

EFFECT OF COATING THICKNESS ON CORROSION PROPERTIES OF PLASMA SPRAYED ALUMINA COATED AZ31B MAGNESIUM ALLOY IN NA CL SOLUTION

* Thirumalaikumarasamy D¹, Shanmugam K² and Balasubramanian V³

¹⁻³ Department of Manufacturing Engineering, Annamalai University, Annamalai Nagar, Tamilnadu-608002, India

ABSTRACT

Alumina coatings with different thicknesses (160, 240, 320 and 400 μm) were deposited on AZ31B magnesium alloy by plasma spraying. The variation in microstructural characteristics and properties of coatings (porosity and hardness) with various thicknesses were investigated. Powders morphology and the microstructure of as-sprayed coatings were characterized by scanning electron microscopy and optical microscopy. The microhardness was measured using a Vickers' indenter. The corrosion behaviour of plasma-sprayed Al_2O_3 coatings in 3.5 wt% NaCl solution at a temperature of 25 °C was evaluated by potentiodynamic polarization test. Experimental results indicated that surface roughness showed no obvious dependence on the coating thickness. However, the porosity of Al_2O_3 coating was increased with increased thickness. The enhanced coating thickness also resulted in decreasing microhardness and reduced corrosion resistance. In this investigation, the Al_2O_3 coating with thickness of 160 μm possesses the lowest porosity level, the highest hardness and superior corrosion resistance.

Keywords: Magnesium, Alumina coating, Atmospheric plasma spraying, Corrosion

1. Introduction

Surface treatments for components made of magnesium alloys are aimed at improving their corrosion resistance and tribological behaviour in order to enhance their life expectancy and service performance in engineering applications [1]. A variety of surface modification procedures have been attempted for the protection of magnesium alloys [2]. Amidst these, Atmospheric plasma spraying (APS) is one of the most preferred techniques as it is capable of producing dense, thick, hard, wear/ corrosion resistant ceramic layers on the surface of magnesium alloys [3].

Thermal sprayed ceramic coatings, such as alumina, zirconia and cordierite, offer cost-effective alternative to modify the component surface properties and are used in a wide range of industrial applications, primarily for wear resistance, thermal barrier and corrosive environment [4]. Some of the applications of alumina are in bearings, valves, pump seals, plungers, engine components, rocket nozzles, shields for guided missiles, vacuum tube envelopes, integrated circuits and railroad components. Alumina coatings are also used for their good wear resistance to solid particles erosion owing to their high hardness and chemical stability, particularly at elevated temperatures [5]. Aluminum oxide coating on metallic substrates has attracted

attention for a broad range of applications including wear resistance, oxidation and hot corrosion resistance, heat and thermal shock resistance and electrical insulation. Al_2O_3 is used extensively for electrical insulation purpose.

Atmospheric plasma spraying (APS), has attracted particular attention for its extremely high temperature, which is essential for dealing with feedstock like oxide and carbide ceramics whose melting temperature is very high. A plasma sprayed coating is built up and the microstructure is formed, when individual, fully or partially molten particles, traveling at a particular velocity, flatten, adhere and solidify on impact with the substrate [6]. This process determines the heterogeneous layered-structure of thermal sprayed coatings consisting of interlamella or volumetric pores, flat plat-like lamellae and weak interface between splats. Due to the high velocity and temperature gradients in the plume, even small changes in the controllable or uncontrollable parameters can result in significant changes in the particle properties and thus in the microstructure of the coatings [7]. Thus, there is a need to put more effort to improve control of the plasma spray process. Statistical process control techniques are being widely used to understand the

*Corresponding Author - E- mail: tkumarasamy412@gmail.com

relationship between the spray parameters and coating properties [8]. Among various spray parameters, the coating thickness attracts less attention though it is generally accepted that the enhanced thickness will increase the amount of residual stress and thus affect the final properties of coating [9]. On the other hand, thicker coatings mean a longer deposition time and higher costs.

From the literature survey [10-12], it was understood that most of the published works have focused on the effects of microcracks and pores on the effective properties of the coatings. However, up to now, there is not much published information on the corrosion performance of thermal sprayed coatings on magnesium alloys with different coating thicknesses. In the current work, Al₂O₃ coatings, as an example of typical thermal sprayed ceramic deposits, were plasma sprayed with different thicknesses onto magnesium substrate and the intrinsic correlation between coating thickness parameter and porosity hardness and corrosion resistance of coating was explored.

2. Experimental Work

Al₂O₃ coatings in thickness of 160, 240, 320 and 400 μm (denoted as A1, A2, A3 and A4 coatings) were deposited on AZ31B magnesium alloy using an APS system 40 kW IGBT based Plasmatron (APSS-II; Ion Arc Technologies, India). A mixture of argon and hydrogen was used as plasma gas. Compressed air was used as substrate cooling gas during plasma spraying. The spraying parameters were given in detail in Table 1. Magnesium alloy coupons with the dimension of 16 \times 15mm were used as substrates. Before spraying, the substrate surface was grit-blasted with corundum, followed by ultrasonic cleaning and degreasing in acetone.

Table 1: Optimized plasma spray parameters used to coat alumina

Parameters	Unit	Values
Power	kW	26
Primary gas flow rate	lpm	35
Stand-off distance	cm	11.5
Powder feed rate	gpm	25
Carrier gas flow rate	lpm	7

Commercially available Al₂O₃ powder with an average particle size of -45+20 μm was used as feedstock. Chemical analysis results revealed the purity to be >99.0 wt.% of Al₂O₃ component in feedstock. Powders morphology and the microstructure of as-sprayed coatings were observed with a scanning electron microscope (SEM; JSM 6400, JEOL, Tokyo,

Japan) and optical microscopy (MIL-7100; MEIJI, Japan). Each coating specimen was mounted in conductive resin, grinded with SiC paper and finally polished with 1 μm diamond slurry. The porosity was analysed as per ASTM B276 standard on the polished cross-section of the coating using optical microscope equipped with image analysing system. Customary metallographic procedures were adopted to polish the cross-section of the coatings. A 200 μm square area was selected on the polished cross-section of the coating, and the image was analysed. The same procedure was repeated at five random locations to find out the average percentage volume of porosity [13].

The surface roughness was measured with 0.5 mm/s traverse speed at 4.8mm length using a surface roughness tester (Model: Mitutoyo SURF TEST 301). The average roughness Ra, defined as the arithmetic mean of departures of the profile from the mean line, was used to quantify the coating surface roughness. The microhardness measurement was made using a Vickers microhardness tester (Model: Shimadzu HMV- 2T). A load of 200 g and a dwell time of 15 s were used to evaluate the hardness. Hardness values were measured at 10 random locations on the polished cross section of a coating.

Electrochemical corrosion tests were carried out using a computer controlled Gill AC potentiostat/frequency response analyser to evaluate the deterioration process of alumina coated specimens in NaCl solutions. A typical three electrode cell, with a saturated Ag/AgCl (saturated with KCl) as reference electrode, a platinum mesh counter electrode and the alumina coated specimen as the working electrode (1cm² exposed area) were used in the tests. The specimens were exposed in the test solution, and a polarization scan was carried out towards more noble values at a rate of 300 mV/min. after allowing a steady state potential to develop. The scan scope was set from -600 mV to +600mV vs. OCP. All electrochemical tests were conducted in triplicate in order to ensure the reproducibility of results. The test specimens were immersed in the solutions for 8 h before potentiodynamic polarization was applied. Photographs of alumina coated specimens were shown in Fig. 1. Potentiodynamic polarization curves of the test specimens were obtained.

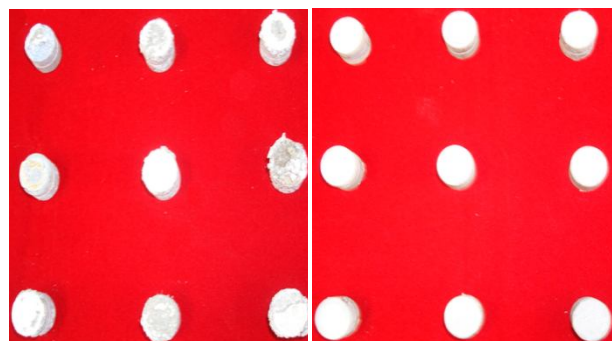
3. Results and Discussions

Evaluation in the SEM was conducted to determine the particle morphology of powders. As shown in Fig. 2, the commercially available Al₂O₃ powders exhibited irregular and angular morphology.

Table 2 Various coating characteristics values as a function of average coating thickness

Samples	Coating thickness (µm)	Porosity (%)	Microhardness (HV _{0.2})
A1	160	4.9	951
A2	240	5.8	927
A3	320	7.3	894
A4	400	8.8	840

The XRD pattern of the alumina powder exhibit α -Al₂O₃ phase as shown in Fig.3. Cross-sectional SEM morphology of as-sprayed coating was shown in Fig. 4. It indicates the typical layered microstructure with inhomogeneously dispersed porosity. Pores indicated by the black area in the microstructure were small with a few exceptions. Besides, no macro cracking was evident. The XRD patterns of the as-sprayed coatings showed that the α -Al₂O₃ and β -Al₂O₃ as presented in Fig. 5 [14].



(a) Before corrosion test (b) After corrosion test

Fig.1 Photographs of alumina coated specimens

Fig. 6 showed the variation of porosity, microhardness and surface roughness as a function of the coating thickness. It can be seen that surface roughness showed no obvious dependence on the coating thickness. With the increase of thickness from 160 to 400 µm the surface roughness of plasma-sprayed Al₂O₃ coating only showed a little variation. However, the porosity of plasma sprayed Al₂O₃ coating ranged from 4.9% to 8.8% and showed an increasing trend with elevated thickness (Table 2).

The enhanced coating thickness also resulted in the decrease of microhardness (Fig. 6). Table 2 showed the values of porosity and microhardness. The porosity and microhardness of A1 coating are 4.9% and 951HV_{0.2}, respectively. While in the case of A4 coating, microhardness decreased at 12% level, and porosity increased at 85% levels. It has been reported that the thicker coating is mechanically weakened with increasing pores and residual stress.

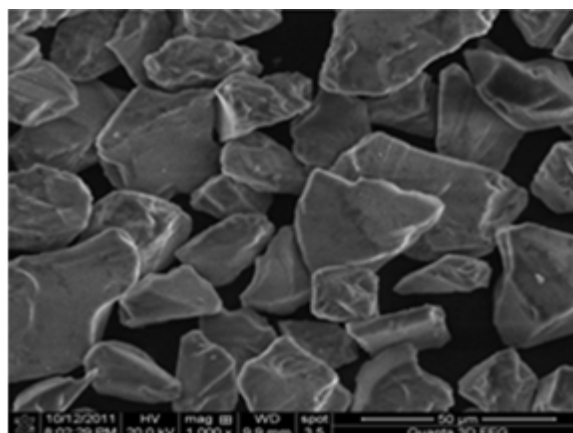


Fig. 2 SEM micrograph of the Al₂O₃ powder

The increase of the porosity will lead to the decrease of coating hardness [15]. Consequently, the higher hardness and lower porosity of plasma-sprayed Al₂O₃ coating can be obtained at lower thickness.

The critical corrosion current density (I_{cp}) as a function of the scanning potential was used to evaluate the coating samples corrosion resistance in 3.5wt% NaCl solution at a temperature of 25°C.

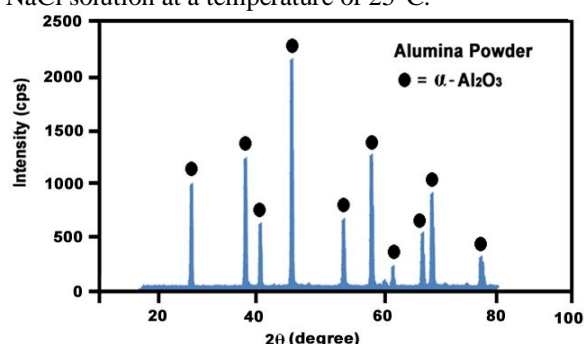


Fig.3 XRD pattern of the alumina powder

The measured results were shown in Fig. 7, for coating thickness as a parameter. As an example, it was given that at the polarization potential of -600mV (vs. Ag/AgCl electrode) the current densities of Al₂O₃ coating samples in thickness of 160, 240, 320 and 400 µm are 45, 164, 202 and 460µA/cm², respectively, while that of the uncoated magnesium sample is at least 25,000 µA/cm². Again, the corrosion resistance of magnesium is greatly improved by the application of Al₂O₃ coatings. From Fig. 7, it also can be drawn that the coating thickness plays an important role on corrosion resistance: the thinner the better.

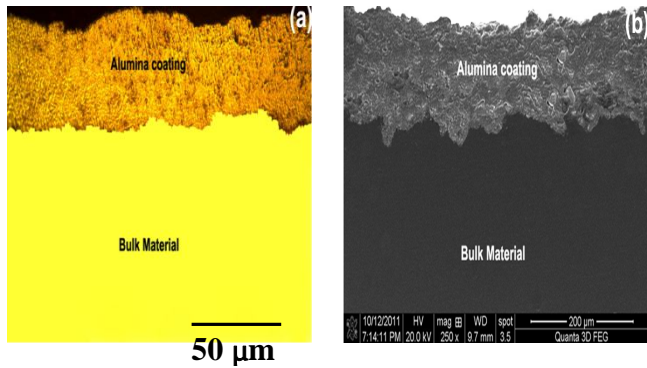


Fig.4 Optical microstructure and SEM image of the coating

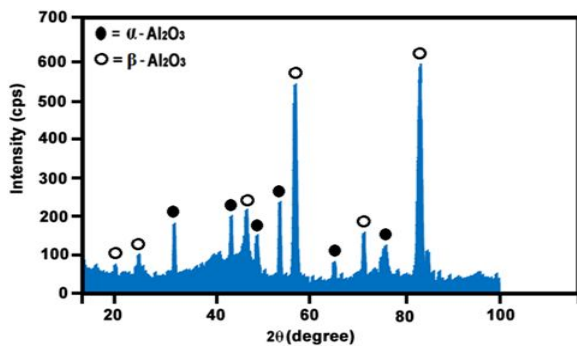


Fig.5 XRD pattern of the alumina coating

It is well known that the coatings obtained by plasma spraying present microstructure with typical types of defects, i.e. pinholes, pores and microcracks [16]. These local defects are formed during or after spraying and act as channels which cause a direct path between the corrosive environment and substrate, leading to rapid local galvanic attacks and corrosion of the base materials. Since I_{cp} arises from the dissolution of magnesium substrate, and can be described approximately as : $I_{cp}=KS$, where K is a constant and S is the total area of microholes in the coating. It is considered that the increase of I_{cp} with increasing thickness is due to the increase in porosity of the plasma sprayed Al_2O_3 coating (Fig. 7).

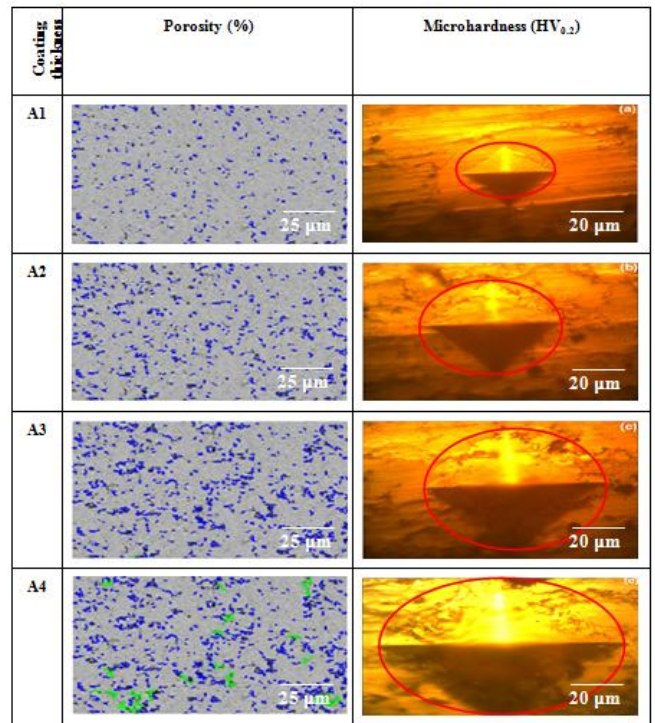


Fig. 5 – Variations of porosity (B) and microhardness (C) as a function of the coating thickness.

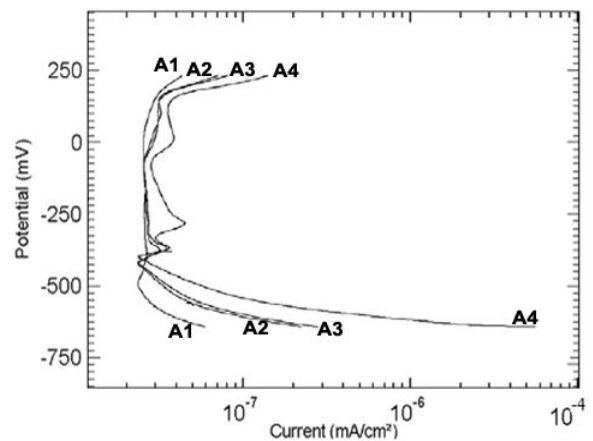


Fig.6 Electrochemical measurement results of samples in 3.5 wt% NaCl solution at a temperature of 25 °C (the thicknesses of A1, A2, A3 and A4 samples are 160, 240, 320 and 400 µm, respectively).

4. Conclusions

The following important conclusions are obtained from this investigation

With the increase of thickness, surface roughness and phase composition of plasma-sprayed Al₂O₃ coatings showed a little change, indicating no obvious dependence of surface roughness and phase composition on thickness parameter.

The porosity of plasma-sprayed Al₂O₃ coating was increased with increasing thickness, which in turn resulted in the decrease of microhardness.

The enhanced thickness lowered the corrosion resistance of plasma-sprayed Al₂O₃ coating.

Acknowledgements

The authors are grateful to the Department of Manufacturing Engineering, Annamalai University, Annamalai Nagar, India, for extending the facilities of Material Testing Laboratory to carry out this investigation. Authors would like to thank Dr.C.S.RAMACHANDRAN, Post Doctoral Research Scholar, State University of NewYork, USA, Mr.R.SELVENDIRAN, Technical Assistant, Manufacturing Engineering for their help with deposition of the coatings.

References

1. Song G L (2005), "Recent progress in corrosion and protection of magnesium alloys", *Adv Eng Mater* Vol. 7: 563–86.
2. Thirumalaikumarasamy D, Shanmugam K, Balasubramanian V (2014), "Developing an empirical relationship to predict corrosion rate of AZ31B magnesium alloy under sodium chloride environment", *Trans Indian Inst Met* Vol.67: 19-32.
3. Psyllaki P P, Jeandin M, Pantelis DI (2001), "Microstructure and wear mechanisms of thermal-sprayed alumina coatings" *Mater Lett* Vol.47: 77–82.
4. Zhijian Yina, Shunyan Taa, Xiaming Zhoua (2011), "Effect of the thickness on properties of Al₂O₃ coatings deposited by plasma spraying, *Materials characterization*", Vol.62: 90 – 93.
5. McPherson R (1989), "A Review of Microstructure and Properties of Plasma Sprayed Ceramic Coatings", *Surf. Coat. Technol.* Vol.173: 39–40.
6. Yugeswaran S, Selvarajan V, Vijay M, Ananthapadmanaban P V, Sreekumar K.P (2009), "Influence of critical plasma spraying parameter (CPSP) on plasma sprayed Alumina–Titania composite coatings", *Ceramics International* Vol.36 :141-149
7. Ozkan Sarikaya(2005), "Effect of some parameters on microstructure and hardness of alumina coatings prepared by the air plasma spraying process", *Surface & Coatings Technology* Vol.190: 388–393.
8. Yongshan Tao, Tianying Xiong , Chao Sun, Lingyan Kong, Xinyu Cui, Tiefan Li, Guang-Ling Song (2010), "Microstructure and corrosion performance of a cold sprayed aluminium coating on AZ91D magnesium alloy", *Corrosion Science*, Vol.52: 3191–3197.
9. Wang L, Fang J C, Zhao Z Y, Zeng H P (2007), "Application of backward propagation network for forecasting hardness and porosity of coatings by plasma spraying", *Surface&Coatings Technology* Vol.201: 5085–5089.
10. Zhang X C , Xu B S, Xuan F Z, Wang H D, Wu Y X, Tu S T(2009), "Statistical analyses of porosity variations in plasma-sprayed Ni-based coatings", *Journal of Alloys and Compounds* Vol. 467: 501–508.
11. Venkataraman R, Dasa G, Singh S R, Pathak L C, Ghosha R N, Venkataraman B, Krishnamurthy R (2007) "Study on influence of porosity, pore size, spatial and opological distribution of pores on micro hardness of as plasma sprayed ceramic coatings", *Materials Science and Engineering A* Vol. 445–446:269–274.
12. Zhang J, Desai V (2005), "Evaluation of thickness, porosity and pore shape of plasma sprayed TBC by electrochemical impedance spectroscopy", *Surface & Coatings Technology* Vol. 190: 98– 109.
13. ASTM B276-05, (2010), "Standard test method for apparent porosity in cemented carbides", *Pennsylvania, American Society for Testing and Material.*
14. Thirumalaikumarasamy D, Shanmugam K, Balasubramanian V (2012), "Influences of atmospheric plasma spraying parameters on the porosity level of alumina coating on AZ31B magnesium alloy using response surface methodology", *Prog Nat.Sci:Mater Int* Vol. 22: 468–479.
15. Costil S, Verdy C, Bolot R, and Coddet C (2007), "On the Role of Spraying Process on Micro structural, Mechanical, and Thermal Response of Alumina Coatings", *J Therm Spray Technol* Vol. 16: 839–843.
16. Celik E, Demirkiran A S, and Avci E (1999), "Effect of grit blasting of substrate on the corrosion behaviour of plasma-sprayed Al₂O₃ coatings", *Surf Coat Technol* Vol. 116:1061–1064.