Corrosion Behavior and Thermal Conductivity of Plasma Sprayed AlN/Al₂O₃ Coating

Hongwei Yang*1, Weiling Luan*2 and Shan-Tung Tu

School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

Plasma sprayed alumina coating has demonstrated great potential in improving the loading capacity and service life of engineering equipments, while the low thermal conductivity limits its application when high heat exchange efficiency is required. In this paper AlN with different proportion was added into the feedstock powder of Al₂O₃, and a series of AlN/Al₂O₃ composite coatings was deposited on mild steel substrate by plasma spray. Its mechanical properties were studied and thermal conductivity was measured by Transient Plane Source (TPS) method. XRD and EDS analysis revealed that most of the Al₂O₃ substrate by plasma spray. Its mechanical properties were studied and thermal conductivity was measured by Transient Plane Source (TPS) method. XRD and EDS analysis revealed that most of the Al₂O₃ in composite coating underwent phase transformation from α phase to metastable γ phase during plasma spraying, and the mass fraction of AlN was decreased comparing with the chemical composition of feedstock powders. With the increase of AlN proportion, the microhardness reduced from 847 Hv of pure Al₂O₃ coating to 685 Hv when the mass fraction of AlN was 0.47, companying with the bond strength decreased from 27.4 to 21.3 MPa, and the corrosion rate decreased by half. The addition of AlN resulted in the increase of thermal conductivity by several times comparing with the original Al₂O₃ coating. [doi:10.2320/matertrans.47.1649]

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1. Introduction

Plasma spraying is a well-established technique for preparation of a wide variety coatings over the past several decades. As sprayed coatings are intensively applied in automobile, aerospace, textile, biomedical, electrical and optical industries due to their merits on wear resistance, thermal barrier, corrosion resistance, biocompatibility and electrical insulation etc.1–4) Aluminum Oxide (Al₂O₃) is one of the most widely applied coating material which shows great effect on improving both wear and corrosion resistance of metallic components.5) However, its relatively low thermal conductivity (from 0.33 to 3.5 W·m⁻¹K⁻¹ according to different authors) inhibits its application on high thermal conversion cases,6,7) such as heat exchanger, wall of the furnace, heat pipe etc. Aluminum nitride (AIN) is regarded as the attractive ceramic materials applicable to the surface modification because of its excellent properties in chemical stability and thermal conductivity, which is usually (320 W·m⁻¹K⁻¹ for single crystal).8) Furthermore, AIN films obtained by various methods including CVD, PVD, reactive sputtering, reactive plasma spraying etc. have been reported. The preparing parameter, crystallographic structure, morphology, anti-oxidation, mechanical properties, as well as the electrochemical corrosion behavior were intensively studied.9,10) However, the AlN coatings made by plasma spraying were rarely reported till now because of its vulnerability to decomposition in high temperature plasma stream.

In this paper, AlN with different proportions was added into the feedstock powder, and a series of AlN/Al₂O₃ composite coatings were deposited on mild steel substrate by Air Plasma Spray process. The spraying parameters were studied, phase and microstructure characterization were investigated by XRD, EDS and SEM. Properties of tensile bonding strength, microhardness, corrosion behavior as well as thermal conductivity were measured. As a comparison, pure Al₂O₃ coating was prepared and studied at the same condition.

2. Experimental Procedures

2.1 Feedstock powder preparation

Commercial AlN(99%) and α-Al₂O₃(99.9%) powders with the average grain size of 20–40 μm were mixed in mass ratios of 40 : 60(R4) and 60 : 40(R6) separately and then milled for 2 hours. 13 mass% polyvinyl alcohol (PVA) adhesive was added into the mixtures for the agglomeration. The prepared mixture was filtered at 200 mesh to protect against powders clogging and enable the homogeneous grain size. At last, the mixed powders were dried in oven at 100 °C for 1 hour, and the grain size of the reconstituted agglomerates varied from 20 to 50 μm, as shown in Fig. 1.

![SEM morphology of the feed stock composite agglomerates.](image)
2.2 Spraying procedure

Mild steel was chosen as the substrate material owing to its low price and widely application in industry. Before the spraying, substrates were degreased ultrasonically in acetone and grit blasted with 80 mesh alumina abrasive. APS-2000 plasma spraying equipment with PG-1S plasma gun (BAM-TRI, China) was used to deposit coatings with a AlN and α-Al2O3 ratio of 4:6 and 6:4. Corresponding specimens were marked as R4 (4:6) and R6 (6:4) respectively. The spraying parameters were summarized in Table 1. Ni/Al bond coating was used to reduce the mismatch of thermal expansion coefficient between ceramics and steel. Bond coating was neglected to samples prepared for thermal conductivity measurements. As a properties comparison, pure Al2O3 coating was prepared and marked as R0. During spraying, compressed air was applied coming from torch to enhance the cooling of substrate and solidification of molten splats. The thicknesses of as-sprayed coatings were measured by micrometer which were about 450 μm.

2.3 Property measurement

The phase composition of as-sprayed coatings were examined by X-ray diffraction (D/max2550, Rigaku, Japan) operating with Cu Kα (λ = 0.154056 nm). Scanning Electron Microscope (JSM-6360LV, JEOL, Japan) equipped with EDS (FALCON, EDAX, America) was used to observe the morphologies of the coatings.

The microhardness measurements were operated by indenting the polished coating surface at a normal load of 9.8 N for 15 s using Vickers hardness tester (HX-1000, Shanghai, China). For each metallurgical surface, the measurement series comprised of 10 indentations, and the distance between indentations was kept greater than three times the indentation diagonal to avoid the effects of stress field from nearby indentations. The tensile adhesion test (TAT) specified by ASTM C 633-79 was used to measure the tensile bonding strength of the coating. A thin layer of E-7 adhesive (Shanghai, China) was used to coat the substrates. After 4 hours of curing at 120°C in oven, the bonded rods were naturally cooled to room temperature. The tensile bonding strength was measured using a universal material tester at a loading speed of 1 mm/min. For the porosity measurement, polished coatings were boiled in distilled water for 1 hour in order to soak the pores with water fully, and Archimedes’ method was utilized.

The corrosion test was performed in 1M HCl solution separately at 80 and 20°C. Mass-loss method was utilized to study the corrosion rate with the uncoated part being masked by epoxy. The mass of the samples were measured with an analysis balance (BP211D, Sartorius, Germany) in every two and five hours preceded ultrasonic cleaning in distilled water to reduce the influence of ions.

Thermal conductivities of coatings were measured by Hot Disk TPS 2500 system (Hot Disk AB, Sweden) operating with thin film sensor (S/N 7854) at 1 W for 20 s, and when measuring the thermal conductivity of the coated substrate, the same system was operated with slab sensor at 0.5 W for 5 s.

3. Results and Discussion

3.1 Phase composition

The phase structure of R4 and R6 coatings showed that the obtained coatings predominantly consisted of γ-Al2O3 and hexagonal AlN. At the same time, a certain content of α-Al2O3 peaks were shown up (see Fig. 2). According to the previous report, the phase transformation of Al2O3 occurs as follows:

- 1200°C → α-Al2O3
- 750°C → β-Al2O3
- 450°C → γ-Al2O3

It has been generally accepted that during quick solidification after the process of impact, γ-Al2O3 will prioritely nucleate if the initial droplet is completely molten for its energy barrier to nucleations is less than that of α-Al2O3. Particles incompletely molten were regarded as the crystallization of pre-existing nuclei of α-Al2O3. A higher content of γ-Al2O3 observed in the coating suggests a higher proportion of the molten powder particles. The existence of α-Al2O3 can also be partly attributed to the reaction of AlN and oxygen in the plasma stream. As for a verification, pure AlN powder was plasma sprayed into distilled water, and XRD investigation displayed that only hexagonal AlN and α-Al2O3 appearing in the collected powder with no γ-Al2O3 being detected (see Fig. 3). In this study, we also carried out the same experiment with α-Al2O3, and the similar XRD profiles was obtained between the collected powder and the as-sprayed deposit on the mild steel substrate, as shown in Fig. 4.

Based on the calculation from the EDS results of presented area for R4 and R6 coatings, we found that most of AlN was retained in the coating, the mass fraction of AlN in R6 and R4 was about 47% and 26% respectively, which is a little decrease from that of source powder (Table 2). The lost of

Table 1: Spray parameters.

<table>
<thead>
<tr>
<th>Ni/Al</th>
<th>R0, R4, R6</th>
</tr>
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<tbody>
<tr>
<td>Primary gas flow rate, Ar (L-min⁻¹)</td>
<td>37</td>
</tr>
<tr>
<td>Auxiliary gas flow rate, H2 (L-min⁻¹)</td>
<td>3.75</td>
</tr>
<tr>
<td>Carrier gas flow rate, Ar (L-min⁻¹)</td>
<td>3.33</td>
</tr>
<tr>
<td>Input power (kW)</td>
<td>36</td>
</tr>
<tr>
<td>Standoff distance (mm)</td>
<td>100–120</td>
</tr>
<tr>
<td>Coating thickness (μm)</td>
<td>150</td>
</tr>
</tbody>
</table>

Fig. 2 XRD pattern of plasma sprayed AlN/Al2O3.
AlN could be attributed to the oxidization and decomposition of AlN in the high temperature plasma stream.

### 3.2 Microstructure

The surface morphology of R6 coating (Fig. 5) clearly displayed that the composites was well melted with a smooth surface companying with some globular pores and micro-cracks. Furthermore, the columnar structures resulted from the splat-splat interaction were evidently found in the morphologies of fractured cross sections (Figs. 6, 7, 8), and splat boundaries were more evident in R4 and R6 coating. Some other features such as interlamellar pores, cracks and globular pores also displayed in the structure. The porosity ratios of the coatings were listed in Table 3, and it was shown that the porosity ratio of the coatings increased with the increasing AlN proportion. The globular pores was related
with the effect of gas entrapment on the coating, while the interlamellar pores could be attributed to improper adhesion at certain places.13) The relaxation of thermal stress during solidification process induced microcracks in the coating.

### 3.3 Tensile bond strength and microhardness

The measurement results of tensile bonding strength of R0, R4 and R6 were shown in Table 4. Comparing with pure Al2O3, the adding of AlN into Al2O3 resulted in the decrease of tensile bond strength, which can be attributed to the high stress level coming from the low thermal expansion coefficient of AlN/Al2O3. The thermal expansion coefficients of Al2O3 and AlN are $8.6 \times 10^{-6} \, ^\circ\text{C}^{-1}$ and $6.09 \times 10^{-6} \, ^\circ\text{C}^{-1}$, as for mild steel, the value is as high as $12 \times 10^{-6} \, ^\circ\text{C}^{-1}$. During plasma spraying the mismatch of thermal expansion between the coating and the bond coat, coupled with the fast cooling rate of the coating material, gave rise to residual tensile stress in coating at the coating-bond interface, which lowered the bond strength of the coating.14) R0 coating displayed the highest bond strength of 27.4 MPa, while the obtained value from R0 sample was 21.3 MPa.

Table 5 illustrated the average microhardness value of the coatings measured on the polished surface. The microhardness of composite coatings reduced with increased proportion of AlN. R0 exhibited the highest microhardness of 847 Hv, while R6 possessed the lowest value of 685 Hv, which can be attributed to the lower hardness value of AlN compared that of Al2O3. As for the bulk materials, Al2O3 exhibits the Vickers hardness value of 24 GPa, Which is about two times of AlN. Besides, the relatively high porosity ratio of the composite coating may serve as another justification.

### 3.4 Corrosion resistance

The comparisons of corrosion properties of R0, R4 and R6 at 20 and 80°C were illustrated in Figs. 9 and 10. The mass change of Al2O3 coating was larger than all those AlN/Al2O3 coatings, and the improved corrosion resistance of composite coatings was more evident at higher temperature of 80°C.

Here we used the following formula to calculate the average corrosion rate.

$$R = (W - W_i)/(S \times T)$$

Where $R$ is corrosion rate, $W$ and $W_i$ indicate the mass of sample before and after corrosion, $S$ is the surface area of the coating and $T$ is the corrosion time.

At 20°C, R0 exhibited the highest corrosion rate of 0.15 mg cm$^{-2}$ h$^{-1}$, while R6 showed the lowest value which was 2/3 of R0. Based on the examination of bulges, we found that the bulging time of R0 was 60 hours, while bulging time of R4 and R6 improved to 70 and 90 hours respectively. The corrosion rate of the coatings increased considerably when the solution temperature rose up to 80°C (see Fig. 10). The improved composition of AlN endowed decreased corrosion rate. R0 displayed the poorest corrosion resistance of 1.72 mg cm$^{-2}$ h$^{-1}$, while R6 had the best anticorrosion property of 0.8 mg cm$^{-2}$ h$^{-1}$, which was less than 1/2 of R0. The bulging examination displayed that R0 bulged after 12 hours in corrosion solution, while R4 and R6 bulged after 16 and 22 hours.
Table 6 Thermal conductivity of R0, R4 and R6 coating.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thermal conductivity (W·m⁻¹·K⁻¹)</th>
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<tbody>
<tr>
<td>R0</td>
<td>0.268 ± 0.006</td>
</tr>
<tr>
<td>R4</td>
<td>0.583 ± 0.028</td>
</tr>
<tr>
<td>R6</td>
<td>0.835 ± 0.028</td>
</tr>
</tbody>
</table>

Table 7 Thermal conductivity of the substrates coated with R0, R4 and R6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity (W·m⁻¹·K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>22.10 ± 0.08</td>
</tr>
<tr>
<td>R4</td>
<td>24.17 ± 0.06</td>
</tr>
<tr>
<td>R6</td>
<td>26.94 ± 0.05</td>
</tr>
</tbody>
</table>

Interconnected porosity such as open pores, pinholes and microcracks in the coating resulted in the reduction of corrosion resistance, by acting as channels which provide direct path between the corrosive environment and the substrate. The metastable γ-Al₂O₃ can react with the corrosive medium, and the corrosion pit accelerates the penetration of corrosive solution through the coating to the substrate, which finally reduced the corrosion resistance of the coating. The better corrosion resistance of AlN/Al₂O₃ coating compared with that of Al₂O₃ coating was attributed to the α-Al₂O₃ thin film formed on AlN during the plasma spraying. Furthermore, the excellent electrochemical corrosion resistance of AlN also took action. The improved reactivity of HCl solution at elevated temperature accelerated the reaction of HCl with γ-Al₂O₃. More corrosion pit was left over in the coating, meanwhile the penetrability of HCl solution rose with increasing temperature, which justified the reduced corrosion resistance of the coatings at higher temperature.

3.5 Thermal conductivity

Table 6 demonstrated the thermal conductivity of as-sprayed coatings. The addition of AlN composition into Al₂O₃ dramatically enhanced the thermal conductivity of coatings. R0 displayed the lowest value of 0.268 W·m⁻¹·K⁻¹, and R6 showed a large increased result which was more than three times of R0. To evaluate the effect of coating process on the thermal properties of the bulk materials, the thermal conductivities of the as sprayed coating samples were also measured. In these measurements, the thickness of the mild steel substrate was 3.5 mm, and the total thickness of the samples was kept at 3.9 mm. Substrate coated with R0 possessed the lowest thermal conductivity of 22.10 W·m⁻¹·K⁻¹, while substrates with R4 and R6 displayed increased results of 24.17 and 26.94 W·m⁻¹·K⁻¹ respectively, as shown in Table 7.

Plasma-sprayed coatings consist of highly anisotropic layered structure with individual splats oriented parallel to the substrate surface, which lowered the thermal conductivity perpendicular to the coating surface. It is estimated that the thermal conductivity of plasma sprayed coatings can be much higher if the forming degree of individual lamellae would be depressed, which will restrict the interfacial thermal contact caused by pores or secondary phases. Here, crystal lattice wave and heat wave are the main media through which heat is transported in ceramic materials, and dispersion as well as interference of the wave result from the pores and cracks in the deposits can justify the low thermal conductivity of the coatings.

4. Conclusions

In order to satisfy the increased requirement on high thermal conductivity of Al₂O₃ coating, a series of AlN/Al₂O₃ composite coatings were deposited by Air Plasma Spray and its properties were studied. XRD analysis showed that most of AlN was retained in the deposits inspite of being oxidized, and Al₂O₃ underwent phase transformation from α phase to metastable γ phase. SEM observation exhibited the composites with well melted columnar structures. Corrosion resistance and thermal conductivity studies showed that with the increase of AlN composition, better and higher corrosion and thermal conductive ability can be obtained, though the addition of AlN resulted in the lower tensile bond strength and microhardness of the coating.

Acknowledgement

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REFERENCES