



## EFFECTS OF ALUMINUM PHOSPHATE SEALANT CONTAINING $\text{Al}_2\text{O}_3$ NANOPARTICLES ON THE HARDNESS AND WEAR RESISTANCE OF THE $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$ PLASMA SPRAYED COATING

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**Abstract.** In the present study,  $\text{Al}_2\text{O}_3$ -40 wt.%  $\text{TiO}_2$  composite coatings were fabricated on medium carbon steel substrate by plasma spraying technique. The coatings were sealed with aluminum phosphate solution containing 5 wt.%  $\text{Al}_2\text{O}_3$  nanoparticles and then heat treated at 400 °C. The phase composition, structure morphology, microhardness and wear resistance of the coating were studied. The study results phase composition of the coatings showed that the coatings were composed  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{TiO}_5$  phase. The compounds  $\text{AlPO}_4$  and  $\text{Al}(\text{PO}_3)_3$  were found in the coating sealed with aluminum phosphate. The coatings sealed with aluminum phosphate containing  $\text{Al}_2\text{O}_3$  nanoparticles have lower porosity density, higher hardness and higher wear resistance than the coating sealed with aluminum phosphate uncontain  $\text{Al}_2\text{O}_3$  nanoparticles and the unsealed coating.

**Keywords:**  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  coating, aluminum phosphate, plasma spraying,  $\text{Al}_2\text{O}_3$  nanoparticles.

### 1. INTRODUCTION

Plasma spraying is a versatile technology to produce protective coatings for facilities in extensive application. Many studies indicate that  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  plasma sprayed coatings have good corrosion, wear and erosion resistance [1 - 11]. However, owing to their lamellar structure and rapid solidification, plasma sprayed coating usually have plenty of cracks and voids. These structural defects provide paths for corrosive species to corrode the substrate, leading to a deleterious effect when these coatings have to perform in an aggressive environment (e.g., seawater). Thus, post-treatments of the as-sprayed coatings are necessary to reduce porosity and enhance the corrosion resistance of the coatings [12].

Laser remelting and high temperature treatments have been applied, but the high thermal inputs may induce microstructural changes of the substrate material, in some cases even lead to cracking of the coatings due to the large residual stress [12]. On the other hand, these methods are very expensive and need very sophisticated equipment. In consideration of the economic and

technical benefits, sealants are widely used, in there, solutions aluminum phosphate was selected and used in many studies. It has been reported that aluminum phosphate sealant could pores decrease obviously and improve wear resistance of the plasma sprayed coatings [12 - 14].

The results of previous studies by the authors have shown that the aluminum phosphate has contributed to reduce the porosity and enhanced protection against corrosion and abrasion of the thermal sprayed coating [15 - 21]. With the desire to improve the properties of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> coating particularly wear resistant, in this study, we will fabricate Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> coating by plasma spraying technology, then the coating is impregnated with aluminum phosphate containing Al<sub>2</sub>O<sub>3</sub> nanoparticles and heat treated at 400 °C. Some properties of this coating will be studied and discussed.

## 2. EXPERIMENTAL

### 2.1. Materials

The main chemical used in the study include NiCr powder size of 15 ÷ 45 µm (China), Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> powder size of 15 ÷ 45 µm (China), α-Al<sub>2</sub>O<sub>3</sub> powder size approximately 150 nm (USA), 85 % phosphoric acid H<sub>3</sub>PO<sub>4</sub> (Germany), aluminum hydroxide Al(OH)<sub>3</sub> powder (Germany), medium carbon steel substrate of composition 98,36 % Fe - 0,13 % C - 0,24 % Si - 1,15 % Mn - 0,12 % (S, P, Ni, ...) by weight.

### 2.2. Preparation of samples

The coatings were prepared by plasma spraying equipment Tafa 3710-PRAXAIR (US) at National Key Laboratory for Welding and Surface Treatment Technologies (NARIME), with the optimized parameters as shown in Table 1. A bond coating of NiCr (thickness about 120 µm) was deposited between the steel substrated and the top Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> composite coating (thickness about 300 µm).

Table 1. Plasma-spraying operating parameters.

Parameters	Bond coating NiCr	Al <sub>2</sub> O <sub>3</sub> -40 wt.% TiO <sub>2</sub> coating
Arc current (A)	380	550
Arc voltage (V)	24	24
Flow rate of primary plasma gas Ar (ml/m)	50	60
Flow rate of secondary plasma gas H <sub>2</sub> (ml/m)	8	8
Spraying distance (mm)	100	100
Powder feed rate (g/m)	30	50

Aluminum phosphate solution was prepared from phosphoric acid (85 % H<sub>3</sub>PO<sub>4</sub>) and aluminum hydroxide Al(OH)<sub>3</sub> powder. The molar ratio P:Al was 3:1. The solution was mixed and slightly heated on a magnetic stirrer until it became clear. Then, 5 wt.% Al<sub>2</sub>O<sub>3</sub> nanoparticles were added to the solution and constantly stirred in 24 hours to get a well dispersed sealant.

Aluminum phosphate solution was stood statically at room temperature for 12 hours and then was slowly scanned on Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coating surface. The sealed coating was stood

at room temperature for 12 hours before heat treatment. The coatings were heat treated according to the process given in Fig. 1. Samples denotations are presented in Table 2.

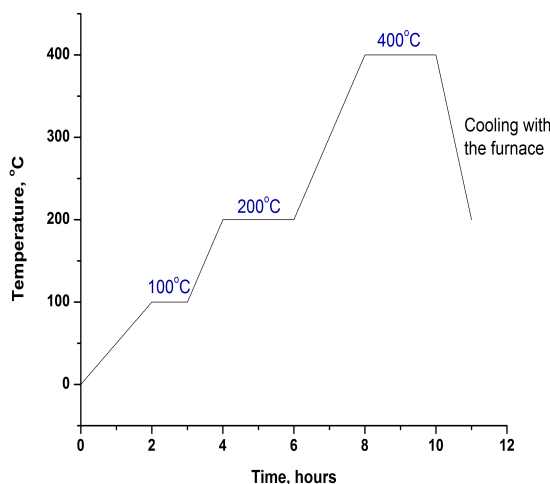


Figure 1. Heat treatment diagram.

Table 2. Samples denotation.

No.	Type of sample	Denote
1	The coating unsealed with aluminum phosphate	AT
2	The coating unsealed with aluminum phosphate, heat treated	AT-T
3	The coating sealed with aluminum phosphate – 0 wt.% $\text{Al}_2\text{O}_3$ nanoparticles, heat treated	AT-P0
4	The coating sealed with aluminum phosphate – 5 wt.% $\text{Al}_2\text{O}_3$ nanoparticles, heat treated	AT-P5

### 2.3. Research Methods

The microstructure was characterized using a scanning electron microscope SM-6510LV (Japan). The microhardness was measured from their cross-sections using AVK-C0/Mitutoyo equipment to TCVN 258-1:2007 standard. The phase composition was done using X-ray diffraction (XRD, X-RAY D5005/ SIEMENS, Gemany) with Cu-K $\alpha$  radiation and the scan step for  $2\theta$  at  $0.02^\circ/\text{s}$ . The wear resistance of the coatings were determined by using a pin-on-disk UMT – 3MT - CETR (US) to ASTM G99:2010 standard. The hardness of Cr pin is 63 HRC. The test was conducted under following conditions: applied constant load of 10 N, radius from the center of the sample to pin of 6 mm, rotational speed of 60 rpm, duration of 1000s.

## 3. RESULTS AND DISCUSSION

### 3.1. The phase composition of the coating

Figure 2 shows the X-ray diffraction patterns of  $\text{Al}_2\text{O}_3$ -40 %  $\text{TiO}_2$  powder and the  $\text{Al}_2\text{O}_3$ -40 wt.%  $\text{TiO}_2$  coating. The results show that, the phase composition of  $\text{Al}_2\text{O}_3$ -40 wt.%  $\text{TiO}_2$  powder before plasma spraying include  $\alpha$ - $\text{Al}_2\text{O}_3$  and rutile- $\text{TiO}_2$  phases. The XRD patterns of the coatings has the appearance of  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{TiO}_5$  phases. Thus, the missing of  $\alpha$ - $\text{Al}_2\text{O}_3$  phase could be because of during the plasma spraying,  $\alpha$ - $\text{Al}_2\text{O}_3$  phase transforms into  $\gamma$ - $\text{Al}_2\text{O}_3$  phase. During plasma sprayed, the  $\alpha$ - $\text{Al}_2\text{O}_3$  and rutile- $\text{TiO}_2$  phases react together to form  $\text{Al}_2\text{TiO}_5$  phases.

AT-P0 and AT-P5 were composed of  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{TiO}_5$  phases, along with compounds of  $\text{AlPO}_4$  and  $\text{Al}(\text{PO}_3)_3$ . However, the characteristic peaks of  $\alpha$ - $\text{Al}_2\text{O}_3$  phase do not appear in XRD spectrum of AT-P5. This is explained by the content of  $\alpha$ - $\text{Al}_2\text{O}_3$  nanoparticles in aluminum phosphate solution is too small. It is difficult to detect by XRD method (its content is below the detection limit of the XRD equipment).

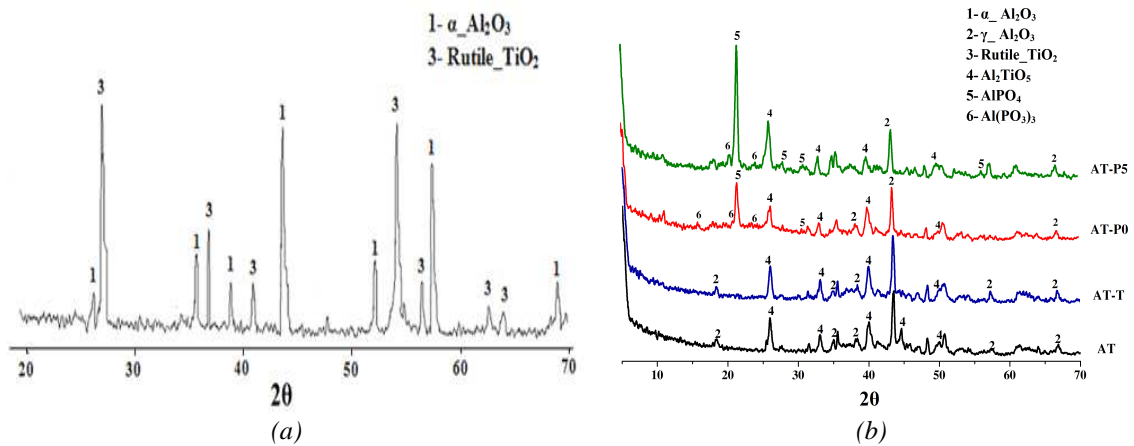


Figure 2. XRD patterns of Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> powder (a) and Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coating (b).

### 3.2. Microstructure and microhardness of the coating

Cross-sectional structure of the Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coating is shown in Figure 3. The thickness of the top Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coating and the bond NiCr coating are about 300  $\mu$ m and 120  $\mu$ m, respectively.

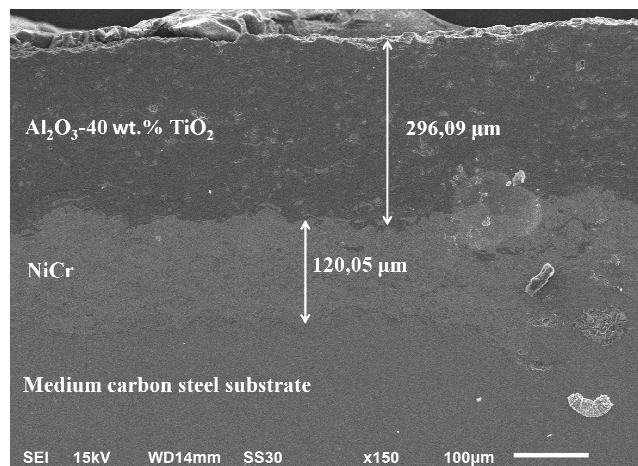


Figure 3. Cross-sectional of plasma sprayed Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coating.

Cross-sectional structure of the plasma sprayed coatings is given in Fig. 4. Cross-sectional surface image of AT-T and AT showed heat treatment to 400 °C without significantly affect to the structure of Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coating. This two coatings were still high porosity and some micro cracks. Meanwhile, the sealed coatings (AT-P0 and AT-P5) have lower density of pores than the unsealed coatings (AT and AT-T). Adding 5 wt.% Al<sub>2</sub>O<sub>3</sub> nanoparticles to aluminum phosphate solution was made the structure of this coating becomes more packed than the remaining coating. The reason is that, after heat treatment to 400 °C, the water in aluminum phosphate solution was evaporated whole, Al<sub>2</sub>O<sub>3</sub> nanoparticles and aluminum phosphate binder into a solid mass fill the pores. Meanwhile, for AT-P0, because of lower specific weight,

aluminum phosphate was shrinkage after the water evaporates. This will create more space in the pores, leading to effective reduction of porous cover.

The microhardness of the coatings was measured from their cross-sections. The measured region were permeable by aluminum phosphate (for AT-P0 and AT-P5 ). Largest distance from the sample surface to the measured position is 30  $\mu\text{m}$ . Results of the microhardness measurement are presented in Table 3.

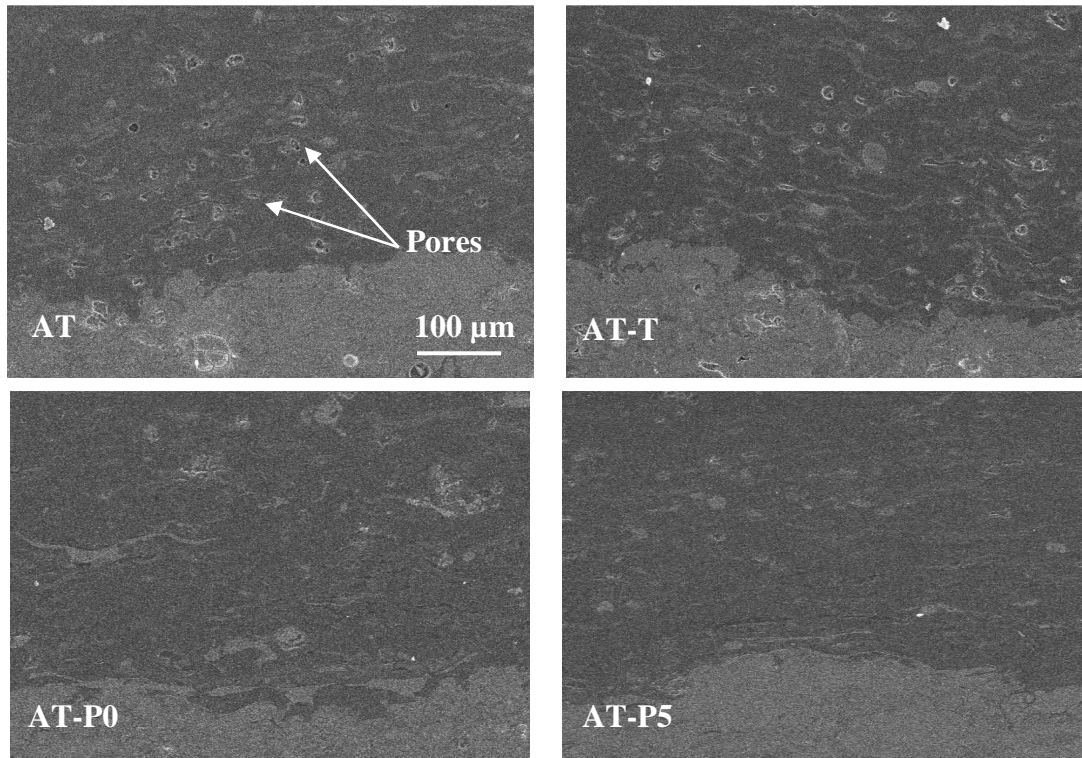


Figure 4. Cross-sectional of the plasma sprayed coatings.

Table 3. Microhardness of the plasma sprayed coatings, scale HV0.2.

Sample	Position 1	Position 2	Position 3	Average
AT	483,2	487,9	478,5	483,2
AT-T	477,8	503,3	483,2	488,1
AT-P0	635,9	644,3	632,4	637,5
AT-P5	713,0	718,6	703,3	711,6

The results showed that the microhardness of the coatings are range from 483.2 to 711.6 HV in ascending order AT, AT-T, AT-P0 and AT-P5. Thus, heat treatment at 400 °C and impregnation with aluminum phosphate were increased the microhardness of the coating. However, if only the heat treatment, the hardness of the coating was not significantly increased (about 1 %). Meanwhile, the hardness of the sealed with aluminum phosphate containing 5 wt.%  $\text{Al}_2\text{O}_3$  nanoparticles and heat treated coating increases about 47 %. The presence of  $\text{Al}_2\text{O}_3$  nanoparticles have also improved the hardness of the coating (increase about 11 %). This is the

result of reduce the porosity of the coating. Moreover,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles very hard and durable also contributed to increase the hardness of the coating.

### 3.3. The wear resistance of the coating

The wear depth is used to evaluate the wear resistant ability of the coatings. The test results of wear resistance are given in Table 4.

Table 4. The wear depth of the coatings.

The coatings	The wear depth, $\mu\text{m}$
AT	158,8
AT-T	127,8
AT- P0	64,9
AT- P5	53,2

The results in Table 4 showed that, AT-P5 had the lowest wear depth corresponding to the highest wear resistance. It was suitable for the results of hardness and porosity above. The wear resistance ability of AT-P5 is about 18 % and 58 % higher than AT-P0 and AT-T, respectively. Thus, the presence of 5 % Al<sub>2</sub>O<sub>3</sub> nanoparticles by weight in aluminum phosphate sealant improved coating's wear resistant ability. The reason is after sealing with aluminum phosphate containing nanoparticles and heat treatment the coating becomes harder and denser.

## 4. CONCLUSION

Al<sub>2</sub>O<sub>3</sub>-40 wt.% TiO<sub>2</sub> coatings had the appearance of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>TiO<sub>5</sub> phases. In the plasma spray process, one part of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase changed to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase interacted with rutile-TiO<sub>2</sub> phase to form Al<sub>2</sub>TiO<sub>5</sub> compound. The sealed coatings with aluminum phosphate also appeared aluminum phosphate compounds of AlPO<sub>4</sub> and Al(PO<sub>3</sub>)<sub>3</sub>.

After sealing with aluminum phosphate and heat treatment, the porosity of the coating decreased. The sealed coating with aluminum phosphate containing Al<sub>2</sub>O<sub>3</sub> nanoparticles has the lowest porosity.

The hardness of heat treated and sealed coating with aluminum phosphate containing Al<sub>2</sub>O<sub>3</sub> nanoparticles increased about 47 %. The presence of 5 wt.% Al<sub>2</sub>O<sub>3</sub> nanoparticles in the coating also improved sealed coating's hardness about 11 %. The hardness of sealed coating with aluminum phosphate and Al<sub>2</sub>O<sub>3</sub> nanoparticles was the highest (HV 711.6).

The wear resistance of the sealed coating with aluminum phosphate containing Al<sub>2</sub>O<sub>3</sub> nanoparticles was about three times higher than the unsealed coating.

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