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Microstructural Investigation of $BaTiO_3$ Plasma Sprayed Coating Deposited by Splash and Disk-Like Splats

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Abstract

In the thermal spray process, particulate materials can be melted by plasma atmosphere due to its high local temperature from 8700 ˚C to 15,000 ˚C. Therefore, the material powders turn into droplets after being melted by injection into the hot flame. Molten droplets are accelerated toward a substrate and form the splats which quickly solidify; finally, the film is formed by pile-up splats. Splat morphology and post treatment can determine the microstructure, mechanical and physical properties of the coating. In this study, $BaTiO_3$ films were deposited onto a mirror polished stainless steel substrates kept at room temperature and 500 ˚C. At the elevated temperatures, the desorbtion of adsorbates and condensate at the substrate surface are the most important factor which change the morphology of the splats, from irregular- splash morphology to disk-like shape. Splat morphology can determine sprayed film microstructure and effect on the coating properties. The morphology of individual splats and the post treated films were studied using scanning electron microscopy. Results indicated that the porosity in the film produced at room temperature was higher than that in the film deposited on the heated substrates. Also, results show post heat treatment can improve physical and mechanical properties of the sprayed coating.

Keywords: Splat Morphology, Heat Treatment, $BaTiO_3$, Air Plasma Spray, Dielectric Properties

1. Introduction

Air plasma spraying (APS) is an important method usually used to produce thick films [1-2]. This method is used in different industries such as gas turbines, automotive and petrochemical industry and can improve engine efficiency. It has been mostly used to produce thermal barrier coatings (TBCs) and anti -wear films [3-5].

Because of progress in technology and the need of new coating, a broad range of engineering materials are used for electrical, magnetic, optical, and medical applications using an atmospheric plasma spraying (APS) method [6]. Among them, Barium titanate, $BaTiO_3$ is so important. BaTiO3 was the first material used to manufacture dielectric and ferroelectric ceramics because of its unique properties [6-7]. Due to recent environmental issues, many studies focus on the lead-free material. Moreover, the excellence of its piezoelectric properties is unsurpassed by any other materials [8].$BaTiO_3$ have a perovskite structure, with the chemical formula of ABO_3 [7]. Ferroelectric properties of $BaTiO_3$ result from its three allotropic transformations [5-8]. In general, $BaTiO_3$ shows different behaviors in the form of thin film, single crystal and Bulk materials [7-10]. The bulk form can be synthesized by solid-state reaction method [7,10]; however, there are different methods to process $BaTiO_3$ thin and thick film. It should be noted that the most important method to produce thick film is plasma spray method and the properties of sprayed thick films are comparable with the bulk materials. By using this method, different substrates with a variety of sizes and shapes can be used and also, the thickness of deposited films can be easily controlled. Additionally, thermal spray methods are a cost-effective, quick and in-situ process [6-7, 10, 11].

In general, because of the formation of cracks, voids, amorphous phase and the non-bounded interface between splats that are usual in the plasma spray process the physical and mechanical properties of the sprayed film are less than bulk materials [9-10]. Xing et al. [12] reported that the electrical properties of sprayed coatings were one-fifth to one-third of bulk materials. In APS, the physical and mechanical properties of the films are related to the morphology of the individual splats [11-12]. In general, in sprayed methods, the film is built up by impingement of molten droplets onto the substrate. Splats are created by flattening and spreading of the impacting droplets. The preheating of the powders and the substrate, roughness and oxidation state of the surface, velocity, spray condition and the angle of the particles on impact can effect on the splat morphology [7]. Among all of them, substrate preheating is an important parameter in APS; there is a transition temperature for all materials, named as (Tt), which above it, the splats morphology of materials on a substrate is changed from a splash/fragmental morphology to a disk-like shape [6-7].

The value of Tt is quite sensitive to the splat material rather than to the substrate [13].

For alumina and zirconia, Tt is around 200 to 250 °C for disc splats deposited on low-carbon steel, aluminum alloys, stainless steel, alumina, and

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zirconia substrates [14]. For ethylene methacrylic acid (EMAA), Tt is around 90-100 °C for deposition onto mild steel [15]. Pakseresht et al. [7] reported that the adhesion strength of coatings on the substrate preheated above the transition temperature was higher than those unheated ones. Substrate surface chemistry also can effect on splat morphology, Tran [16] studied the effects of surface chemistry on splat morphology during the plasma spray process. Aluminum substrates were heated thermally and hydrothermally to grow specific types of hydroxide and oxide layers on the surface. Nickel-chromium single splats were then sprayed onto the pre-treated mirror polished substrates. It was indicated that splats with splash morphology formed on samples where a thin layer of hydroxide was present on the substrate surface. It was concluded that splat formation and morphology were sensitive to surface chemistry; particularly the concentration and thickness of the hydroxide layer at the surface substrate. The lower the amount of surface hydroxide, the better the splat formation and morphology [16].

It should be noted that by changing the splat morphology from splash morphology to disk-like, the physical and mechanical properties of the sprayed coating could be improved. Also, post heat-treatment can reduce the poor contact between splats results in improvement in the coating structure. Previous investigations explained that improvement in splat morphology and reduce non-bounded interface between splats play a key role in increasing the physical and mechanical properties of plasma sprayed film. In our previous investigation, the transition temperature of $BaTiO_3$ deposited on SS was determined around 300 °C [7]. In this research, the individual splats were collected on a mirror polished substrate held at two different temperatures, and microstructure of coating before and after heat treatment were studied. Also, the effect of substrate preheating on dielectric properties of plasma sprayed $BaTiO_3$ thick film was investigated.

2. Materials and Methods

$BaTiO_3$ Powders with the purity of 99% and average initial particle size of 1-10 µm used in this investigation were prepared from Alfa Company (product No. 12348). To increase the flow ability of commercial powders, they were granulated. Fig. 1. shows the morphology of granulated powders.

The average size range of the granulated powders was nominally −60-80 µm. The substrates used in this study were stainless steel (AISI 316L) disks, the external diameter of the samples was 20 mm and the thickness was 0.3 mm. Before plasma spraying, the substrates were grit blasted with alumina particles and the substrate roughness increases to 3.5 ± 0.5 µm then the substrates were cleaned in an ultrasonic bath with acetone solution.

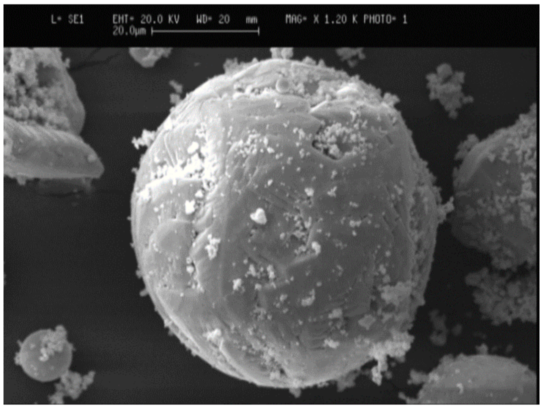

Fig. 1. Morphology of granulated powder.

In order to study the splat morphology, the substrates surface should be mirror polished to remove surface roughness. The substrates were prepared by polishing with grit paper. The substrates were finally polished both with 0.3 µm and 0.05 µm Al_2O_3 to reach nanoscale roughness.

$BaTiO_3$ film was sprayed by a Plasma Technique AG; Metco 3MB gun in air. Argon gas was the primary plasma gas and hydrogen gas was added as the secondary gas. To deposit the single splat, a stainless steel plate with holes of 1 mm in diameter to permit limited particles to reach the substrate was placed perpendicularly to the plasma jet at the distance of 20 mm ahead of the substrate.

$BaTiO_3$ single splats were collected on the mirror polished substrates kept at room temperature and 500 °C. Before spraying, the mirror polished substrate was pre-heated by the plasma torch. During spraying, the substrate temperature was monitored using optical pyrometer. Table. 1. Given typical atmospheric plasma spray parameters and condition used for the single splat collection.

Table. 1. Experimental spraying conditions.

Parameter	**Film**	**Splat collection**
Current (A)	500	500
Voltage (V)	60	60
Primary gas, Ar (Scfh)	65	65
Secondary gas, H2 (Scfh)	15	15
Spray distance (mm)	80	80
Powder feed rate (g/min)	20	10

The splats morphology and microstructure of $BaTiO_3$ deposited films were analysed using scanning electron microscopy (SEM: S360, Cambridge, UK.). To remove the apparent amorphous phase and improve the coating properties, the films were heat treated in air at 1050 °C for 3 h with a heating rate of 10 K min^{-1}. The amount of prosities were estimated by image analysis software (Image J) from the SEM image of the polished cross -section of samples.

For the electrical properties, top surface of the film was contacted by sputtered gold electrode and the substrate was also used as a bottom electrode. The dielectric properties (relative permittivity and dielectric loss) were measured by the LCR-meter (model Precision LCR Meter 8110G) at 1 kHz and with 1 V AC perpendicular to the coating surface. All measurements were performed at the same humidity condition [17]. The relative permittivity of materials (ε_r) was related to the material dimensions and it was calculated from measured capacities, C_P, according to the following equation:

$$C_P = \varepsilon_0 \times \varepsilon_r \times A/t \qquad (1)$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}; A/t [m] is defined as the ratio between the area of guarded electrode and the thickness of the layer [17].

3. Results and Discussion

3.1. Splat Morphology

The splats morphologies are shown in Fig. 2. and Fig. 3. Accordingly, the splashed / fragmented and disk-shaped splats are the morphologies related to the as-prepared and preheated substrates at 500 °C, respectively. It is clear with increasing the substrates temperature, splats morphology tends to be disk-shaped and also, splashing is decreased. It is clear that the splats morphology completely turned into disk-shape at 500 °C. In this situation, perfectly disk-shaped splats without any projection around the splat could be found on the surface of the substrate. The difference in splat morphology was related to the surface condition and the wetting characteristics of the substrate at higher temperatures [7, 18].

There are two factors affecting the wettability of the substrate. The first factor includes the substrate roughness. Higher surface roughness causes higher wettability of the substrate. Cedelle et al. [18] showed that the wettability of droplets could be enhanced by increasing the substrate temperature and showed changes in the surface topology could improve thermal contact resistance between substrate and splats and wetting behaviour of droplets in impact [7]. The second factor includes the amount of condensates/adsorbents on the surface of the substrates and the composition, thickness, and morphology of the oxide layer on the substrate surface which affected by the preheating rate, temperature and time. The thickness of the oxide layer can effect on substrate roughness, and thus modifies the substrate wettability. Besides, a higher content of condensates or adsorbents on the surface of the substrates decreases the wettability of the substrate. Accordingly, splashing occurred during flattening of the molten droplet at low substrate temperature because of condensates/adsorbents at the substrate surface. Actually, evaporable substances and the water were desorbed by substrate preheating; thus, the droplets impacted a clean surface and disk-shaped splats formed on the substrate. However, when there are evaporable adsorbents on the surface of the substrate which can evaporate after the impactions of the high temperature droplets, the fragmented droplets were formed and subsequently, the splashed splat morphology achieved [7].

Fig. 2. Top surface morphology of fragmented and splashed splat collected at room temperature.

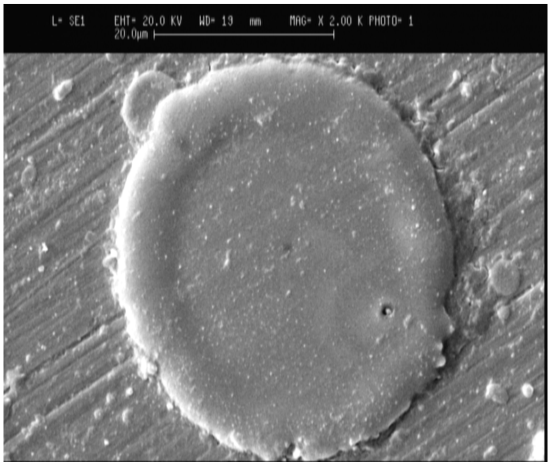

Fig. 3. Top surface morphology of Disk-like splat collected at high temperature.

3.2. Morphology of the Fracture Surface

The performance and properties of coatings deposited by thermal spray depend on the quality of contact between the coating and the substrate and between deposited layers [7, 18]. Plasma sprayed and HVOF coatings are characterized by a highly anisotropic lamellar structure. Fig. 4. and Fig. 5. Show the SEM micrographs of the cross-sectional morphology of the fractured film on as-prepared and preheated substrates, respectively. In the case of conventional substrate, the micrograph showed poor contact between splats. Micro-cracks, non-bounded interfaces between splats and pores were the common defects of the sprayed coatings. Forming the pores were because of some reasons such as evaporation of the adsorbed substances, bubble formation from the gases, extensive splashing of the droplets upon impact and poor contact between splats [19-21]. Measuring the porosity value at the cross-section of the coatings showed that fraction of porosity was decreased from 12.7% to 3.1% for the coating on a preheated substrate (500 °C), in comparison with the conventional one. It should be noticed that, for the preheated substrate, the adsorbed substances evaporated, caused reduce in plashing; thus, the porosity value and space between splats were decreased.The film is formed by pile-up many individual splats and created the lamellar structure with columnar grains is obvious from Figs. 4. and 5. In the case of pre-heated substrates, the microstructures were more uniform, showing the improved contact between the splats, and the growth of columnar grain through the splat-splat boundary [7]. This kind of microstructure causes the well- bounded lamellar layers that can create more bonding ratio between lamellae in sprayed film. Mechanical and physical properties of the sprayed coating depend on the contact of those splats with the underlying layers and substrate surface. So, coating with uniform microstructure has higher mechanical and physical properties than conventional one [6-7].In heat-treated samples the better contact between the substrate and droplets was a consequence of the evaporation of contaminants and enhanced heat transfer between the molten droplets and substrate, finally changing the splat morphology [7-8].

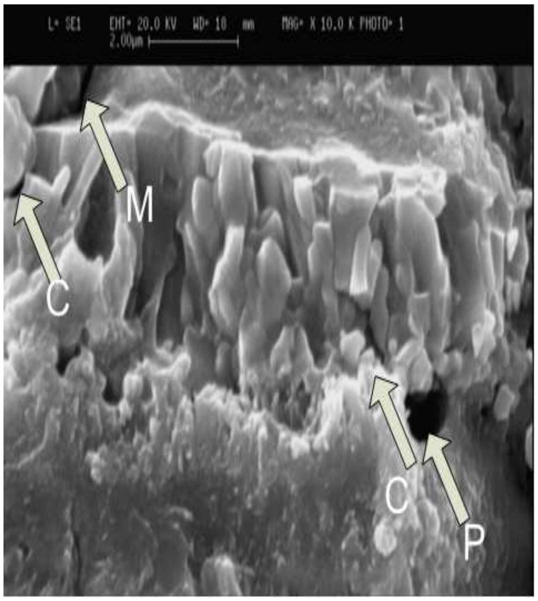

Fig. 4. Fracture surface of film deposited on substrate held at room temperature (C: Poor contact between splats, P: Pore, M: Micro-Crack).

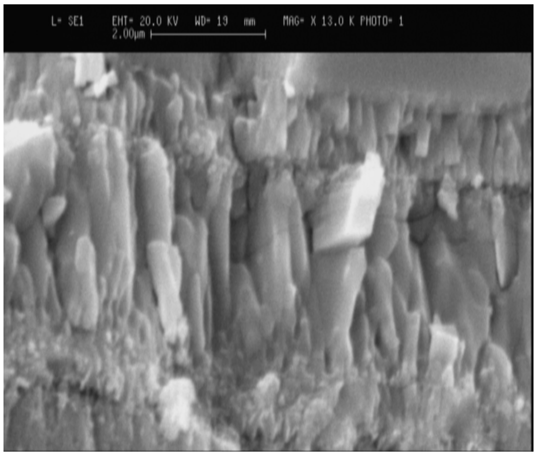

Fig. 5. Fracture surface of film deposited on substrate held at high temperature.

3.3. Effect of Post Heat Treatment on Microstructure of Coating

Fig**.** 6**.** Shows cross-sectional morphology of the fractured $BaTiO_3$ film after the heat treatment. As can be seen, some of the defects in sprayed coating start to sinter and heal after post heat treatment. The micro-cracks, porosities, splats, and un-melted areas can be clearly seen in this Fig. 6. The inter-splat bonding and coherency across the splat boundary improved after heat treatment of the film. The process of heat treatment generally produces bridging interfaces between the splats in close physical vicinity, decreases the porosity and micro-crack content, and increases the contact area between the splats [6]. Moreover, some inter-splat interfaces, porosities, and large voids remain relatively unaffected in the structure.

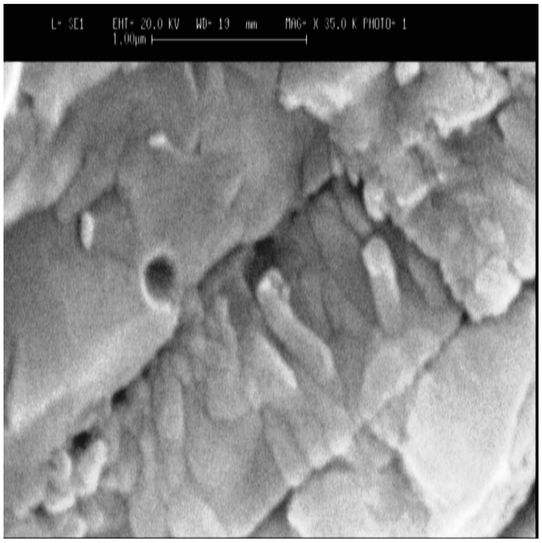

Fig. 6. Fracture surface of film after heat treatment.

3.3. Dielectric Properties

The microstructure of deposited film has the major effect on dielectric properties of the sprayed film such as dielectric constant and dielectric loss, influenced by the splat morphology and post-treatment process [6-7]. The level of adhesion between lamellar structures formed during the plasma spraying and the amounts of pores and cracks strongly influences mechanical, thermal, as well as electrical properties of the sprayed coatings [6-7].The relative permittivity values would be reduced because of limited interlamellar bonding in coating deposited by splash splats. The air trapped in pores and inter-splat cracks can reduce relative permittivity values as can be seen in Fig. 4. So, the relative permittivity of the conventional coating is less than that for the coating with disk-like splats.

Fig. 7. shows the results related to the electrical properties of both coatings, the results showed that the amount of relative permittivity for coating produced by splash splats and disk-like splats was 120 and 465, respectively. This increase is due to the coating morphology improvement. It is clear that the relative permittivity for the plasma sprayed films is low and loss tangent is more in comparison with the bulk $BaTiO_3$ and it is due to the presence of common defects such as the interfaces between splats and the lamellae structure in sprayed coatings that are the factors decline the mechanical and physical properties of the plasma sprayed film in comparison with the bulk $BaTiO_3$. It should be noted that after heat treatment the amount of relative permittivity was increased in conventional samples due to improvement in microstructure and these phenomena haven’t seen in samples with disk- like splats [10].

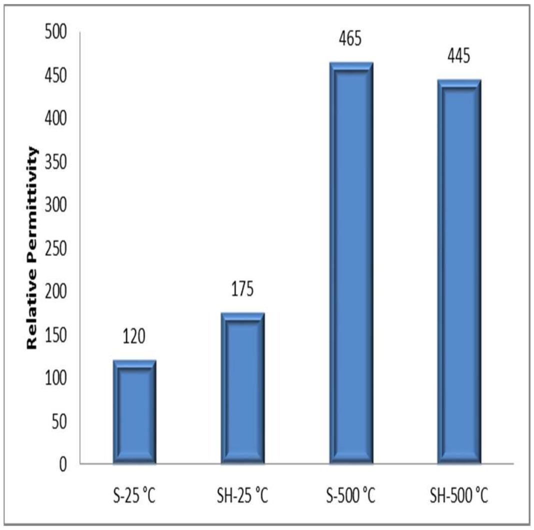

Fig. 7. Comparison of the relative permittivity of deposited films onto the substrate with different temperatures (S-25 °C, SH-25 °C (heat treated sample), S-500 °C and SH-500 °C (heat treated sample)).

4. Conclusions

1. The properties of coatings and splats are affected significantly by the substrate surface conditions, such as surface wettability, surface roughness, transition temperature and surface chemistry.
2. Splat morphology can effect on final sprayed coating structure. For some materials, there is a transition temperature which above this temperature splat morphology changed from splashed morphology to disk like- morphology.
3. Coating with disk-like splat has higher physical and mechanical properties than the conventional one.
4. By changing splat morphology, the amounts of porosities reduce from 12.7% to 3.1%.
5. The relative permittivity increase after heat treatment due to an increase in the contact area between the splats.

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