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Novel double ceramic coatings based on $Yb_2Si_2O_7/La_2(Zr_{0.7}Ce_{0.3})_2O_7$ by plasma spraying on C_f/SiC composites and their thermal shock behavior

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ABSTRACT

$Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (or LZ_7C_3) ceramic powders have been synthesized by solid-state reaction using constituent oxide powders as starting materials in appropriate molar ratios. The fabricated powders were subjected to spray drying treatment for subsequent syntheses of coatings. Double ceramic layer coatings based on $Yb_2Si_2O_7$ as interlayer and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ as the top coat are synthesized on C_f/SiC composite coupons by air plasma spraying (APS). Coatings are subjected to thermal shock testing between 400 °C and 1500 °C in a gas burner rig experiment. X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), and thermogravimetry with differential scanning calorimetry (TG/DSC) were performed on the processed products. Our studies show that the LZ_7C_3 powders after undergoing through the plasma flame result in the formation of coating dominant in pyrochlore structure. Bulk part of the LZ_7C_3 based coatings was found intact with the substrate on thermal shock testing, however, with the presence of cracks in the surface and its partial transformation into constituent oxides. Meanwhile, evaporative loss of cerium happens on progressed thermal cycling. The chemical nature of interaction across the interface was assessed by heating $Yb_2Si_2O_7$ and LZ_7C_3 powders and carrying out the XRD. At 1275 °C for 24 h, almost no reactions took place. However, on heating at 1475 °C for 24 h, microchemistry of the resulted powder is also characterized by the presence of decomposed phases of LZ_7C_3 and the reaction products, especially the cerium based di-silicate.

1. Introduction

Ceramic matrix composites (CMCs) are among the top candidate materials for technological applications requiring high temperature, corrosive and erosive environments, etc. [1–3]. However, the CMCs with carbon fiber reinforcements, especially the C/C composites are prone to oxidation when subjected to higher temperatures (>450 °C) in air. One of the possible solutions to overcome this drawback is their matrix modification such as through development of C_f/SiC or C_f/C-SiC ceramic matrix modified composites. Another way to boost the applicability window of these materials is the application of suitable coating or set of coatings suitable against oxidation, high temperatures, erosion, etc. The selection of protective coating materials for composites containing carbon reinforcements and silicon as one of their matrix ingredients is restricted by some of the requirements such as low thermal conductivity, close match of the coefficient of thermal expansion (CTE), high melting points, phase stability/durability during service environments, low elastic modulus, good adherence to the substrate, low sintering rate, porous microstructure, chemical compatibility to the substrate, etc. [4–6]. Therefore, the number of materials that can be used as new environmental and thermal protection materials is very limited and in addition, no single material satisfies all requirements.

Among the interesting candidates for thermal protection and environmental protection, the rare earth zirconates especially those materials with the mixture of pyrochlore and fluorite structures, lanthanum–zirconium–cerium composite oxide $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ or LZ_7C_3 show promising thermo-physical properties and have attracted great attention. Bulk LZ_7C_3 has a low thermal conductivity value (0.87 W m^{-1} K^{-1}, 1273 K) and it has been proposed as a promising thermal protection material [6–10].

However, due to large differences in the CTEs of LZ_7C_3 (9 ppm/°C) and C_f/SiC composite whose average CTE value from 100 °C to 1500 °C is calculated to be 2.64 ppm/°C (in our separate studies), the coating may come under large stresses, resulting in the possible delamination of the coating. In order to cope with it, interface modification, applying a buffer layer with intermediate CTE value and having strong credentials in terms of environmental protection and thermal protection, is one of the options. The studies have shown that rare earth silicate materials, especially the $RE_2Si_2O_7$ (RE = rare earth) are found to offer compatible CTE values to those of SiC containing ceramics and ceramic matrix composites. The importance and vitality of the $RE_2Si_2O_7$ systems have been discussed and verified in various studies in the

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literature [11–14]. They are the great choices as far as good environmental protection and thermal protection are concerned. However, for advanced thermal protection systems, the materials with even lower thermal conductivities and sintering resistance are required for short and long term applications in various applications of aeronautics and astronautics. Therefore, in these studies, we have produced the sandwiched structures with LZ_7C_3 as top coat and with the intermediate ytterbium di-silicate layer which is already an established material in connection to its high oxidation resistance with low evaporation rates, low permeability, etc. Meanwhile, the CTE of ytterbium silicate $Yb_2Si_2O_7$ is of the order of 4 ppm/°C and thus can contribute positively in decreasing the CTE induced thermal stresses. It should be emphasized that the performance of LZ_7C_3 coatings in extreme environments with temperature up to 1500 °C has not been verified. However, due to its exotic properties, it is considered as one of the protective materials for metallic/alloy substrates. As a matter of fact, the concept of multilayer (ML) is an effective way to overcome the shortcomings of any individual layer ultimately giving enhanced protection of the substrate. Usually, the multilayer includes an erosion resistant layer as the outer layer, a thermal barrier layer, a corrosion–oxidation resistant layer, a thermal stress control layer and a diffusion resistant layer. Based on the DCL coating system, the top ceramic layer should have a low thermal conductivity and high phase stability, and it acts as a thermal insulator to protect the inner layer.

There has been, however, no data available on the performance of $Yb_2Si_2O_7/LZ_7C_3$ double ceramic layers prepared by plasma spraying in open literature. In this work, we firstly have fabricated the $Yb_2Si_2O_7$ and LZ_7C_3 powders by solid-state reaction method and these powders after spray drying are air plasma sprayed on C_f/SiC coupons. The coated coupons are then subjected to thermal shock testing between 400 °C and 1500 °C in a gas burner rig. The study, by necessity, is also phenomenological in nature because the sandwiched structure constitutes ceramic oxides with different structural characteristics, therefore, a preliminary knowledge of the nature and the severity of interactions of phases and emergence of new phases (if any) and thermal shock behavior of the DCL or its transformations (if any) would be the main concerns.

2. Experimental

2.1. Solid-state reaction syntheses and spray-drying treatment

The $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ powders were fabricated by solid-state reaction method. The starting materials SiO_2 and Yb_2O_3 with purities >99.99% for making $Yb_2Si_2O_7$ and La_2O_3, CeO_2 and ZrO_2 with purities >99.99% for preparing $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ were first separately heated at 1000 °C for 2 h in a box furnace. The powders were later ball-milled and sieved to achieve the similar particle size distribution. Deionized water based suspensions were prepared by mixing the constituent oxide powders in appropriate molar ratios for the fabrication of $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$. These suspensions were thoroughly mixed in crucibles for >24 h with zirconia balls. After mixing, the suspensions were completely dried in an oven at 120 °C for several hours. Now the dried powders taken in appropriate molar ratios were ready for subsequent high-temperature reaction, which was carried out at around 1450 °C for 12 h. As a result of high temperature heat treatment, $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ were formed according to the chemical reactions $2SiO_2 + Yb_2O_3 = Yb_2Si_2O_7$ and $La_2O_3 + 0.6CeO_2 + 1.4ZrO_2 = La_2(Zr_{0.7}Ce_{0.3})_2O_7$.

For spray drying of the solid-state reaction fabricated $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ powders, the ball-mill ground powders were mixed with gum arabic powder and tri-ammonium citrate $(NH_3)_3C_6H_5O_7$ in de-ionized water. The suspensions were ball mixed for >50 h for preparation of uniform and homogenous liquid feedstock for spray drying [15]. Centrifugal spray dryer (GZ-S5, Jiangsu Wuxi Yangguang Co. of Spray Drying Machines), with drying capacity of 5 kg water/h, Φ_{in} (inside diameter) of drying chamber 1.4 m, and air as drying medium has been used for the said purpose.

2.2. Plasma spraying and thermal shock testing of the coatings

The atmospheric plasma spraying (APS) of the spray dried powders was carried out by using the Sulzer Metco plasma-spraying unit with F4-MB gun. Table 1 shows the deposition parameters of plasma spray processing for $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ coatings on C/SiC composite coupons. Prior to fixing the C_f/SiC coupons in the sample holder for plasma spraying, the coupons were grit blasted followed by acetone cleaning. In grit blasting, the sand particles were accelerated with compressed air aiming the stream of particles at the surface of the composite coupons. Thermal cycling performance of the plasma sprayed double layer ceramics with $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ as the top coat on C_f/SiC substrate was investigated between ~400 °C and 1500 °C using a gas burner rig. For this purpose, the coated samples were thermally cycled by means of a gas torch by heating them at a temperature of 1500 °C for 6 min duration, and subsequently; the coatings were cooled to around 400 °C in 3 min duration. This makes one cycle. The average ramping rate from 400 °C to 1500 °C was 18 °C/s in these studies. The process was repeated for multiple thermal cycles, and the surface temperature of coating was monitored by infrared radiation pyrometer ($\lambda = 9.6–11.5$ μm).

2.3. Characterization

The fabricated powders and coatings were analyzed using X-ray diffraction for phase identification and optical and scanning electron microscopes for surface morphology. Electron microscopy was mainly carried out by XL-30 FEG Philips SEM equipped with an EDS. X-ray diffraction studies were carried out by Bruker D8 Advance Diffractometer in Bragg-Brentano geometry with an incident monochromatic Cu Kα radiation with wavelength $\lambda = 1.5406$ Å. The operation voltage and current were maintained at 40 kV and 40 mA, respectively. The chemical interactions of $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ in a molar ratio of 1:1 were studied by a simultaneous thermal analysis apparatus. For this purpose, Netzsch STA449 F3 system was used from room temperature to about 1400 °C in air atmosphere with a constant heating rate of 10 °C/min.

3. Results and discussion

3.1. Microstructural characterization of $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ powders

The XRD patterns of $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ powders are shown in Figs. 1(a) and 2(a), respectively. The crystal structure of the fabricated $Yb_2Si_2O_7$ powders is monoclinic; with space group C2/m no. 12 and JCPDS card #25-1345. In addition, the XRD pattern in Fig. 1(a) also reveals some peaks such as those at 2θ ~23.02°, 25.40°, 30.63°, 41.41°, 41.60°, and 50.58°, belonging to Yb_2SiO_5 impurity phase with JCPDS card #40-0386. In general, the peaks were found shifted slightly rightward representing the smaller d values, implying the contracted unit cell.

Table 1
Plasma spraying parameters for the manufacture of $Yb_2Si_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ coatings on C_f/SiC composite.

Spray distance (mm)	Voltage (V)	Current (A)	Plasma gas (S.L.P.M)	Carrier gas Ar (S.L.P.M)	Powder feed (g/min)
110	62	650	Ar = 46, H_2 = 8	2.6	30

S.L.P.M (Standard Litres per Minute).