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Synthesis, spray granulation and plasma spray coating of lanthanum phosphate nanorods for thermal insulation coatings

M. Midhun[a], A. Pragatheeswaran[b], S. Sankar[a], K. Shijina[a], M. Firozkhan[a], A. Peer Mohamed[a], P.V. Ananthapadmanabhan[b,c], K.G.K. Warrier[a], U.S. Hareesh[a,*]

[a] Materials Science and Technology Division, CSIR, National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695019, Kerala, India
[b] Centre for Scientific and Applied Research, PSN College of Engineering and Technology, Tirunelveli 627152, India
[c] Bhabha Atomic Research Centre, Mumbai, India

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ABSTRACT

Nanorods of lanthanum phosphate obtained by a wet chemical precipitation route were granulated to obtain sizes in the range of 10–15 μm by spray drying from aqueous slurry of 35 wt% solid loading and 2 wt% of PVA binder. The powders thus obtained displayed enhanced flowability and were plasma sprayed on to stainless steel substrates resulting in the formation of adherent coatings of 150–180 μm thickness. These coatings were characterized using electron microscopy, X-ray diffraction analysis and Raman spectroscopy. X-ray analysis indicated phase instability of $LaPO_4$ during plasma spraying resulting in the formation of oxy and polyphosphates of lanthanum ($La_2P_4O_{13}$ and La_3PO_7). However, post deposition heat treatment of coated samples at 1100 °C for 2 h resulted in the reversible formation of stoichiometric lanthanum orthophosphate ($LaPO_4$). Raman spectral analysis was used to confirm the phase structure of the coatings deposited at various plasma input powers. The coatings obtained were found to effectively lower the thermal conductivity of the substrates from ~24 W/mK to less than 19 W/mK (~10%) even at 200 °C.

1. Introduction

Lanthanum phosphate ($LaPO_4$) has been realized as a versatile material by virtue of excellent properties like thermal phase stability, high melting temperature, low thermal conductivity/diffusivity and chemical inertness [1–4]. The thermal expansion coefficient of $LaPO_4$ is comparable to that of common ceramic oxides such as alumina and zirconia [5]. However, inherent property of $LaPO_4$ when compared to other high temperature materials is the very low thermal conductivity (1.30 W/mK at 1000 °C), due to its high mean atomic mass and also the structural similarity to network silicates with various arrangements of corner and edge-sharing PO_4 tetrahedra making the material suitable for thermal insulation applications [6]. Nevertheless, maintaining La-PO_4 stoichiometry during the synthesis of $LaPO_4$ has been one of the persistent problems due to which it's wide spread usage in high temperature applications is limited [7]. Although many reports are available for the synthesis of $LaPO_4$ nanoparticles over the years [8–14], a versatile sol-gel process involving precipitation- peptization mechanism has been proven effective to control the stoichiometry [15]. The sol-gel process also has the upper hand over other conventional methods due to the low temperature processing and easy processibility in large scale synthesis.

Atmospheric plasma spray (APS) coating is one of the proven methods for the preparation of ceramic-based thermal barrier coatings. APS deposition often enabled high deposition rates and the highly porous coating thus resulted is employed as high efficiency thermal barrier coatings. YSZ is one of the well-recognized ceramic materials for thermal barrier coatings. However, thermal stability issues related to the formation of t′- ZrO_2 during deposition and its subsequent conversion to tetragonal and monoclinic phases during temperature cycling limits the life of the coatings for long duration applications. Hence, it is desirable to explore new ceramic materials as thermal barrier coatings usable beyond 1200 °C [16–19].

As the sol-gel synthesis of $LaPO_4$ yields nanorod morphology [20,21], these particles cannot be used directly for the plasma spray coating owing to issues associated with the flowability. Due to this very reason, a post-synthesis modification is considered essential to convert the rod shaped $LaPO_4$ into flowable granules having spherical morphology. Spray granulation is a simple technique where the slurries containing a dispersion of particles are atomized to soft agglomerates

* Corresponding author.
E-mail address: hareesh@niist.res.in (U.S. Hareesh).

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forming granules of few tens of microns in size (10–200 μm) [22]. In the present study, nanorods of $LaPO_4$ formed by the precipitation step in a modified sol-gel process were converted to uniform spheres/granules using spray granulation. The granules obtained were then plasma sprayed to form adherent $LaPO_4$ coating over steel substrates for application in the field of thermal insulation. The phase instability issue observed for $LaPO_4$ was addressed by an annealing process to obtain phase pure $LaPO_4$ coating over steel substrates.

2. Experimental procedure

2.1. Synthesis of $LaPO_4$

$LaPO_4$ powder was synthesized following the sol-gel process as reported elsewhere [20]. The precursors used were Lanthanum Nitrate (Star Earth Minerals Ltd., India 99.9%) and orthophosphoric acid (SD Fine Chem. Ltd., India 88%). For the synthesis of 100g of $LaPO_4$, 27.2 mL orthophosphoric acid solution was added drop wise to 0.05 M solution of lanthanum nitrate under vigorous stirring. A white precipitate was formed, which was further flocculated using ammonia solution (Merck India Ltd., 25%) at pH 7. Stirring was continued for 1 h and the solution was then allowed to stand overnight. The mother liquor was decanted and the sediment was separated by centrifugation. The precipitate was washed several times using hot distilled water for the complete removal of nitrates and excess phosphates. The filtrate was then dried and powdered after a final wash with ethyl alcohol. The powder was later sieved and calcined at 800 °C.

2.2. $LaPO_4$ slurry preparation

The 800 °C calcined powders were used to prepare the slurry for spray drying. $LaPO_4$ powder was made into aqueous slurry using distilled water and the pH was adjusted to 2 using 10% HNO_3 solution. The slurry was homogenized by ball milling for 10 h using alumina grinding media of 5 mm size. 2 wt% polyvinyl alcohol (PVA) solution was added to the slurry as binder. The pH was again adjusted to 2 and further ball milled for another 2 h. Slurries with varying solid loading (from 20 to 50 wt% $LaPO_4$) were prepared for measuring the viscosity.

2.3. Spray granulation

The spray dryer used was Spray Dryer-SPD-P-111, (Techno search Instruments Ltd., Mumbai, India) with compressed air as drying medium. $LaPO_4$ slurry was fed into the cyclone chamber using a peristaltic feed pump at the rate of 2–5 mL/min and atomized using the two-fluid nozzle atomization process. The inlet and outlet temperatures were maintained at 160–180 °C and 100–120 °C respectively. Spray granulated $LaPO_4$ powders were collected from the collecting chambers and were analyzed for distribution and shapes.

2.4. Plasma spray deposition

Plasma deposition was carried out using a 40 kW atmospheric plasma spray facility developed at the Laser & Plasma Technology Division (L & PTD) Bhabha Atomic Research Centre (BARC). The torch consists of a thoriated-tungsten cathode (10 mm diameter) with conical tip and copper anode nozzle, 7 mm diameter. The electrodes were cooled by water and a teflon insulator separates the electrodes. Argon gas was used as the primary plasma gas and powder carrier gas. Nitrogen was used as the secondary plasma gas. Alumina grit blasted stainless steel 304 (SS 304, 25×20×2 mm) substrates were used for plasma spray deposition. The arc voltage was kept at 40 V and the input power was varied from 10 to 18 kW by varying the arc current. All the other parameters like powder feed rate, plasma gas and carrier gas flow rates were kept constant. The torch traverse speed (average) is about 2 m/min. The passes were continuous and 10 passes were used for each coating.

2.5. Characterization

Viscosity values of the slurries with varying solid loading were measured using Modular Compact Rheometer, MCR102 (Anton Paar, Austria). Rigaku Miniflex-II X-ray diffraction unit was used for analyzing the phase composition of the feedstock powder and coated samples. Diffraction patterns were recorded in two-theta range from 10°–60°. The scanning rate was fixed at 2°/min for all the samples. Microstructure analysis of the feedstock powder, surface and cross section of the coatings were carried out using Carl Zeiss model EVO 40 electron microscope. The spray-coated samples were carefully cut and the cross-sectioned samples were mounted in a cold setting epoxy resin and allowed to cure at room temperature for 24 h. The mounted samples were polished using emery papers of grit size ranging from 400 to 2500 and final polishing was done with diamond paste (3–0.25 μm size). These cross-sectioned samples were used to analyze the microstructure of $LaPO_4$ coatings. In order to observe porosity and other features, SEM images of microstructures were taken at 1000 X (five micrographs were used for obtaining the average porosity manually). In order to make the samples conductive for electron microscopy, the samples were sputter-coated with gold using Quantum Innovations sputter coating unit. TEM micrographs for the $LaPO_4$ powder were obtained using FEI Tecnai 30 G2 S-TWIN microscope at an accelerating voltage of 300 keV. Raman spectra of the feedstock and plasma spheroidized powders were recorded using Labram-HR 800 spectrometer equipped with an excitation radiation of wavelength λ=514.5 nm from an argon-ion laser. (In order to avoid the substrate contamination while removing the coating from the substrate after deposition, free-standing $LaPO_4$ samples obtained by the plasma spheroidization under identical experimental conditions of plasma spray deposition were used for recording Raman spectra. Thermal conductivity of the samples (bare and coated) was measured by the laser flash technique using thermal conductivity analyzer (Flash Line TM2000 Anter Corporation, USA). Steel was used as the standard reference material (with known values of specific heat and density). From the thermal diffusivity results thermal conductivity (**λ**) was derived using the equation;

$$\lambda = \alpha C p \rho \quad (1)$$

where α is the thermal diffusivity, Cp is the specific heat and ρ is the density. Specific heats of the samples were determined by the instrument in correlation with the standard reference (steel) while densities of the samples were measured using Archimedes principle in order to account for the substrate and the coating.

3. Results and discussion

The TEM micrographs of $LaPO_4$, as precipitated and calcined are given in Fig. 1. $LaPO_4$ precipitate formed under the mentioned synthesis conditions yielded particles with nanorod morphology having~15–20 nm diameter and approximately 500 nm length. The formation of the nanorods during the process is in accordance with anisotropic feature of the units arising from the room temperature sol-gel process adopted, following the spherical growth diffusion model [15]. The rod morphology is maintained even after calcination at 800 °C (Figs. 1b and c). The EDAX pattern provided in Fig. 1d shows peaks corresponding to La, P and O and this confirms the formation and purity of $LaPO_4$.

X-Ray diffraction patterns presented in Fig. 2 provides the phase evolution during calcination. The as-precipitated powder after drying at 80 °C indicated $LaPO_4$ phase in hexagonal form. Nearly all the major peaks are indexed to $LaPO_4$ and no other impurity phases are detected. On calcination, the $LaPO_4$ transformed crystallographically from hexagonal to pure monoclinic phase. Here also, all the peaks are indexed to monoclinic phase of $LaPO_4$.