Titanium Coatings Plasma Sprayed with/without a Shroud

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Titanium Coatings Plasma Sprayed with/without a Shroud

Hong Zhou[1,*], Cheng Peng[2], Zhi Liu[3], Mohammad Al-Rawi[1] and Jai Kanna[1]

[1] Centre for Engineering and Industrial Design, Waikato Institute of Technology, Hamilton, 3240, New Zealand;

[2] Technical Centre, GAC Motor Co. Ltd., Guangzhou 511434, China

[3] Science and Technology ltd., Hamilton 3210, New Zealand.

[*] zhouhong.nz@gmail.com

Abstract. Titanium coatings were deposited by plasma spraying with and without a shroud. The as-sprayed titanium coatings were then microstructurally examined. A comparison in microstructure between titanium coatings with and without the shroud was carried out. Based on the analytical results, it showed that the shroud played a critical role in protecting the titanium particles from oxidation. The presence of the shroud in the plasma spraying brought about a better heating of the particles in the plasma jet due to a mitigation of air entrainment with the shroud, thus a reduction in coating porosity was obtained. An enhanced microstructure in the shrouded titanium coatings were observed compared to the air plasma sprayed counterpart.

1. Introduction

Titanium and its alloys have been extensively used due to their good corrosion resistance and high specific strength. This illustrates their early success in the aerospace and the chemical processing markets [1-2]. Other industries like architecture, medicine, power generation, marine, sports and leisure, and transportation are also seeing an increased application of titanium [1-4]. As we know, a self-sealing oxide layer can be formed on the surface of titanium and its alloys when exposed to oxygen. The dense film provides a strong resistance to various corrosive chemical media [5- 6]. However, the metal is expensive because of the difficulty in processing. Processing for titanium must be carefully carried out in an inert atmosphere.

Thermal spray technologies have been developed throughout the major sectors of engineering industry for component protection and reclamation. These technologies allow combining a thin layer of high value material onto cheap structural materials. Plasma spraying is considered as the most flexible coating technique among them since there are plenty of materials for coating to meet various different requirement [7-8]. But titanium and its alloys are not very suitable for plasma spraying because they become reactive at high temperatures and have a strong affinity with oxygen titanium, nitrogen and hydrogen. Consequently, plasma spraying of titanium coatings in ambient air becomes challenging. Meanwhile, coating porosity may be increased due to oxidation of these metals and mechanical properties of coating would be degraded [9-10]. The spraying process for titanium should be carried out carefully in an inert atmosphere or vacuum to prevent from oxidation. Within the area of thermal spray, controlled atmosphere plasma spray, low pressure plasma spray, or vacuum plasma spray can offer an inert or vacuum atmosphere. They have been the potemtial techniques applied for titanium fabrication since they can form dense coatings with low oxygen content [11-14]. Some

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researchers reported that a good corrosion resistance like that of bulk titanium can be reached if proper spraying parameters were optimized [12, 14]. However, these processes are very expensive, and limited only to the small components.

Shrouded plasma spray can potentially produce titanium coatings at a low oxide containing level and be applicable for large components and when spraying under field conditions. The plasma spray torch is modified by using a gas-shrouded attachment [15-22]. The shroud attachment physically shields the plasma jet. A gas shroud surrounds the plasma jet after exiting the shroud attachment. Kinos et al [23] fabricated both titanium and tantalum coatings by shrouded plasma spraying. In his study, oxidation during plasma spraying was reduced with a shrouding system. Porosity and oxide content were minimized by optimizing the spraying parameters.

To avoid oxidation in plasma-sprayed coatings, feedstock should be melted, impacted onto substrate and solidified without contacting with appreciable amounts of oxygen. In the present study, a solid conical shroud was used to plasma spray titanium powders to reduce the oxide content in the coatings [24, 25]. The low-cost shrouding system can be operated in an open-air situation. Air plasma sprayed titanium coatings without the shroud were also deposited under the same plasma spraying parameters. The difference in microstructure between the two types of titanium coating has been investigated in terms of microstructure.

2. Experimental procedure

2.1. Materials and methods

Titanium powder was commercially available from Xi'an Lilin company, China, which was used to fabricate titanium coating. The powder's particle size has a range of 20 - 90 μm. The morphology of the titanium powders is shown in figure 1, which illustrates that the titanium powders presents irregular shapes.

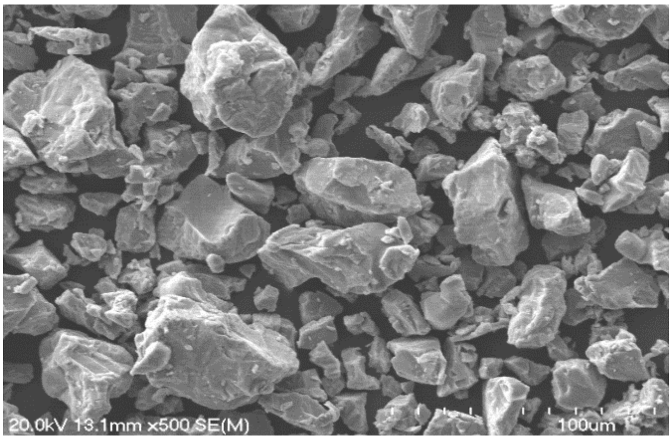

Figure 1. The particle morphology of the titanium powders

A shroud has been used for the fabrication of titanium coatings by plasma spray [24,25]. A plasma gun SG-100 from Praxair surface technologies, USA, with and without the shroud, was taken to plasma spray the titanium powder. The plasma gun on a 6-axis robot moved in a raster pattern to spray the samples. The substrates were some rectangular plates of mild steel with size of 100 ×25 ×3 mm^3. They were degreased, and sand blasted before plasma spraying. Table 1 presents the parameters for plasma spraying with and without the shroud. The spraying parameters were the same except for a shroud gas flow in the plasma spray process with the shroud. For plasma spraying with the shroud, argon was used as an external shrouding gas at the exit, and the flow rate of argon is 300 slpm.

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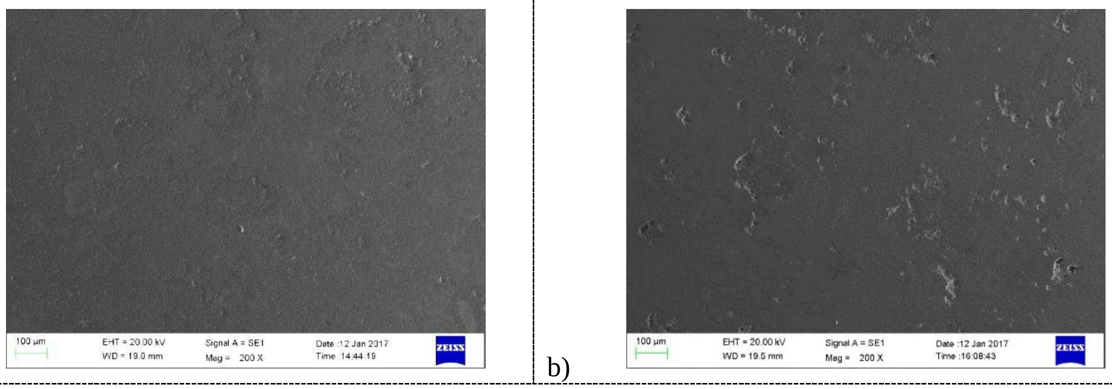
2.2. Characterization
Samples of cross sections of the titanium coatings sprayed with and without the shroud were metallographically prepared for microstructural analysis. Scanning electron microscope (SEM, Hitachi S4700, Japan and Zeiss EVO 18, German) with second electron and back scatter electron was used to observe the microstructure and morphology of the specimens.

Table 1. The parameters for plasma spraying with and without the shroud

Spray parameter	setting
Voltage, V	80
Current, A	800
Argon, Primary gas, slpm	85
Helium, Auxiliary gas, slpm	18
Feed rate of powder, g/min	30
Passes of spray	10
Distance of spray, mm	100
Transverse moving speed, mm/s	500
Nozzle	"Mach II"–forward injection anode nozzle

3. Results and discussion
The titanium coatings with and without the shroud were microstructurally analysed on the polished cross sections, as presented in figure 2. The SEM images reveals that a dense cross section at a low level of porosity in the shrouded titanium coating has been obtained; the pores in the titanium coating with the shroud are small, sparse and scattered. Whereas the titanium coating plasma sprayed without the shroud possesses a lot of porosity; the pores are relatively large and gathered into strips. This demonstrates that the presence of the shroud attachment resulted in a reduction in the porosity of titanium coating. In principle, there is a shielding effect of the shroud and the external shrouding gas, which would significantly mitigate the contact of in-flight molten titanium particles with the ambient air. This enabled the plasma spraying with the shroud to delay the corresponding drop in temperature. On the other hand, the reduction in air entrainment with the shroud could extend hot core of the plasma jet, and then increased the dwell time of particles in the plasma [20]. Thus, a better particle heating during the in-flight time was expected for the plasma spraying with the shroud, which led to more titanium particles fully molten at higher temperatures and a good splat spreading on the substrates. This helped to generate a dense microstructure and decrease the porosity in the shrouded plasma sprayed titanium coatings.



a) b)

Figure 2. SEM images showing the polished cross sections for a) plasma sprayed Ti coating with the shroud and (b) air plasma sprayed Ti coating without the shroud.

The back-scattered electron (BSE) images of the titanium coatings with and without the shroud are presented in figure 3. Backscattered electrons are normally sensitive to the atomic mass of the nuclei from which they scatter. Consequently, heavier element that backscatters more efficiently appears brighter than lighter element in a BSE image. Therefore, the BSE images contain compositional information. In figure 3, the lightest contrast features were identified as the titanium splats, the grey features were titanium oxides and the darkest contrast features were identified as porosity. The images show that there exist some titanium oxides in both the titanium coatings. However, the shrouded titanium coating presents much fewer grey areas than the unshrouded counterpart, which implies less oxidation took place during the shrouded plasma spraying. Most of the titanium oxides and porosity in both titanium coatings are located at the pass boundaries, which can be verified by many large grey or the titanium oxide stringers with some dark spots distributed along the pass boundaries in the images. This suggests that the dominating oxidation in the plasma spraying with and without the shroud might be the post deposition oxidation, which associated with the build-up of titanium coating when the spray gun moved away from the deposited material at each pass. As the plasma gases exited the torch or the shroud, they mixed with air to generate a high temperature, oxygen rich environment, which gave rise to the post oxidation. The shrouded titanium coating presented a much lower level of titanium oxides at the pass boundaries, which is clearly shown in figure 3a. It is postulated that the low oxygen in the plasma jet and a high external shroud gas flow which prevented the surrounding air ingress around the periphery of the shroud that was near the surface, could reduce the extent of titanium oxide formation at the pass boundaries during the shrouded plasma spraying. It was also observed that several thin submicron size (thickness) titanium oxide stringers homogeneously and broadly distributed within both types of titanium coating. The submicron titanium oxide stringers should be associated with splat formation, and more densely distributed in the titanium coatings without the shroud. During the plasma spraying without the shroud, air entrainment into the plasma resulted in molten or semi-molten particles being easily oxidized on the particle surface; the particles then impacted onto the substrate and flattened during splat spreading. Finally, those submicron titanium oxide stringers were formed at splat boundaries. In the shrouded titanium coatings, only a few of submicron titanium oxide stringers were observed. This can be explained that the shroud attachment and external shroud gas were able to create an effective shielding, which allowed the splats to form in a low oxygen environment. Thus, there were less submicron titanium oxides generated during the shrouded plasma spraying.

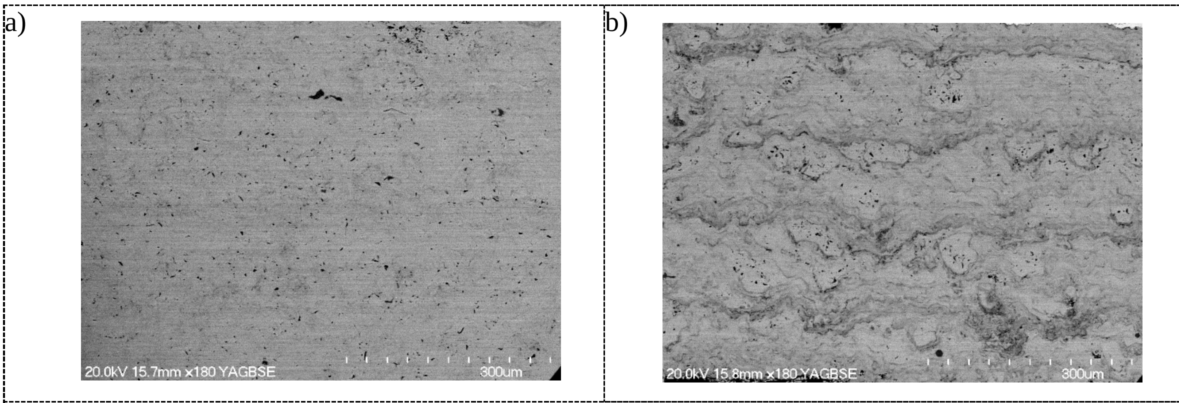


Figure 3. BSE images showing the polished cross sections for a) plasma sprayed Ti coating with the shroud and (b) plasma sprayed Ti coating without the shroud.

Figure 4 shows the SEM images of fractured cross-section for the plasma sprayed titanium coatings with and without the shroud. It is clear to observe that there exists a lamellar structure in the shrouded titanium coating, as shown in figure 4a. This is a typical structure for plasma sprayed coatings. Some voids in the titanium splats and some porosity in between the titanium splats could be observed. The splats with thin thickness were closely contacted within the titanium coating. None of unmelt particle was found in the titanium coating plasma sprayed with the shroud. In the spraying process, a plasma flame was produced by the ionization process of an argon gas, and the feedstock powders were injected into the plasma flame. The plasma could heat the titanium particles to a molten state. The titanium particles then impacted on the substrate, spread and quickly solidified to build up the titanium coating and the lamellar structure was then formed in the coatings. The presence of the shroud led to a better heating of particle during the plasma spraying. A higher temperature resulted in a better molten state of the particles. Therefore, the splats could spread fully when impacting upon the substrate and formed a dense lamellar structure with low porosity. Figure 4b presents the laminas in the shrouded titanium coating with thickness of about 1-2 μm, and the laminas have a nanosized columnar microstructure. The rapid heterogeneous nucleation should take the responsibility for the generation of the columnar nanostructure. The nucleation normally occurs at the cooler boundaries of the flattened droplets at large undercooling. The titanium coating without the shroud showed a different structure as seen in figure 4c. The lamellar structure is not clearly observed, whereas some solid particles with pores inside indicated that the molten state of splat during spraying was not well achieved. Some micrometre-sized particle could also be seen in the figure, which resulted from the droplets from well molten splats at impact or at the end of flattening.

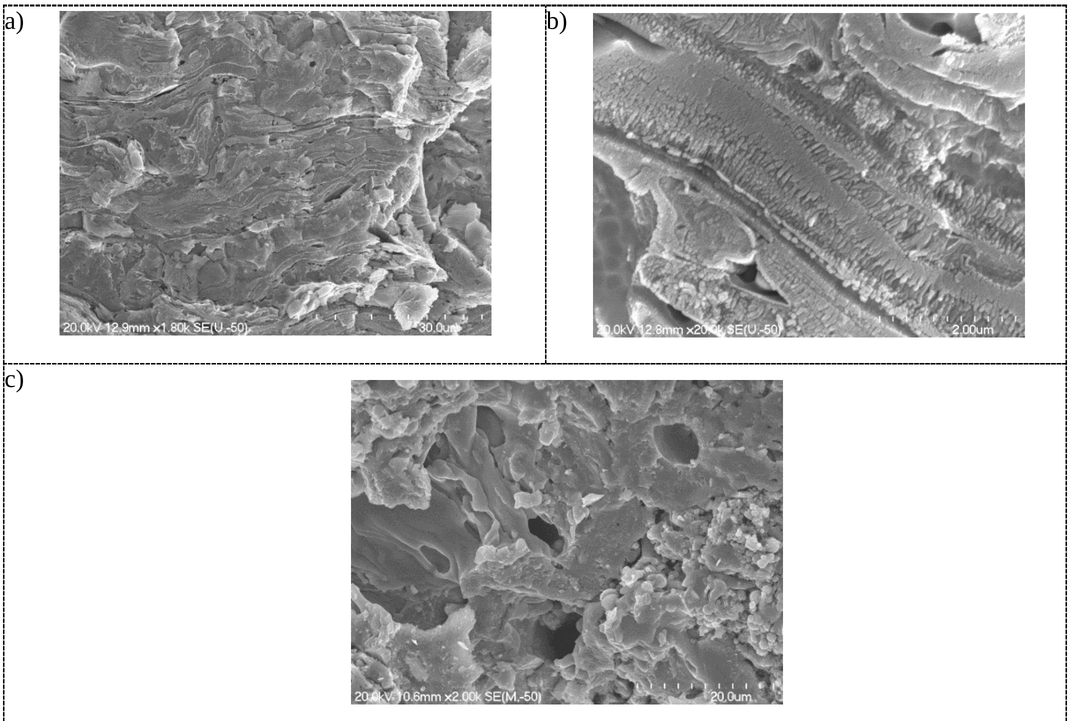


Figure 4. SEM images of fractured cross sections. a & b) plasma sprayed Ti coatings with the shroud at different magnification; c) plasma sprayed Ti coatings without the shroud.

4. Conclusion

This work presents the feasibility of using the shroud to fabricate titanium coatings by plasma spraying, and air plasma sprayed titanium coatings were also deposited under the same conditions. Microstructural characterisation was carried out for both titanium coatings. The physical isolating of the shroud attachment and the external shroud gas resulted in a better heating of in-flight titanium particles and resulted in a reduction in terms of coating porosity. The titanium coating with the shroud had a dense and reinforced microstructure; meanwhile, the titanium coating plasma sprayed without the shroud possessed a high porosity.

References

[1] Leyens C, Peters M. Titanium and titanium alloys. Weinheim (Germany): Wiley-VCH GmbH & Co. KGaA; 2003; 6-18.
[2] Inagaki I, Takechi, T, Shirai Y. Application and features of titanium for aerospace industry. Nippon Steel and Sumitomo Metal Technical Report. 2014; 106: 22-27.
[3] Gangwar K, Ramulu M. Friction stir welding of titanium alloys: A review. Materials and Design. 2018; 141:230-255.
[4] Zhou H, Gabbitas B, et al. Titanium and titanium alloy coatings for corrosion protection, In: Zhou L, Chang H, editors. Proceedings of the 12th World Conference on Titanium, V3; 2011 June 19-24; Beijing, China, Science press; 2012 : 1287-1291.
[5] Kitashima T, Kawamura T. Prediction of oxidation behavior of near-α titanium alloys. Scripta Materialia. 2016; 124: 56-58.
[6] Rajabi A, Mashreghi A, Hasani S. Non-isothermal kinetic analysis of high temperature oxidation of Ti–6Al–4V alloy. J. alloys and Compounds. 2020; 815: 151948.
[7] Fauchais P, Vardelle M, Goutier S. Latest Researches Advances of Plasma Spraying: From Splat to Coating Formation. Journal of Thermal Spray Technology. 2016; 25(8): 1534-1553.
[8] Fauchais P, Montavon G, Bertrand G. From Powders to Thermally Sprayed Coatings. Journal of Thermal Spray Technology. 2010; 19(1-2): 56-80.
[9] Matthews S. Shrouded plasma spray of Ni-20Cr coatings utilizing internal shroud film cooling. Surface and coating technology. 2014; 249:56-74.
[10] Gan J, Berndt C. Review on the Oxidation of Metallic Thermal Sprayed Coatings: A Case Study with Reference to Rare-Earth Permanent Magnetic Coatings. Journal of Thermal Spray Technology. 2013;

22(7):1069–1091.
[11] Kawakita J, Kuroda S, Fukushima T, et al. Dense titanium coatings by modified HVOF spraying. Surf. Coat Technol. 2006; 201:1250–1255.
[12] Steffens H, Erturk E, Busse K. A comparison of low-pressure arc and low-pressure plasma sprayed titanium coatings. J. Vac. Sci. Technol. 1985; A3:2459-2463.
[13] Gan J, Berndt C. Titanium Powder Metallurgy: Science, Technology and Applications. Amsterdam (Netherlands): Elsevier Academic Press; 2015. Chapter 23, Thermal spray forming of titanium and its alloys; p. 425-446.
[14] Lugscheider E, Lu P, Haeuser B, et al. Optimized vacuum plasma-sprayed titanium coatings. Surf. Coat. Technol. 1987; 32:215-226.
[15] Liu T, Zheng L, Zhang H. Effect of Solid Shield on Coating Properties in Atmospheric Plasma Spray Process. Journal of Thermal Spray Technology. 2016; 25(8):1502-1515.
[16] Mukherjee B, Kumar R, Islam A, et al. Evaluation of strength-ductility combination by in-situ tensile testing of graphene nano platelets reinforced shroud plasma sprayed Nickel-Aluminium coating. J. alloys and Compounds. 2018; 765: 1082-1089.
[17] Kim J, Kang K, Yoon S.et al. Enhancement of metallic glass properties of Cu-based BMG coating by shroud plasma spraying. Surface and Coating Technology. 2011; 205(8-9):3020-3026.
[18] Chen Q, Peng X, Yang G, et al. Characterization of Plasma Jet in Plasma Spray-Physical Vapor Deposition of YSZ Using a <80 kW Shrouded Torch Based on Optical Emission Spectroscopy. J. Thermal Spray Technology. 2015; 24: 1038-1045.
[19] Gawne D, Zhang T, Liu B. Computational analysis of the influence of a substrate, solid shield and gas shroud on the flow field of a plasma jet. Surface and Coating Technology. 2002; 153: 138-147.
[20] Chen H, Pfender E, Heberlein J. Improvement of plasma spraying efficiency and coating quality. Plasma Chemestry and Plasma Processing. 1997; 17: 93-105.
[21] Li J, Li C, Yang G, Li, C. Effect of vapor deposition in shrouded plasma spraying on morphology and wettability of the metallic Ni20Cr coating surface. Journal of Alloys and Compounds. 2018; 735:430-440.
[22] Vetrivendan E, Jayaraj J, Ningshen S, et al. Argon Shrouded Plasma Spraying of Tantalum over Titanium for Corrosion Protection in Fluorinated Nitric Acid Media. Journal of Thermal Spray Technology. 2018; 27(3):512-523.
[23] Kinos T, Chen S, Siitonen P, et al. Densification of plasma-sprayed titanium and tantalum coatings. J. Thermal Spray Technol. 1996; 5:439-444.
[24] Zhou H, Liu Z, Luo L. Microstructure and phase composition of titanium coatings plasma sprayed with a shroud, in Proceedings of the MATEC Web of Conferences, Qingdao, China, 25-27 August 2017.
[25] Zhou H, Liu Z, Luo L. Microstructural characterization of shrouded plasma sprayed titanium coatings. J. Manuf. Mater. Process. 2019; 3(4): jmmp3010004.