WC-CoCr Coatings Sprayed by High Velocity Oxygen-Fuel (HVOF) Flame on AA7050 Aluminum Alloy: Electrochemical Behavior in 3.5% NaCl Solution

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In the present work, the electrochemical behavior of WC-CoCr coatings with 10 (W10), 15 (W15) and 20 (W20) torch passes sprayed by High Velocity Oxygen-Fuel (HVOF) flame on AA7050 aluminum alloy substrate, evaluated in 3.5% NaCl solution, were compared using open-circuit potential (Eoc) measurements, electrochemical impedance spectroscopy (EIS) and polarization curves. The coating surfaces and their cross sections were characterized by X ray diffraction and the Rockwell-C hardness test, and also by optical (OM) and scanning electron microscopy (SEM) before and after the corrosion tests. The electrochemical data showed that sample W10 presented higher corrosion resistance than the others in chloride solutions. In some tests, aluminum salts on the coating surface were identified by EDS, indicating the corrosion of the substrate. And using aluminon, aluminum ions were detected and analyzing the surface via stereomicroscopy, hydrogen bubbles were observed, both showing that the electrolyte reached the substrate and galvanic corrosion possibly occurred. The physical characterization showed that sample W10 presented a lower number of cracks and pores, justifying its higher corrosion resistance.

Keywords: corrosion resistance, EIS, HVOF, WC-CoCr, aluminum alloy

1. Introduction

Aluminum alloys have been chosen for the production of structural components of aircraft since about 1930. Although polymer matrix composites are being used extensively in high-performance military aircraft and also specified for some applications in modern commercial aircraft, AA7050 aluminum alloys are the overwhelming choice for the plate, extrusions, hand and die forgings of aircraft structural parts. Other applications require very high strength materials coupled with high resistance to exfoliate corrosion, avoid stress-corrosion cracking and promote high fracture toughness and fatigue resistance1,2.

All structural materials are susceptible to some degradation from the environment, and aluminum alloy products used in aircraft are not an exception. Aluminum alloy products corrode in a localized manner either by pitting, intergranular attack or exfoliation3,4. It is well known that pitting corrosion in the AA7050 aluminum alloys is usually associated to constituent particles, and pitting may have a marked effect on the fatigue properties of these materials. Also, light metals in general exhibit very poor tribological properties resulting in severe superficial wear5.

To increase the corrosion resistance and improve tribological properties of aluminum alloys in highly erosive environments, high-wear and corrosion-resistant coatings are proposed and these are sprayed onto the alloy using the HVOF (High Velocity Oxy-Fuel) method. The thermal spray process is by far the most versatile modern method for surface treatment in terms of economy, range of materials applied and protected, and the scope of application6. The HVOF powder spray process represents a state-of-the-art method to apply thermal spray metallic coatings. It combines a fuel like kerosene, propylene, and so on, which burns with a large amount of oxygen to produce a flame with a relatively low temperature (around 3000 °C) and an extremely high gas-molecule velocity. This velocity may reach values near 2000 m/s (for HVOF) in contrast to about 100 m/s (flame spraying) or 1000 m/s (plasma spraying). It can result in very dense and tightly adherent coatings, having low residual stresses with little or no oxidation6. Thus, the HVOF process can be largely used for applying powder materials with a relatively low melting point and those which are subjected to thermal degradation at high temperatures7.

When coatings are applied using a high quality process and under strict quality control procedures, the coatings can provide a very effective barrier to prevent any corrosion occurring at the coating/substrate interface. In this situation, it is very important to consider that coating corrosion itself can occur and its initiation and propagation associated with composite microstructure features are of great importance. The three main issues related to the corrosion performance of thermal spray coatings are (i) protection of the substrate, (ii) corrosion of the coating itself, and (iii) galvanic processes between the coating and the substrate8.

Powders sprayed using HVOF can afford different coating properties according to their manufacturing, initial characteristics (composition, shape, morphology, etc.) and spray parameters. The cermet powders consisting of carbides and metallic binder are highly suitable for HVOF spraying because the high velocities and low temperatures involved cause no melting of carbides, diminishing their thermal degradation. Thus, carbide-based powders such as WC-CoCr
and Cr, Cr2-NiCr are the best candidates for application using HVOF. The first one provides hard and dense coatings with good adhesion and resistance against abrasion and erosion, particularly in aqueous solutions, and the second exhibits good friction resistance, high resistance against abrasion, erosion and corrosion at temperatures up to 815 °C, not exceeding 900 °C, and also high corrosion resistance in gases containing sulphur. Among numerous types of thermal spray coatings, the tungsten-carbide/cobalt based ones are widely used in industry, in general to protect steels, when abrasion, sliding, fretting, corrosion and erosion resistance are required. The WC-CoCr coatings are also used as an alternative to hard chromium plating. The hard WC particles in the coating provide high hardness and wear resistance, while the metal binder (CoCr, Ni or Co) gives the necessary coating toughness. Almost all applications have been made on steels, being scarce on aluminum and their alloys mainly due to the residual stress. For aluminum alloys and other light metals or their alloys covered with ceramic coatings, the high contraction of the substrate during the cooling period causes compressive thermal stresses due to their low coefficient of thermal expansion. As a consequence, coating delamination at the coating/substrate interface and/or within the coating can occur. So successfully applying these coatings on aluminum alloys is still a difficult task. Although some thermally sprayed coatings have been recently applied on aluminum and other substrates, no significant effect of the substrate on their mechanical and tribological properties was observed. However, only morphological and mechanical characterization was performed on these coating/aluminum-based systems and no electrochemical studies were found. This means that this work is one of the first to deal with electrochemical tests of WC-based coated aluminum alloys. Considering the possible applications of these coatings in different environments composed mainly of water-based solutions containing soluble salts, it is very important to investigate their corrosion behavior in aqueous medium.

In this work, the corrosion resistance and some mechanical properties of WC-CoCr thermal spray coatings sprayed on an AA 7050-T7 aluminum alloy with different numbers of torch passes were studied. The corrosion resistance was studied using electrochemical techniques: open-circuit potential (E_{ocp}), electrochemical impedance spectroscopy (EIS), and polarization measurements (CP) in unstirred and aerated 3.5% NaCl solution.

2. Experimental Procedure

An AA 7050-T7 aluminum alloy with a nominal composition of 6.1 wt. (%)Zn, 2.2 wt. (%)Cu, 2.1 wt. (%)Mg, 0.05 wt. (%)Si, 0.08 wt. (%)Fe, 0.01 wt. (%)Mn, 0.0 wt. (%)Cr, 0.11 wt. (%)Zr, 0.02 wt. (%)Ti and the balance being Al was used as substrate. Prior to the spraying process, rectangular (100 x 20 x 5 mm³) samples were degreased with acetone and grid blasted with Al₂O₃ (grade 24) to get a surface with a mean roughness of around 5 µm.

The WC-CoCr coatings were obtained via HVOF spraying (CPT-Universitat de Barcelona) using a DJH 2700 gun, applying 10 (W10), 15 (W15) and 20 (W20) torch passes, using an oxygen (253 L/min) and propylene (69 L/min) mixture to partially melt the powder particles and spray them onto the aluminum alloy substrate. The powder selected was a commercial 86WC-10Co4Cr (wt. (%)) from Sultzer Metco, Diamalloy 5844, which is an agglomerated sintered powder having a particle size of 45 ± 11 µm, and also a cobalt-chromium matrix with well-distributed fine WC particles (average size of 1 µm).

In this work, we decided to study only samples prepared with a number of torch passes equal to or less than 20, to avoid the formation of visible cracks, which result from inappropriate coatings. These coating thicknesses were chosen for the following reasons: Studies of cermet coatings on steel substrate showed that increasing the thickness of a nobler coating implies in an increase of the barrier effect, delaying the electrolyte attack and consequently, increasing the corrosion resistance. In thermal spray technique, especially for HVOF, thick coatings accumulate stresses, which can cause a detachment at the coating/substrate interface as a means of relieving this stress. But there is another way to relieve stress, as can be seen in Figure 1, which can be influenced by the number of torch passes. The effect of the number of torch passes can be visibly seen for coated aluminum alloys: in Figure 2a, the coating was built up with 30 torch passes (a thinner sample) while in Figure 2b, 20 torch passes were applied onto the aluminum alloy substrate. It is possible to observe cracks on the surface of the sample prepared with 30 torch passes and immediately after spraying some coating fragments were expelled out from it, indicating a highly stressed coating.

The microstructure of all coatings was studied using a scanning electron microscope (SEM) coupled to an X-ray energy dispersive analyzer (EDS). The coating thickness was evaluated from digital optical micrographs using MATROX INSPECTOR image software, and the following coating thickness values were found: 180, 280 and 370 µm for W10, W15 and W20 samples respectively. An Otto
Wolpert–Werke indenter was used for the Rockwell C with a load of 1471 N for the adhesion tests (CEN/TS 1071-8 standard). This test method causes layer damage adjacent to the boundary of the indentation. On each sample, three indentations were produced.

The corrosion resistance of the coated aluminum alloy was evaluated by electrochemical measurement of the as-sprayed HVOF coated samples in 80 mL of aerated and unstirred 3.5% NaCl solution at 25 °C. An Ag|AgCl|KCl(sat.) electrode connected to the working solution through a Luggin capillary was used as reference along with a Pt network as auxiliary electrode.

Finally, a working electrode of each coated sample was placed at the bottom of an electrochemical cell, exposing a geometric area of 0.8 cm² to the solution.

The E_{oc} and EIS measurements were made using EG&G Parc-273 and Solartron-S11255 systems. The EIS tests were performed applying 10 mV (rms) to the E_{oc} value, starting from 5 x 10^4 to 10^{-2} Hz with 7 points/decade once the open-circuit potential attained an almost constant value, which meant that a steady-state condition had been reached (26 hours of immersion). Polarization curves were recorded after the EIS experiments for all samples in the potential range of −150 to +350 mV vs. the E_{oc} at 0.166 mV/s using an EG&G Parc-273 potentiostat coupled to a PC.

The surface of the W15 sample was examined during the immersion tests (up to 8 hours) in 3.5% NaCl + aluminon solution using a stereomicroscope model QUMIN Q734- ZT. The aluminon (C_{22}H_{23}N_{3}O_{9}), a reagent confected using Aurintricarboxylic Acid and Ammonium Salt, which turns red in the presence of aluminum ions.

### 3. Results and Discussion

#### 3.1. Structural characterization:

**WC-CoCr powder and coatings**

Figure 3 shows micrographs of the powder used to obtain the coatings. It is possible to observe that pores are present, which could facilitate heat distribution and promote better particle melting or semi-melting.

To characterize the powder, a XRD pattern (Figure 4) was recorded and phases, such as WC, Co₄W₂C and Cr were identified.
(Figure 4a). When the powder was submitted to the HVOF flame, some changes on the XRD pattern were observed. The following phases were found in the coating: WC, W2C, CoO, W and Cr2O3-CoO (Figure 4b). Phases W, CoO, W and Cr2O3-CoO derived from the thermal decomposition of the powder during spraying.

Figure 5 shows SEM images for sample W15 as-sprayed using the HVOF technique. W15 and W20 samples presented a high quantity of pores and cracks, mainly on sample W20. On the contrary, sample W10 is homogeneous, well-compacted, and the WC phase is well-distributed such that there is a lower quantity of pores; and cracks were not observed in this coating.

3.2. Electrochemical characterization

3.2.1. Open-circuit potential (EOC) measurements

For all samples, the EOC values were measured for 26 hours of immersion in 3.5% NaCl solution (Figure 6). For all samples and until 5 hours of immersion, the open-circuit potential increased. The potential oscillations observed in all curves can be related to the electrolyte penetration and hydrogen bubble formation by the chloride attack, mainly to the substrate. For AA 7050 aluminum alloy, the EOC stabilized around -0.60 V. For samples W15 and W20, the EOC values increased up to the 5 and 10-hour mark, respectively, and after diminished to reach a stabilized value at around -0.78 V, which is lower than that measured for the aluminum alloy. For W10, the EOC increased slowly up to the end of the experiment (around -0.5 V). The continuous increase in the EOC values for the W10 sample could be mainly associated to the aluminum oxide/hydroxide formation inside and at the bottom of the pores, suggesting a slight attack on the aluminum alloy and/or to the coating itself (metallic matrix). It is well-known that coatings prepared using HVOF present lower porosity than coatings prepared using other thermal spray techniques, but considering the corrosion resistance, this porosity is enough for the electrolyte to penetrate and attack the substrate. For samples W15 and W20, more oscillation occurred in the EOC values than for the W10 sample, which can be attributed to the increase in the number of pores and cracks in the thicker coatings. Other reasons for potential oscillations can be attributed to the different reactions involving chloride attack mainly to the substrate resulting in pitting corrosion, hydrogen evolution and galvanic micro-cell formation between the tungsten carbide, matrix phases and the substrate. Additionally, due to the higher stress present in the thicker coatings, delamination between layers inside the coating and near the substrate was observed. It is possible that the EOC values for samples W15 and W20 after 10 hours of immersion reflect a high influence of the pitting potential value, while for the aluminum alloy substrate, a pitting / repassivation process is still occurring as time passes during the experiment, producing an almost constant and higher potential. Probably, the EOC value for the aluminum alloy diminishes at much longer immersion times, when pits are larger and no repassivation is possible. Therefore, one possible path for electrolyte to penetrate up to substrate is through cracks, pores and inner layers or coating detachment.

The presence of pores and cracks, mainly for thicker coatings sprayed on light metals or their alloy, can be related to the thermal stress. Thermal stresses appear when materials are heated or cooled causing thermal effects and defects in the materials. Some of these thermal effects include thermal stress, strain, and deformation. The first effect here considered is thermal deformation. Thermal deformation simply means that as the “thermal” energy (or temperature) of a material increases, the vibration of the atoms/molecules that comprise the material also increases, which results in what can be considered a stretching of the molecular bonds, causing the material to expand.

One problem of these coatings is how to know when the electrolyte has reached the substrate. According to literature, Al3+ ions react with aluminon (trimmonium salt of aurin tricarboxylic acid) to form a dye, which has been used for the colorimetric determination of Al(III) species. Thus, a 3.5% NaCl + aluminon solution was prepared and used as electrolyte. When the chloride ions reached the substrate, as the Al substrate is less noble than the coating, its corrosion is accelerated via a galvanic process. As a result, Al3+ ions are liberated into the solution and a red complex with aluminon is formed. Using a stereomicroscope coupled to a camera and a computer, it was possible to observe the coating surface for long immersion times (Figure 7). Figure 7a and b shows the surface of sample W15 where no bubbles or red points are seen. After two hours of immersion, red spots are observed at the sample surface due to the complex formation indicating the penetration of the electrolyte through the coating and reaching the substrate. Thus, it is clear that the aluminum corrosion process has already started. After three hours (Figure 7c), hydrogen bubbles also appeared on the surface. Increasing the immersion time, the attack on the substrate continued and the corrosion products increased on the coating surface (Figure 7d). The same test was performed for samples W10 and W20. Hydrogen bubbles and red spots were only observed...
after 6 hours of test for sample W10 while they were observed after a shorter time for sample W20 than for W15.

3.2.2. EIS measurements

Figure 8 shows the impedance diagrams for samples W10, W15 and W20 obtained after 26 hours of immersion in unstirred and aerated 3.5% NaCl solution. The complex plane plots (Figure 8a) for sample W10 show one well-defined semicircle at high frequencies and another not well-defined at low frequencies; while for samples W15 and W20 only one time constant was observed. The time constant for sample W15 appeared at intermediate frequencies. This means that for sample W10, the first process occurring at higher frequencies (1-10 Hz) and with a phase angle around 70 degrees (Figure 8b) is related to the coating, and that the one appearing at lower frequencies (0.1-0.01 Hz) and having a phase angle below 30 degrees is due to the substrate. In the case of samples W15 and W20, only one time constant at low frequencies was observed, which was mainly attributed to the substrate response, since the coating itself of sample W20 cannot protect the substrate against corrosion in 3.5% NaCl solution. The highest total impedance value was obtained for sample W10.

It is also observed that as the number of torch passes increases, the total impedance value decreases. The total impedance values were: around 30, 1 and 0.4 kΩ for samples W10, W15 and W20, respectively. This means that the thermal stress within the coating depends on the number of torch passes and influences the corrosion resistance values of the coating/substrate system.

A similar analysis can be made from the phase angle read from the Bode plots. The maximum phase angles for samples W10, W15 and W20 are 70, 45 and 38 degrees respectively. This indicates that sample W10 presents the most capacitive behavior when compared to the others. This fact can be attributed to the structure of the W10 coating, which due to its lower thickness and defect concentration is less stressed than the others. Due to these factors, it can delay the electrolyte attack on the aluminum substrate. Therefore, the electrolyte takes more time to penetrate the coating and reach the substrate. For samples W15 and W20, the lower phase angles observed are related to a higher accumulation of stress and defects, which facilitate the attack on the substrate by the electrolyte, diminishing the capacitance and resistance of the coating/substrate system. Defects are more easily attacked by the electrolyte, increasing the coating...
porosity, facilitating electrolyte penetration to within the coating, and consequently promoting corrosion reactions. When only one time constant is observed (samples W15 and W20), an overlapping of two time constants may have occurred, since the time constant related to the coating may have moved to lower frequencies and that related to the substrate may have moved to higher frequencies. This phenomenon occurs when the coating is degraded and the substrate is easily reached by the electrolyte.

Figure 9 shows EIS diagrams for sample W10 as a function of the immersion time. The total impedance value decreased with time, indicating a deterioration of the coating and substrate. This means that the coating only acts as barrier against electrolyte penetration for a certain period, which was higher for sample W10 than for the others. These results call attention to the importance of diminishing the level of stress in the coating, since the consequence is the formation of pores and cracks. The stress can be reduced by optimizing all spraying parameters, mainly when light metallic materials (soft materials) are coated with hard metallic-ceramic coatings.

As the sample thickness can be a cause of stress, it is important to remember that the thickness values measured for samples W10, W15 and W20 were: 180, 280 and 370 µm, respectively, and each torch pass layer (sublayer) had a thickness of around 19 µm.

After the immersion tests, the samples were observed using a SEM and for the W10 sample no cracks or delamination was observed even after 30 hours of immersion in 3.5% NaCl solution. However for samples W15 and W20, delamination between the sublayers was observed after 30 hours of immersion in the electrolyte (Figure 10). This occurred because when the electrolyte penetrates the coating, a galvanic pair can be formed between the coating and substrate accelerating the corrosion process. Corrosion products such aluminum and other ions can be formed and diffuse out of the coating surface, and salts can also precipitate within the coating between the coating sublayers (those formed in the successive torch passes) and at the coating/substrate interface, causing coating detachment from the substrate. The detaching of the coating may also be related to stress created during the thermal spray process and stress created by the salt precipitation within the coating and at the coating/substrate interface.

### 3.2.3. Polarizations curves

After EIS measurements, polarization curves were obtained (Figure 11). As expected and based on the results obtained from the other techniques, sample W10 presented a higher corrosion potential and a
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Figure 10. SEM cross-section images for sample W15 (a, b) and sample W20 (c) after 30 hours immersed in aerated and unstirred 3.5% NaCl solution.

Figure 11. Polarization curves for samples W10, W15, W20 and AA7050 Al alloy in aerated and unstirred 3.5% NaCl solution after 26 hours of immersion at 25 °C and at 0.166 mV.s⁻¹.

lower corrosion current. The corrosion potential values were: –0.58 V (sample W10), –0.67 V (AA7050 aluminum alloy), –0.78 V (samples W15 and W20) and the corrosion current values were: 1.4 µA.cm⁻² (sample W10), 1.7 µA.cm⁻² (AA7050 aluminum alloy), 5.0 µA.cm⁻² (sample W15), and 6.4 µA.cm⁻² (sample W20), suggesting that the thermal stress and defects define the behavior of the coating.

3.3. Rockwell-C hardness tests

In this work, one of the most important aims was to make the coating adhere to the substrate surface. As the thermal expansion coefficients (CTE) of the coating and the aluminum alloy are very different, during the cooling of the sample, the high contraction of the light metallic alloy (substrate) causes compressive thermal stress in the coating, mainly in the ceramic coating materials due to their low CTE values. This can cause coating delamination in the coating/substrate interface or within the coating itself. The thermal stress can also be related to the thickness of the coating mainly for substrates with low hardness and low melting point compared to that of the coating.

A qualitative indication of the effect of the stress accumulated in the coatings was assessed by a Rockwell-C hardness tester, using the same load (1471 N) for all samples.

Figure 12 shows micrographs of sample W5 (a sample with 5 torch passes, prepared only for the hardness measurement), and of samples W10, W15 and W20 after the Rockwell-C hardness measurement. Comparing the images of samples W5 and W10 (Figure 12a and 12b), it is possible to observe a lower number and smaller cracks than is seen for samples W15 and W20 (Figure 12c and 12d). Literature suggests that a small number of radial cracks (less than five) is evidence of good adhesion and toughness; whereas the presence of both branched (ramified) cracks and lakes of delamination mean low adhesion between the sublayers.

Important information can be also obtained from Figure 13, which shows a SEM cross-section image of sample W20 after the electrochemical measurement was taken. It is possible to observe a cracked structure and this rupture can be attributed to the Al salts that precipitated into the coating, which increase the stress present between layers, causing a detaching of the outer layers.

Another indication of the presence of stress between sublayers can be seen for sample W10 in Figure 14. The distance between cracks...
is around 20 µm (20.8, 18.3, 24.5 and 17.3 µm without angle correction) in the outer sublayers. This information helps us to explain the reason why samples with lower thickness presented higher corrosion resistance; and this was found to be as a consequence of their lower thermal stress thus giving a lower defect concentration.

4. Conclusion

During the building up of the WC-CoCr coating using the high velocity oxy-fuel (HVOF) spraying process, new phases such as W₂C, CoO, W and Cr₂O₃-CoO were produced, which were not present in the original powder.
The number of torch passes influences the electrochemical behavior in 3.5% NaCl solution for coatings sprayed via HVOF on AA7050 aluminum alloy substrate. The thinner coating presented the highest corrosion resistance.

Sample W10 showed no cracks and/or coating detachment after immersion in NaCl solution for 26 hours, probably due to the lower thermal stress created during the thermal spray process.

The number of cracks and pores are higher for samples W15 and W20 and are responsible for electrolyte penetration into the coating, which leads to lower corrosion resistance in NaCl solution. For these samples, after only two hours of immersion in chloride solution, aluminum ions and bubbles of hydrogen were detected on the coating surface, clearly indicating the chloride attack on the substrate.

All electrochemical techniques used gave coherent results indicating the W10 coating as the best among the coatings studied.

Comparing samples W15 and W20, it is possible to observe a higher number of cracks for sample W20 than for W15. This may be due to the higher thermal stress detected in sample W20. And finally, the Rockwell-C hardness tests indicate a low adhesion between sublayers for thicker samples, which could contribute to increase the number of cracks and pores.

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