Corrosion resistance of double ceramic composite layer

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Abstract: This present work WC-12% Co/Al2O3 coatings were deposited on AISI 304L stainless steel by means of plasma spray process by different deposition techniques and parameters. Surface roughness parameters for coating specimens measured by TalySurf Taylor-Hobson W6. The polarization studies in 3.5% NaCl conducted to evaluate the corrosion resistance of coated samples. The results showed that the parallel coating deposition process indicates high values of microhardness than the perpendicular coating deposition technique. In addition the smoothness of surface is increased when the fine grains are used as a final layer. The parallel coating deposition process has higher corrosion resistance than the perpendicular coating deposition technique. It was also found that the samples coated by WC-12% Co coarse grains and the second layer of Al2O3 fine grains had better corrosion resistance than the other grain combination of Fine WC-12% Co and Coarse Al2O3 grains.

Keywords: Plasma coating, coarse grain, fine grain, coating direction, surface roughness, corrosion

Introduction
Plasma spraying is an effective surface engineering technology that has been widely applied in various industrial fields [1–3]. Plasma spraying coating can improve the contact fatigue resistance, wear resistance, and corrosion resistance in metal components such as rollers in paper manufacturing, shafts and screws in petrochemical processes, and transmission shafts in construction machinery and cars. In addition, the plasma spraying technology can be applied to a wide range of materials, such as ceramics, pure metals or alloys, and polymeric materials [4, 5]. Corrosion-resistant coatings produced by plasma spraying have exhibited good benefits in certain conditions. It is well known that Al2O3, Al2O3+TiO2, Cr2C3+NiCr, NiAl, NiCrAl, ZrO2 and WC-Co powders used in plasma coatings are resistant to specific corrosion media which are widely employed in industry. With respect to environmental and material factors affecting corrosion processes, 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. Many factors influence the corrosion, including their quality and structure [6, 7]. Gray Aluminum oxide Al2O3 ceramic is a powder of a very high melting point and it is a good coating of sliding wear resistance as it is very hard bond layer. In condition of co-existence of wear and corrosion connected pores and micro-cracks in the coating result in decrease of wear and corrosion resistance. The pitting corrosion caused by the connected pores and micro-cracks in the coating can decrease the corrosion resistance of the plasma sprayed coating greatly. At present, 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. Sealing treatments are not suitable for the coating under the conditions in existence of wear and corrosion. Laser remolding can only decrease the connected pores, but it is difficult to eliminate the connected pores and micro cracks [8]. Increasing thickness by doubling layer of ceramics coatings 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. Tungsten carbide-cobalt (WC-Co) based materials used extensively in industry in their sintered as well as thermally sprayed forms for applications requiring abrasion corrosion, sliding, and erosion corrosion resistance. The hard WC particles form 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 [9]. The tribological and tribo-corrosion performance of the WC-12% Co will be related to their mechanical and corrosion properties as well as deposition parameters, microstructure and actual composition. For example, the anisotropic microstructure of thermally sprayed WC-12% Co coatings, changes when its sprayed in a direction parallel to the substrate and when sprayed in a vertical direction to the substrate, also the grain types weather its fine or coarse grains all of these conditions influence the coating properties and performance against corrosion of surface. The aim of this work is to evaluate the corrosion resistance of AISI 304L stainless steel, coated with WC-12% Co/Al2O3 using plasma spray process by different deposition techniques and parameters.
2. Experimental details

2.1 Plasma spray deposition

Substrate used in this study was AISI 304L stainless steel, with the dimensions of 25x20x2 mm. These specimens were grit-blasted with grade 45 alumina grit in order to improve the adherence of the coating and to provide a surface roughness in the range of 2.3 to 3.6 μm [10]. Specimens were then cleaning in especially developed hot vapor washing tanks followed by Trichlorethane and Trichlorotrifluoromethane solutions as a finishing cleaning operation. In the plasma spray process, material flows through a plasma arc and the molten particles are projected through inert gas stream with high velocity to give a coating with some degree of metallurgical bonding. Thus, plasma spraying is a complex process in which experience and reliable machinery are very important. Recently, developing composite materials of ceramics, has become necessary to keep up with highly progressed industries. On the other side, the choice of the couple of composite powders needs some investigations to reduce the inevitable troubles arising from using two different type of coated powders which have different physical, chemical, and thermal properties. Ceramic material is superior in resistance of corrosion, but inferior in impact toughness and machining. Therefore, it is suitable for ceramic material to be applied onto metal substrates as reinforcement material. It is known that the thickness of coating layer is usually obtained by spraying the substrate materials in one direction. The spray gun used in some machines is to be fixed in a specific location meanwhile the pieces to be coated are rotating around the machine spindle in one direction facing the sprayed powder. This motion is continuously until the required coated thickness gained. Actually it was aim of the study is to obtain a layers coating composite ceramic materials using plasma spray technique, taking into account the particle size, the type of coatings powder and the direction of coat. Can we here display an image using scanning electron microscope (SEM) for each type of powder coatings used in the research basis before work mixing coatings for them via plasma method, as shown in Fig.1.(a and b).

The proposed work is to change the direction of coating after getting a certain value of thickness. This is very easy to be achieved by changing the fixation of specimens around the axis by 90o. In this case, the next layers of coating are in a direction normal to the previous ones. However, the spraying process occurred in parallel and in traversal paths by using gray aluminum oxide of Metco 101 NSC as coarse grain and AMDRAY 187F fine grain. Also by the same way spraying powder of tungsten carbide (WC) – 12% cobalt (Co) of Metco 71 VFNS as fine grain and AMDRY 301C as coarse grain.

2.1.1 Specimens were coated with composite powders

Bilayer of coating powders of (Al₂O₃) and (WC-12%Co) have been plasma sprayed using (APS) equipment with a F4-MB gun as the following procedure:

a- Specimens were coated by using spraying powders of (AMDRY- 301C ) followed by (AMDRAY 187 F ) in the same directions.

b- Specimens were coated by using spraying powders of (Metco 71 VFNS ) followed by (Metco 101 NSC ) in the same directions.

c- Specimens were coated by using spraying powders of (Metco 71 VFNS ) as a first layer followed by (Metco 101 NSC ) in normal the first directions.

d- Specimens were coated by using spraying powders of (AMDRY- 301C ) followed by perpendicular layer of (AMDRAY 187 F ).

Table 1 shows the powder specifications and Table 2 lists the different depositions techniques used for each sample.

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**Table 1. Powder specifications.**

<table>
<thead>
<tr>
<th>Powders</th>
<th>Density g/cm³</th>
<th>Melting Temperature °C</th>
<th>Grain Size μm</th>
<th>Coating Hardness Kp/mm²</th>
<th>HV 0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gray Aluminum Powder</td>
<td>4.05</td>
<td>1788-2000</td>
<td>Fine = 5-25</td>
<td>Coarse = 12-40</td>
<td>HV 1000</td>
</tr>
<tr>
<td>Tungsten Carbide(WC)</td>
<td>13.75</td>
<td>Co is melting at 1459</td>
<td>WC is melting at 2777</td>
<td>.45-5 μm</td>
<td>HV 2000</td>
</tr>
</tbody>
</table>

**Table 2. The different depositions techniques on each sample.**

<table>
<thead>
<tr>
<th>WC= AF</th>
<th>Coarse tungsten carbide parallel to fine aluminum oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>WF= AC</td>
<td>Fine tungsten carbide parallel to coarse aluminum oxide</td>
</tr>
<tr>
<td>WF ┴ AC</td>
<td>Fine tungsten carbide vertical to coarse aluminum oxide</td>
</tr>
<tr>
<td>WC ┴ AF</td>
<td>Coarse tungsten carbide vertical to fine aluminum oxide</td>
</tr>
</tbody>
</table>
2.2 Electrochemical test
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.

3. Results and discussion
3.1 Surface roughness parameters and microhardness test results.
The results of some surface roughness parameters measured by Talsurf Taylor-Hobson W6 for coating specimens using different powders of (WC-12% Co) and Al2O3 are given in Table (3). Moreover, the results of microhardness tests are listed in the same table. On the other hand, the talsurf paper trace of coated specimens used in this work is shown in Fig. (2).

Table 3. Surface roughness parameters and microhardness values for coated specimens using different powders.

<table>
<thead>
<tr>
<th>No</th>
<th>Coating Cases</th>
<th>Surface Roughness Parameters</th>
<th>Microhardness Values</th>
<th>HV20</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WC = AF</td>
<td>Ra 14.8 µm, Rtm 29.4 µm, S 52 µm, Sm 122 µm, Aq 130 µm, Sq 14.5 degree</td>
<td></td>
<td>753</td>
</tr>
<tr>
<td>2</td>
<td>WF = AC</td>
<td>R 84.4 µm, Rtm 30.4 µm, S 54 µm, Sm 169 µm, Aq 140 µm, Sq 15 degree</td>
<td></td>
<td>559</td>
</tr>
<tr>
<td>3</td>
<td>WC-12% AF</td>
<td>Ra 4.02 µm, Rtm 24 µm, S 29 µm, Sm 88 µm, Aq 80 µm, Sq 21.6 degree</td>
<td></td>
<td>603</td>
</tr>
<tr>
<td>4</td>
<td>WF-4 AC</td>
<td>Ra 4.44 µm, Rtm 25 µm, S 30 µm, Sm 92 µm, Aq 85 µm, Sq 22.1 degree</td>
<td></td>
<td>608</td>
</tr>
</tbody>
</table>

the results support the correlations among the microhardness and the surface roughness parameters when the grain size of powders referred. The using of fine grain gives a dense structure where the cohesive force between particles are higher than that if the coarse grains sprayed. Therefore, it is expected that, the microhardness value is enhanced. Additionally, the vaporization of the grains, either totally or partially, depending on their size and the elimination of the smallest grains by means of air curtains located perpendicularly to the particles trajectory and the porous volume of the coating is indeed doubled when the mean diameter of the powder grains increases from 25 to 45 µm [11]. The smoothness of surface is increased when the fine grains are used as a final layer, where they fill the wide distance among the peaks of coarse grains as shown in Fig.2. The macrographs shown in Fig (3) indicate less separation if the coarse grains are the lining and those fine are the outermost layer. This is due to that, the fine grains filled the voids in the coarse grain. In addition there is no separation and contamination between the two layers and gives better homogeneous structure and hence improved the hardness properties of the coated specimens [12, 13], see table (3) The coating with composite layer considered in this investigation gives good conclusion with parallel direction for plasma coating layers, the lining and face layers. Therefore, it can conclude that, the coating layer in the same direction gives stronger layer where the mechanical and tribological properties are improved. The considered result of this work display good result obtained in transversal coating where the machine equipped by two-sprayed gun enable the spraying action had done without separate time. With composite powder, this discrete time is still inevitable due to change the gun and spraying gas where each powder should be sprayed by specified gas. In addition, the change of grain size and direction of coating need some time. This implies to redesign the plasma spray coating machine to develop the facilities necessary to continue the spraying action by different powder, different grain size and different direction without split process. So, the parallel direction coating of composite powders indicate high values of microhardness. Moreover, the coating in traversal direction to preceding one developed smooth surface where the result quoted in table(3) pointed out improving in surface roughness parameters. There is a decrease in vertical such as Ra, Rt, and S, Sm respectively. This denotes, the peaks of surface roughness are become less high as well as the valleys are less deep considering the vertical parameter [13 ] see Fig. 2-b and Fig.2-d. In addition to that, the decrease of the spacing surface roughness measures; S and Sm indicate the shortening of the distance of peak and adjacent valley and in the same time determine the decrease of space between the successive peaks i.e. less voids and hence smarter surface resulted and consequently the mechanical and tribological properties are improved [14]. This aforementioned concept supported by the hybrid parameter λq, the average of the wavelength, and Δq, the root mean square slop. The result provide a drop in value of λq in case of traversal coating rather than the coating process in the same direction as clear from table(3). As matter of fact, the increase of average slop Δq in normal coating highlights that; the peaks become very sharp, which always correlated by the super finishing processes. Therefore, the other surface roughness parameters such as λq, S, Sm, Ra and Rpm recorded improvement in the surface
smoothness. This is explained by that, the normal coated layer fill the spaces and distance between the peaks. However, the choice of this couple of powders needs some investigation and experimentation work to select the powders proper to compose the composite layer. Apart from the experimental results, it is seemed that, the (WC-12% Co) powders predict a good lining layer for (Al2O3) outermost layer where it is used as a binder for it to the substrate piece. This present work introduces two approaches for improving the surface roughness and mechanical properties for sprayed coating layers. The first modification proposed to use fine grain sized powder in spraying the upper layer followed the coarse one with the bottom layer. The second trial assumes to change the coating direction of the top layer to be traverse the lower layer.

3.2 Corrosion test:
In plasma coatings, open circuit potential (OCP) measurements and potentiodynamic polarization scans have been widely used to evaluate the corrosion behavior [15-18]. The OCP-time plots for the coating samples as a function of time are shown in Fig. 4 and the results recorded in Table (4).

Table 4. Terminal potential values in the OCP.

<table>
<thead>
<tr>
<th>Coating Cases</th>
<th>Starting value</th>
<th>Finishing value</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC=AF</td>
<td>-0.392</td>
<td>-0.389</td>
</tr>
<tr>
<td>WF=AC</td>
<td>-0.398</td>
<td>-0.445</td>
</tr>
<tr>
<td>WC⊥ AF</td>
<td>-0.430</td>
<td>-0.528</td>
</tr>
<tr>
<td>WF⊥ AC</td>
<td>-0.490</td>
<td>-0.498</td>
</tr>
</tbody>
</table>

It seems that the OCP of the coating sample WC=AlF has increased from -0.392 V to -0.389 V. On the contrary, all other coating samples showed a higher initial OCP, tending to a decreased potential. In this study, the open circuit 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 corrosion. Figure 5 shows the potentiodynamic polarization curves of the plasma-sprayed coatings by using perpendicular and parallel deposition techniques in 3.5%NaCl. It can be seen all coatings indicated typical pitting corrosion behavior, with a breakdown potential, as evidenced by the hysteresis loop formed by the forward and reverse potentiodynamic scan [19]. As shown in Fig 5.a the coating sample WC=AlF showed passivity breakdown at -0.35 V while the coating sample WF=AlC showed passivity breakdown at -0.3 V. It is also shown that WF=AlC had greater anodic dissolution than WC=AlF and its polarization curve shifted to the left, which means that WC=AlF showed better corrosion resistance than the WF=AlC. In Fig. 5.b the coating sample WC⊥ AlF indicated passivity breakdown at -0.2 V while the coating sample WF⊥ AlC showed passivity breakdown at +0.01 V. It is also seen that a large passive range ~ 0.32 V for the coating sample WC⊥ AlF. In addition the coating sample WF⊥ AlC showed greater anodic dissolution compared with WC⊥ AlF which means that the coating sample WC⊥ AlF is better corrosion resistant than the coating sample WF⊥ AlC. Corrosion current density (Icorr) is directly proportional to the corrosion rate of the material. The corrosion current density of the samples were determined from the potentiodynamic polarization curves using Tafel extrapolation method and summarized in Table (5). It is obvious that, the coating sample WC= AlF has the least corrosion current density 0.301 µA/cm² with most noble corrosion potential -0.362 V. The WF= AlC comes next with Icorr 0.5015 µA/cm². Both samples were coated by parallel deposition technique but the difference is that the WC= AlF sample was coated by Coarse Tungsten Carbide and Fine Aluminum Oxide while the WF= AlC was
coated by Fine Tungsten Carbide and Coarse Aluminum Oxide. The third smallest corrosion current rate was that of WC ┴ AlF 2.4974 μA/cm², which is sprayed by perpendicular deposition technique and was coated by Coarse Tungsten Carbide and Fine Aluminum Oxide. Finally the highest corrosion current density was that of WF┴ 10.1575 μA/cm², and that sample was coated by perpendicular deposition technique and was coated by Fine Tungsten Carbide and Coarse Aluminum Oxide. No doubt, the grain size and its order as well as the direction of coating have prevalent effects on both the surface topography and the indentation microhardness of the coated face which has consequently affected the corrosion resistant property. In addition to that, through the overlapping of one lamination over the other, the sprayed coating is built up. An improved structure, "i.e. a less porous structure with a better bond" can be achieved when the new lamination of droplets take up their natural form inbetween the other previous laminations [20].

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 corrosion potential values of the parallel-coated samples were higher than values of the perpendicular coated samples, which leads to indicate that 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 [21]. Another observation, the grain type combination also showed a great influence on the corrosion behavior of the plasma coatings [22], the coarse WC-12% Co covered by fine Al2O3 showed a much better corrosion resistance than the fine WC-Co covered by coarse Al2O3. The reason is that the WC-12% Co is the first layer deposited on the substrate surface and then the Al2O3 is deposited on this coating layer. Coarse grains have much more microcracks and pores than the fine grains. So when this layer combination of plasma coat was made the fine Al2O3 made a strong barrier and cover for the microcracks and pores in the coarse grains of WC -12% Co. 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 WC-12% Co coarse grains. So this combination of grains decreased the rate of uniform corrosion and showed a better corrosion behavior than the other combination which was fine WC-12% Co covered by coarse Al2O3.

3.2.1 Microstructure of corroded specimens

The SEM micrograph of the surface morphology of coated specimens after corrosion test is given in Fig.6. The figure shows clearly the pitting corrosion in all samples and it shows general corrosion in the perpendicular coated samples. Apparently, Fig. 6(a, b) shows that parallel coating specimens are more corrosion resistance than the perpendicular specimens. In addition the parallel coating specimen WC= AlF in Fig. 6a is very good corrosion resistance. The perpendicular coating specimen WC ┴ AlF in Fig. 6-c is more corrosion resistance than WF┴ AIC. As shown in Fig. 6-d WF┴ AlC suffered severe corrosion. The microstructure confirms the results obtained from polarization curves and OCP.

4. Conclusion

The Corrosion behavior and performance of Plasma WC-12% Co/Gray Al2O3 Coatings on AISI 304L stainless steel surface has been studied related to the deposition parameters, Grain types (fine and coarse grains). Based on the above results and discussion, it can be concluded that:

1- This work display 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

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Table 5. Electrochemical parameters calculated from the polarization curves.

<table>
<thead>
<tr>
<th>Coating Cases</th>
<th>E_Corrosion (V)</th>
<th>I_Corrosion (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC= AF</td>
<td>-0.362</td>
<td>0.301</td>
</tr>
<tr>
<td>WF= AC</td>
<td>-0.462</td>
<td>0.5015</td>
</tr>
<tr>
<td>WC ┴ AF</td>
<td>-0.538</td>
<td>2.4974</td>
</tr>
<tr>
<td>WF ┴ AC</td>
<td>-0.406</td>
<td>10.1575</td>
</tr>
</tbody>
</table>
well as the amount of expensive fine grain sized powder.

2. The surface roughness of plasma spray coating plays an important role in determining the mechanical and corrosion performances of WC-12% Co/Al2O3 bilayer coatings.

3. The parallel coating deposition process indicate high values of microhardness than the perpendicular coating deposition technique.

4. The parallel layers of plasma coatings deposition technique had a better corrosion behavior and resistance than the perpendicular plasma coatings.

5. The parallel layers of coating specimen WC=AlF has the best corrosion resistance between the coated specimens with lowest current density 0.301 µA/cm².

6. 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 Al2O3 showed a much better corrosion resistance than the fine WC-12% Co covered by coarse Al2O3.

Fig. 6. SEM of corroded surface of (a) WC=AlF (b) WF= AlC (c) WC┴AlF (d) WF┴ AlC

References


