Investigation on the Tribological Behaviors of as-sprayed Al_2O_3 Coatings With the Effects of MoS_2 Lubricant and External Loads

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Research Article

Keywords: Plasma spraying, Al_2O_3 - MoS_2 coating, Mechanical properties, Tribological behaviors

Posted Date: October 23rd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-95757/v1>

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Abstract

The Al_2O_3 - MoS_2 ceramic-based lubricating coating was prepared via introducing MoS_2 dry film lubricant into the pores and cracks of thermal-sprayed Al_2O_3 coating by facial paint spraying method. The microstructure, mechanical properties and tribological behaviors of the as-received Al_2O_3 - MoS_2 coating were thoroughly evaluated. The results illustrated that MoS_2 was mainly concentrated on the shallow surface of the Al_2O_3 coating, and thus more uniform, more compact and smoother Al_2O_3 - MoS_2 coating was obtained. Meanwhile, the mechanical properties of the Al_2O_3 coating did not change significantly after the introduction of MoS_2 . The tribological experiments illustrated that compared with the Al_2O_3 coating, the friction coefficient and specific wear rate of the Al_2O_3 - MoS_2 coating under different loads were greatly reduced due to the generation of the lubricating layer. Especially under the load of 5 N, the friction coefficient was as low as 0.36, and the wear rate ($1.49 \times 10^{-5} \text{ mm}^3 \times (\text{N} \times \text{m})^{-1}$) was almost 17 times lower than that of Al_2O_3 coating ($2.53 \times 10^{-4} \text{ mm}^3 \times (\text{N} \times \text{m})^{-1}$). This research established a new and simple way to prepare ceramic-based self-lubricating coatings by using temperature-sensitive solid lubricants.

1. Introduction

With the continuous development and improvement of science and technology, traditional materials in some emerging industries have been far from satisfying the needs of the requirements. Especially in the field of electronics and aerospace, the materials are required to have the properties of oxidation resistance, high-temperature resistance and wear resistance [1–4]. Although metal and alloy materials possess good toughness, machinability and conductivity, their wear resistance, corrosion resistance and high-temperature resistance are poor [5–7]. Ceramic materials are widely used due to making up for the deficiency of metals and alloys. However, due to the high friction coefficient of ceramic materials, it is difficult to achieve the degree of oil-free lubrication [8–10]. Therefore, the research on the tribological properties of ceramic materials has been paid attention to the scientific field.

Ceramic materials have the advantages of light weight, high strength, super hardness, high-temperature resistance, wear resistance, corrosion resistance and good chemical stability. They are extensively applied in the fields of space mechanism, engine parts, dynamic sealing parts, high-speed cutting tools, which become one of the best options of coating materials for wear-resistant parts [11–14]. However, ceramic materials are characterized by high brittleness, low fracture toughness and high elastic modulus due to the bond properties of ionic bond and covalent bond. Therefore, hard and brittle ceramic materials are difficult to be milled, planed or grinded, which limits the application of engineering structures [15–17]. Driven by this demand, surface engineering technology has been developed and improved by leaps and bounds. Ceramic coating deposited on the metal substrate with good strength and toughness can organically combine the high toughness and shaping of metal materials with the wear resistance, corrosion resistance and heat resistance of the ceramic coating, giving full play to the comprehensive advantages of the two materials [18–21].

As a protective surface coating of mechanical parts, plasma-sprayed Al_2O_3 coating has attracted more and more attention. However, there are essential differences between the covalent/ionic bond of ceramic and the metal bond of metal. Therefore, the plasticity of ceramic material is limited, and its ductility is far lower than that of metal. The instinctive brittleness of ceramic coatings is the main factor causing abrasive wear, which seriously inhibits the widely application of the ceramic coating in frictional parts [15, 18, 22]. Therefore, the study and evolution of self-lubricating ceramic coating with long service life is extremely important to solve the tribological and lubrication problems of mechanical parts under harsh working conditions. At present, most of the studies were reported that the solid lubricants were mixed with the feedstock powders to prepare ceramic-based self-lubricating wear resistant coatings [23–25]. However, some commonly used solid lubricants (such as C, MoS_2 , PTFE) have a low melting point and are apt to oxidize or fail in the high-temperature flame of plasma spraying (up to 15000K) [26, 27]. It is possible to provide the ceramic-based coatings with lubricating properties by depositing lubricants covered with metal Ni, but owing to the bad compatibility between ceramics and metals as well as the introduction of soft lubricating phase. As a result, the prepared coating presents more cracks and pores, resulting in poor mechanical properties (hardness, bonding strength, etc.) [28, 29]. It has been reported that the tribological properties of ceramic coatings under dry friction environment could be improved via introducing lubricating phases into the pores or textures holes of the as-sprayed ceramic coatings. Li et al. [30] have prepared micro-textured holes on 8YSZ coatings by a pulsed laser, and then the modified polytetrafluoroethylene (M-PTFE) emulsion solution was injected to the textured holes by vacuum impregnation. Ultimately, the self-lubricating ceramic-based coating with the low friction coefficient and ultra-high wear resistance was acquired. Besides, Zhao et al. [31] in-situ synthesized Ag in the micro defects of as-sprayed zirconia coating by chemical synthesis process, which also endows the ceramic coating excellent lubrication performance. However, these post-treatment methods were cumbersome, and the high-temperature process also has an impact on the coating structure.

Based on the above analysis, in the present paper, in consideration of the inherent defects such as pores and cracks in the as-sprayed ceramic coating, MoS_2 dry film lubricant was introduced into the micro defects of the Al_2O_3 coating by facial paint spraying method. The Al_2O_3 - MoS_2 coating with lubricating characteristics was obtained without affecting any performances of the original ceramic coating. The friction and wear experiments were conducted to study the tribological behaviors of the Al_2O_3 - MoS_2 coating under different loads. Meanwhile, the wear mechanism of Al_2O_3 - MoS_2 coating was clarified to realize the long-term lubrication of ceramic coating and endowed the ceramic coating with excellent lubrication performance.

2. Experimental

2.1. Preparation of Al_2O_3 coating

The Al_2O_3 coatings were deposited onto 316L stainless steel substrates ($\phi 25\text{mm} \times 7.8\text{ mm}$) by an APS-2000A system (Beijing, China). The Al_2O_3 powders (purity > 99.9 wt%), of which a particle size distribution

of 5–45 μm , were purchased from Sulzer Metco (USA) used as the feedstock in this study. The plasma gun was fixed by a six-axis robot (Switzerland) to realize the uniform coatings by finely dominating the spraying distance or passes. Before depositing Al_2O_3 coatings, the substrates were grit-blasted to roughen their surfaces with a GS-943 sandblasting machine (Beijing, China) followed by ultrasonically clean with acetone to eliminate residual fine silica powders, oils and other impurities. To reduce the residual thermal stress between ceramic coating and metal substrate, a NiCrAlY bonding layer with a thickness of $\sim 100\ \mu\text{m}$ was fabricated before depositing Al_2O_3 coating. The thickness of the Al_2O_3 coating was kept within the limits of $300 \sim 350\ \mu\text{m}$, which was measured using a digital micrometer with a high-resolution of $1\ \mu\text{m}$. The detailed plasma spray parameters used in this study were described in the previous report [32].

2.2. Preparation of Al_2O_3 - MoS_2 coating

Commercially available MoS_2 dry film lubricant was mainly applied to improve the lubrication performance of the Al_2O_3 coating while filling its pores. The detailed spraying process was referred as follows. The suspension of MoS_2 dry film lubricant was sprayed on the surface of the Al_2O_3 coating via taking a manual gun at a pressure of about 0.3 MPa and the tilt angle of about 45° . The distance between the coating and the gun was controlled within $30 \sim 35\ \mu\text{m}$. After the spraying was completed, the Al_2O_3 - MoS_2 coating was placed in atmospheric environment for 30 min to dry naturally. Finally, the samples were obtained by polishing slightly with 8000 mesh sandpaper. The schematic diagram of the preparation of Al_2O_3 - MoS_2 coating was exhibited in Fig. 1.

2.3. Characterization of Al_2O_3 powders and as-received coatings

The morphologies of powders, as-received coatings and their worn surfaces were characterized by a scanning electron microscope (SEM, JSM-5600LV) with an energy dispersive X-ray spectrometer (EDS). An OLYCIA m3 image microscope has been contracted to examine the porosity of as-sprayed coatings. X-ray diffraction (XRD, Cu-K α radiation) analysis was confirmed to measure the crystal structures and phase composition of powders and coatings. The hardness and elastic modulus of the polished coatings were determined by nano-indentation equipment (Switzerland). The applied load was 40 mN with a dwelling time of 10 s. Then, an average of 5 times was reported for each specimen to evaluate mechanical properties. Raman spectroscopy (LabRAM HR Evolution) was used to determine the phase analysis of the wear scars under different frictional conditions. The 3D morphologies, the roughness and section profile of the wear scars were measured by Micro-XAM-3D non-contact surface profiler (ADE Corporation, Massachusetts, USA). The worn surfaces of counterparts were characterized using an optical microscopy.

2.4. Friction and wear test

Friction and wear behaviors of the coatings sliding against Al_2O_3 ceramic balls ($\phi 6$ mm, commercially available) were conducted by a ball-on-disc configuration (CSM, Switzerland) with a linear reciprocating mode at room temperature. The sliding tests were executed in an air environment with a sliding velocity of 10 cm/s, the amplitude of 2.5 mm and a total sliding distance of 300 m. The friction coefficients were continuously recorded by a connected computer. The applied normal loads of 5 N and 10 N were selected. The specific wear rates of coatings were estimated as: $K = V/FL$, where K indicates the wear rate (mm^3/Nm), V indicates the wear volume (mm^3) that determined by a Micro-XAM-3D non-contact surface profiler, F means the external load (N) and L implies the sliding distance (m). It is worth emphasizing that three separate measurements were observed under the same situation, and the average values were cited in this study.

3. Results And Discussion

3.1. Characterization of powders and coatings

The morphology of Al_2O_3 feedstock powder has doubtless considerable performance implications on microstructure, mechanical properties and tribological behaviors of Al_2O_3 coating. Therefore, it is of great importance to analyze the size and shape of Al_2O_3 powder. Figure 1 showed the typical micrographs of Al_2O_3 powders used in this study. Obviously, the Al_2O_3 feedstock powders exhibited an irregular blocky or angular shape resulted from the crushing and fusing process or its intrinsic brittleness. However, the powders were complete with the particle size range was about 5–45 μm . Due to the narrow particle distribution and small particle size, the powders can be full-melted during the spraying process, thus ensuring the compact coating.

It is generally known that the surface topography (such as microscopic appearance and surface roughness) and composition analysis are important parameters to measure the whole properties of the ceramic coating. Figure 3 exhibited the SEM morphologies of the spreading behavior of a single molten particle as well as the top surface and cross-section morphologies of as-sprayed Al_2O_3 coating. As shown in Fig. 3(a), the spreading of the molten particle was discontinuous and many cracks existed in the ceramic splat, which was mainly attributed to the stress in splat during the rapid cooling process. In fact, the sprayed particles were stacked and deposited in successively, resulting in incomplete overlaps along with cracks and pores in the Al_2O_3 coating. This could be explained by SEM morphologies of the top surface and cross-section of Al_2O_3 coating (Fig. 3(b) and (c)). As exhibited in Fig. 3(b), the top surface of the as-sprayed Al_2O_3 coating was very rough with a surface roughness of about 5.49 μm . Meanwhile, many protrusions, pores, semi-molten particles and cracks presented on the surface of the Al_2O_3 coating, while most ceramic particles were completely melted and spread in the form of a pancake. The defects in ceramic coating mainly came from incomplete infiltration between ceramic splats, cracks caused by stress change during rapid cooling and pores formed by airflow during spraying [33, 34]. Besides, from the cross-section of Fig. 3(c) that the coating has compact structure and the porosity was about 11.6%. The pores observed from the cross-section mainly came from two aspects: one is the inherent pores in

the coating, the other is the grain pulling out or brittle spalling caused by mechanical force during the mechanical polishing process. Therefore, it can be inferred that the real porosity of the coating was less than 11.6%. Additionally, as shown in Fig. 3(d), the ceramic coating, the bonding layer and the metal substrate were tightly integrated, thereby greatly increasing the bond strength between ceramic coating and metal substrate, which is conducive to the enhancement of general properties of the ceramic coating.

Figure 4 displayed the XRD patterns of Al_2O_3 powder and as-sprayed Al_2O_3 coating. The distinction of the spectral peaks indicated that phase transition occurred during plasma spraying. The spectrum of Al_2O_3 powder showed that the original powder was composed of stable $\alpha\text{-Al}_2\text{O}_3$ without other visible characteristic peaks. Additionally, it can be found that metastable $\gamma\text{-Al}_2\text{O}_3$ was the principal phase of the Al_2O_3 coating, which is mainly due to the fact that the nucleation energy of $\gamma\text{-Al}_2\text{O}_3$ was lower than that of $\alpha\text{-Al}_2\text{O}_3$. The molten Al_2O_3 droplets impacted on the substrate, $\gamma\text{-Al}_2\text{O}_3$ formed priority in the rapid cooling process with a rate of $\sim 10^5\text{-}10^6$ K/s [35]. However, it should be noted that $\alpha\text{-Al}_2\text{O}_3$ was still contained in the coating after spraying, which mainly came from semi-molten or un-molten ceramic particles.

Figure 5 displayed the polished surface of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating and the corresponding EDS analysis. Compared with Al_2O_3 coating, the defects of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating were reduced and its surface density was significantly improved, which is largely ascribed to the filling of MoS_2 . This can also be confirmed by the EDS mapping that corresponds to the surface of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating. Mo and S elements were exposed on the top surface of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating, indicating the MoS_2 was successfully introducing to the Al_2O_3 coating. From Fig. 6, the MoS_2 diffraction peak was detected in the XRD spectrum of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating, which further confirmed the introduction of MoS_2 . Besides, from the optical photos that spraying MoS_2 lubricant (Fig. 1), a black substance was attached on the surface of Al_2O_3 coating. This also can be explained by the fact that the MoS_2 lubricant was successful introduced into ceramic coating.

To further confirm the introduction of MoS_2 into the Al_2O_3 coating, the enlarged cross-section of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was characterized by SEM, and the corresponding EDS mapping was analyzed, the results are shown in Fig. 7. From the SEM morphology with higher magnification of the cross-section of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating, it can be found that the coating exhibited a typical lamellar structure and high density. Meanwhile, Mo and S elements were identified on the top surface and the interior of the coating, suggesting that MoS_2 was successfully introduced into the coating by facial paint spraying method. However, due to the high density of Al_2O_3 coating and the small impact pressure of MoS_2 dry film lubricant by external spraying, MoS_2 only entered the shallow surface of the coating and did not penetrate into the interior of the coating. Besides, EDS mapping showed that MoS_2 was mainly concentrated on the shallow surface of the coating. In conclusion, this post-treatment method endowed the ceramic coating with special properties. Since friction and wear usually occurred on the surface or interface, it is an effective method to improve the tribological behaviors of ceramic coating.

3.2. Mechanical properties

The mechanical properties of the materials are intimately related to the preparation method, the selected parameters as well as the pre-treatment or post-treatment process, which have a great impact on the tribological behaviors of the coating. It is absolutely interesting and extremely significant to take a further examination of the mechanical properties of the coatings. Hardness is a kind of indentation hardness that reflected the ability of a measuring goal to resist another hard goal. Besides, due to the indentation area was small and the depth was shallow, the values of hardness acquired can further reflect the mechanical strength of the coatings. Therefore, nano-indentation technology was used to test the mechanical properties of the polished surface of the Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating. The typical loading-unloading curve was shown in Fig. 8. During the testing, the hardness and elastic modulus of the coating was directly recorded by the system, and the corresponding elastic failure strain (H/E) and plastic deformation resistance (H^3/E^2) were calculated. At the same time, the elastic recovery rate ($w_{\text{rev.}\%}$) of each coating was calculated according to the loading-unloading curve, and the calculation formula is as follows [36]:

$$W_{\text{rev.}\%} = \frac{d_{\text{max}} - d_{\text{res}}}{d_{\text{max}}} \times 100\%$$

where w_{rec} is the elastic recovery rate, d_{max} is maximum displacement and d_{res} is the residual displacement. The calculation results are shown in Table 1. The hardness of the Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was similar. This can be ascribed to the two reasons: on the one hand, the depth of nano-indentation is between 300–500 nm, indicating that the curve obtained by the nano-indentation test has little correlation with coating defects; on the other hand, if the diamond Berkovich indenter pressed into the defects, the standard curves cannot be obtained.

Table 1
Mechanical properties of Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating

Properties	Al_2O_3 coating	$\text{Al}_2\text{O}_3\text{-MoS}_2$ coating
Hardness (GPa)	11.53 ± 0.37	12.39 ± 0.41
Elastic modulus (GPa)	133.29 ± 1.56	141.26 ± 1.69
Elastic strain energy (H/E)	0.087 ± 0.0023	0.088 ± 0.0017
Plastic Deformation Resistance (H^3/E^2)	0.086 ± 0.0019	0.095 ± 0.0026
Elastic Recovery (%)	50.27 ± 0.57	44.87 ± 0.39

Generally speaking, hardness (H) and elastic modulus (E) have great effects on the tribological behaviors of materials. Generally, high hardness also meant a high elastic modulus (Table 1) [37, 38]. As expected,

the hardness of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was slightly higher than that of Al_2O_3 coating. It is generally true that the wear resistance enhanced with the increase of hardness and elastic modulus. Besides, according to the research of S. Ehtemam-Haghighi et al. [39], H/E and H^3/E^2 determined by the nano-indentation method can be used as more appropriate parameters to predict the friction life of the parts. The elastic failure strain (H/E) indicated the wear resistance of the material, a high of H/E represented better wear resistance. Besides, H^3/E^2 was related to the plastic deformation resistance, a high of H^3/E^2 suggested better plastic deformation resistance. The H/E and H^3/E^2 of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating were slightly higher than those of the Al_2O_3 coating. The phenomenon can be understood by the fact that the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating has higher toughness, which corresponding to the high wear resistance.

3.3 Friction and wear behavior

To elucidate the effects of MoS_2 lubricant on the friction and wear properties of Al_2O_3 coating, the variations and curves of friction coefficient and wear rates of Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating coupled with Al_2O_3 ball under various sliding conditions are shown in Fig. 9. It can be found that the friction coefficient curves exhibited different trends under different sliding conditions. Because of the non-lubricity of Al_2O_3 coating, the friction coefficient was higher and reached to 0.58. Besides, the friction curve reached a relatively stable level after a short fluctuation, which is mainly due to the brittle fracture of Al_2O_3 coating sliding against the hard Al_2O_3 ball in the initial stage. The abrasive debris formed in the friction process existed in the wear scar, hence result in the abrasive wear in the continuous friction process accompanied by the fluctuation of friction coefficient. With the continuous sliding friction, the ceramic debris would be pressed into fine debris and constantly extruded the grinding marks, and finally, the friction coefficient reached a steady level. However, on account of that the introduction of MoS_2 , the friction coefficient of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was lower than that of Al_2O_3 coating. Under the load of 5 N, the friction coefficient was lower (0.36) and the friction curve was relatively stable. This indicated that a continuous lubricating layer was formed. The friction coefficient curve fluctuated in the later stage of the sliding friction due to the generated Al_2O_3 wear debris was not removed in time, and leading to slight abrasive wear. Under the load of 10 N, the friction coefficient was increasing gradually and then reached to a steady level after 150 m tribological test. This may be attributed to the generation of a more continuous and complete lubricating layer at the initial stage. However, with the friction going on, the ceramic debris was produced under the high load, which destroyed the lubricating layer. As a result, the friction coefficient of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating increased gradually.

Under different sliding conditions, the variation tendency of specific wear rate of Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was consistent with that of the average friction coefficient (Fig. 9 (b)). It is found that compared with Al_2O_3 coating, $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating exhibited better wear-resistance ability. Concretely, the specific wear rate of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating under the loads of 5 N and 10 N was $1.49 \times 10^{-5} \text{ mm}^3 \cdot (\text{N} \cdot \text{m})^{-1}$ and $1.92 \times 10^{-5} \text{ mm}^3 \cdot (\text{N} \cdot \text{m})^{-1}$, respectively. In contrast, the specific wear rate of Al_2O_3 coating at 5 N was $2.53 \times 10^{-4} \text{ mm}^3 \cdot (\text{N} \cdot \text{m})^{-1}$, which is almost 17 times higher than that of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating under the

same conditions. The results illustrated that the wear resistance of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was improved with the introduction of MoS_2 lubricant. The development of the MoS_2 lubricating layer effectively reduced the friction coefficient and specific wear rate of ceramic coating, which was also consistent with the analysis results of the mechanical properties of the coatings.

In order to obtain insight into the influence of MoS_2 on the wear mechanism of Al_2O_3 coating, the morphology of worn surfaces was investigated with SEM. Figure 10 exhibited the SEM morphologies and EDS mapping of the wear tracks of Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating under various sliding conditions. As can be seen clearly from Fig. 10(a), there is a great number of fine debris on the worn surface of the Al_2O_3 coating that caused slight abrasive wear. This can be explained by the fact that the interfacial bonding among the deposited splats is relatively weak in the thermal-sprayed ceramic coatings [29, 40]. As a result, the cracks induced by the sliding friction would propagate along the interfaces among the splats, which consequently lead to the brittle micro-peeling. The flake spalling marks or pits on the worn surface further proved that the Al_2O_3 coating undergone the serious splat delamination sliding against the Al_2O_3 ball, which is the important factor for the large wear rate of the Al_2O_3 coating. Contrastively, the worn surface of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating under 5 N was relatively smooth (Fig. 10(b)), which was mainly attributed to the generation of the MoS_2 lubricating layer. Furthermore, uniformly distributed Mo and S elements were detected in the EDS mapping, implying the formation of evenly MoS_2 tribo-film on the worn surface. Besides, it is pointed out that some Mo and S elements were accumulated in the pores on the worn surface, which mainly came from two aspects: one is the original MoS_2 introduced into the pores of the coating; and the other is the MoS_2 lubricating layer squeezed into the pores. As a result, the friction coefficient and wear rate of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was greatly reduced. Under 10 N, the worn surface of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was smooth, while micro-cracks and spalling defects emerged due to the brittle fracture induced by fatigue under high load (Fig. 10(c)). Although the MoS_2 tribo-film was formed, the contact stress under high load was large. This means the cyclic stress on the worn surface of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating under 10 N was larger than that of at 5 N. Therefore, the generation of ceramic abrasive would destroy the lubricating layer, leading to the increase of friction coefficient and wear rate.

The three-dimensional morphologies (denoted as 3D) and cross-section profile are more instinctive parameters to estimate the wear loss of the coatings. Figure 11 displayed the 3D topographies as well as the cross-section profiles of the wear scars of the Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating under different sliding conditions. Evidently, the comparison indicated that the 3D morphologies of the two coatings well corresponded to their respective wear rates. To be specific, the size of the wear tracks of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was small but with obvious parallel grooves or scratches presented on the wear tracks, especially at 10 N (Fig. 11(b) and (c)). This fact should be attributed to the destruction of the MoS_2 lubricating layer by ceramic debris, resulting in the slightly abrasive wear characteristics. Different from the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating, the wear tracks of Al_2O_3 coating was wider and deeper under the same friction condition without obvious scratches or grooves. It is mainly due to the serious peeling off of ceramic coating during the

friction process. Ultimately, a more extreme wear loss was caused by splat delamination. These peeled ceramic debris were pressed into fine wear debris, of which were removed from the wear tracks, and some were filled into the pores of the coating, eventually, leading to a smooth worn surface. This is one of the reasons that the friction coefficient curve could keep stable (Fig. 9 (a)).

For an aim of comparison or verification of the formation of the MoS_2 lubricating layer in the process of reciprocating friction and wear, the experiments concerning the Raman of worn surface of the two kinds of coatings were conducted accordingly. The Raman spectrum of polished surface and worn surface of Al_2O_3 coating as well as the worn surface of Al_2O_3 - MoS_2 coating under different loads were shown in Fig. 12. It is pointed out that the Raman peaks of Al_2O_3 coating were enhanced under the action of repeated tangential frictional force or heat, indicating that the crystallization of Al_2O_3 coating was increased after friction (Fig. 12(b)) [41, 42]. Besides, a strong MoS_2 characteristic peak was detected on the worn surface of the Al_2O_3 - MoS_2 coating (Fig. 12(c) and (d)), suggesting the MoS_2 tribo-film was generated on its worn surface. The formation of MoS_2 tribo-film effectively reduced the level of shear stress, led to lower friction coefficient and less plastic deformation in the subsurface and hence reduced the wear rates. Besides, it was found from Fig. 12(d) that the characteristic peak of MoO_3 presented on the worn surface of Al_2O_3 - MoS_2 coating under 10 N, implying that MoS_2 was oxidized during the wear [43, 44]. According to the tribological applications in the atmospheric environment, the failure of the MoS_2 lubricating layer was partly due to oxidation, which is the reason of many wear mechanisms [43]. Combined with the previous SEM analysis (Fig. 10(c)), the MoS_2 lubricating layer of Al_2O_3 - MoS_2 coating was damaged or peeled off under the load of 10 N, leading to the increase of the friction coefficient and specific wear rate. Except for the damage of ceramic abrasive, part of the reason was the oxidation failure of the MoS_2 lubricating layer. It is reassuring that MoS_2 peak was still detected in the Raman spectrum of Fig. 12(d), indicating that MoS_2 was not completely oxidized. The friction coefficient of Al_2O_3 - MoS_2 coating was lower than that of Al_2O_3 coating that confirmed the existence of the MoS_2 lubricating layer (Fig. 9). It is concluded that the superior friction and wear properties of Al_2O_3 - MoS_2 coating were mostly given to the formation of the MoS_2 lubricating layer.

The tribological properties of the coatings can also be further explored by comparing and analyzing the morphologies of their counterparts. Figure 13 exhibited the optical micrographs of the worn surface of the counterparts coupled with Al_2O_3 coating and Al_2O_3 - MoS_2 coating under the corresponding frictional conditions. It was obvious that the worn morphologies of the counterparts were in good agreement with the wear degree of the coatings (Fig. 11). The worn surface of the Al_2O_3 ball presented an oval shape sliding against the Al_2O_3 coating (Fig. 11(a)), which corresponded to the large wear rate and deeper wear track of the coating. Besides, the worn surface of the counterpart presented scratches and some attachments, it can be inferred that the attachments were the debris formed by the peeling off of the Al_2O_3 coating. However, due to excellent friction-reducing ability, the worn surface of the Al_2O_3 ball was regular circular coupled with Al_2O_3 - MoS_2 coating (Fig. 11(b)). The adhesion substances were found on the Al_2O_3 ball, suggesting that the MoS_2 lubricating layer transferred to counterpart. The existence of the

lubricating layer reduced the direct contact between the friction pair and the coating, thus endowing the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating with a lower friction coefficient and wear rate. However, the lubricating layer was not continuous which is probably due to the damage of ceramic debris produced during the friction. That is the major reason that the friction coefficient of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating was higher than that of pure MoS_2 under the same conditions [45]. Besides, it was found that there is a lot of wear debris around the wear track of counterpart, which means wear debris was removed in the tribological test. The wear morphology of the Al_2O_3 ball under the load of 10 N was similar to that of at 5 N, but the wear area was larger than that of 5 N. However, the slight scratches presented on the counterpart (Fig. 13 (c)), which also corresponded to the wear track morphology of the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating at the load of 10 N. It is also proved that the existence of lubricant not only reduced the wear damage of the coating but also greatly reduced the destruction to the counterpart.

4. Conclusions

Al_2O_3 coating was deposited by atmospheric plasma spraying technology. Then, MoS_2 dry film lubricant was introduced into the micro-defects of Al_2O_3 coating by facial paint spraying method. The $\text{Al}_2\text{O}_3\text{-MoS}_2$ ceramic-based coating was obtained. The microstructure, mechanical properties and tribological properties of Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating were analyzed, respectively. And the following main conclusions were obtained:

- (a) MoS_2 lubricant was successfully introduced into the micro-defects of Al_2O_3 coating by facial paint spraying method, and the compactness of the coating surface was improved. However, due to the limitation of coating properties and the post-treatment process, MoS_2 lubricant only entered the shallow surface of the coating and did not penetrate into the interior of the coating. Besides, the mechanical properties of the Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating are basically similar.
- (b) During the friction process, the Al_2O_3 coating showed seriously brittle micro-peeling and abrasive wear. However, the $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating exhibited better friction-reducing and wear-resistance ability under the same friction conditions. During the sliding process, a MoS_2 lubricating layer was built on the worn surface. The soft phase MoS_2 can reduce the shear stress and relieve the internal stress of the lubricating layer, which significantly improved the tribological properties of the as-sprayed Al_2O_3 coating. However, the oxidation of MoS_2 occurred with the increase of the load, and the friction and wear performances were slightly worse than that of low load.
- (c) The formation of the MoS_2 lubricating layer reduced the friction coefficient and wear rate of the ceramic coating, meanwhile, the wear degree of the counterpart was also alleviated. The lubricating layer formed in the friction process transferred to the counterpart. The existence of the lubricating layer reduced the immediate contact between the friction pair and the coating, thus optimizing the tribological properties.

Declarations

Acknowledgements

This research is financially supported by the National Natural Science Foundation of China (Grant No. 52075409). The authors also appreciate constructive comments of the reviewers.

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Figures

Figure 1

Schematic diagram of the preparation of Al₂O₃-MoS₂ coating.

Figure 2

SEM micrographs of Al₂O₃ feedstock powder.

Figure 3

SEM images of the Al₂O₃ sputter (a), as-sprayed Al₂O₃ coating (b) and its polished cross-section ((c) and (d)).

Figure 4

XRD spectra of Al_2O_3 powder and as-sprayed Al_2O_3 coating.

Figure 5

SEM images of polished Al₂O₃-MoS₂ coating and corresponding element mapping.

Figure 6

XRD spectra of $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating.

Figure 7

SEM images of the cross-section of Al₂O₃-MoS₂ coating and corresponding element mapping.

Figure 8

Load-unload curves of the polished surfaces of Al_2O_3 coating and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating.

Figure 9

The friction coefficient curves (a) and wear rates (b) of Al₂O₃ coating and Al₂O₃-MoS₂ coating under various conditions.

Figure 10

SEM images of the wear tracks and corresponding element mapping of Al₂O₃ coating (a) and Al₂O₃-MoS₂ coating ((b) 5N and (c) 10N).

Figure 11

3D topographies and sectional profiles of the wear tracks of Al₂O₃ coating ((a) and (d)) and Al₂O₃-MoS₂ coating ((b) (e) 5N and (c) (f) 10N) (The locations of the sections of each topography image are marked by blue line).

Figure 12

Raman spectra of the polished Al_2O_3 coating (a) as well as the wear tracks of Al_2O_3 coating (b) and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating ((c) 5N and (d) 10N).

Figure 13

The optical micrographs of the worn surfaces of the friction pairs sliding against Al_2O_3 coating (a) and $\text{Al}_2\text{O}_3\text{-MoS}_2$ coating ((b) 5N and (c) 10N).