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Performance evaluation of plasma sprayed yttria coatings on high density graphite for cathode processor applications

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Abstract

Cathode processing in the pyrochemical reprocessing of spent metallic nuclear fuels encompasses melting and consolidation of uranium deposit obtained from the electro-refining step. Ceramic coated High density graphite (HDG) is considered for process crucibles in the cathode process. Thermal cycling behaviour of plasma sprayed yttria coated HDG discs with NiCrAlY bond coat was investigated at 1000 and 1100 °C in vacuum. Each thermal cycle comprised soaking for 1 h at the isothermal temperature followed by furnace cooling to ambient temperature. The microstructure and elemental composition of the as-received and thermal cycled yttria coated samples were analysed by scanning electron microscopy coupled with energy dispersive spectroscopy. Phase identification of the coating, performed by X-ray diffraction and laser Raman spectroscopic techniques confirmed the presence of only cubic phase in the as-received as well as thermal cycled samples. Yttria coating failed after 35 thermal cycles at 1000 °C and 19 cycles at 1100 °C. Micro-cracks developed after three uranium melting experiments at 1300 °C could be owing to phase change in the bond coat.

Keywords: B. Surfaces; D. Carbon; D. Y_2O_3; E. Nuclear applications

1. Introduction

Non-aqueous pyrochemical processing route has been proposed for the reprocessing of spent metallic fuels, to be discharged from future fast breeder reactors in India [1]. Pyrochemical reprocessing [2] involves several steps/processes, which include salt purification, electro-refining, cathode processing and fuel casting. Electro-refining process is carried out at 500 °C using molten salt mixture (LiCl–KCl) as the electrolyte, under ultra high pure (UHP) argon atmosphere [2,3]. Uranium and U–Pu mixture are electro transported to solid ferritic steel and liquid cadmium cathodes, respectively. The solid cathode deposit contains dendrites of heavy metal (mainly uranium), salts and cadmium. After electro-refining step, cathode processor operation is performed at about 1300 °C [2,4], for the purpose of (a) removing the entrained salt and cadmium from the uranium electrodeposits by vaporization and (b) for consolidating the dendritic deposits. The composition of the cathode processor ingots is adjusted, induction melted and homogenised to the desired composition in the next operational step of injection casting. Considering the long term uninterrupted service of all these operations, involving molten chloride salts and uranium in high radioactive environment in the pyrochemical reprocessing plants, selection of the structural materials for the components and accessories, require to be based on the above environment considerations. Hence, corrosion resistance of the structural materials and equipment in molten chloride salts as well as in molten uranium at high temperatures, in the range 500–1300 °C is of prime importance for pyrochemical reprocessing. High density graphite (HDG) is considered as one of the candidate materials for salt purification, lid, liners and cathode processor as well as fuel casting crucibles [5] due to its good thermal shock resistance and high temperature strength. In addition to these characteristics, the crucible used for cathode processing and fuel casting should exhibit good thermal cycling life and should be inert to molten uranium [6]. The studies conducted earlier in the authors' laboratory, revealed the need for a proper ceramic

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coating over high density graphite [7] to explore the possibility of using it for cathode processing application. Since pyrochemical reprocessing is a batch process, the ceramic coated structural materials should withstand the rigorous testing of several heating and cooling cycles, to assess the durability and integrity of the coating for applications at high temperatures.

Atmospheric plasma spray (APS) process has been widely employed to obtain various ceramic coatings, for the protection of structural materials from corrosion. Yttria stabilized zirconia (YSZ) deposited by plasma spray process was used as a corrosion resistant coating to handle LiCl–KCl molten salt at high temperatures, due to its good thermal shock resistance and low thermal conductivity [8]. The standard Gibb's energy change for the reactions of U with ZrO_2 and Y_2O_3 in the temperature range 300–2000 °C confirmed that both ZrO_2 and Y_2O_3 are chemically inert towards uranium [9]. The compatibility of YSZ coating with molten uranium, evaluated in a previous study also showed satisfactory performance of the coating in liquid uranium [9].

Jagadeesh Sure et al. [8] deposited NiCrAlY bond coat over high density graphite discs and PSZ top coat by plasma spraying, for containing LiCl–KCl molten salt at 600 °C. They evaluated the performance of the coated HDG discs and had reported that PSZ coating exhibits good corrosion resistance in molten salt, up to 2000 h. Several researchers investigated the nature and behaviour of plasma sprayed thermal barrier coating of YSZ with various bond coats on different substrates [10,11]. Berndt et al. [12,13] studied the thermal cycling behaviour of plasma sprayed ZrO_2–12 wt% Y_2O_3 coatings, with and without the bond coat of Ni–Cr–Al–Zr, at 1200 °C and their cracking behaviour was followed by acoustic emission techniques. The influence of plasma spray parameters such as plasma arc current, spray distance and powder feed rate on the thermal shock resistance of plasma sprayed YSZ coatings was studied at 1200 °C by Joshi and Srivastava [14]. They observed that plasma spray parameters affect the durability of coating and had reported that the major factors which determine the life of coating are the nature of the bond coat material and the thickness of top coat. Khan et al. [15] performed thermal cycling studies with YSZ coated nickel based super alloys at 1020 °C. These authors reported that delamination of the coating started from the extreme edge of the samples, quenched in water as well as forced air. They also observed more thermally grown oxide (TGO) at the edges than at the central portion of the sample. Thermal cycling studies performed in air environment indicated that oxidation of the bond coat occurs owing to the growth of TGO, during exposure of a thermal barrier coating (TBC) at high temperatures [16,17]. The growth of TGO with increasing number of thermal cycles was believed to play a crucial role in the life of the coating, as it induces strain energy for crack propagation and ultimately resulting in the spallation of coating. Nagaraj et al. [18] evaluated the thermal shock resistance of plasma sprayed yttria coating on tantalum substrate. The coated sample was subjected to controlled heating and cooling cycles between 27 and 1327 °C, in an induction furnace under argon atmosphere. The coatings deposited using in-house sintered yttria powder and commercially available powder were found to withstand thermal loads up to 26 and 6 cycles, respectively.

In the present study, yttria top coating with NiCrAlY bond coat was developed on HDG substrate, by plasma spray process and the durability of the coating during thermal cycling was evaluated, for the purpose of employing yttria coated HDG crucible in cathode processing application. Uranium melting experiments were conducted over the coated surface of HDG discs, to ascertain the integrity of the coating. As the performance of plasma sprayed ceramic coating on HDG during thermal cycling entirely depends on the microstructure of the coating, microstructural characterization of the coating was also carried out to understand the mechanism for the failure of coating.

2. Experimental

2.1. Yttria coating on high density graphite

High density graphite disc samples of dimensions 25 mm dia and 5.5 mm thickness were fabricated and the top surface of the samples was pressure blasted with alumina grit (size: 16 mesh) to obtain a rough surface in order to get adherent coating. These surface-treated samples were deposited with 50 μm thick NiCrAlY (Amdry 962) bond coat and 250 μm thick yttria (PAC2100P1) top coat by atmospheric plasma spray process, using a METCO 9MB plasma gun at M/s. Plasma Spray Processors, Mumbai. The parameters employed for plasma spray process for the deposition of bond coat and top coat are given in Table 1. The HDG samples were coated on the top flat/curved surface only, as shown in Fig. 1a and b.

2.2. Thermal cycling studies

The yttria coated samples were subjected to thermal cycling studies, after vacuum sealing them in quartz ampoules at 10^{-3} bar pressure (Fig. 1c). Vacuum sealing was required to prevent the oxidation of the HDG substrate in ambient air, as well as to simulate the salt purification step of pyrochemical reprocessing. Thermal cycling experiments were carried out in a box type furnace, at the temperatures 25–1000 and 25–1100 °C, until the failure of coatings. The schedule for heating and cooling cycles is shown in Fig. 2. The vacuum sealed, yttria coated HDG samples

Table 1
Parameters for atmospheric plasma spraying of yttria coatings on high density graphite.

Process parameters (units)	NiCrAlY bond coat	Yttria top coat
Plasma arc current (A)	500	600
Arc voltage (V)	75	70
Primary gas (psi)	100	100
Secondary gas (psi)	50	50
Powder feed rate (g/min)	60	45
Spray distance (mm)	150	100
Argon gas flow rate (l/min)	96	97
Carrier gas flow rate (l/min)	37	37
Type of gun used	9MB	9MB