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Properties of alumina–titania coatings prepared by laser-assisted air plasma spraying

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Abstract

Studies have shown that microstructures formed by post-laser remelting of air plasma sprayed coatings exhibit densification but also numerous macrocracks due to the rapid cooling and thermal stresses. In laser-assisted air plasma spraying (LAAPS) process, the laser beam interacts simultaneously with the plasma torch in order to increase the temperature of the coating and possibly remelt the coating at the surface. As a result, the microstructure is partially densified and macrocracks, which are generally produced in the post-laser irradiation treatment, may be inhibited. In this paper, LAAPS was performed to improve the hardness and wear resistance of Al_2O_3 –13% TiO_2 coatings. These coatings prepared by air plasma spraying (APS) are widely used to protect components against abrasive wear at low temperatures. The coating microstructure was characterized by SEM and X-ray diffraction. The mechanical characterization was done by hardness measurements, erosive wear tests and abrasion wear tests. Results showed that laser assistance may improve the microstructural and mechanical properties. Phenomena involved in LAAPS of alumina–titania coatings are discussed in this paper.

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Keywords: Laser-assisted air plasma spraying; Alumina–titania; Erosive wear; Abrasive wear

1. Introduction

Alumina–titania coatings produced by air plasma spraying (APS) are widely used to protect components against abrasive wear at low temperatures [1–3]. However, APS ceramic coatings contain connected porosities and the properties of these coatings, such as high temperature corrosion resistance, toughness and abrasive resistance, may thereby be reduced. To improve these properties, various methods have been proposed, such as impregnation with polymers or ceramics, seal sintering with liquid alloys and post-laser irradiation [4–12]. Laser irradiation may be an interesting method for densifying the microstructure of the ceramic coatings. However, in post-spraying configuration, i.e. the laser treats the coating after its deposition, the formation of macrocracks is difficult to be suppressed [4,6–8,10,13,14].

During rapid solidification after the laser irradiation, the contraction of a high material volume induces stresses into the coating. These stresses are finally relaxed by the formation of macrocracks. Laser-assisted air plasma spraying (LAAPS) consists of APS with the simultaneous laser beam irradiation, the APS gun and the laser head being coupled. This method has been studied to deposit ZrO_2 ceramic with Ni-based bond coat [4–7,13,14], Cr_3C_2 cermets [15], Al_2O_3 based ceramic [1,12,16] and TiNi metallic alloy [17]. This process enables control of the coating microstructure in a single process. Molten and semi-molten particles are sprayed from a plasma torch, and the heat of the particles impinging on the substrate may be controlled by laser irradiation depending on the laser parameters. According to recent studies, LAAPS seems to be effective in preventing the formation of macrocracks and in maintaining an appropriately densified microstructure [4–7,13,14]. The remelted thickness in one pass is lower in the case of LAAPS than in the case of laser post-treatment. Consequently, the stresses induced during the layer solidification are lower and the macrocrack appearance may be inhibited. In this study, alumina–titania coatings were prepared by laser-assisted air plasma spraying using a

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continuous 2 kW Nd:YAG laser. Wear resistance properties were evaluated in relation to changes in the coating microstructure. The properties of such coatings were compared with those of as-sprayed APS coatings.

2. Experimental set-up

Fig. 1 shows the experimental set-up of LAAPS. The laser head and the APS gun (SG100, Praxair, Concord, NH, USA) were coupled on a 6-axis robot and move at a transverse speed of 0.6 m s^{-1} . The laser beam was adjusted at the centre of the particle footprint on the substrate surface (particle footprint of around 10-mm diameter). The particle stream was almost normal to the surface sample, while the angle between the laser beam and the plasma spray was set at 45° .

Al_2O_3 –13% TiO_2 powder (Metco 130) was used to deposit 500- μm thick coatings on low carbon steel substrates (length: 76.2 mm, width: 25.4 mm, thickness: 12.7 mm). A Ni–Cr–Al–Y 150- μm -thick bond coat (Praxair Ni-164-2 powder) was applied by APS to improve the adhesion of ceramic coatings. LAAPS was not used during the bond coat deposition. Substrates were grit-blasted before spraying. The spray parameters employed in this work are listed in Table 1. The spraying parameters of the Al_2O_3 –13% TiO_2 coating were chosen based on previous experiments with different torches and spray parameters. All these coatings were abrasion-tested and the coating sprayed with the parameters listed in Table 1 exhibited the highest abrasion wear resistance and was chosen as the benchmark for the current experiment. During spraying, a cooling system (air jets) was applied to reduce the coating temperature, which was monitored by using an optical pyrometer. The maximum coating temperature, while depositing coatings to a thickness of approximately 500 μm , did not exceed 170 $^\circ\text{C}$.

LAAPS was carried out using a 2000 W continuous wave Rofin Sinar Nd:YAG laser of 1.064- μm wavelength and a 1-mm diameter optical fiber. A lens with a 200-mm focal length focussed the laser beam and the laser power was adjusted to 1650 W on the workpiece surface. The laser irradiation density is calcu-

Fig. 1. Experimental set-up for laser-assisted air plasma spraying.

Table 1

Spray parameters used for the APS torch

	Al_2O_3 –13% TiO_2	Ni–Cr–Al–Y
Plasma gun type	SG100	SG100
Nozzle exit internal diameter (mm)	8	8
Powder injector internal diameter (mm)	2	2
Primary gas (Ar) flow (l min^{-1})	50	50
Secondary gas (l min^{-1})	1.6 (H_2)	23.6 (He)
Current (A)	800	700
Voltage (V)	38.8	35.8
Power (kW)	31	25
Carrier gas (Ar) flow (l min^{-1})	7	6.5
Powder feed rate (g min^{-1})	20	30
Spray distance (mm)	63	63

lated by the ratio of laser power applied on the sample to the surface of laser beam irradiating the sample. The changes of laser irradiation density offered during LAAPS was controlled by adjusting the out-of-focus distance of the laser beam irradiating the specimen surface (see Fig. 1), whereas the plasma spray parameters were maintained constant for all samples. The relationship between out-of-focus distance, spot diameter of the laser beam and laser irradiation density is shown in Table 2. Distribution of the laser beam evolved from a top hat profile at the focus point to a gaussian profile at an out-of-focus position [4].

The coatings were vacuum-impregnated with a low viscosity epoxy and then polished to a mirror finish (diamond with grain size of 1 μm). The cross-section microstructures were evaluated via scanning electron microscopy (SEM). Phases were identified by X-ray diffraction (2θ from 20° to 80°) using a Bruker AXS D8-Discover diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1542 \text{ \AA}$, step = 0.05° , step time = 2.5 s, 40 kV, 40 mA). Vickers measurements were performed on coating cross-sections with a load of 3 N in the case of micro-hardness measurements (15 indentations per sample) and 50 N in the case of crack propagation analysis (5 indentations per sample). The slurry-erosion test was carried out using an in-house built set-up. Alumina #100 (20–360 μm) was employed as erodent. The liquid part of the slurry was made with neutral pH deionised water and the erodent concentration was 0.66% by weight. The slurry jet had a constant flow rate of 1 l min^{-1} (6.6 g min^{-1} of alumina particles) and a constant velocity of 20 m s^{-1} . The slurry-erosion resistance was evaluated at an impinging angle of 90° during 5 min for each sample. Three samples were tested for each of the different coating types produced in the study. The volume of the material abraded away during the slurry-erosion test was measured via optical profilometry. The abrasion resistance of the coatings was tested following the ASTM standard G65-00

Table 2

Relationship between out-of-focus distance, spot diameter of the laser beam and laser irradiation density

Out-of-focus distance (mm)	Spot diameter (mm)	Power density (W mm^{-2})
30	6	60
40	8	34
50	10	22
60	12	15
70	14	11

(procedure D-modified) [18], also known as the dry sand/rubber wheel test. In this test, a stationary coated sample (coating surface) was pressed against a rotating rubber-coated wheel (114.3-mm radius — 200 rpm) with a force of 45 N. Silica sand (212–300 μm) was fed (300–400 g min^{-1}) between the coating and rubber wheel until the wheel travelled over the equivalent linear distance of 1436. Prior to being submitted to this test, the surfaces of the coatings were prepared by grinding with diamond wheels to produce a flat surface. The ground coatings exhibited roughness values (R_a) of approximately 0.2 μm . Two samples were tested for each types produced in the study. The volume of the material abraded away during the abrasion test was measured via optical profilometry [19].

3. Results

Fig. 2a shows a typical cross section of an APS alumina–titania coating. The microstructure shows lamellar splat morphology with interlamellar pores, typical of plasma sprayed coatings. Fig. 2b, c and d show the changes of the microstructure obtained by LAAPS at laser power densities of 60, 34 and 22 W mm^{-2} . A well-bonded between the coating and the bond coat was obtained. The density of the microstructure of LAAPS coatings increased with the laser irradiation density increasing from 11 to 60 W mm^{-2} . This is experimentally observed by looking at the microstructures of an APS and a

LAAPS coating (34 W mm^{-2}) in Fig. 3. It is noticed that under cracks and pores were healed by using the laser-assisted deposition under optimum conditions. On the other hand, in the case of out-of-focus distance equal or lower than 30 mm, the laser irradiation density was too high, equal or superior to 60 W mm^{-2} . This leads to an excessive melting thickness, inducing higher stresses and the debonding of the alumina–titania coatings (Fig. 2b). A similar phenomenon has been reported in many studies on laser remelting of APS ceramic coatings [4,6,7]. Due to the high laser density, excessive coating melting takes place under the irradiation area. Then a large contraction of the melted ceramics occurs in an extremely short period of time due to rapid cooling. This causes the appearance of large cracks parallel and normal to the sample surface and, in extreme cases, the debonding of the coating, as shown in Fig. 2b.

On the other hand, when the laser irradiation density decreases from 34 to 11 W mm^{-2} , the coating melting is mostly absent and the coatings are defect-free. At 34 W mm^{-2} , some cracks were still observed as shown in the Fig. 2c, nevertheless their number and size were small compared to coating processed with higher laser density. For a laser irradiation density lower than 34 W mm^{-2} , these macrocracks were not observed by optical microscopy (Fig. 2d). In this case, the contraction of the coating during the solidification was smaller than one obtained at higher laser density as the regions of contraction were limited to the upper layers of the coating. At high

Fig. 2. Cross-sectional SEM micrographs of a) an APS coating and LAAPS coatings at b) 60 W mm^{-2} , c) 34 W mm^{-2} and d) 22 W mm^{-2} .

Fig. 3. Cross-sectional SEM micrographs of a) as APS coating and b) LAAPS coating at 34 W mm^{-2} .

magnification (Fig. 3a), the SEM observation of an APS coating revealed intralamellar microcracks in the splats. With the LAAPS use, the intralamellar microcracks in the splats were inhibited or strongly reduced (Fig. 3b). These microcracks can be inhibited by the heating effect of laser irradiation. This makes the sprayed particles to cool at a slower speed, limiting the thermal stress. Moreover, the laser irradiation can partially remelt the upper layers of the alumina–titania coatings during the process. This may cause the elimination of microcracks by densification of the molten splats.

As shown in Fig. 4, XRD phase analysis revealed that the as-sprayed coating predominantly consists of the metastable $\gamma\text{-Al}_2\text{O}_3$ phase. The thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ phase is present only in small quantity. Early experiments with thermally spray alumina deposits showed that the metastable $\gamma\text{-Al}_2\text{O}_3$ structure was produced rather than $\alpha\text{-Al}_2\text{O}_3$ [20]. This can be explained based on nucleation kinetics; $\gamma\text{-Al}_2\text{O}_3$ is more easily nucleated from the melt than $\alpha\text{-Al}_2\text{O}_3$ because of a lower interfacial energy between crystal and liquid and, at sufficiently rapid cooling rates, the metastable form is retained at room temperature [20]. The same observation can be done on the coatings obtained by LAAPS as shown in the XRD pattern of Fig. 4a carried out with a laser irradiation density of 22 W mm^{-2} . At this laser irradiation density, macrocracks were not observed by optical microscopy (see Fig. 2d). The LAAPS coatings

Fig. 4. XRD patterns of alumina–titania coatings obtained by a) LAAPS with a laser irradiation density of 22 W mm^{-2} , b) APS without laser.

mainly consist of the metastable $\gamma\text{-Al}_2\text{O}_3$ phase. However, as shown by the relative height and number of diffraction peaks, a higher quantity of the stable $\alpha\text{-Al}_2\text{O}_3$ may be formed. This characteristic may be related to a slower solidification rate of the molten phase during spraying. Indeed, the solidification rate is reduced by the laser heating effect increased by the thermal barrier effect of the lower alumina–titania layers. As a matter of fact, the low thermal conductivity of the lower layers can reduce the heat transfer by thermal conduction, and hence decrease the solidification rate. This lower solidification rate can cause the partial equilibrium solidification and the precipitation from the metastable $\gamma\text{-Al}_2\text{O}_3$ to the stable $\alpha\text{-Al}_2\text{O}_3$. The formation of $\alpha\text{-Al}_2\text{O}_3$ during LAAPS is highly desirable because this phase exhibits improved mechanical properties when compared

Fig. 5. Hardness evolution of APS and LAAPS coatings as a function of the laser irradiation density. The hardness of APS coatings and its standard deviation are shown by the dark and the dash lines, respectively.

to γ - Al_2O_3 [21]. This may help the enhancement of the anti-wear performance of the coatings, as shown afterwards.

Fig. 5 shows the hardness in the cross section of APS alumina–titania coating (dark line) and coatings obtained by LAAPS, laser irradiation density evolving from 11 to 34 W mm^{-2} . Hardness values of LAAPS coatings obtained with a laser irradiation higher than 13 W mm^{-2} were higher than that of the APS coating (1093 HV). The maximum value was 1210 HV, corresponding to a hardness increase of 11% compared with the APS coating. As shown in Fig. 5, the hardness increases with the increase of the laser irradiation density. Similar observations have been reported by several authors [4,6]. Fig. 5 indicates a good linear correlation between hardness and laser irradiation density ($r^2=0.77$).

LAAPS improved the erosive wear resistance in the laser irradiation density range of $15\text{--}22 \text{ W mm}^{-2}$, as reported in Fig. 6a. Outside this range, the wear rate was higher than $12.2 \text{ mm}^3 \text{ kg}^{-1}$, the value measured on the APS coatings. The best result was achieved for a laser irradiation density of 18 W mm^{-2} , leading to a wear rate of $10.8 \text{ mm}^3 \text{ kg}^{-1}$ and

erosion resistance improvement of 12%. Fig. 6b shows the abrasive wear resistance evaluated on the coating surface obtained by APS and LAAPS. The volume loss of the APS coatings was about 17.6 mm^3 . This value was reduced by the LAAPS use, up to a minimum value of 11.0 mm^3 with a laser irradiation density of 22 W mm^{-2} . The volume loss during abrasive wear is then reduced by 38%. As shown in Fig. 6b, the volume loss decreased considerably with an increase of the laser irradiation density from 11 to 22 W mm^{-2} . On the other hand, the volume loss increased between 22 to 34 W mm^{-2} , although it was always lower than the one of APS coatings.

4. Discussion

The improvement of hardness obtained using the LAAPS process can be explained by different factors. First, the sample surface temperature was raised by the laser beam irradiation. Moreover, this heating effect was increased by the thermal barrier effect of lower alumina–titania layers. This local heating may result in an increase of the substrate wettability to the sprayed particles, an increase of the bonding areas between the splats and therefore the strengthening of the bonding force between the splats (Fig. 3). This phenomenon was highlighted by Kuwashima et al. [22] in the case of $\text{Cr}_3\text{C}_2\text{--Ni--Cr}$ splats deposited by laser-assisted HVOF and Jiang et al. [23] in the case of Mo splats deposited by LAAPS. This strengthening of the bonding force between the splats can be also observed by the crack propagation measurement produced during Vickers indentation [24]. Fig. 7 shows the formation of these cracks on an APS coating (Fig. 7a) and a LAAPS coating (Fig. 7b); this latter coating was obtained with a laser irradiation density of 18 W mm^{-2} , leading to the higher wear resistance. Five Vickers indentations at a load of 50 N for 15 s were carried out on the cross section of each coating. The indenter is aligned such that one of its diagonals is parallel to the substrate surface. The total length of the major crack ($2c$) parallel to the substrate surface that originated at or near the corners of the Vickers indentation was measured. The mean crack lengths were respectively $745 \mu\text{m}$ (standard deviation of $110 \mu\text{m}$) and $333 \mu\text{m}$ (standard deviation of $33 \mu\text{m}$) for APS and LAAPS coatings, respectively. Based on the indentation load (P) and crack length ($2c$), the crack propagation resistance was calculated according to the relation $P/c^{3/2}$ where P is in Newton and c in meter [25]. The calculated crack propagation resistances were $7.2 \text{ MPa m}^{1/2}$ for the APS coating and $23.6 \text{ MPa m}^{1/2}$ for the LAAPS coating. This strengthening improvement of the bonding force among the splats associated with the partial precipitation of α - Al_2O_3 instead of γ - Al_2O_3 can explain the hardness increase in LAAPS coatings observed in Fig. 5.

The benefits of LAAPS on the erosive and abrasive wear resistance may result from the following factors. Firstly, the intralamellar microcracks in the splats were inhibited by the laser irradiation. This phenomenon decreases the fracture and the removal of the coating splats during the impacts of erosive particles or the scratch effect of the abrasive particles. Secondly, as shown previously, LAAPS resulted in the strengthening improvement of the bonding force between the splats. This

Fig. 6. Relationship between laser irradiation density and a) erosive wear rate and b) abrasive wear rate for LAAPS coatings. The wear rates of APS coatings and their standard deviation are shown by the dark and the dash lines, respectively.

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