



# A comparative study on corrosion behavior of ceramic coatings via plasma spray process in 3.5% NaCl solution

## دراسة مقارنة لسلوك التآكل الخاص بالطلاء السيراميك بطريقة البلازما في محلول يحتوي 3.5% صوديوم كلوريد

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### KEYWORDS:

*Plasma coating; coarse grain; fine grain; coating direction; corrosion*

*المخلص العربي:- في عملية رش البلازما، يتم تدفق المواد من خلال قوس البلازما والجسيمات المنصهرة من خلال تيار غاز حامل مع سرعة عالية على صفائح الفولاذ المقاوم للصدأ لإعطاء طلاء مع درجة من الترابط التعديني. تناقش هذه الدراسة فعالية حجم الجسيمات ونوع الطلاء والاتجاه على تآكل طلاء السيراميك في محلول كلوريد الصوديوم 3.5%. تم استخدام طريقتين لإعداد العينات المطلية. الطريقة الأولى هي استخدام مسحوق ذو الحبيبات الخشنة في الرش كطبقة أولى تليها طبقة من الحبيبات الناعمة. تفترض الطريقة الثانية تغيير اتجاه الطلاء للطبقة العليا بالنسبة للطبقة السفلى. تم ترسب WC-12% Co/Al<sub>2</sub>O<sub>3</sub> على الفولاذ المقاوم للصدأ عن طريق عملية رش البلازما بواسطة تقنيات ترسب مختلفة. ولأغراض المقارنة، تم استخدام مجموعة من العينات المطلية Al<sub>2</sub>O<sub>3</sub>، WC-12%Co. تم إجراء قياسات الاستقطاب بوتنشيوديناميك لتحديد سلوك التآكل للعينات المختلفة في 3.5% كلوريد الصوديوم. وأظهرت النتائج أن مقاومة التآكل تعتمد بشدة على نوع الطلاء واتجاه الطلاء. والعينة ذات طبقات متوازية من الطلاء لديها أفضل مقاومة للتآكل بين العينات المختلفة بمعدل تآكل 0.425 ملم / سنة.*

**Abstract**— In the plasma spray process, material flows through a plasma arc and the molten particles are projected through an inert gas stream with high velocity on AISI 304L stainless steel sheet to give a coating with some degree of metallurgical bonding. This study discusses the effectiveness of particle size, type of coating and direction on the corrosion of ceramic coating in 3.5 % NaCl solution. Two approaches were used for preparing coated specimens. The first modification proposed to use coarse grain sized powder in spraying as the first layer followed by the fine one. The second trial assumes to change the coating direction of the top layer to be traversing the lower layer. WC-12% Co/Al<sub>2</sub>O<sub>3</sub> coatings were deposited on AISI 304L stainless steel by means of a plasma spray process by different deposition techniques. For comparative purposes, a set of ceramics coatings via plasma spray process was employed on a substrate with Al<sub>2</sub>O<sub>3</sub>, and WC-12% Co. Potentiodynamic polarization measurements were carried out to determine the corrosion behavior of the plasma-sprayed-coatings in 3.5% NaCl. The results showed that the corrosion resistance depends strongly

on the type of coating and on its direction of coating. The grain type combination showed a great influence on the corrosion behavior of the plasma coatings, the coarse WC-12% Co covered by fine Al<sub>2</sub>O<sub>3</sub> showed a much better corrosion resistance than the fine WC-12% Co covered by coarse Al<sub>2</sub>O<sub>3</sub>. The parallel layers of coating specimen has the best corrosion resistance between the coated specimens with lowest corrosion rate 0.425 mm/year.

### I. INTRODUCTION

THE plasma spraying coating can enhance the contact fatigue resistance, wear and corrosion resistance in metal components as rollers in paper manufacturing, shafts and screws in petrochemical processes, and transmission shafts in construction machinery and cars. Moreover, the plasma spraying technology can be applied to a wide range of materials, such as ceramics, pure metals or alloys, and polymeric materials [1,2]. Corrosion-resistant coatings produced by plasma spraying have exhibited good benefits in certain conditions. It is well known that Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>+TiO<sub>2</sub>, Cr<sub>2</sub>C<sub>3</sub>+NiCr, NiAl, NiCrAl, ZrO<sub>2</sub> and WC-Co powders which are used in plasma

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coatings are resistant to specific corrosion media which are widely engaged in industry. The corrosion behavior of plasma sprayed coatings depends on the following elements: corrosive media, substrate and their surface state, environmental temperature, composition, structure, porosity, thickness, adhesive strength and other properties of the coatings [3,4]. The pitting corrosion caused by the connected pores and micro-cracks in the coating may decrease the corrosion resistance of the plasma sprayed coating. Many means have been put forward to solve the pitting corrosion problem in ceramic coating such as sealing treatment, laser remolding, and increasing the thickness of the coating by spraying more than one ceramic layer over each other. [5]. Increasing thickness by doubling layer of ceramic coating increases toughness and is one of the best ways to decrease the connected pores in the coating and accurate covering of the substrate by the coating due to the high thermal stress induced in the process of spraying, and this always depends on the deposition processes and techniques of the ceramics spraying. Aluminum oxide ( $Al_2O_3$ ) has a very high melting point and it is a good coating because of a very hard bond layer. Tungsten carbide-cobalt (WC-Co) based materials used extensively in industry in their sintered as well as thermally sprayed forms for applications requiring abrasion, sliding, and erosion corrosion resistance. The hard WC particles from the major wear-resistant constituent of these materials, while the cobalt binder provides toughness and cohesion. Properties such as hardness, wear resistance and strength influenced primarily by the WC grain size and volume fraction and with thermally sprayed coatings also by varying the porosity and the carbide and binder (Co) phase composition [6,7]. The anisotropic microstructure of thermally sprayed WC-12% Co coatings, changes when it's sprayed in a direction parallel to the substrate and when sprayed in a vertical direction to the substrate, also the grain types whether it's fine or coarse grains all of these conditions influence the coating properties and performance against corrosion of the surface. The aim of this work is to compare the corrosion resistance of AISI 304L stainless steel, coated with WC-12% Co/ $Al_2O_3$  using a plasma spray process by different deposition techniques and parameters and AISI 304L stainless steel coated with  $Al_2O_3$ , and WC-12% Co.

TABLE 1  
POWDER SPECIFICATIONS

Powders	Density g/cm <sup>3</sup>	Melting Temperature °C	Grain Size µm	Coating Hardne ss Kp/mm <sup>2</sup> HV0.1
Aluminum oxide Powder	4.05	1788-2000	Fine = 5-25 Coarse = 12-40	HV 1000
Tungsten Carbide(WC)- Cobalt(Co) WC-12%Co	13.75	Co is melting at 1459 WC is melting at 2777	-45+5	HV 2000

## II. EXPERIMENTAL DETAILS

The substrate used in this study was AISI 304L stainless steel, with the dimensions of 25×20×2 mm. These specimens were grit-blasted with grade 45 alumina grit to improve the adherence of the coating and to provide a surface roughness in the range of 2.3 to 3.6 µm. After that the specimens were cleaned in specially developed hot vapor washing tanks followed by Trichlorethane and Trichlorotrifluorethane solutions as a finishing cleaning operation. The ceramic coatings were carried out via atmospheric plasma spray (APS) equipment with a F4-MB torch. Table.1 shows the powder specifications and Table.2 lists the different deposition techniques used for each sample. Coating structure was examined using scan electron microscope.

Electrochemical test was conducted in 3.5% NaCl solution prepared prior to each test using distilled water. All electrochemical experiments were conducted with a Gamry PCI300/4 Potentiostat / Galvanostat/Zra analyzer. It was connected to a PC. The Echem Analyst software (version 5.21) was used for all electrochemical data analysis. A three-electrode cell composed of a specimen as a working electrode, platinum. Counter electrode, and saturated calomel electrode (SCE) as a reference electrode used for the tests. Tafel polarization tests were carried out using a scan rate of 0.5 mV/min at room temperature.

TABLE 2.  
THE DIFFERENT DEPOSITIONS TECHNIQUES ON EACH SAMPLE.

Coating Cases	Specimens code	Depositions Techniques
WC⊥WF Perpendicular coating (WC-12% Co)	W1	Coarse grain sized powder of tungsten carbide followed the fine one of tungsten carbide normal to be traverse the lower layer
WC= WF parallel coating (WC-12% Co)	W2	Coarse grain sized powder of tungsten carbide followed the fine one of tungsten carbide to be the same coating direction
AIC⊥AIF Perpendicular coating ( $Al_2O_3$ )	A1	Coarse grain sized powder of aluminum oxide followed the fine one of aluminum oxide normal to be traverse the lower layer
AIC = AIF parallel coating ( $Al_2O_3$ )	A2	Coarse grain sized powder of aluminum oxide followed the fine one of aluminum oxide to be the same coating direction
WC= AIF parallel coating (WC-12% Co/ $Al_2O_3$ )	WA1	Coarse grain sized powder of tungsten carbide followed the fine one of aluminum oxide to be the same coating direction
WF= AIC parallel coating (WC-12% Co/ $Al_2O_3$ )	WA2	Fine grain sized powder of tungsten carbide followed the coarse one of aluminum oxide to be the same coating direction
WC⊥AIF Perpendicular coating(WC-12% Co/ $Al_2O_3$ )	WA3	Coarse grain sized powder of tungsten carbide followed the fine one of aluminum oxide normal to be traverse the lower layer
WF⊥AIC Perpendicular coating(WC-12% Co/ $Al_2O_3$ )	WA4	Fine grain sized powder of tungsten carbide followed the coarse one of aluminum oxide to be traverse the lower layer

III. RESULTS AND DISCUSSION

A. Microstructures

The SEM micrographs of plasma-sprayed-coatings (PSC) are given in Fig.1. It is shown that (PSC) may exhibit porosity, oxides, un-melted particles and inclusions. The ceramic coatings of perpendicular spray direction denoted by (W1 for WC-12%Co, A1 for Al<sub>2</sub>O<sub>3</sub>) shows more porous structure compared to the parallel coatings denoted by (W2 for WC-12%Co, A2 for Al<sub>2</sub>O<sub>3</sub>) as shown in Fig.1(a-d). For instance, the WC-12% Co coating exhibits high porosity with large pore sizes and relatively wide distribution. For Al<sub>2</sub>O<sub>3</sub> coating, the defects were mainly in the form of micro pores, and no visible micro cracks were found in it as illustrated in Fig.1 (c, d). The pores are caused by the splashing of particles on impact with deposited material [8]. It may be due to voids resulting from the poor deformation of partially melted particles. These pores can have different sizes and exceedingly intricate shapes [9]. The presence of pores, cracks, and localized compositional variations could degrade corrosion resistance [10].

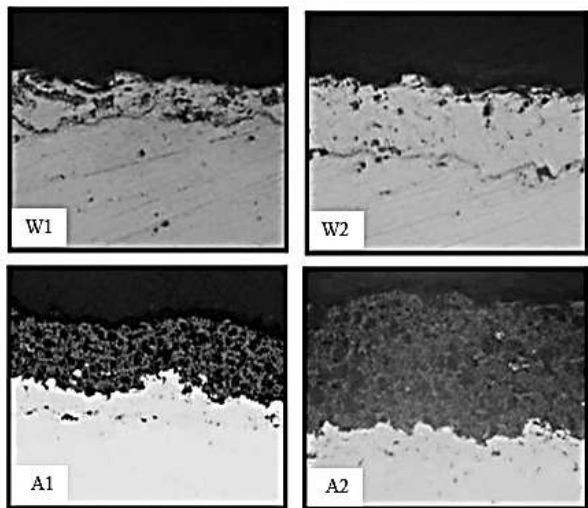


Fig.1 Microstructure of coated specimens W1, W2 coated by WC-12 % Co and A1,A2 Coated by Al<sub>2</sub>O<sub>3</sub>

Figure.2 indicate less separation if the coarse grains are the lining and those fine are the outermost layer. Because of the fine grains filled the voids in the coarse grain. As shown in Fig.2 (a, c) the parallel coating was more homogeneous than the perpendicular one Fig.2 (b, d). The homogeneous structure improved the corrosion properties of the coated specimens [11, 12]

B. Corrosion test:

The corrosion results were summarized in table (3). As shown in table (3) the corrosion potentials of the perpendicular coated samples show more negative values compared to the parallel-coated samples, which means that the perpendicular deposits had active surfaces and higher thermodynamic tendency to corrode. The corrosion potential of the specimen

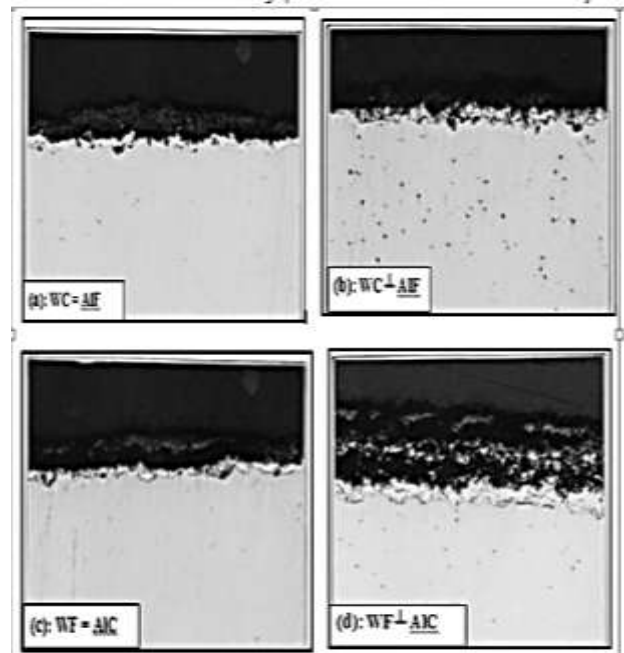


Fig.2 Microstructure of coated specimens with WC-12% Co/Al<sub>2</sub>O<sub>3</sub>

W1 was more negative as compared to the specimen W2. As well as the corrosion potential of the specimen A1 was more negative than the specimen A2. The parallel coated specimen with WC-12% Co/Al<sub>2</sub>O<sub>3</sub>, WA1 verified the most noble corrosion potential (-0.362 V). As it is evident from the table (3) that the parallel coatings have shown more corrosion resistance as compared to perpendicular coatings. In addition, the coated specimens with Al<sub>2</sub>O<sub>3</sub> (A1, A2) were more corrosion resistance than the coated specimens with WC-12%Co (W1, W2).

TABLE 3. ELECTROCHEMICAL PARAMETERS CALCULATED FROM THE POLARIZATION CURVES.

Coating Cases	Specimens code	E Corrosion (V)	Corrosion rate(mm/year)
WC⊥WF	W1	-0.720	2.393
WC=WF	W2	-0.688	0.981
AIC⊥AIF	A1	-0.436	1.156
AIC=AIF	A2	-0.369	0.724
WC=AIF	WA1	-0.362	0.425
WF=AIC	WA2	-0.462	0.615
WC⊥AIF	WA3	-0.538	3.197
WF⊥AIC	WA4	-0.406	7.124

On the other hand, the parallel coated specimens with WC-12% Co/Al<sub>2</sub>O<sub>3</sub>, (WA1, WA2) have shown higher corrosion resistance as compared to other specimens. The corrosion rate of the specimens with parallel coatings, WA1 and WA2 was 0.425 and 0.615 mm/year respectively.

Whereas the corrosion rate is maximum in case of the specimen WA4. The corrosion rate of this specimen recorded 7.124 mm/year.

Figure 3, 4 shows the potentiodynamic polarization curves of the plasma-sprayed coatings by using perpendicular and parallel deposition techniques in 3.5%NaCl. The corrosion behavior shown in Figs.3 & 4 confirmed that the coating process greatly influenced the coating performance. Figure 3.a shows that the corrosion potential of specimen W2 was shifted toward the noble direction compared with specimen W1. In addition, the passive range for the specimen W2 was larger than W1. Similar trend was also observed for the specimens A1, A2 in Fig 3.b. As shown in Fig 4.as the specimen WA2 had greater anodic dissolution than the specimen WA1 and its polarization curve shifted to the left, which confirm that WA1 showed better corrosion resistance than the WA2. In Fig. 4.b. the specimen WA4 showed greater anodic dissolution compared with WA3 which means that the specimen WA3 is better corrosion resistant than the specimen WA4.

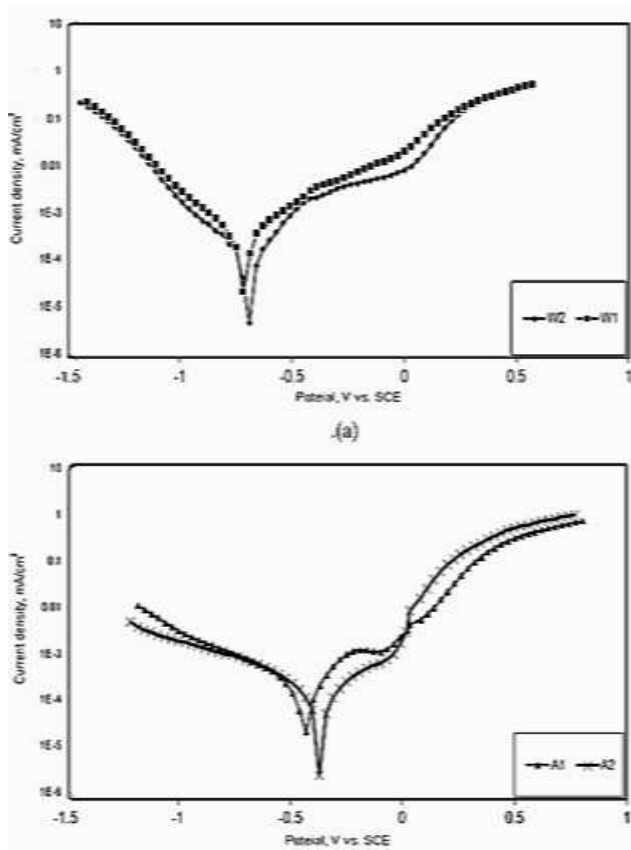


Fig.3 Polarization curves of coated specimens (a) Specimens coated by WC-12 % Co and (b) Specimens Coated by Al<sub>2</sub>O<sub>3</sub>

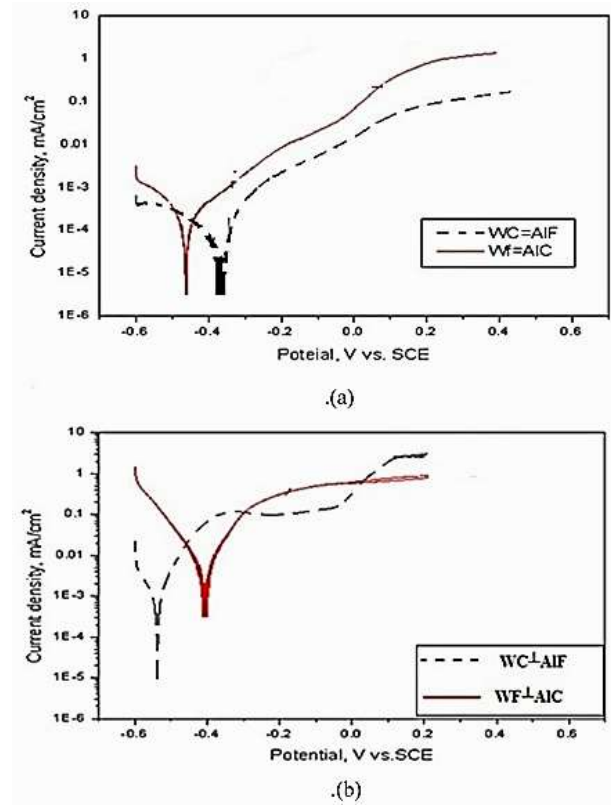


Fig.4 Polarization curves of coated specimens with WC-12% Co/Al<sub>2</sub>O<sub>3</sub>

The grain size and its order as well as the direction and the type of coating have prevalent effects on the corrosion resistant property of the coated specimens. As a general observation, the results confirmed that the parallel deposition technique exhibited a markedly better corrosion resistant ability than the perpendicular deposition technique by virtue of more noble corrosion potential. The parallel coating deposition technique's passive layer was strong and provided more corrosion resistance and protection than that of the perpendicular coating deposition technique. The improvement in corrosion resistance of parallel coatings may be attributed to the chemical stability of the coating layer, which acts as barriers for the corrosion process by reducing the holes and gaps on the surface and consequently preventing the corrosive pits from growing up [13,14]. Another observation, the grain type combination also showed a great influence on the corrosion behavior of the plasma coatings, the coarse grain covered by fine grain (W2, A2, WA1, WA3) showed a much better corrosion resistance than the fine grain covered by coarse grain (WA2, WA4b). The reason is that coarse grains have much more microcracks and pores than the fine grains. So when this layer combination of plasma coat was made the fine grain made a strong barrier and cover for the microcracks and pores in the coarse grains. This due to better strong passive layer which was a strong barrier for the electrolyte in the cell used in the corrosion test (NaCl) to pass to the coarse

grains. So this combination of grains decreased the rate of uniform corrosion and showed a better corrosion behavior than the other combination [15].

#### IV. CONCLUSION

The Corrosion behavior of Plasma WC-12% Co/ Al<sub>2</sub>O<sub>3</sub> Coatings on AISI 304L stainless steel surface has been studied related to the deposition parameters, Grain types (fine and coarse grains). For comparative purposes, a set of ceramics coatings via plasma spray process was employed on a substrate with Al<sub>2</sub>O<sub>3</sub>, and WC-12% Co. This work displays the economic view of coating process where the expensive cost of this process can be reduced through using the bilayer of coarse grain powder followed by fine grain powder for bilayer coating powder. This lead to decrease the coating thickness as well as the amount of expensive fine grain sized powders. It can be concluded that the parallel layers of plasma coating deposition technique had a better corrosion behavior and resistance than the perpendicular plasma coatings. The parallel layers of coating specimen WC= AIF (WA1) has the best corrosion resistance between the coated specimens with lowest corrosion rate 0.425 mm/year. The grain type combination also showed a great influence on the corrosion behavior of the plasma coatings, the coarse WC-12% Co covered by fine Al<sub>2</sub>O<sub>3</sub> showed a much better corrosion resistance than the fine WC-12% Co covered by coarse Al<sub>2</sub>O<sub>3</sub>.

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