

Experimental Study On Corrosion Behavior Of Different Ceramic Plasma Coatings In Sulfuric Acidic Solution

Kh. Abd El-Aziz

Abstract — Ceramic coatings materials are considered to be optimal in their applications as compared with metallic or organic coating materials, which are used under different environmental conditions. In this study, the corrosion behavior of austenitic steel substrates with different types of ceramic coating materials was investigated. The corrosion tests was carried out using Gamry PCI300/4 analyzer in a 0.5M H₂SO₄ solution as a corrosive environment. The corrosion behavior of ceramics coatings using plasma spray process was employed on a substrate with multilayers deposition of Al₂O₃, WC-12% Co and WC-12% Co/Al₂O₃ using atmospheric plasma spray (APS) equipment by using different parameters and deposition techniques. The microstructure of the coatings and corroded coatings were characterized by SEM. It was concluded that the corrosion resistance depends strongly on the type of coating material. Specimen which was coated by WC-12% Co/Al₂O₃ exhibited lower corrosion rate (8.8 mm/year) as compared with other types of coating materials. The corrosion potential of coated specimen was shifted toward the noble direction compared to uncoated specimen.

KEYWORDS: Ceramic coatings; Al₂O₃; WC-12% Co; Coatings; Plasma spray; Corrosion protection.

1. INTRODUCTION

Coating is the most commonly used process for, reducing, preventing or controlling corrosion due to an available and possible variation of coating materials and coating processes for different conditions and applications [1]. Plasma spraying is an operational surface engineering technology that has been commonly useful in various industrial fields [2-4]. Plasma spray coating is selected because of low cost, easiness and high deposition rate. However, coating of ceramic using plasma spray technique leads to higher inherent porosity which helps the electrolyte to attack on substrate which in turn leads to corrosion. Different ceramics coating materials help in avoiding the corrosion, as Al₂O₃, ZrO₂, WC-12% Co and TiO₂ [5]. Alumina offers electric insulation and low thermal conductivity; low friction coefficient and good corrosion resistance in both saline and acid environment. Alumina coating is generally useful in these applications involving sliding wear together with exposure to corrosive environment. WC-Co coatings are composed of WC particles disseminated in a metallic Co matrix [8]. This type of coating reveals the high temperature and abrasion resistance of ceramics and the ductility of metallic materials. Owing to these properties, WC-Co coatings are extensively used for applications where high mechanical performance and corrosion resistance are required, such as for airplane landing gear, and rollers in paper industries [9]. Many factors influence the corrosion characteristics of coatings, including their quality and structure. The porosity is usually used as a parameter of the structure of plasma sprayed coating [10]. Therefore, reduction of porosity of the sprayed coatings plays a key role in improving the corrosion resistance of the coatings. To overcome these issue bilayered coatings of Al₂O₃ and WC-12%Co has been used in present paper. The aim of this study

is to evaluate the corrosion resistance of austenitic stainless steel, coated with Al₂O₃, WC-12%Co and WC-12% Co/Al₂O₃.

2. EXPERIMENTAL PROCEDURE

The substrates used in this study were austenitic steel with the dimensions 25x20x2 mm. The specimens was coated with Al₂O₃, WC-12%Co and WC-12% Co/Al₂O₃. The characterizations of different coating materials are given in

Table 1. Coating materials characterizations.

Coating materials	Density (g/cm ³)	Melting Temperature °C	Grain Size (μm)	Coating Hardness HV0.1
Aluminum oxide Powder	4.05	1788-2000 °C	15-40	HV 1000
Tungsten Carbide (WC) - Cobalt (Co) (WC-12%Co)	13.75	1459 °C for Co 2777 °C for WC	25-45	HV 2000

Table (1). The ceramic coatings were carried out via atmospheric plasma spray (APS) equipment with a F4-MB torch. Surface coatings were produced using a plasma spray parameters as presented in Table (2). Electrochemical tests were conducted in 0.5 M H₂SO₄ solution prepared prior to each test using distilled water. All electrochemical experiments were conducted with a Gamry PCI300/4 Potentiostat/Galvanostat/Zra analyzer, connected to a PC. The Echem Analyst Software (version 5.21) was used for all electrochemical data analysis. A three electrode cell was used in these experiments. Tafel polarization tests were carried out using a scan rate of 0.5 mV/min at 25 °C. Specimens with exposed surface area of 1.5 cm², were used as a working electrode. Prior to electrochemical tests, the specimens were cathodically cleaned for 15 min at -1500 mV (SCE) to remove the air-formed oxide film. The applied routine automatically selects the data that lies within the Tafel region (±250 mV with

- ^a Mechanical Engineering Department, Taif University, Taif, 21974-888 Saudi Arabia
- ^b Materials Engineering Department, Zagazig University, Zagazig, P.O. Box 44519 Egypt

respect to the corrosion potential). The microstructure of tested specimen after corrosion was examined using scan electron microscope.

Table 2. Spray parameters for plasma burner PT F4-HB/ F4-MB.

Spray parameters	Unit	Aluminum Oxide		Tungsten Carbide-	
		Powder		Cobalt	
		(Al ₂ O ₃)		(WC-12%Co)	
Plasma gases	-	Ar/ H ₂		Ar/ He	
Amperage	A	500		820	
Voltage	V	70- 72		57-60	
Plasma gas flow	SLPM	47/ Ar and 12/ H ₂		74/Ar and 122/ He	
Powder flow	g/min	30		30	
Carrier gas flow	SLPM	2.5		2.6	
Anode diameter	mm	normal		6 (inside)	
Spray distance	mm	100		125 - 130	
Powder injector	mm	1.8		2	
Cooling		air		Air or CO ₂	

3. RESULTS AND DISCUSSION

3.1. Corrosion behavior

Fig. 1 displays polarization curves of coating specimens and uncoated specimen in 0.5 M H₂SO₄ solution. In this figure, it is obvious that the best corrosion protection was found for specimen coated by WC-12% Co/Al₂O₃. Moreover, a significant shift of the anodic curves towards higher current values was observed for polarization curves of uncoated specimen. The results illustrated in Fig.2 and Fig.3 show that the ceramic coating type greatly influenced the coating performance. As shown in Fig.2, uncoated specimen had the highest corrosion rate (75.6 mm/year).

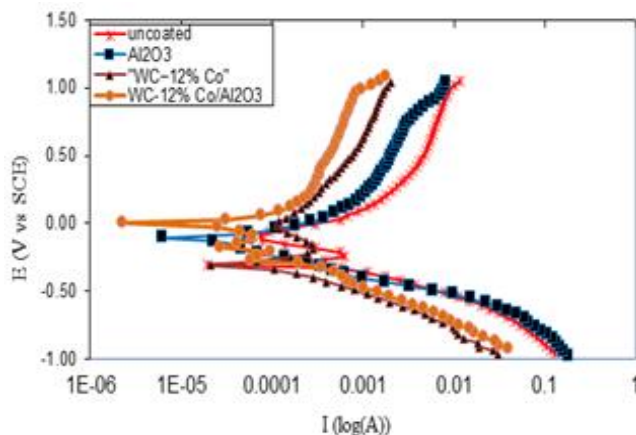


Fig. 1: Polarization curves of coating specimens and uncoated specimen in 0.5 M H₂SO₄ solution.

Specimen which was coated by WC-12% Co/Al₂O₃ has a lower corrosion rate (8.8 mm/year) as compared with other type of coating. According to Fig.3 the corrosion potential of coated specimen was shifted toward the noble direction compared with uncoated specimen. The corrosion potential

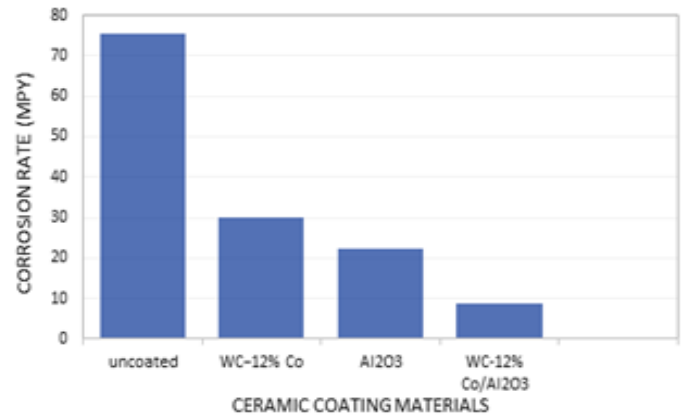


Fig.2: Corrosion rates of coated samples with different ceramic coatings.

of uncoated specimen recorded -299 mV. While the corrosion potential of coated specimen with Al₂O₃ was -113 mV. The results confirm that WC-12% Co/Al₂O₃ coating exhibited a significantly better corrosion-resistance than the other coatings by virtue of more noble corrosion potential.

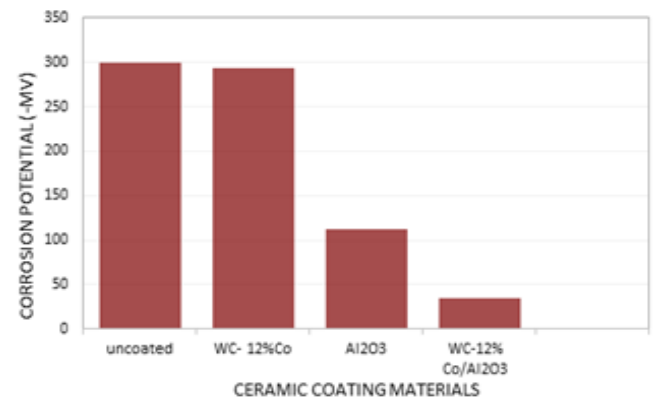


Fig.3: Corrosion potential of coated sample with different ceramic

As shown in Fig.4, the Nyquist plots for uncoated and coated specimens also supports the findings in Fig.2. The plasma coated sample exhibits higher corrosion resistance in tested solution H₂SO₄, while uncoated specimen suffered from severe corrosion. Ceramic coating of WC-12% Co/Al₂O₃ appears to afford significantly higher protection compared with the other coating specimens. Dosta et.al. [8] concluded that the WC-12Co coating was effective in corrosion resistance for the duration of 400 h of immersion in 3.5% NaCl solution. At extensive immersion times, dissolution of the Co phase and the loss of WC particles led to the creation of interconnected porosity, letting access of the solution and corrosion of the substrate. The low thickness, higher porosity, and possibly a larger quantity of defects were accountable for frailer performance of this coating. Celik et al. [11] studied the effect

of grit blasting of substrate on the corrosion behavior of plasma sprayed Al_2O_3 coatings and they

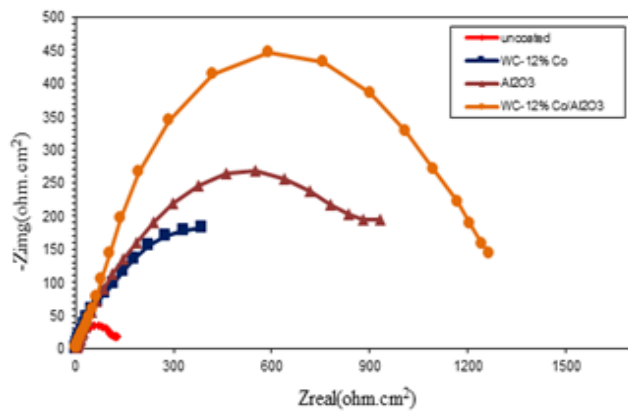


Fig.4: Nyquist plots of samples with different coatings in 0.5M H_2SO_4

identified that the corrosion resistance of the alumina coatings increased with decreasing porosity and coating thickness. Dianran et al. [12] investigated the corrosion behavior of Al_2O_3 based ceramic composite coatings in dilute HCl solution and they reported that the connected porosity in the Al_2O_3 based ceramic composite coatings rises with the open porosity and

is independent of the density of the coating. The as-sprayed alumina coatings (Al_2O_3 -APS) revealed a poor corrosion performance in the test solution due to their high degree of interconnected pores simplifying the penetration of aggressive species towards the bulk material [13]. Indermeet et.al. [5] noticed that in Al_2O_3 surface coating, Al_2O_3 was seen as major phase while Fe_2O_3 was noticed as minor phase by XRD, SEM/EDS analysis. The formation of Fe_2O_3 might be due to diffusion of Fe from the base alloy through the porosities in the alumina coating. However, they were noticed that the ZrO_2 and Al_2O_3 ceramic coating supported to improve corrosion resistance of these coatings. Carbajal et.al. [14] reported that the surface coating of stainless steel by SiO_2 - Al_2O_3 ceramic coating exhibited good indication of corrosion resistance in 1 M HCl solution and in 1 M H_2SO_4 solution. In addition, the more positive E_{corr} was obtained by coated specimens. Furthermore, the resulted corrosion rate values were smaller than the resulted corrosion rate from uncoated material.

It is clear from previous studies that the source of the deterioration of the coatings was clearly revealed by the presence of porosities and microcracks that acts as connecting pathways for the corrosive environments. In addition, the use of one type of coating material as Al_2O_3 or WC+ 12%Co alone may be contained more porosity than the use of two types of ceramic materials as WC-12% Co/ Al_2O_3 as a surface coating material.

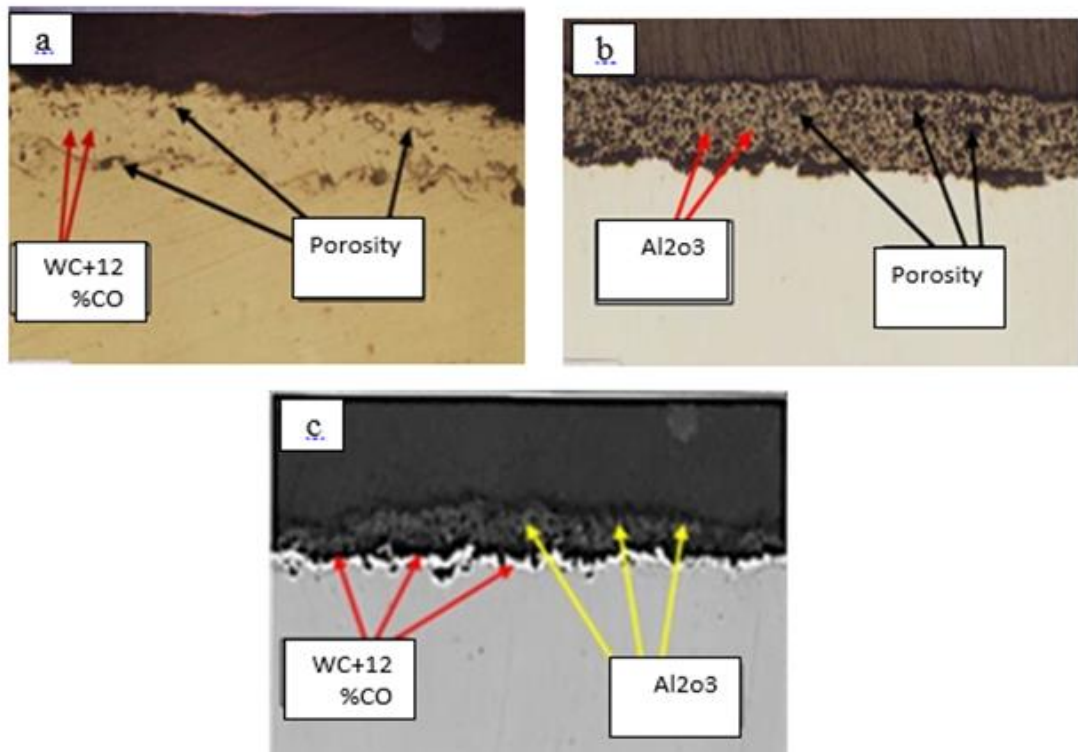


Fig.5: The micrographs of substrates with; (a) WC-12%Co coating, (b) Al_2O_3 coating, and (c) WC-12% Co/ Al_2O_3 .

3.2. Microstructure

The micrographs of the surface morphology of coated specimens with different types of coating materials is given in Fig.5. The plasma spray coating usually exhibit porosity, oxides, un-melted particles and inclusions. From Fig.5, it is clear that WC-12% Co coating exhibits higher porosity with

large pore sizes and relatively wide distribution than Al_2O_3 coating. The presence of pores could degrade corrosion resistance [15]. Fig. 6 shows the SEM microstructure of the corroded surfaces with different coating materials. Apparently, the uncoated specimen suffered severe corrosion as shown in Fig.6a. On the other hand, Fig.6 (b-d) shows that the coating

of the specimens with different ceramic coatings improves corrosion resistant of the substrates. In addition, the specimen coated with WC-12% Co/ Al_2O_3 ceramic coating exhibited a very good corrosion resistant, which is attributed to the high dense coating surface with a minimum number of pores as indicated in Fig.5-c and Fig. 6-d.

4. CONCLUSIONS

The experimental results in this present research indicated that the corrosion behavior is affected by the types of surface coating materials. Uncoated specimen revealed the highest corrosion rate (75.6 mm/year). The surface coating process improved the corrosion resistance of the base metal. The

defects in Al_2O_3 coating layer were relatively few compared to WC-12%Co coating, and hence, the corrosion resistance of the substrates with Al_2O_3 coating was higher than that of the substrates with WC-12%Co coating. The best corrosion resistance was achieved in case of using WC-12%Co / Al_2O_3 coating. In addition, the corrosion potential of coated specimen was shifted toward the noble direction as compared with uncoated specimen.

ACKNOWLEDGMENT

The author would like to express their deepest gratitude to Associated prof. Dalia Saber for her help and useful instructions during this research.

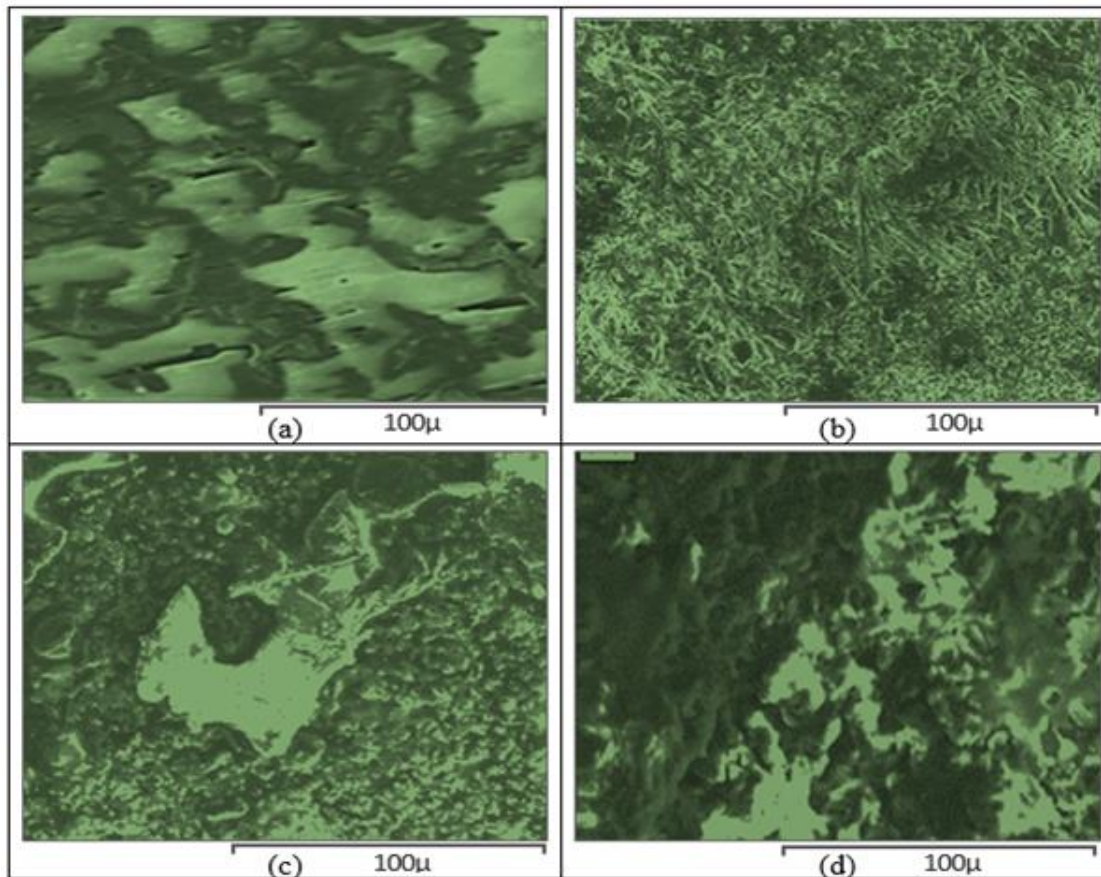


Fig.6: SEM micrographs of corroded surface; (a) without coating, (b) with Al_2O_3 coating, (c) with WC+12%Co coating, and (d) with WC+12%Co/ Al_2O_3 coating.

REFERENCES

- [1] Dana H. Abdeen ,Mohamad El Hachach, Muammer Koc and Muataz A. Atieh, "A Review on the Corrosion Behaviour of Nanocoatings on Metallic Substrates", *Materials* 2019, 12, pp. 210.
- [2] H.L. Yu, W. Zhang, H. M. Wang, "Bonding and sliding wear behaviors of the plasma sprayed NiCrBSi coatings", *Tribol. Int.* 2013; 66, pp.105-113.
- [3] Y.L. An, G.L. Hou, J. Chen, X.Q. Zhao, G. Liu, H.D. Zhou,J.M.Chen, "Microstructure and tribological properties of iron-based metallic glass coatings prepared by atmospheric plasma spraying", *Vacuum* 2014;107, pp.132-140.
- [4] Z.Q. Zhang , H.D.Wang, B.S. Xub,and G.S. Zhang, "Characterization of microstructure and rolling contact fatigue performance of NiCrBSi/WC-Ni composite coatings prepared by plasma spraying", *Surface & Coatings Technology* 2015; 261, pp. 60–68.
- [5] Indermeet Singh , Khushdeep Goyal, Rakesh Goyal, "Evaluations of Hot Corrosion Behavior of Al_2O_3 Thermal Spray Coatings with ZrO_2 Reinforcements on T-91 Steel " *Universal Journal of Mechanical Engineering* 7(4): pp. 224-230, 2019.
- [6] B. Matthes, E. Broszeit, J. Aromaa, H. Ronkainen, S.-P. Hannula, A. Leyland, A. Mathews, "Corrosion performance of some titanium-based hard coatings", *Surface and Coatings Technology* 49 (1991), pp. 489.

- [7] F.S. Pettit, Summary Abstract, "The requirements for developing corrosion resistant", *Journal of Vacuum Science & Technology*. A4 (1986), pp. 3025.
- [8] S. Dosta, M. Couto, J.M. Guilemany, "Cold spray deposition of a WC-25Co cermet onto Al7075-T6 and carbon steel substrates", *Acta Mater.* 61 (2013), pp. 643–652.
- [9] L. M. Berger, "Hard Metals as Thermal Spray Coatings", *Powder Metall.* 50 (2007) 205–214.
- [10] C.J. Li and A. Ohmori, "Relationships Between the Microstructure and Properties of Thermally Sprayed Deposits", *J. Therm. Spray Technol.*, 2002, 11(3), pp. 365-374.
- [11] E. Celik, I. Ozdemir, E. Avci and Y. Tsunekawa, "Corrosion behavior of plasma sprayed coatings", *Surface & Coatings Technology* 193 (2005), pp. 297-302.
- [12] Dianran Yan, Jining He, Xiangzhi Li, Yangaia Liu, Jianxin Zhang and Huili Ding, "An investigation of the corrosion behaviour of Al₂O₃ based ceramic composite coatings in dilute HCl solution", *Surface and Coatings Technology* 141 (2001), pp.1-6.
- [13] D. Thir., K. Shanmugam And V. Balasubramanian, "Influences of Spraying Parameters on Porosity Level And Corrosion Rate Of Atmospheric Plasma Sprayed Alumina Coatings On Az31b Magnesium Alloy", *Journal of Materials Science and Engineering with Advanced Technology* Vol. 8, Number 1, 2013, pp. 27-53.
- [14] G. Carbajal-de la Torre¹, M.A. Espinosa-Medina², A. Martinez-Villafañe³, "Study of Ceramic and Hybrid Coatings Produced by the Sol-Gel Method for Corrosion Protection", *The Open Corrosion Journal*, 2009, 2, pp.197-203.
- [15] N. Ahmed, M.S. Bakare, D.G. McCartney, and K.T. Voisey, "The Effects of Microstructural Features on the Performance Gap in Corrosion Resistance between Bulk and Hv of Sprayed Inconel 625", *Surf. Coat. Technol.*, 2010, 204 (14), pp. 2294-2301.