also considered that the Y_2O_3 coating layer exhibited good consolidation with only a few small pores due to its relatively low melting temperature of 2440 °C compared with the poorly consolidated HfN, TiC, and ZrC layers with melting temperatures in excess of 3000 °C [27]. Thus, the consolidation of the coated discs was generally good except the slurry-spray-coated Y_2O_3 layer. Further, the pores of the coated discs were small closed pores, except the slurry-spray-coated layer.

SEM micrographs of the ceramic-coated graphite discs after five thermal cycles at 1450 °C are presented in Fig. 2. The coated discs were examined for signs of coating deterioration. The Y_2O_3 slurry-spray-coated disc, as shown in Fig. 2-(a), had numerous large pores, which indicated the porous condition of the coating layer. The Y_2O_3 slurry–spray coating was much significantly porous than the other specimens, and cracks were not formed in the specimen after five thermal cycles due to its high porosity. The porosity of the slurry-spray-coating after five thermal cycles remained approximately 33% higher than those of the plasma-spray coatings, as described in Table 2. The Y_2O_3 plasma-spray-coated disc, the multiple-layer-coated disc with CVR-formed SiC, and the plasma-spray Y_2O_3, which are depicted in Fig. 2-(b) and (d), respectively, had denser states and a few definite cracks perpendicular to the substrate surface after 5 cycles. This potentially resulted from the slight differences in thermal expansion between the coating and the graphite substrate. The Y_2O_3-st. ZrO_2 plasma-spray-coated disc, which is depicted in Fig. 2-(c), had some micro-cracks due to thermal shock after five thermal cycles; however, the cracks were not interconnected. Hence, the thermal cycling tests of the ceramic plasma-spray

Table 2
Summarized results of coating layers on the graphite substrate after thermal cycling and melt dipping test.

No.	Coating method	As-coated state		Thermal-cycled		Melt-dipped
		Consolidation	Porosity (%)	Microstructure	Porosity (%)	
1	Slurry-spray (Y_2O_3)	Poor	18.4	Open pores	38.6	Partial degradation
2	Plasma-spray (Y_2O_3)	Excellent	4.9	A few cracks	3.6	Sound state
3	Plasma-spray (8 mol% Y_2O_3-st. ZrO_2)	Good	3.9	Micro-cracks, not interconnected	4.1	Extensive reaction
4	CVR (SiC) + Plasma-spray (Y_2O_3)	Excellent	4.2	A few cracks	2.9	Sound state

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