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Tribological Properties of Plasma Sprayed Alumina, Alumina–Titania and Alumina–Zirconia Coatings

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Alumina, alumina–titania and alumina–zirconia coatings were formed on stainless steel (AISI 304L) via atmospheric plasma spraying. The surface morphology, elemental composition and phase structure of the as-sprayed coatings were investigated by scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. The influence of feedstock powder nature on the tribological properties of the coatings were measured under dry-sliding conditions. The energy dispersive X-ray spectroscopy measurements indicated that the amount of zirconium and titanium on the surface of the coatings was 0.76 wt.% and 3.9 wt.%, respectively. The friction coefficient and wear rate of the steel substrate was 0.75 and 1.29×10^{-4} mm^3/(N m), respectively. It was demonstrated that the addition of titania or zirconia enhanced the friction coefficient of the composite alumina coatings up to 0.63 and 0.65, which was $\approx 12\%$ and $\approx 16\%$ higher when compared to alumina coating. In addition to the increase of the friction coefficient values, all as-sprayed coatings demonstrated superior wear resistance when compared to the steel substrate.

topics: plasma spraying, alumina–zirconia, alumina–titania coatings, tribological properties

1. Introduction

Alumina coatings have found a pre-eminent place in the engineering industry owing to their varied merits such as high hardness, resistance to wear, insulation characteristics, durability, etc. The alumina coatings are widely used for the protection of the metallic surfaces in order to increase the lifetime of various parts [1–3]. One of the more efficient ways to produce these coatings on metallic surfaces is by plasma spraying. The advantages resulting from applying this process are high flame temperature, increased particle velocity, commendable surface properties, etc. [4–6]. The tribological properties of the coatings are quite dependent on the plasma spraying parameters as well on other parameters, e.g. the additive material used.

Within plasma-spraying parameters the torch power, spraying distance and plasma–gas composition are some of the imperatives [4–7]. Scientists quite often used an argon–nitrogen or argon–hydrogen plasma. It is uncommon, however, to find an air–hydrogen plasma [8–10], although the reduction of the process cost, versatility and efficacy seem to be relatively better, as we observed in our previous work [7].

Al_2O_3 coatings in general have a high wear resistance but their toughness is not as high as the former property's. To make up for this, an inclusion of a material such as zirconia may ensure both high strength and toughness [11]. The friction coefficients and wear rates of as-deposited and mechanically post-treated (dry blasting process and mechanical abrasive polishing) alumina coatings were found to be in the range from 0.6 to 0.8 and the wear rates were $\sim (1–3) \times 10^{-5}$ mm^3/(N m) [12]. In another case, the friction coefficient of alumina varied from 0.61 to 0.75 with different material grades [9]. With a reinforcement of 25 wt.% of zirconia into alumina, it was found that the friction coefficient was 0.45, indicating a tribological condition of superior hardness and toughness as compared with the properties of the individual materials [11]. Another additive such as titania makes a higher improvement of the coating properties possible as it aids in the proliferation of the fracture toughness: the resistance to fracture in the presence of inevitable defects/cracks, as well as the reduction of the porosity due to lower melting temperature of TiO_2 [13, 14]. It was demonstrated that with 3 wt.% of TiO_2 to Al_2O_3, the friction coefficient subject to plasma spraying conditions was found to be between 0.68 and 0.80 and with 13 wt.% of titania it was between about 0.66 and 0.77, respectively [15, 16]. The addition of zirconia and titania into alumina coating improves the toughness, corrosion resistance and could result in better tribological properties [11, 15–17]. It should be noted that the applied plasma spraying technique for the formation of the coatings on thick and large-size metallic parts is quite common [1]. However, it is a challenge to spray high quality coatings on the thin metallic parts due to overheating of the samples.

Our work, therefore, aims to study the structure and tribological properties of air–hydrogen formed plasma sprayed coatings on thin substrates of pure alumina, alumina–zirconia (Al_2O_3–5 wt.% ZrO_2) and alumina–titania (Al_2O_3–3 wt.% TiO_2).

2. Experimental

The substrates for coating samples were prepared from AISI 304L steel and the dimensions were $40 \times 10 \times 1.5$ mm^3. The plasma torch used in this work for the preparation of coatings was designed and produced at the Lithuanian Energy Institute. Total air flow rate of 3.7 g/s was used for plasma jet formation and the additional air flow rate of 0.75 g/s was used for powder transportation into the plasma torch. In order to increase the plasma temperature inside the reactor nozzle and to intensify the heat transfer between the plasma jet and powder particles, the ≈ 0.1 g/s flow rate of hydrogen was injected. Al_2O_3 (ALO-101), Al_2O_3–3 wt.% TiO_2 (ALO-105) and ZrO_2 (ZRO-113/114) powders were used to produce the coatings. The powders were procured from PRAXAIR Surface Technologies, USA. The mixture of alumina and zirconia powders of Al_2O_3–5 wt.% ZrO_2 was prepared. The feedstock powders were dried before the deposition. The aluminium was sprayed as bonding coating in order to increase the adhesion between ceramic coatings and the substrate. The samples were placed in the distance of 70 mm from the plasma torch nozzle and the spraying lasted for 40 s. The plasma torch arc current during the experiments was constant and equal to 200 A, which provided the plasma torch power of 40 kW. Such experimental conditions resulted in the mean plasma temperature at the injection place of the powders equal to 3820 ± 50 K, while the mean temperature of plasma at the exit nozzle of plasma torch was 3600 ± 50 K. More detailed information on the experimental setup and the methodology for plasma parameter calculations is found in [7].

The Hitachi S-3400N scanning electron microscope (SEM) and a portable surface roughness tester Mitutoyo Surftest SJ-210 Series (Version 2.00 with standard ISO 1997) was used for the surface morphology and roughness analysis of the coatings, respectively. The energy dispersive X-ray spectroscopy (EDX) method (Bruker Quad 5040 spectrometer, AXS Microanalysis GmbH) was used for determining the elemental composition of the sprayed coatings. The structure of the coatings was analysed using X-ray diffraction (XRD) (Bruker D8 Discover) with a standard Bragg–Brentano focusing geometry in a 5°–80° range using the CuK$_\alpha$ ($\lambda = 0.154059$ nm) radiation. A ball-on-flat configuration on a tribometer (UMT-2, Bruker, USA) was used for measuring the tribological properties of prepared coatings and initial steel substrate. The sliding velocity of 0.05 m/s for 3000 s (distance of 150 m) with a constant normal load of 1.0 N was used for the tests. All tribological tests were performed in dry-sliding conditions at 21 °C and relative humidity RH = 20 ± 5%. As a counterpart, the 10 mm diameter Al_2O_3 ball (purity 99.5% and grade 10) was employed. The 3D white-light optical interferometer (Counter GT-K0, Bruker, USA), with the use of software Vision64 was applied for the examination of the amount of material removed from the coatings during the tribological tests.

3. Results and discussion

The surface images of the deposited coatings are given in Fig. 1. The surface microstructure of the Al_2O_3 coating demonstrates the presence of lamellar splats with a very low number of the partly melted particles (Fig. 1a, b). It should be noted that the microsize pores and microcracks were observed on the surface of the sprayed coating. The surface morphology of alumina–titania coating was quite similar to that of the Al_2O_3 coating (Fig. 1c, d). The insignificant increase in the amount of fully molten splats and a slight reduction of pores was observed. The surface of the alumina–zirconia coating was rather nonuniform in nature and larger size particles and more micropores were observed (Fig. 1e, f). The insignificant changes in the surface morphology of the coatings are related to the nature of the additive powders. The melting temperature of titania is lower than that of the ZrO_2 powder, thus a more homogeneous coating with smaller size particles and less amount of pores was formed. It was demonstrated that the reduction of the porosity in Al_2O_3 coatings increases the microhardness and density of as-sprayed coatings [5]. Meanwhile, the production of interlaminar cracks would reduce the mechanical properties of the coatings [5, 17].

The surface roughness of the plasma sprayed alumina, alumina–zirconia and alumina–titania coatings was measured. It was estimated that the surface roughness R_a and root-mean-square roughness R_q values were very similar for pure alumina, i.e., 2.82 μm and 2.85 μm, and for alumina–titania, i.e., 3.54 μm and 3.57 μm. In the case of the alumina–zirconia coating, its roughness was the highest, namely $R_a = 3.5$ μm and $R_q = 4.4$ μm. Better melting (due to lower melting temperature) and bonding capabilities exhibited by titania in comparison to zirconia could be the reason for the reduced surface roughness. Further, the melting temperature

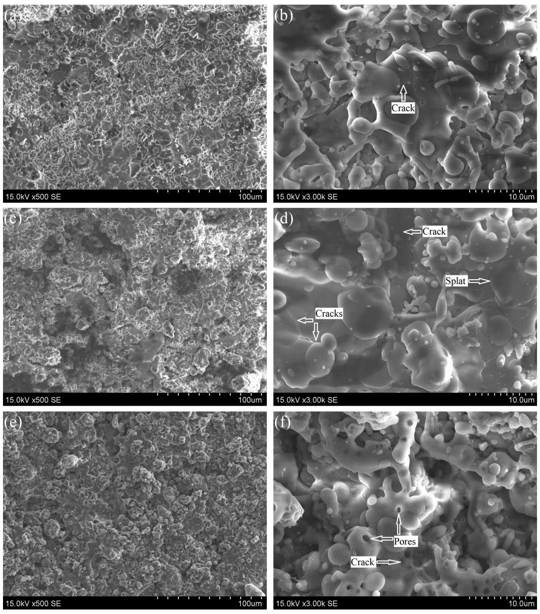

Fig. 1. SEM images of deposited coatings of Al_2O_3 (a, b), Al_2O_3–3 wt.% TiO_2 (c, d) and Al_2O_3–5 wt.% ZrO_2 (e, f).

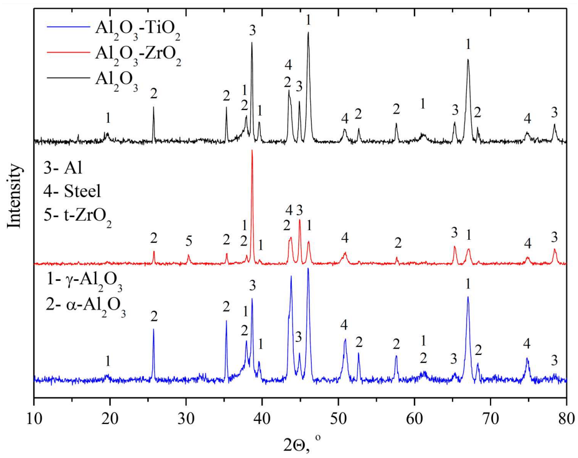

Fig. 2. The XRD patterns of Al_2O_3, Al_2O_3–5 wt.% ZrO_2 and Al_2O_3–3 wt.% TiO_2 coatings.

of Al_2O_3 is about 2050 °C and the melting temperature of ZrO_2 is about 2680 °C [17]. Consequently, the addition of ZrO_2 into the alumina powder resulted in higher surface roughness. The roughness of the polished steel substrate was $R_a \approx 0.25$ μm and $R_q \approx 0.32$ μm.

The EDS measurements were used to investigate the surface composition of the deposited coatings. The Al_2O_3 coating consisted of aluminum ($\approx$ 50.3 wt.%) and oxygen ($\approx$ 48.5 wt.%) with a low amount ($\approx$ 1 at.%) of impurities related to the composition of the powder and carbon. The alumina–titania coating consisted of Al ($\approx$ 46.4 wt.%), O ($\approx$ 48.7 wt.%) and Ti ($\approx$ 3.9 wt.%). The oxygen content was $\approx$ 47.1 wt.%, aluminum — 51.0 wt.%, while zirconium's amount was $\approx$ 0.76 wt.%, when the alumina–zirconia powders mixture was used. It should be noted that all coatings have a low amount of impurities mainly related to the composition of feedstock powders. Goral et al. [18] demonstrated that even in nanostructured Al_2O_3–13TiO_2 coatings, the elemental composition varied considerably: for Al from 43.9 at.% to 49.1 at.%, for O from 46.1 at.% to 50.0 at.% and for Ti from 2.7 at.% to 4.0 at.% [18].

The XRD patterns of pure Al_2O_3 and Al_2O_3 composite coatings are presented in Fig. 2. Both rhombohedral α-Al_2O_3 and cubic γ-Al_2O_3 phases were present in all coatings [5, 14]. The peaks corresponding to various orientation α-Al_2O_3 were found at 25.7°(012), 35.4°(104), 38.0°(110), 43.5°(113), 52.6°(024), 57.7°(116) and 68.4°(300). The signal relating γ-Al_2O_3 phase was obtained at 19.6° (111), 37.8°(311), 39.6°(222), 46.0° (400), 61.1° (511) and 67.0° (440) [5, 19]. The peaks located at $\approx$ 38.6°, 44.9°, 65.3° and 78.4° were attributed to the adhesive aluminum layer. The peaks found at $\approx$ 43.8°, 50.9° and 74.8° are due to the steel substrate. Since the amounts of ZrO_2 and TiO_2 in the feedstock powder were relatively small, the phase composition of composite coatings did not differ much when compared to the pure Al_2O_3 coating. In the Al_2O_3–TiO_2 coating, it was impossible to distinguish peaks corresponding to TiO_2 since their intensities were much lower when compared to the signal of Al_2O_3 peaks. In the case of Al_2O_3–ZrO_2 coatings, only one additional low intensity peak of tetragonal t-ZrO_2 (101) was obtained and it was located at 30.2° [11, 17]. Although the addition of Ti or Zr oxides did not change the positions of main peaks or introduce significant amounts of new phases, it did influence the relative concentrations of α-Al_2O_3 and γ-Al_2O_3. The most common method to evaluate relative α-Al_2O_3 and γ-Al_2O_3 concentrations is described in [19]. Calculations were done using:

$$\gamma\text{-Al}_2\text{O}_3(\%) = \frac{I_{\gamma\text{-Al}_2\text{O}_3(400)} \times 100\%}{I_{\gamma\text{-Al}_2\text{O}_3(400)} + I_{\gamma\text{-Al}_2\text{O}_3(113)}}, \quad (1)$$

where $I_{\gamma-\text{Al}_2\text{O}_3(400)}$ and $I_{\gamma-\text{Al}_2\text{O}_3(113)}$ are the highest intensity peaks corresponding to γ-Al_2O_3 and α-Al_2O_3 phases.

According to the calculations, the pure alumina coating consisted of 66.3% gamma phase and 34.7% alpha phase, alumina–titania coating — 62.1% γ-Al_2O_3 and 37.9% α-Al_2O_3 phase and the composition of alumina–zirconia coatings were 49.5% γ-Al_2O_3 and 50.5% α-Al_2O_3. The XRD results indicated that the gamma phase dominates over α-Al_2O_3 phase in alumina and alumina–titania coatings. It indicates that most of the feedstock particles were fully melted in air–hydrogen plasma and due to rapid solidification of the aluminum oxide splats on the steel substrate, γ-Al_2O_3 phase was formed [5, 7, 14, 17]. Rong et al. [20] observed that the addition of yttria into the alumina coatings reduced the γ-Al_2O_3 phase content,

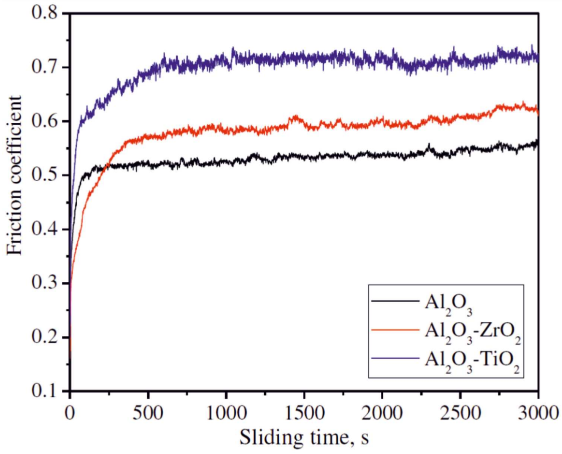

Fig. 3. Friction coefficient curves of as-sprayed coatings.

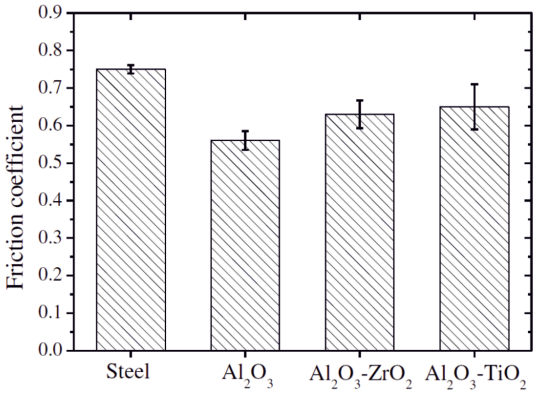

Fig. 4. Friction coefficient values of as-sprayed coatings and steel substrate.

due to the chemical reaction, reduced surface tension and interfacial energy. The addition of the zirconia powder could induce the same processes which lead to the stabilization of α-Al_2O_3 phase and enhance its fraction in the Al_2O_3-ZrO_2 coating. It was demonstrated that the microhardness of α-Al_2O_3 is higher than that of γ-Al_2O_3 phase [17]. Di Girolamo et al. [14] have shown that the addition of 3 wt.% TiO_2 into alumina reduced the microhardness values, despite the enhancement of α-Al_2O_3 phase fraction in the coating.

It could be perceived from Fig. 3 that the curves of the friction run of pure alumina were the least and with alumina–titania — the highest. The running-in state of pure alumina was the shortest, clocking at $\approx$ 250 s, whereas with alumina–titania it was the highest, namely $\approx$ 750 s. The friction coefficient curves for Al_2O_3, Al_2O_3–ZrO_2 and Al_2O_3–TiO_2 coatings ranged from 0.17–0.56, 0.16–0.61 and 0.2–0.71, respectively (Fig. 4). It could clearly be seen that with additives such as zirconia and titania, which in general increase the toughness of the material, the average friction coefficient was also higher. With the spread of the additives being ploughed-out with a reciprocating action of the counter body,

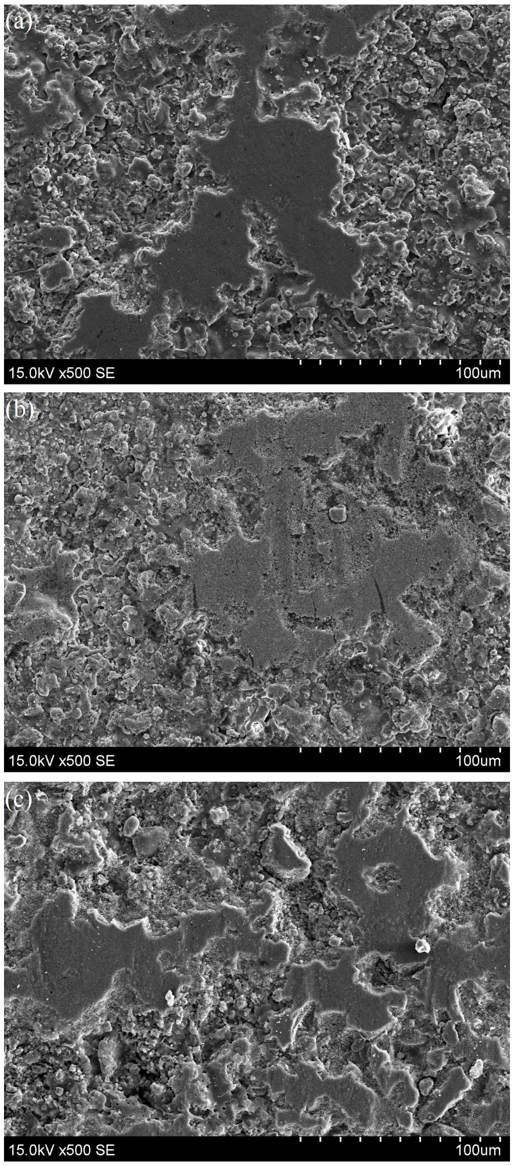

Fig. 5. SEM images of worn surfaces of Al_2O_3 (a), Al_2O_3–3 wt.% TiO_2 (b) and Al_2O_3–5 wt.% ZrO_2 (c) coatings.

the coating in any case was not completely destroyed (a sign of it having the COF close to unity). Thus, the friction runs of the coatings were well within the safety limits, not indicating substantial coating-delamination/destruction as also seen from the SEM images (Fig. 5).

The average friction coefficient measured to be the steady state average taken from 2000–3000 s indicated that pure alumina, alumina–zirconia and alumina–titania had an ascending nature to the tune of 0.56 ± 0.025, 0.63 ± 0.037 and 0.65 ± 0.06, respectively. The COF of the steel substrate was, however, recorded to be the highest at 0.75 ± 0.011. It was obtained that the friction coefficient of Al_2O_3–15 wt.% ZrO_2 composite coating at 3 N load was 0.75. However, the variation of sliding time, sliding speed and applied load has huge influence on the friction coefficient values [21].

The elemental composition was measured at wear scars regions of the as-sprayed coatings. It should be noted that the gold layer was deposited on the as-sprayed coatings in order to obtain better images for 3D white-light optical interferometer. The EDS measurements were performed at 500× magnification at several places and average values were calculated. The alumina oxide coating was composed of aluminum (43.7 wt.%) and oxygen (36.6 wt.%), while the amount of gold was ≈ 18.3 wt.%. The surface composition of alumina–zirconia coating was Al (38.3 wt.%), O (43.2 wt.%), Zr (1.0 wt.%) and Au (16.4 wt.%). Aluminum (32.3 wt.%), oxygen (32.5 wt.%), titanium (2.7 wt.%) and gold (31.6 wt.%) were obtained in the wear scars of alumina–titania coatings. The wear scars of the sprayed coatings are shown in Fig. 5. The surface morphology after tribological tests of all coatings was very similar. The wear scars in the contact area were non-continuous and no additional cracks or delamination of the coatings were observed. It indicates good toughness and high adhesive strength between individual splats in the as-sprayed coatings [22]. The abraded areas on the surface of the coatings were obtained. However, the existence of the smoothened zone indicates that the Al_2O_3 ball interacted only with a limited surface area of the coatings. As a result, only very slight peeling of the highest hills was caused. The 3D interferometery was used to measure the profiles of wear scars. However, the surface roughness values between the non-affected and wear scars areas were in the same range. Thus, the amount of the removed material was very low and it was impossible to properly determine the wear rate of the coatings. The normalized wear rate (NWR) of the all as-sprayed coatings were found to be immeasurable owing to plastic deformations with no defined wear depth. However, for the steel substrate the NWR was determined to be 1.29×10^{-4} mm^3/(N m). This clearly indicates that the wear resistance of the as-sprayed coatings was definitively superior.

4. Conclusions

The Al_2O_3, Al_2O_3–ZrO_2 and Al_2O_3–TiO_2 coatings were deposited by plasma spraying. The elemental composition measurements indicated that the titanium and zirconium concentration in the Al_2O_3–3 wt.% TiO_2 and Al_2O_3–5 wt.% ZrO_2 coatings was 3.9 wt.% and 0.76 wt.%, respectively. The incorporation of ZrO_2 into the Al_2O_3 powders enhanced (≈ 24%) the surface roughness of the coating. The γ-Al_2O_3 phase content in Al_2O_3 coating was almost twice as high as the phase fraction of α-Al_2O_3. Meanwhile, the amount of γ-Al_2O_3 phase fraction in the Al_2O_3–ZrO_2 was reduced and became equal to the α-Al_2O_3 phase. The friction coefficient of the Al_2O_3 coating was the lowest (≈ 0.56) and was ≈ 25% lower when compared to the 304 L steel. The friction coefficients of the as-sprayed Al_2O_3–ZrO_2 and Al_2O_3–TiO_2 coatings were 0.63 and 0.65, respectively. The surface views after the friction tests demonstrated that only a slight surface damage was obtained for as-sprayed coatings. The wear scars were non-continuous and only an insignificant peeling of the hilltops on the surfaces was observed. Meanwhile, the wear rate of AISI 304 L steel was 1.29×10^{-4} mm^3/(N m). The obtained results demonstrated that the as-sprayed coatings exhibited a superior wear resistance in dry sliding conditions and could significantly extend the service life of metallic parts under low load conditions.

Acknowledgments

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