Microstructural Characterization Of Plasma Sprayed $LaPO_4$ Based Coating

Shubhra Bajpai[1*], G. Sumanth[2], Ayashkant Mekap[3], D. Debasish[1], R. K. Satpathy[4], B. R. Mishra[5]
[1]Advanced Materials Technology, CSIR-Institute of Minerals & Materials Technology, Bhubaneswar, India
[2]Department of Metallurgical and Materials Engineering, National Institute of Technology, Surathkal, India
[3]Department of Energy Science and Engineering, Indian Institute of Technology, Mumbai, India
[4]Defence Metallurgical Research Laboratory (DMRL), India
[5]Indian Rare Earths Limited (IREL), India

DOI: 10.3578/jecsi .68.1&2.2019.34

Abstract

Deposition of lanthanum phosphate coating was carried out using 80 kW atmospheric plasma spray system. Spherical powder for the same, in the size range 22-45 ìm, was obtained by spray drying. The thickness of the coating was controlled in the range of 275-325 ìm in order to have sufficient adhesion strength. The compatibility of $LaPO_4$ towards plasma spraying and its parameter such as plasma forming gas flow rate have been studied using microstructural characterization. High gas flow rate was found to be favorable for synthesizing quality coating with which high amount of porosity can be tailored leading to further decrease in thermal conductivity of the coatings. X-Ray Diffraction and FESEM study revealed the presence of $LaPO_4$ and the formation of a secondary phase i.e. La_2O_3 which is further confirmed by Micro-Raman spectroscopy. The formation of La_2O_3 phase can be reduced to some extent by controlling the rate of flow of plasma forming gas.

Keywords: Plasma spraying, Micro-Raman, FESEM
*Corresponding Author: Shubhra Bajpai, email: sbajpai@immt.res.in, shubhrabajpai@gmail.com, Ph: +91-674-237-9194, +91-7735561650

1. Introduction

Lanthanum phosphate ($LaPO_4$), also known as monazite, is considered as a technologically potential material for corrosion and thermal barrier applications by virtue of its corrosion resistance, thermal stability, relatively high thermal expansion coefficient (10.5×10^{-6} @1273 K), and low thermal conductivity (1.8 W m^{-1} K^{-1} @973 K) and high melting temprature (2343K) [1]. Lanthanum phosphate is reported to have good corrosion resistance in environments containing sulphur and vanadium salts and is reported to be non-reactive with many molten metals[2]. It has also been used for thermal insulation, catalytic, and sensor applications[3]. Lanthanum phosphate ($LaPO_4.0.5H_2O$), prepared by chemical route occurs in hexagonal structure and known as rhabdophane. It is stable up to about 550 °C. Beyond this, it loses the water and forms the monazite phase with monoclinic structure. The rhabdophane-monazite phase change is irreversible [4,5]. Researchers, presently, attempting to find usage of lanthanum phosphate to coat tundish, casting die and other components which can be utilized to prevent the base metal from corrosive attck of liquid metal including uramium etc[6-8].

As lanthanum phosphate consists high melting temperature, plasma spraying apperas to be a good choice for coating deposition of the same. A major advantage of plasma spray processes vis-a‘-vis other competing deposition techniques is that virtually any material that melts at high temperature can be deposited with high deposition rate. Plasma spraying utilizes the high temperature and high enthalpy of the thermal plasma medium

to heat the coating material to a molten or semi-molten state and propel the molten particles onto a substrate, where these particles solidify to produce adherent coatings which can be of thickness as high as 200 - 300 μm[9].

In view of the above advantages, plasma spraying has been identified as a suitable method to prepare $LaPO_4$ coatings. In this contribution, we present the results of thermal plasma sprayed lanthanum phosphate coating developed using a 80 kW plasma torch. Coatings were found to be adhrent and detailed reults are presented and discussed below.

Material and experimental details

The coating deposition was carried out using atmospheric plasma spray unit using PS50 torch (M/s Metallization,UK) and input parameters utilized fo rthe same are mentioned in table 1.

Table 1: Plasma spray deposition parameter

Deposition Parameters	**Bond coat (NiCrAlY)**	**Top coat ($LaPO_4$)**
Current (amp)	650	700
Voltage(volts)	39	51.4
Power (KW)	25.5	36-37
Primary gas flow (Ar) (slpm)	40	20-40
Secondary Gas flow (H_2) (slpm)	Nil	0.5-0.8
Carrier Gas flow (Ar) (slpm)	3	3
Powder feed rate (rpm)	8	8
No. of passes	5	15
Spraying distance (in cm)	8	8
Substrate temperature after coating (°C)	60 – 80	below 100

Prior to coating, the 316L SS substrates were sand blasted with alumina grits for better mechanical bonding of the melted coating powders. Before lanthanum phosphate top coat deposition, NiCrAlY bond coat (~100-200 μm) was deposited using spray grade powder of same material composition (make HC stark, Germany, particle size range: 22-45 μm) on the substrate in order to reduce the residual thermal stresses between substrate and ceramic coating which may arise due to CTE mismatch [10]. In other words, it increases the adhesive strength of the top ceramic coat. During the deposition process it was ensured that substrate temperature should not go beyond 100 °C.

Results & discussion

Lanthanum phosphate particles (4-7 μm) were agglomerated and spray dryed to obtain the flowable powder, also known as spray grade powder, for plasma spraying. Figure 1 shows field emission scanning electron microscope (FESEM) images of the as obtained and spray dryed powder paticles. After spray drying, powder particles were found to be spherical in nature as shown in Fig. 1 (b) and (c).

Further, particle size distribution of the spray dryed powder was obtained using laser based particle size analyser (PSA, Malvern Panalytical Ltd, Hydro 2000MU) and is shown in figure 2. The powder distribution suggests that about 90% of the powder particle size (by volume) fall below 50ìm size range and, therefore, are suitable for plasma spray deposition. The cross-sections of the powders reveal spherical shapes of which some of them were found hollow which is typical of spray drying. Hollow particles can be melted or softened more easily hence the it is expected that the coatings to have less or no unmelted particles [11]. The aboriginal particles which make the spherical agglomerates are below 6-7ìm.

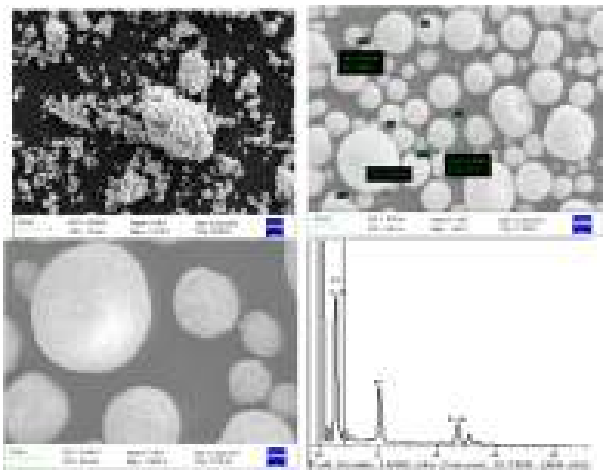


Fig. 1 FESEM of $LaPO_4$ powder (a) as obtained; (b), (c) spray dryed; and (d) energy dispersive spectra of the same



Fig. 2 Particle size analysis of spray dryed powder

X-ray diffraction (XRD) of $LaPO_4$ powder was carried out using x-ray diffractometer (Pan Analytical) with a copper Ká x-rays. XRD pattern of the powder is shown in the Fig. 3. X-ray diffraction of the powder showed a monazite structure which is a high temperature phase[5]. This monazite phase consists a monoclinic structure. This phase of $LaPO_4$ remins stable upto 2000 ^oC in vaccum at which point it melts, however in air it decomposes to Lanthana at 1400 ^oC.

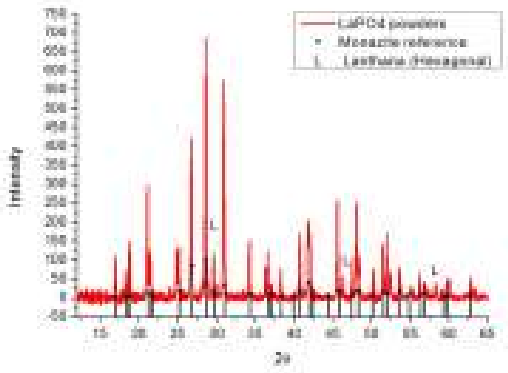


Fig. 3 X-ray diffraction of $LaPO_4$ powder

Further, using the same powder top layer coating deposition was performed using PS 50 plasma torch with the power of 35KW on 316L stainless steel substrates. Effect of primary gas flow was studied within the same coating by making a multilayer of three different conditions. The primary gas, Ar, was varied as 20, 30 and 40 standard liter per minute (slpm). The drop in current, due to reduction in primary gas was compensated by secondary gas which is H_2. Thickness of each layer was kept around100ìm. However, in the light that $LaPO_4$ decomposes at temperatures around 1400 ^oC, the coatings microstructure holds information that be used to understand the effect of primary gas flow.

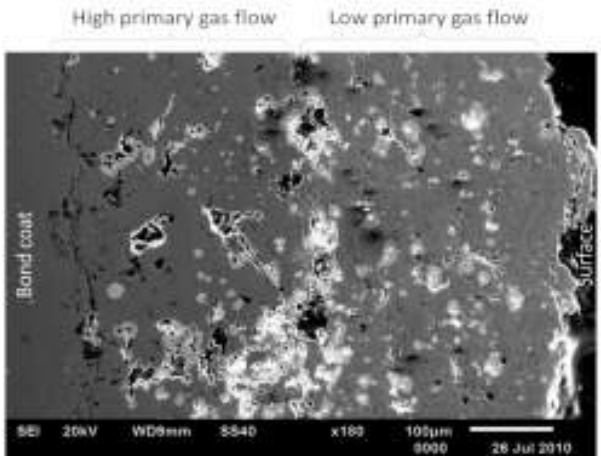


Fig.4 (a) Optical micro-graph of coating cross-section, (b) at higher magnification

The optical image at low magnification shown in figure 4 revealing that the thickness of the bond coat is about 230 ìm and top ceramic coat of $LaPO_4$ is about 300 ìm. The higher magnification opitcal image is shown in figure 4(b). It is clearly visible that the coating near the substrate interface has larger pores and the coating towards the surface has smaller pores. This could be one of the effects of primary gas flow reduction which can be envisaged as an increase in duration spent by the particles in plasma plume thus giving rise to lower porosity in the upper layers. At higher primary gas flow the particles reside in the plume for a shorter time before striking the surface. This might result in a lower temperature of the particles which are less malleable giving rise to larger pores.

The scanning electron microscope (SEM) image shown in figure 5 reveals a clear difference in the top layer and the bottom layer of the top coat. The top layer appear brighter than the dark layer also the top layer shows alternating dark and bright bands of size ~3 ìm. It can be recalled that $LaPO_4$ disintegrates according to reaction given below at temperatures close to 1500 ^oC . The reaction product lanthana has a higher mean atomic number of 65 as compared to $LaPO_4$'s 39. Due to this, lanthana appear brighter than $LaPO_4$.

$$LaPO_4 \rightarrow La_2O_3 + P_2O_5 \uparrow \quad (1)$$



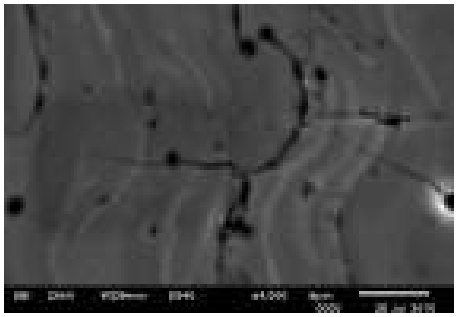


Fig.5 SEM image showing the bright and dark contrast between top and bottom layer. Inset image shows banding in the top layer

The dark lower layer of top coat indicates lower disintegration of $LaPO_4$ while the top layer which has been deposited using a lower primary gas shows higher amounts of disintegration of $LaPO_4$ to Lanthana. Raman spectra shown in figure 6 validates this argument. Graph compares the raman spectra for powders and coating top surface along with references for $LaPO_4$ monazite phase and also the Lanthana.

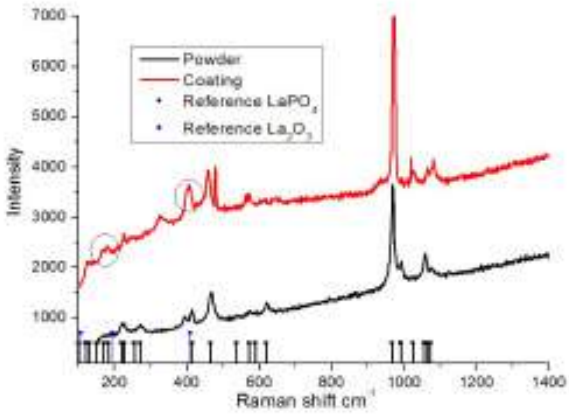


Fig. 6 Raman spectra of precursor powders and deposited coating

Conclusions

Lower primary gas setting shows higher disintegration of $LaPO_4$ hence, is not a suitable for the coating deposition for the purpose of thermal shielding of substrates. Higher primary gas rate during plasma deposition shows lesser disintegration of $LaPO_4$. At the same time, it shows higher porosity. Higher porosity can further

decrease the thermal conductivity of the coating which is beneficial for thermal shielding application. Hence, it may be concluded that higher primery gas rate is beneficial for the coating deposition purpose.

Acknowledgements

Authors are thankful to Director, CSIR-IMMT for giving permission to publish the results. In-house funding from CSIR-IMMT, Bhubaneswar (grant no. OLP-97) is acknowledged for this work.

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