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Technical Report

Microstructural and tribological characterization of air plasma sprayed nanostructured alumina–titania coatings deposited with nitrogen and argon as primary plasma gases

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A B S T R A C T

Air plasma sprayed nanostructured Al_2O_3–13wt%TiO_2 coatings were deposited as a function of critical plasma spray parameter (CPSP), defined as the ratio of arc power to primary gas flow rate, using nitrogen and argon as the primary plasma gases. Microstructural features including percentage of α-Al_2O_3 phase, percentage of partially melted/unmelted regions, microhardness, and wear characteristics were evaluated for the deposited coatings. Effect of CPSP on microstructural and wear characteristics of coatings deposited with nitrogen was found to be relatively small. In contrast, significant effect of CPSP on coating characteristics was found for coatings deposited with argon. In wear tests, while strong effect of normal load on weight loss was observed for coatings deposited with nitrogen, weight loss for coatings deposited with argon was nearly independent of applied normal load, at least for coatings deposited at the highest CPSP.

1. Introduction

Plasma sprayed alumina–titania coatings are used in several applications because of their high wear resistance, heat and thermal shock resistance, oxidation and hot corrosion resistance and electrical insulation. They are also attractive as they bond well with metallic bond coats, resist wear, solid particle erosion and have high hardness and chemical stability even at elevated temperatures. Plasma sprayed coatings from nanostructured agglomerated alumina–titania powders have received considerable attention in recent past owing to their improved properties over that of the corresponding coatings from conventional powders. For instance, Jordan et al. [1] reported enhanced cracking and spallation resistance for nanostructured alumina–titania coatings as compared to the corresponding conventional coatings. Luo et al. [2] showed that under optimized conditions nanostructured coatings showed a nearly 100% higher crack growth resistance as compared to the toughness for conventional coatings. Tian et al. [3] demonstrated that nanostructured coatings exhibited much higher fretting wear resistance than conventional coatings in fretting wear tests against 52100 steel balls. Ibrahim et al. [4] showed that rotating beam fatigue specimen coated with nanostructured alumina–titania coatings exhibited about 2–3 times higher life than specimen coated with corresponding conventional coatings and about 4 times higher life than uncoated specimen.

Shaw et al. [5] studied wear characteristics of air plasma sprayed conventional and nanostructured alumina–13wt% titania coatings. It was found that nanostructured coatings show better wear characteristics as compared to conventional coatings. Lin et al. [6] studied effect of temperature on tribological properties of both conventional and nanostructured alumina–3wt% titania coatings deposited by atmospheric plasma spraying. Tests were conducted using silicon nitride ball in the temperature range from room temperature to 600 °C. It was found that wear resistance of nanostructured coatings was superior to that of conventional coatings except at room temperature.

Bounazef et al. [7] correlated plasma spraying process parameters such as primary and secondary gas flow rates, carrier gas flow rate and powder injection distance, with wear characteristics of plasma sprayed alumina–titania coatings. It was found that there is a combined effect of spray temperature and in-flight particle characteristics on the wear resistance of the alumina–titania coatings. Wang et al. [8] investigated abrasive wear resistance of conventional (Metco-130) and three nanostructured alumina–titania powders: Al_2O_3–13wt%TiO_2, Al_2O_3–13wt%$TiO_2 + CeO_2$, and Al_2O_3–13wt% $TiO_2 + CeO_2 + ZrO_2$. Abrasive wear resistance of nanostructured coatings was far superior to that of corresponding conventional coatings. Among nanostructured coatings, wear

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volume was lowest for coatings containing CeO_2 and ZrO_2. Guessasma et al. [9] obtained sliding wear characteristics of plasma sprayed alumina–titania coatings using pin-on-disc wear tests. It was found that the friction coefficient increases with increase in applied load and sliding velocity. Rico et al. [10] investigated dry sliding wear performance of nanostructured and conventional Al_2O_3–13wt%TiO_2 coatings. Nanostructured coatings were seen to exhibit enhanced wear resistance at all conditions considered.

Bolelli et al. [11] used pin-on-disc and dry sand–steel wheel tests to study wear resistance of three plasma sprayed ceramic coatings: Al_2O_3, Al_2O_3–13%TiO_2, and Cr_2O_3. Wear resistance of coatings was correlated with that of well-known platings (such as Cr electroplating) and HVOF-sprayed cermets (WC–17%Co, WC–10%Co–4%Cr). Alumina coatings displayed highest wear resistance in dry sand–steel wheel tests. Tian et al. [12] studied three body abrasive wear characteristics of plasma sprayed conventional (Metco-130) and two nanostructured Al_2O_3–13wt%TiO_2 coatings (regular and plasma densified powders). Coatings deposited from plasma densified powders were seen to have nearly three times higher abrasive wear resistance than conventional coatings. The coatings from densified nanostructured powders had homogenous and dense coating microstructure. They also possessed the highest hardness, crack growth resistance, scratch resistance, and three body wear resistance.

In addition to uniform mixing of constituents, enhanced performance of nanostructured coatings has also been attributed to the bi-modal nature of the microstructure. As noted e.g. by Lima et al. [13], *bi-modal* coating microstructures form when complete melting of a fraction of agglomerated particles is prevented, and then unmelted and partially melted particles appear as inclusions within the fully melted matrix. As observed by Lima and Marple [14], formation of bi-modal microstructures is also aided by different melting points for the constituents of the powders. For example, while titania in alumina–titania powders has a melting point of 1855 °C, alumina has a melting point of 2072 °C. As first pointed out by Gell et al. [15], critical plasma spray parameter – defined as the specific power input to the plasma gas – controls the percentage of partially melted (PM) regions in nanostructured coatings and thereby has a strong effect on properties of these coatings.

Goberman et al. [16] investigated the effect of CPSP on volume fraction of PM regions and γ-Al_2O_3 phase in conventional and nanostructured coatings. Volume fraction of PM regions in nanostructured coatings was seen to decrease with increasing CPSP. The γ-Al_2O_3 phase was seen to increase with CPSP until a certain stage and decrease then onwards. Nanostructured coatings deposited using argon as the primary plasma gas at lowest CPSP of 300 contained about 50% PM region and about 70% γ-Al_2O_3 phase. On the other hand, conventional coatings were seen to be composed of nearly completely fully melted splat structure. Song et al. [17] studied the effect of plasma spraying conditions such as spraying distance and critical plasma spray parameter (CPSP) on wear performance of nanostructured alumina–titania coatings. It was found that the hardness of the coatings increased with increasing CPSP and decreasing spray distance. Wear resistance was higher at higher CPSPs.

Even though, nitrogen is more widely available and cheaper as compared to argon, nearly all earlier works, analyzed performance of nanostructured alumina–titania coatings deposited using argon as the primary plasma gas. In this work, we study microstructural and wear characteristics of air plasma sprayed Al_2O_3–13wt%TiO_2 coatings deposited using conventional and nanostructured agglomerated powders with nitrogen as the primary plasma gas. For comparison purpose, nanostructured coatings are also obtained using argon as the primary plasma gas. As CPSP controls the volume fraction of unmelted/partially melted regions in coatings, which in turn control the coating properties, nanostructured coatings deposited with nitrogen as well as argon are obtained as a function of CPSP.

2. Experimental details

2.1. Substrate preparation

Coatings in all cases were deposited on AISI 1020 steel substrates of 65 × 55 × 5 mm size. A power saw was used to cut coupons from long plates of 55 mm width and 5 mm thickness. An Alex NH 500 surface grinder was used to grind the top and bottom faces of substrates to remove the oxide layers and generate flat surfaces with a surface roughness of about 0.1 μm. Before plasma spraying, substrates were grit blasted inside a suction type grit blasting cabinet (Sandstorm, Bangalore, India) using alumina grits of mesh size 24 at 100 psi air pressure and 100 mm stand-off distance to increase average surface roughness to around 6 μm for providing better mechanical anchorage between bond coat and substrate. Grit blasting also helps in removing the oxide layer that forms during time gap between surface grinding and grit blasting. Next, the grit blasted substrates were cleaned ultrasonically for about 10 min in iso-propanol bath to remove dust and any other foreign matter present on substrate surfaces. Substrates, prepared using the said procedure were then pre-heated to around 200 °C using the plasma gun, with nitrogen/argon as only plasma gases, before depositing the bond coat. Pre-heating was done to remove grease, oily substances, water vapour, etc., and produce a clean, nascent surface for depositing the bond coat and the pre-heating temperature was monitored using a non contact type pyrometer.

Coatings were deposited using Sulzer Metco 3MB plasma gun mounted on a CNC *X*–*Y* table. Nitrogen/argon and hydrogen were used as primary and secondary plasma gases. Nitrogen was also used as the carrier gas for carrying powders from powder feeder to the gun. Process parameters used for depositing the coatings are shown in Table 1. For all coatings, spraying was done at a spray angle of 90°. Two auxiliary air jets, parallel to the plasma flame, were used to cool the substrates during deposition process and to remove any unmelted and weakly bonded powder particles from coating surfaces. Ni–20%Cr bond coats of about 100–150 μm were deposited prior to depositing alumina–titania ceramic top coats of about 250–350 μm thickness. For further analyses, specimens of 10 × 5 × 5 mm size were cut from coated samples, using a low speed diamond saw. Cross sectional specimens for metallographic examination were prepared from sliced coupons.

2.2. Microstructure characterization

Coatings microstructures were observed using a Zeiss Evo 60 scanning electron microscope (SEM) and a Zeiss Supra 40 field emission scanning electron microscope (FE-SEM). Volume percentages of partially melted/unmelted regions in nanostructured coatings were obtained using the following procedure. At a given CPSP, for each coating, ten SEM/FE-SEM images were taken at fixed magnification of 1000×. Images were printed on A4 sheets and via visual inspection partially melted/unmelted regions were identified and cut out. The initial weight of the sheet and the cumulative weight of partially melted/unmelted regions were used to calculate the area/volume fraction of partially melted/unmelted regions in the images. The volume fraction of the white coloured titania rich regions has also been computed using this procedure. X-ray diffraction studies were carried out using a PANalytical X'pertPRO PW1070 instrument with Cu Kα radiation and operating at 40 kV voltage and 30 mA current, scanning step of 0.0167° and step time of 0.13 s. Hardness measurements were made using a LECO LM 700 microhardness tester with a Vickers indenter at 100 g load and 15 s dwell time. Ten readings were taken for each coating.