Corrosion–fatigue properties of a 4340 steel coated with Colmonoy 88 alloy, applied by HVOF thermal spray

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Abstract

The corrosion–fatigue behavior of a quenched and tempered AISI 4340 steel has been evaluated under two different conditions: (a) uncoated; and (b) grit-blasted with alumina and coated with a thermal-sprayed Colmonoy 88 alloy (220 \( \mu \)m in thickness), employing a high-velocity oxygen fuel (HVOF) gun. The tests were conducted under rotating bending conditions employing a 4-wt.% NaCl solution. The results indicated that the fatigue behavior of the coated material under this condition is very similar to that previously reported after testing in air. The fatigue cracks were nucleated at the alumina particles deposited in the matrix of the substrate steel during blasting rather than at corrosion pits formed during testing. Therefore, the corrosion–fatigue strength of the coated substrate has been found to be controlled by the same mechanism that governs the fatigue behavior of the material in air. The fatigue strength of the uncoated substrate tested in the NaCl solution has also been found to be significantly less than that in air and that, if the substrate steel is coated with the Colmonoy alloy, its corrosion–fatigue life increases substantially. The microscopic observation of the fracture surfaces also showed that under some alternating stress conditions, the substrate–deposit interface can be severely cracked giving rise to the detachment of the deposit from the substrate steel. The fatigue performance of the material under the two conditions analyzed has been quantified by determining the Basquin parameters from the fatigue life curves obtained. \( \copyright \) 2001 Elsevier Science B.V. All rights reserved.

Keywords: Corrosion–fatigue behavior; HVOF; Colmonoy 88 alloy

1. Introduction

It is a well-known fact that both ceramic and metallic coatings deposited by thermal spraying can improve a number of surface properties of metallic substrates such as abrasive wear, thermal exposure, oxidation, chemical attack and corrosion, which make them suitable for their employment in many different fields such as automotive, aircraft, military, steelmaking and energy. Also, such deposits are widely used for restoring worn or undersized high strength steel parts and components which, in service, could be subjected to severe cyclic loading under aggressive environments and therefore where corrosion–fatigue properties could be of utmost importance. In spite of this, the study of the corrosion–fatigue behavior of metallic substrates thermally sprayed-coated with such deposits has been rather limited [1–5].

Tokaji and co-workers [5], for example, carried out
an investigation on the corrosion–fatigue behavior and fracture mechanisms of a medium carbon steel coated with different sprayed materials. In this investigation, samples of the steel substrate were thermally sprayed with Cr$_2$O$_3$, WC-12% Co, Ni-11% P and Al-2% Zn and tested under rotating bending conditions in a solution of 3% NaCl. Some of the Cr$_2$O$_3$ coatings were deposited as a top coating on a layer of Ni-5% Al previously sprayed on the fatigue specimens. According to the authors, the corrosion–fatigue process of the first three coatings was basically the same, in the sense that the corrosive fluid could be supplied from the surface of the coating to the substrate through cracks that were initiated during fatigue cycling, as well as pores present in the coatings.

Therefore, corrosion pits were generated in the substrate that gave rise to the subsequent nucleation of fatigue cracks. However, it was also reported that when the Cr$_2$O$_3$ deposits were sprayed on the Ni-Al undercoatings, the corrosion–fatigue strength of the composite material was slightly improved as compared with the uncoated substrate, since the undercoating layer could impede the penetration of the corrosive fluid. Also, the samples sprayed with WC-12% Co coatings exhibited improved corrosion–fatigue strength because of the high cracking resistance of the ceramic deposit and its low porosity.

On the contrary, the Ni-11% P coatings showed poor cracking resistance and therefore, the corrosion–fatigue properties of the deposited samples was similar to that observed for the uncoated substrate. Finally, the Al-2% Zn coatings displayed anodic dissolution with consequent cathodic protection of the substrate, leading to a corrosion–fatigue resistance of the composite material similar to that observed for the substrate tested in air. This investigation concluded that a dual coating consisting of a WC-12% Co on an undercoating of Al-2% Zn was very effective at low alternating stresses and gave rise to an incremental improvement in the corrosion–fatigue properties of the substrate steel.

Thus, the present investigation has been conducted in order to study the corrosion–fatigue behavior of an AISI 4340 steel which has been oil-quenched and tempered prior to grit blasting with Al$_2$O$_3$. It was coated using HVOF thermal spray with Colmonoy 88 (a Ni–W–Cr–Si–Fe–B–C alloy) of approximately 220 μm in thickness to compare the results obtained with those of the uncoated steel, in order to quantify the effectiveness of such a metallic coating in improving the corrosion–fatigue strength of the substrate material.

2. Experimental techniques

The present investigation has been carried out with samples of an AISI 4340 steel with the following composition (wt.%): 0.41 C; 0.69 Mn; 0.24 Si; 0.25 Cu; 0.79 Cr; 0.23 Mo; and 1.73 Ni. This material is widely used in the production of automotive crankshafts and rear axle shafts, aircraft crankshafts, connecting rods, propeller hubs, gears, drive shafts, landing gear parts and heavy duty parts of rock drills. The alloy was provided as bars of approximately 16-mm diameter and 6 m in length. Such bars were cut to pieces of approximately 90 mm in length for machining fatigue samples of a gauge diameter of 6.35 mm, shoulder diameter of 12.7 mm and a curved gauge length of 38.1 mm along the cord, machined following a continuous radius of 58.73 mm. The material was already provided in the quenched and tempered condition from which 50 samples were machined. All the specimens were subsequently ground with successive SiC papers grit 100–1200 and polished mechanically in order to have similar polished, mirror-like surfaces before testing.

The 25 samples to be coated were subsequently cleaned, pre-heated and grit-blasted with Al$_2$O$_3$ particles grit 24, at a pressure of 621 kPa and a distance of 30 cm normal to the surface of the specimens. They were then thermally sprayed at Plamatec Ingenieros C.A. (Guarenas, Venezuela), employing a HVOF JP-5000 gun under the following conditions: fuel pressure (kerosene), 1.17 MPa; oxygen flux, 11.75 l s$^{-1}$; nitrogen flux, 0.23 l s$^{-1}$; spraying distance, 330 mm; fuel flux, 0.0063 l s$^{-1}$; and powder (Colmonoy 88) at a feeding rate of 1.5 g s$^{-1}$. The commercial powder employed had the following nominal composition (wt.%): 17.0 W; 15.0 Cr; 3.0 B; 3.5 Fe; 4.0 Si; 0.75 C; and Ni bal.

According to the studies conducted by Gil and Staia [6], this commercial powder has a spherical morphology which is typical of the atomization process employed for powder production. These authors also reported that the particle size varied from 22 to 66 μm (as determined from the laser method) with a circle of an equivalent diameter of approximately 31.5 μm. These results were corroborated by means of image analysis and it was also reported that the form factor of the particles was approximately 0.85. The deposit had a thickness of approximately 220 μm. Gil and Staia [6] also determined the porosity of the sprayed alloy and reported that it was mainly influenced by the spraying distance and that it could vary between approximately 3.7–6.2%.

Regarding the hardness of the coating, Hernández et al. [7] in a previous investigation reported that such a property decreased slightly as the distance from the substrate–deposit interface increased. Near the interface, the hardness was found to be approximately 700 ± 85 HVN$_{300}$, whereas near the surface it was observed to decrease to approximately 650 ± 85 HVN$_{300}$.

Fatigue tests were carried out under rotating bending conditions (Fatigue Dynamics, RBF-200, Walled
Lake, USA) at a frequency of 50 Hz and alternating stresses of 270, 333, 382, 449 and 515 MPa, for the uncoated substrate, which corresponds to 24, 29, 33, 39 and 45% of the tensile strength of the uncoated substrate, respectively. Also, the blasted and thermally-sprayed samples were tested at alternating stresses of 463, 482, 500, 518 and 542 MPa, which corresponds to 50, 53, 54, 56 and 59% of the tensile strength of the substrate, respectively. Thus, in order to determine the corrosion–fatigue strength of each material condition, the number of samples tested exceeded the minimum number of specimens required in S–N testing for reliability data according to the ASTM standard 739 (12–24 samples). Therefore, the testing procedure followed in the present work allowed a replication greater than 80%. It is also important to mention that the alternating stresses applied to the coated samples were calculated taking into consideration the thickness of the deposit. The corrosive medium employed was a 4-wt.% NaCl solution.

The fracture surfaces of some of the blasted and coated samples that failed at a number of cycles close to the mean, at the lowest and highest alternating stresses, were examined by means of SEM techniques, in order to study more closely the initiation sites of the fatigue cracks, the general morphology of the fracture surfaces, the behavior at the substrate–deposit interface and the role of the metallic deposit in the corrosion–fatigue mechanisms of the substrate steel. The SEM observations were conducted on a Hitachi S-2400 (Japan) with EDS facilities, at a constant potential of 20 kV.

3. Experimental results and discussion

3.1. Evaluation of the corrosion–fatigue behavior

As already mentioned, the uncoated samples were tested at alternating stresses in the range of 270–515 MPa, which corresponded to approximately 0.24–0.45 of the ultimate tensile strength (UTS) of the material, whereas the blasted and coated specimens were tested at stresses in the range of 463–542 MPa, corresponding to 0.50–0.59 of the UTS. Thus Fig. 1 illustrates the mean number of cycles to fracture ($N_f$) as a function of the alternating stress applied to the material for the substrate and blasted/coated specimens. For comparison, the behavior of the substrate and coated specimens tested in air has been included. The dashed lines represent the behavior of the coated material taking into consideration the diameter correction.

![Fig. 1. Number of cycles prior to fracture ($N_f$) as a function of the alternating stress applied to the material for the substrate and blasted/coated specimens. For comparison, the behavior of the substrate and coated specimens tested in air has been included. The dashed lines represent the behavior of the coated material taking into consideration the diameter correction.](image-url)

Table 1

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>Number of cycles to fracture</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>351000</td>
<td>398700</td>
<td>405200</td>
</tr>
<tr>
<td>333</td>
<td>272100</td>
<td>278600</td>
<td>317500</td>
</tr>
<tr>
<td>382</td>
<td>134800</td>
<td>147600</td>
<td>150300</td>
</tr>
<tr>
<td>449</td>
<td>81000</td>
<td>81200</td>
<td>84400</td>
</tr>
<tr>
<td>515</td>
<td>58700</td>
<td>61100</td>
<td>62400</td>
</tr>
</tbody>
</table>
if testing is conducted in air. This behavior has been thoroughly investigated in a previous study [7] which resulted in the conclusion that such a reduction can vary between approximately 95.8–97.4%, at alternating stresses in the range of 463–663 MPa. This behavior was found to be associated with the alumina particles that were retained into the matrix near the surface of the specimens, after grit blasting. Such particles were observed to act as stress concentrators that gave rise to the early nucleation of fatigue cracks that subsequently propagated throughout the cross-section of the specimens.

Fig. 1 also shows that when the uncoated substrate is tested in NaCl, the fatigue life of the material is reduced much more significantly. Thus, in the alternating stress range of 590–665 MPa, where the fatigue behavior of the uncoated substrate in air was first evaluated [7], the reduction in fatigue life varies between approximately 81.8–94.5%. However, as expected and observed in curve (b) of Fig. 2, such a reduction is not a linear function of the stress applied to the material, but on the contrary, it is highly nonlinear.

Thirdly, Fig. 1 also illustrates that if the substrate specimens are grit-blasted and HVOF coated with the alloy, the fatigue life displayed by the composite material is very similar to that determined for the coated samples tested in air, without taking into consideration the correction for diameter effects. However, it is also apparent that the effectiveness of the metallic coating in improving the corrosion–fatigue strength of the substrate is significantly dependent on the alternating stress applied to the material. At elevated stresses of the order of 535 MPa both the uncoated and the thermally-sprayed substrates behave very similarly and the reduction in fatigue life of the uncoated steel in relation to the coated condition is only approximately 0.22%.

However, at alternating stresses of the order of 435 MPa, the reduction in fatigue life of the uncoated specimens in relation to the coated ones increases significantly to approximately 94.5%. Curve (a) in Fig. 2 illustrates the change in reduction in fatigue life of the uncoated substrate in relation to the thermally-sprayed one, as a function of the alternating stress, both tested in NaCl. However, these estimations of reduction in fatigue life for the uncoated substrate can be considered as ‘conservative’ since all the calculations were carried out by taking into account the deposit thickness for computing the alternating stresses applied to the coated specimens.

If such stresses were re-computed without considering the thickness of the deposit, the corresponding fatigue curves, as well as the curve that describes the consequent reduction in fatigue life of the uncoated specimens, would be modified as shown by the dashed lines in Fig. 1 and curve (a’) in Fig. 2. Accordingly, in the alternating stress range of 470–535 MPa, the reduction in fatigue life of the uncoated substrate would be much more pronounced, of approximately 99.8–98.2%, respectively. Therefore, it can be concluded that by HVOF coating the base steel with this metallic deposit, it is possible to increase significantly the corrosion–fatigue performance of the substrate in the NaCl solution.

The fact that the number of cycles to failure can be represented as a linear function of alternating stress in a double logarithmic scale indicates the validity of a simple parametric relationship similar to the one ear-

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### Table 2

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>Number of cycles to fracture</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>463</td>
<td>132300</td>
<td>336900</td>
<td>368900</td>
</tr>
<tr>
<td>482</td>
<td>154500</td>
<td>215200</td>
<td>256000</td>
</tr>
<tr>
<td>500</td>
<td>76800</td>
<td>87000</td>
<td>155000</td>
</tr>
<tr>
<td>518</td>
<td>132300</td>
<td>142100</td>
<td>143000</td>
</tr>
<tr>
<td>542</td>
<td>31600</td>
<td>49962</td>
<td>63900</td>
</tr>
</tbody>
</table>

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![Graph](image-url)
Table 3
Parameters involved in the Basquin relationship for the conditions tested

<table>
<thead>
<tr>
<th>Condition</th>
<th>A (MPa)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>13697.5</td>
<td>0.301</td>
</tr>
<tr>
<td>Grit-blasted and coated</td>
<td>919.2</td>
<td>0.050</td>
</tr>
</tbody>
</table>

lier proposed by Basquin [9] for the description of this kind of data, of the form:

\[ S = A N^{-m} \]  \hspace{1cm} (1)

where \( A \) and \( m \) represent constants that depend on both material properties and testing conditions. The fatigue strength coefficient and exponent of the material are represented by \( A \) and \( m \), respectively. Table 3 summarizes the values of the parameters \( A \) and \( m \) for the three sets of data represented in Fig. 1.

The above equation and the correct determination of the parameters involved in it, are of upmost importance for the prediction of the corrosion–fatigue behavior of any component made of this steel that could be thermally-sprayed with this particular deposit, either to improve its corrosion and abrasive wear resistance, or to restore its dimensions after severe wear in service. Thus, such a relationship constitutes the basis for the design of parts and components against high cycle corrosion–fatigue failure in such an aggressive medium.

3.2. Evaluation of the fracture surfaces of the samples

The fracture surfaces of some of the coated samples were examined by means of SEM techniques in order to study more closely their morphology and to assess the role of the Colmonoy 88 deposit in the fracture process. Fig. 3, for example, illustrates the general fracture surface of a specimen tested at an alternating stress of 463 MPa. Thus it can be observed that, after fracture, the Colmonoy deposit looks partially delaminated from the substrate, at the substrate–deposit interface, due to the propagation of secondary cracks. Thus at this particular stress level, it would be expected that the reduction in fatigue strength observed in these samples, in comparison with the behavior displayed by the uncoated substrate tested in air, could in part be related to such a delamination of the coating.

It is believed that the lack of continuity at several locations along the substrate–deposit interface, could leave the substrate material and just part of the deposit

Fig. 3. (a) General fracture surface of a specimen tested at an alternating stress of 463 MPa. The final fracture of the sample occurred due to the propagation of several merging cracks. The origin of two such cracks (A and B) have been pointed out. (b) and (c) represent a detailed view of sites A and B, respectively. In both cases, the nucleation of the fatigue cracks is associated with \( \text{Al}_2\text{O}_3 \) particles (P) that were deposited onto the periphery of the substrate (S) during blasting. The presence of a large number of fracture steps (FST), visible as radial markings emerging from the substrate–deposit interface, indicates the transcryalline propagation of the cracks during early stages of the fatigue process.
as the load-carrying elements of the coated specimen during testing. Therefore, the diameter correction carried out to re-compute the alternating stresses applied to the samples during testing would be only partially justified. However, at present there is not sufficient experimental evidence to show that the coating delaminates prior to failure and therefore, it could also be possible that the entire coating acted as a load-carrying element up until fracture and that delamination occurred at failure.

The analysis of the fracture surface shown in Fig. 3 also illustrates that the fatigue process occurs as a result of nucleation of a large number of cracks along the periphery of the substrate at the substrate–deposit interface.

Two such sites of crack initiation have been identified as A and B. Consequently, the last section of the specimen that failed by ductile fracture is observed to have shifted towards the upper central part of the cross section of the sample. Thus, Fig. 3a, b shows a detailed view of the sites identified as A and B, respectively. Here, it is observed that, similarly to the blasted and blasted/coated samples tested in air [7] under corrosion–fatigue conditions, the final fracture also takes place due to nucleation of fatigue cracks at the Al$_2$O$_3$ particles present in the matrix, deposited during grit blasting. In particular, Fig. 3b shows the presence of a number of fracture steps and radial markings on the substrate, which characterize the transcrystalline propagation of the fatigue cracks from such sites.

On the other hand, Fig. 4a illustrates the general fracture surface of a HVOF coated sample tested at 542 MPa in which again a large number of crack initiation sites at the substrate–deposit interface can be observed. Such sites are revealed by the presence of a number of fracture steps that propagate from the interface as clearly visible radial markings. Fig. 4b–d shows some sections of the fracture surface at the substrate–deposit interface. The fracture steps that emerge from the interface can be seen to be associated with alumina particles that remained from the blasting process.

At this stress level, the deposit is observed to be completely detached from the substrate due to the presence of secondary cracks that run parallel to the interface. Also, at some locations on the fracture surface it was possible to observe few cracks within the Colmonoy deposit, as shown in Fig. 4b,c. Finally, Fig. 5 represents a detailed view of Fig. 4b in which it can be appreciated more clearly the fracture process along the substrate–deposit interface and the fracture steps that emerge from it, indicating again the transcrystalline

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**Fig. 4.** (a) General fracture surface of a coated specimen tested at 542 MPa. (b), (c) and (d) represent a magnified view of sites A, B and C, respectively. Severe secondary cracking (SC) along the substrate (S)–deposit (D) interface can be clearly observed. Locations A and B also show secondary cracks (SC) along the Colmonoy alloy. The three locations also show the presence of Al$_2$O$_3$ particles (P) at the interface.
Fig. 5. Detailed view of Fig. 4b illustrating secondary cracks along the substrate (S)–deposit (D) interface and the Colmonoy alloy. Fracture steps (FST) emerging from the interface are also clearly visible. At this alternating stress level the deposit (D) is almost completely detached from the substrate (S).

propagation of the main fatigue crack during the early stages of the fatigue process.

These microscopic observations provide an explanation for the fatigue results presented in Fig. 1, which indicate that under the present conditions the Colmonoy 88 deposit exerts effective protection of the substrate against the action of the corrosive fluid. Thus, it is apparent that the time required for nucleation of the fatigue cracks at the alumina particles deposited at the substrate surface after blasting, and their subsequent propagation, is much shorter than that required for the penetration of the NaCl solution through the coating and the formation of corrosion pits on the substrate periphery that subsequently gave rise to the nucleation of fatigue cracks at such sites.

This fracture mechanism differs significantly from that described by Tokaji and co-workers [5] for the materials analyzed, according to which the corrosive medium is supplied to the surface of the substrate through cracks initiated during fatigue cycling and/or pores present in the coating. Accordingly, once the corrosive solution reaches the steel substrate, corrosion pits are formed and the adjacent interface delaminates. Subsequently, cracks are initiated from the corrosion pits and the final fracture occurs due to the propagation of the cracks. Therefore, according to these authors, the controlling mechanism during the corrosion–fatigue testing of the coated samples would be the transportation of the corrosive solution and consequently, the corrosion–fatigue strength would be significantly influenced by the resistance of the coating to cracking under cyclic loading, the volume fraction of pores present in the deposit and its adhesive strength.

The present work, on the contrary, indicates that the corrosion–fatigue strength of the coated substrate is controlled by the same mechanism that governs the fatigue behavior of the material in air, namely the presence of alumina particles in the substrate matrix at the substrate–deposit interface which act as fatigue initiation sites.

4. Conclusions

The corrosion–fatigue behavior of a quenched and tempered AISI 4340 steel previously blasted with Al₂O₃ particles of grit 24, at a pressure of 621 kPa, subsequently HVOF thermally spray-coated with Colmonoy 88 alloy of approximately 220 μm in thickness and tested in a 4-wt.% NaCl solution, has been found to be very similar to that previously reported after testing in air. The microscopic observations of the fracture surfaces of the samples tested indicated that the fatigue cracks were nucleated at the alumina particles deposited in the matrix of the substrate steel during blasting rather than at corrosion pits formed during testing. Therefore, the corrosion–fatigue strength of the coated substrate has been found to be controlled by the same mechanism that governs the fatigue behavior of the material in air. The fatigue strength of the uncoated substrate tested in the NaCl solution has also been found to be significantly less than that in air. At
alternating stresses in the range of 590–665 MPa, the reduction in fatigue life has been observed to vary between 81.8–94.5. However, if the substrate steel is coated with the Colmonoy deposit, its corrosion–fatigue life is increased substantially. Thus, in the stress range of 435–535 MPa, the reduction in fatigue life of the uncoated substrate, in relation to the Colmonoy-deposited steel was observed to vary between approximately 0.22–94.5%, this without taking into account the diameter correction for the calculation of the alternating stress. If such a correction is taken into account, the reduction in fatigue life increases to approximately 99.8–98.2% in the same stress range. The microscopic observation of the fracture surfaces also indicated that under some alternating stress conditions, the substrate–deposit interface can be severely cracked giving rise to delamination of the deposit from the substrate steel.

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