Plasma current effects on the microstructure of solution precursor plasma spray YSZ coatings

R.Sudarshan1,a, Sriram Venkatesh2b,K. Balasubramanian3c, P. Karuna purnapu Rupa4
1Geethanjali Collge of Engineering and Technology, Cheeryal(V), Keesara (M), RR Dist, Telangana, India
2University College of Engineering, Osmania University, Hyderabad, India
3Non Ferrous Materials Technology Development Centre, Kanchanbagh, Hyderabad, India
4rsujo1@gmail.com,b)venkatmech@yahoo.com, c)director@nftdc.res.in
Corresponding Author: R. Sudarshan, rsujo1@gmail.com

Abstract -The Solution Precursor Plasma Spray (SPPS) process has been used for obtaining Zirconia coatings as Thermal Barrier Coatings (TBCs). In this study an in house developed Zirconyle nitratesolution precursor plasma spray setup has been used. In this process the coating is built up by horizontal and vertical passes of the plasma torch across the substrate. The microstructural characterizations of coatings were carried out by scanning electron microscope (SEM) and X-ray diffraction (XRD). Significant effect of plasma current has been observed on the zirconia coatings.

Index Terms—Solution precursor, Plasma Spray, TBCs, Plasma current

1. Introduction:
Thermal spraying is an advanced materials processing technique which has found wide acceptance in many high technology industries. High temperature, high velocity flame is produced to heat, melt and spray material introduced into the flame. In general, thermal spray coatings have a very fine (micron sized) grain structure. Nano grained deposits and nanosized particles have superior properties compared to conventional materials. Reduction of the particle size of the thermal spray feedstock improves the homogeneity and properties of coatings.

The Liquid Precursor plasma spray (LPPS) is using to a great extent driven by the gas turbine industry, Automobile industry and in particular the manufacturing of the thermal barrier coatings (TBC) that protects the surfaces of metallic parts in the hottest zones of gas turbines used for the generation of electricity and propulsion of aircraft [1-2].

The thermal spray processes have been using the different kind of powder feed stocks such as for the coating. It has been widely used for various purposes like to protect from corrosion, improve durability and oxidation resistance properties at high temperature and it can reduce the metal service temperature [3-4]. The Solution Precursor Plasma Spray is recently developed for the fine spray. It is same as the existing conventional spraying processes with the only difference that instead of powders the feed is in the form of solution precursor. The liquid solution precursor material is injected into the plasma jet by a nozzle. Rapid heat-up and vaporization of precursor droplets in the formation of particles, which will be heated and accelerated to the substrate to generate coatings. In order to gain a better quality and performance of the coating, liquid precursors are sprayed into the plasma jet to generate finely structured coatings [5]. Deposition of small, melted particles leads to fine microstructure with the improvement in certain mechanical properties like hardness and strength. The different kinds of solutions or suspension precursors have been used for the different purposes. With normal APS process it’s not possible to feed powder with size finer than 5-10μm due to the effects of surface forces on powder flow [6]. The atomized droplets of precursor undergo rapid
evaporation and breakup in the plasma [7]. The precursor droplets fed into the plasma regions at different temperature will experience different physical and chemical reactions. The high power plasma is necessary for SPPS adherent coatings [8]. Deposition parameters of low distance of substrate and high power lead to the formation of low density and rough coatings [9] the crystallinity decreased [10] and the poor deposition efficiency [11,12] increase in the particle velocity, porosity and surface temperature[12]. Applied plasma current influences the chemistry and morphology of atmospheric pressure plasma deposited coatings [12–16]. By increasing the plasma current or decrease it the particle velocity will increase or decrease respectively [17]. The pumping effect decreases as the plasma current decreases [18]. The investigations have been carried out for the effects of processing parameter (plasma current) in the SPPS and to understand their implications and improving of this process. The microstructural characterizations of coatings were carried out by scanning electron microscope (SEM) and X-ray diffraction (XRD).

2. Experimental setup:
An in house prepared solution precursor Zirconyl Nitrate has been used as a liquid precursor for the present study. The solution precursor Plasma Spray (SPPS) was carried out using a robotic plasma spray system equipped with a liquid spray unit. The gun was connected to a 6 axis ABB robot for precession maneuvering. Argon and Hydrogen gases were used as a primary gas and secondary gas respectively. The argon flow rate was maintained as 20 NLPM and hydrogen was 10 NLPM. For the coating characterization studies SS 430 of 50mm X 50mm X 2mm substrates were grit blasted before the coating deposition. Coating thickness for all the deposits was maintained at 500 ml/min. The SPPS process is schematically shown in fig.1. involves spraying of the liquid precursor into plasma plume through an atomizing nozzle.

The coatings were characterized by SEM and XRD. Compositional analysis was carried out by EDS attached to the SEM.

3. Results and discussion:
The parameters of plasma spray and Injection for the liquid feedstock are shown in the following Tables.1 & 2

Table:1. Plasma Spray Parameters

| Parameters    | Sample 1 | Sample 2 | Sample 3 |
|---------------|----------|----------|----------|
| Operating Gas | Ar, H2   | Ar, H2   | Ar, H2   |
Argon flow rate (NLPM) at 5.5 bar

| Parameters                        | Sample 1 | Sample 2 | Sample 3 |
|-----------------------------------|----------|----------|----------|
| Atomising Gas                     | N2       | N2       | N2       |
| Precursor Feed Rate (ml/min)      | 500      | 500      | 500      |
| Precursor Tank Pressure (Bar)     | 5        | 5        | 5        |
| Atomising Pressure (Bar)          | 1        | 1        | 1        |

Table: 2 Injection Parameters for Liquid Precursor Feedstock

The plasma arc current was increased during experimentation is 400 – 600 amp. The flow rate of primary and secondary gas was kept constant 20 and 10 NLPM respectively. The liquid precursor injection parameters were kept constant throughout the experimentation.
Fig. 2: SEM images of Sample 1 (400amp) at different magnifications.

Fig. 3: EDS of the sample 1 (400amp)

| Element | Weight % | Atomic % |
|---------|----------|----------|
| O       | 34.45    | 65.41    |
| Al      | 0.78     | 0.88     |
| Si      | 0.42     | 0.46     |
| S       | 5.19     | 4.91     |
| K       | 1.79     | 1.39     |
| Cr      | 4.68     | 2.74     |
| Cu      | 1.27     | 0.61     |
| Y       | 3.93     | 1.34     |
| Zr      | 16.91    | 5.63     |
| Fe      | 30.57    | 16.63    |
| Total   | 100      | 100      |
The uniform coating has been obtained shown in Fig.2. SEM observations show the presence of very small cracks of 200 to 300 microns. No pores were observed in the sample 1. EDS shows the presence of oxygen, zirconium, Yttrium, Ferrous and other elements also. XRD pattern of the coating is shown in Fig. 4. Broad peaks were not observed because of the coating thickness is very less. The peaks were not matched with zirconia.

Fig. 4 XRD for Sample 1 (400 amp)
Fig. 5: SEM images of Sample 2 (500amp) at different magnifications.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O       | 52.47   | 80.90   |
| S       | 6.96    | 5.36    |
| K       | 2.86    | 1.80    |
| Ca      | 0.44    | 0.27    |
| Cu      | 8.68    | 3.37    |
| Zn      | 1.65    | 0.62    |
| Y       | 5.10    | 1.41    |
| Zr      | 19.74   | 5.34    |
| Fe      | 2.09    | 0.92    |
| Total   | 100     | 100     |

Fig. 6: EDS of the sample 2 (500amp)
Fig. 7: XRD of the as coated sample S2 (500amp)

The uniform coating has been obtained shown in Fig. 5. No pores and cracks were observed by the SEM observations but it shows the different phases in the sample 2. EDS shows the presence of oxygen, zirconium, Yittrium, and other elements. XRD pattern of the coating is shown in Fig. 7. Broad peaks were not observed because of the coating thickness is very less. The peaks were not matched with zirconia. But as compared to sample 1 coating thickness the coating thickness of sample 2 is little bit high.
Fig. 8: SEM images of Sample 3 (600amp) at different magnifications.

Fig. 9: EDS of the sample 3 (600amp)

| Element | Weight% | Atomic % |
|---------|---------|----------|
| O       | 46.03   | 77.39    |
| S       | 7.63    | 6.4      |
| K       | 3.4     | 2.34     |
| Zn      | 9.03    | 3.72     |
| Y       | 4.81    | 1.46     |
| Zr      | 28.49   | 8.40     |
| Fe K    | 0.61    | 0.29     |
| Total   | 100     | 100      |
The uniform coating has been obtained but the surface roughness is there in sample 3 shown in Fig.8. SEM observations show the presence of small pores and distributed uniformly. It has not clear that the pores are inter linked in SEM observations as shown in sample 3. EDS shows the presence of oxygen, zirconium, Yitrrium, and other elements also. XRD pattern of the coating is shown in Fig.10. Broad peaks were observed. The peaks matched with zirconia. However, the coating was dense and the thickness is also more in sample 3 than the sample 1 and sample 2.

4. Conclusion
In this experiment only one parameter the current has changed from 400 to 600 amp and the other parameters are constant. As current increases the density of coating is increasing and also the thickness of coating is increasing. Small cracks are observed in sample 1, no pores and cracks were observed in sample 2, and the pores and cracks are observed in sample 3.

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Fig.10: XRD of the as coated sample 3 (600amp)
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