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## $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$ nanocomposite coating deposition on Titanium by Air Plasma Spraying

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### Abstract

Titanium has low wear and corrosion resistance due to its low hardness. The corrosion and wear resistance of titanium are improved using various surface modification methods such as coating with sufficient materials.  $\text{Al}_2\text{O}_3$  based microparticles' coatings have interesting mechanical properties. Mechanical properties of alumina can be improved with several techniques such as applications of alumina nanoparticles instead of microparticles and also adding ceramics such as  $\text{TiB}_2$ . Air Plasma Spraying is a physical method for coating, which is one of the most commercial and economical coating techniques. The aim of this work is to coat  $\text{TiB}_2$ - $\text{Al}_2\text{O}_3$  Nanocomposite on commercially pure titanium by Air Plasma Spraying method. Spraying process was operated at two steps. In this research, the effect of current on melting of  $\text{TiB}_2$ - $\text{Al}_2\text{O}_3$  Nanocomposite and microstructure of coatings was investigated. Surface characteristics were evaluated using Field Emission Scanning Electron Microscopy (FESEM). The microstructure of the coatings consisted of two distinct regions and was completely melted and quenched as splats, and the other one was incompletely melted.

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**Keywords:** Titanium;  $\text{Al}_2\text{O}_3$ - $\text{TiB}_2$  Nanocomposite; Coating; Air Plasma Spraying

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## Introduction

Titanium and titanium alloys are used in many industries containing aerospace, marine, biomedical, etc. They have special properties including high strength, corrosion resistance and low density [1, 2], but these properties are not suitable for some applications and therefore they are coated for special applications. Ceramics are the most commonly applied materials as coating materials. An alumina ceramic has characteristics of high hardness and high corrosion resistance [3,4]. Aluminium oxide ( $\text{Al}_2\text{O}_3$ ) or alumina possess chemical and thermal stability, relatively good strength, thermal and electrical insulation characteristics combined with availability in abundance, therefore it is attractive for engineering applications. Alumina has several allotropic forms [5,6], but only the usual type or  $\alpha$ -alumina is considered here. Alumina has melting temperature of about 2040 °C [7]. There has been great interest in producing composite materials using  $\text{TiB}_2$  as a reinforcing phase; since the excellent mechanical properties of  $\text{TiB}_2$  enhance the overall performance of the composites [8,9].  $\text{Al}_2\text{O}_3$  has good mechanical properties, but using alumina nanoparticles [10-11] instead of microparticles and also adding ceramics such as  $\text{TiB}_2$  improves its properties [12-13].

There are various surface modification technologies to improve corrosion and wear resistance of titanium and its alloys. These methods have three categories: mechanical, physical and chemical methods, which are classified according to the formation mechanism of the layer on the material surface. Thermal spraying is a physical method and a process in which materials are thermally melted into liquid droplets and impacted energetically to the surface on which the separated particles stick and condense. Thermal spraying methods contain flame spraying, plasma spraying, arc spraying, detonation gun spraying, laser spraying and high velocity oxy-fuel (HVOF) spraying, which are widely used in the industry. Plasma spraying is usually used to form ceramic coatings. Plasma spraying contains two methods: a) Air Plasma Spraying (APS) and b) Vacuum Plasma Spraying (VPS) [1, 14]. Air plasma spraying is an important industrial method for preparing protective coatings to improve component performance [15]. H. C. Cheng *et al.* coated  $\text{Al}_2\text{O}_3/\text{TiB}_2$  composite by APS [17] and axial plasma spray [12].

In this study, 70%  $\text{Al}_2\text{O}_3$ -30%  $\text{TiB}_2$  nanocomposite were deposited on commercially pure titanium substrate by Air Plasma Spraying. The effect of current parameter on amount of melted and microstructure of coating was studied.

## Materials and Methods

Commercially pure titanium grade II with 10mm length, 10mm width and 4mm thickness was used as the coating substrate. The substrate composition is given in Table 1. The average particle diameter of  $\alpha$ - $\text{Al}_2\text{O}_3$  (MERCK) and  $\text{TiB}_2$  (Sigma Aldrich) powders were around 80nm and 10 $\mu\text{m}$ , respectively. In order to prepare the coating composition,  $\alpha$ - $\text{Al}_2\text{O}_3$  (70 wt%) and  $\text{TiB}_2$  (30 wt%) powders were mixed. The mixed  $\alpha$ - $\text{Al}_2\text{O}_3/\text{TiB}_2$  powder composition was granulated before spraying.

Table 1: Chemical analysis of titanium grade II

| Element | Ti   | Ni    | Cu    | Fe    | W     | Pb    | Mo    |
|---------|------|-------|-------|-------|-------|-------|-------|
| Percent | 99.8 | 0.067 | 0.047 | 0.648 | 0.025 | 0.007 | 0.021 |

The substrate surface was cleaned by washing and sonicating in acetone and ethanol. The cleaned substrate was sandblasted and heated at 250 °C. The composition was coated on the substrate in two steps, namely step A and step B, with air plasma spray method. The plasma spray parameters for each step are presented in Table 2.

Vickers microhardness amounts measured on the cross-section of sprayed coatings in accordance with ASTM E384-16. Surface roughness ( $R_a$ ) of coatings measured with TR 100 Surface Roughness tester.

Table 2: Spraying process parameters of two coatings

| Parameters                 | Step A    | Step B  |
|----------------------------|-----------|---------|
| Current                    | 500 A     | 600 A   |
| Ar (Pressure)              | 100 psi   | 100 psi |
| H <sub>2</sub> (Pressure)  | 50 psi*   | 50 psi  |
| Ar(Flow rate)              | 75 scfh** | 75 scfh |
| H <sub>2</sub> (Flow rate) | 15 scfh   | 20 scfh |
| Spray Distance             | 8 cm      | 8 cm    |

\* psi = pound per square inch

\*\* scfh = standard cubic feet per hour

## Results and Discussion

Figures 1 and 2 show the FESEM of the plasma sprayed 70% Al<sub>2</sub>O<sub>3</sub>-30% TiB<sub>2</sub> coating step A and step B, prepared under conditions given in Table 2. FESEM images of coating A show that the majority of particles are spherical and non-melted. It can be seen from Fig.1 that the coating A is highly porous, which results in low level of hardness of the coating. In addition, such a large number of non-melted particles decreases the coating adhesion to the substrate. The interface of Al<sub>2</sub>O<sub>3</sub>-TiB<sub>2</sub> is Ti and O atoms. There is a strong covalent bonding between atoms in the interface of Al<sub>2</sub>O<sub>3</sub>-TiB<sub>2</sub> [16], which may be one of the reasons for the non-melted areas.

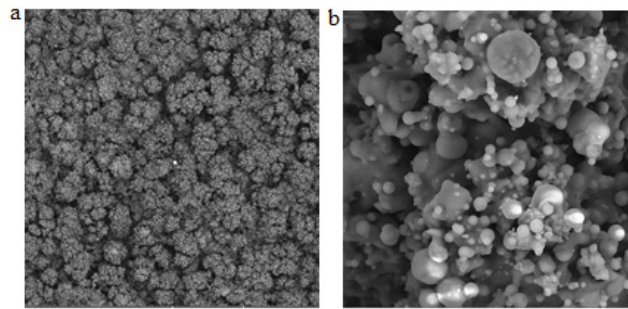


Figure 1. FESEM images of sprayed coating A, on the scale of a) 500 μm; b) 10 μm

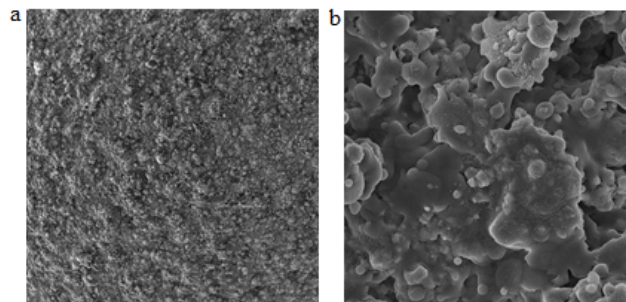


Figure 2. FESEM images of sprayed coating B, on the scale of a) 500 μm; b) 10 μm

In order to improve the hardness and the adhesion of the coating, it should be heated to higher temperatures. Therefore, in the step B, the current was increased to 600 A to achieve higher temperature than the one in step A. The FESEM image of coating B (Fig.2) shows completely melted and incompletely melted areas that the TiB<sub>2</sub> microparticles are remained non-melted in the matrix of coatings, which originate from high melting point of TiB<sub>2</sub> (about 2980 °C [17]). Molten alumina plays the role of carrier of titanium diboride particles. In addition, increasing

the hydrogen gas flow rate in step B, compared to step A, leads to more homogeneous coating in step B. The hydrogen gas is thermal conductor. Increasing its flow rate leads to generate of stronger plasma and more heat.

Figure 3 shows the FESEM of cross-section of coatings A and B. The thickness of coatings A and B are around 100  $\mu\text{m}$  and 40  $\mu\text{m}$ , respectively. It can be seen that cross-section of coating A is destroyed, but cross-section of coating B has good quality. Image b in Figure 3 represents good adhesion between coating and substrate. The surface and cross-section of coating does not show any crack. The reasons for the absence of cracks can be two reasons: a) preheating of titanium substrate b) the amounts of the coefficient of thermal expansion of titanium and titanium diboride are close together (coefficient of thermal expansion of Ti,  $\text{TiB}_2$  are  $8.6 \times 10^{-6}/^\circ\text{C}$ ,  $8.1 \times 10^{-6}/^\circ\text{C}$ , respectively [18]). Therefore, their temperature tolerance is almost the same, so thermal tension is not created.

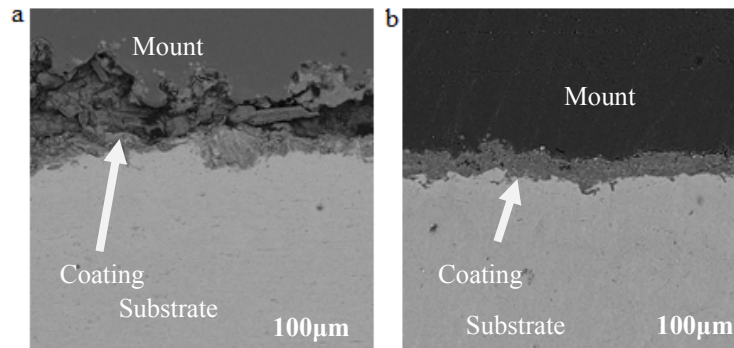


Figure 3. FESEM images of cross-section of coating a) A; b) B, on the scale of 100 $\mu\text{m}$

Microhardness amount of coating B is measured at three different points on the cross-section, with an average of 1145HV25. Microhardness measurement of coating A was not possible, due to its high porosity and its degradation. Surface roughness average of coatings A and B obtained 8.33 and 4.67  $\mu\text{m}$  respectively. The reasons for the more surface roughness of coating A respect to B is high surface porosity and the non-melted particles.

## Conclusions

The results reveal the effects of plasma current and hydrogen gas flow rate on coatings quality. Produced thermal energy under current 500 A was not adequate for melting the  $\text{Al}_2\text{O}_3\text{-TiB}_2$  powder. Increasing the current from 500 A to 600 A, resulted in melting  $\text{Al}_2\text{O}_3$  nanoparticles, while  $\text{TiB}_2$  microparticles remained non-melted (because of their high melting point). The porosity of 70%  $\text{Al}_2\text{O}_3\text{-30% TiB}_2$  nanocomposite coated under the current 500 A is higher than the one under 600 A. The porosity of the coatings is a consequence of non-melted particles ( $\text{Al}_2\text{O}_3$  and  $\text{TiB}_2$ ). The coating with current 500 A presented poor adhesions to the substrate compared to the one with 600 A, due to the presence of non-melted particles. Increasing the hydrogen gas flow rate, increased the temperature of plasma and led to more homogeneous coating.

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