Microstructure of Coatings Obtained by High Velocity Oxygen-Fuel Spraying (HVOF)

P.H. Suegama[1]; C.S. Fugivara[1]; A.V. Benedetti[1*]; J. Fernández[2]; J. Delgado[2] and J.M. Guilemany[2]
[1]Dep. Físico-Química, Instituto de Química, Universidade Estadual Paulista, UNESP. CP 355, 14801-970 Araraquara, SP, Brazil. E-mail:benedeti@iq.unesp.br
[2]CPT Thermal Spray Center. Materials Engineering. Dept. Enginyeria Química i Metal-lúrgia. Universitat de Barcelona, C/Martí i Franquès 1. E-08028 Barcelona, Spain

Abstract

Corrosion behaviour of 75%Cr_3C_2-25%NiCr coatings deposited on 42CrMo6 steel by High Velocity Oxy-Fuel spraying (HVOF) was investigated. Three coatings were studied; two of them using different spraying parameters (standard and optimized) and third one submitted to a thermal treatment.

The electrochemical behaviour of the coated steels was evaluated by means of Open Circuit Potential (E_{corr}), Electrochemical Impedance Spectroscopy (EIS) and Polarization measurements (CP). The structural characterization has been performed by Optical and Scanning Electron Microscopy (SEM-EDS), before and after immersion in aerated H_2SO_4 0.5M solution. The standard sample showed a strong substrate influence during immersion due to the rapid electrolyte penetration through the coating, reaching the steel substrate. It was concluded that the thermal treatment performed during thermal spraying improved the coating behaviour against corrosion as the electrolyte did not reach the steel even after 1 month of immersion.

Keywords: Cr_3C_2-NiCr, thermal spraying, HVOF, corrosion.

Introduction

Coatings obtained by thermal spray techniques have been used in many industrial applications due to the possibility of applying many different materials, from polymers to ceramics, at relatively low cost, easy and fast application without dimension restrictions and good reproducibility [1]. They are used in many applications where wear and abrasion resistance are required [2]. Thermally sprayed metallic coatings can easily be applied to large surfaces, which makes them very attractive for using as corrosion resistant coatings [3]. The HVOF technique, among other spraying processes, involves low temperature and high velocity of the powder particles, which leads to an improvement in the properties of the coatings when compared to other thermal spraying processes and coatings [4]. The powder injected into a HVOF gun is sprayed onto a steel substrate due to the combustion of a propylene and oxygen gas mixture. The spraying of several torch passes produces a dense and homogeneous layer where it is possible to find defects as pores, macro and microcracks, and oxides produced during the flying, melting and depositing of the particles [5]. These are important drawbacks of the Cr_3C_2-NiCr coatings to be used for steel corrosion protection, due to the fact that the electrolyte can reach the steel substrate, being preferentially corroded in the galvanic pair formed between steel and a nobler coating [6].

The aim of this work is to characterize the effect of the spraying parameters on the corrosion behaviour of such systems and to link it with the structural characterisation made before and after corrosion testing. An attempt to improve the coating homogeneity was also done by means of thermal treatments with the gun flame. This was done in order to try to close pores and cracks produced during the powder deposition and to relax stresses made during the quenching of the melted sprayed powder [7].

Materials and Methods

A ferritic-perlitic 42CrMo6 grid blasted steel was used as a substrate (**table 1** for composition). An Amdry-5420 powder with a nominal composition of 75%Cr_3C_2-25%NiCr was sprayed using a Sulzer Metco CDS-PT gun for High Velocity Oxy-Fuel equipment (HVOF). Mixtures of propylene, oxygen, and nitrogen were used as spraying gases. The spraying parameters are shown in **table 2**.

Samples **A** and **B** were obtained using a standard and optimized parameters respectively [8]. Sample **Q3** was thermal treated during the coating formation using the flame of the gun (without powder) immediately after the first layers of the coating were sprayed. After that, the rest of the layers were immediately sprayed in order to achieve a similar coating thickness to be compared with **A** and **B** coated samples.

The electrochemical cell was composed by a Hg/Hg_2SO_4 $K_2SO_{4,saturated}$ electrode, connected to the solution through a Luggin capillary, which was used as a reference electrode, and a Pt network was used as an auxiliary electrode. A Pt electrode of small area, connected to the reference electrode by a non-electrolytic capacitor of 10 µF, was used as the fourth electrode to minimize the ohmic dropping effects and noise [9] in the EIS experiments. The coated sample was fixed at the bottom of the cell and a geometric area of 0.33 cm^2 was exposed to the solution.

An aerated and unstirred H_2SO_4 0.5 M solution was used as electrolyte and the immersion time was kept around 24 hours for one sample and 1 month for the other. During this period, open circuit potential (E_{corr}) measurements were recorded for 24 hours in order to study the corrosion behaviour of such coated samples vs. time. EIS and CP tests were also done. EIS tests were performed after reaching a free electrode potential stability, applying 5 mV rms and running from 50 kHz to 1mHz at 7 points/decade. CP tests were recorded from –0.1 to 0.35 V/E_{OC}, at 0.16 mV s^{-1}. All samples were characterized before and after 1 and 30 days of immersion in H_2SO_4 0.5 M solution. Structural characterization was carried out using an Olympus Optical Microscope (OM) and a TOPCON SM-300 Scanning Electron Microscope (SEM) coupled to an Energy Dispersive Spectrometer detector (EDS).

Results and Discussion

Structural characterisation of the coated steels showed well-bounded coatings with a thickness comprised between 200 and 300 µm. Large cracks or a porosity level above *ca.* 3% were not detected by means of the coatings cross-section analysis [10]. It was also noticed that **A** coated steel was more porous than **B** and **Q3** coated samples, which indicates that the spraying parameters used to prepare **B** and **Q3** coatings produced a more homogeneous coating in agreement with a more energetic flame than the **A** sprayed samples.

Figure 1 shows cross-section of the **A** coated steel obtained by means of Scanning Electron Microscopy. It can be seen the presence of Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ carbides (a), embedded in a NiCr matrix with different composition (b) analysed by using of EDS. Cracks (c) and pores (d) produced during spraying were also found in all samples. Chromium oxides formed during spraying were also detected in the splat interboundaries (e) produced during the build-up of the coating from melted powder particles.

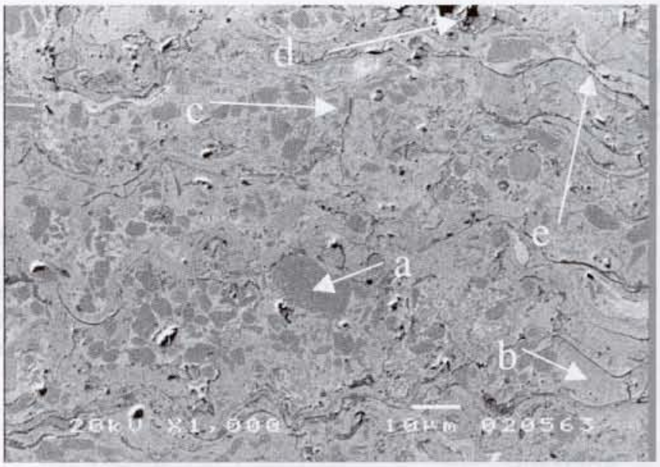


Fig. 1: SEM cross-section image of the **A** sample.

The main difference between **Q3** and the other two samples (**A** and **B**) is the presence of small cracks caused by the thermal treatment performed in such sample (**figure 2**).

Such thermal treatment performed between the spraying of the first layers and the other ones seem to have a stress-relaxation effect. Chromium oxide was also detected inside of such cracks, which were preferentially located in the layers that suffered thermal treatment and close to the substrate. The upper layers of the coating showed a structure similar to **B**, without this kind of cracks.

During the first hour of the immersion test, **A** sample showed ferrous oxide spots coming from the steel substrate to the surface, while **B** coated steel showed pitting attack 4-5 hours later. Surface of **Q3** remained almost unaltered after more than 1 month of immersion and ferrous oxide was not detected on the coating surface.

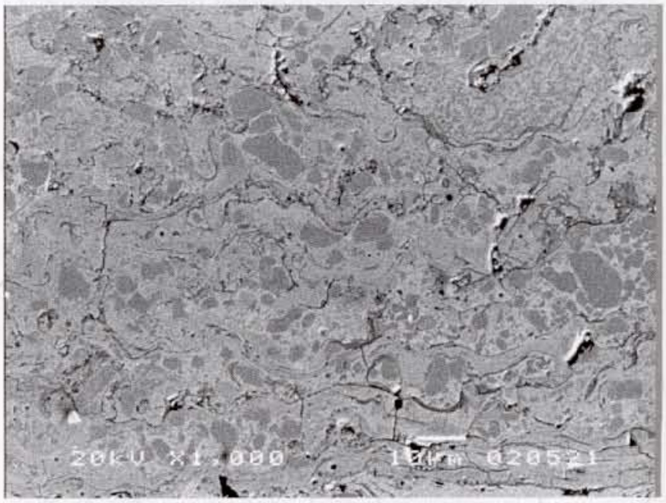


Fig. 2: SEM cross-section image of the thermal treated **Q3** sample, close to the substrate.

Figures 3 and **4** show OM cross-section images of the **A** coated steel after 1 and 30 days of immersion, respectively. The first sample shows that the electrolyte penetrated through the coating, reaching the steel, which was corroded, while after 30 days of immersion the coating was completely depleted. The same behaviour was observed for **B** coated steel. Notice that **Q3** coating depleting was not found after the same immersion period was characterized (**figure 5**), which means that the electrolyte did not reach the substrate yet.

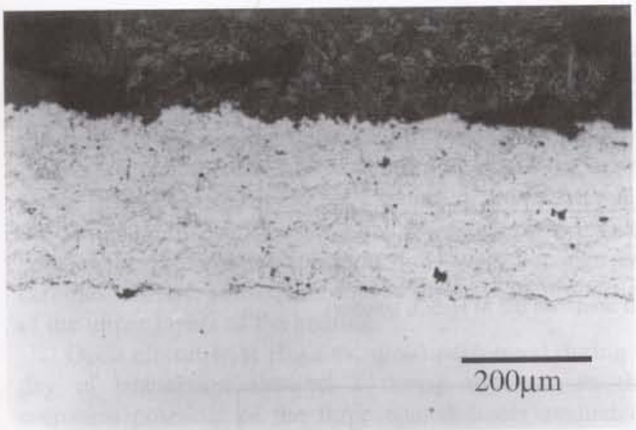


Fig. 3: OM cross-section image of the **A** sample after 24 hours of immersion in aerated and unstirred H_2SO_4 solution.

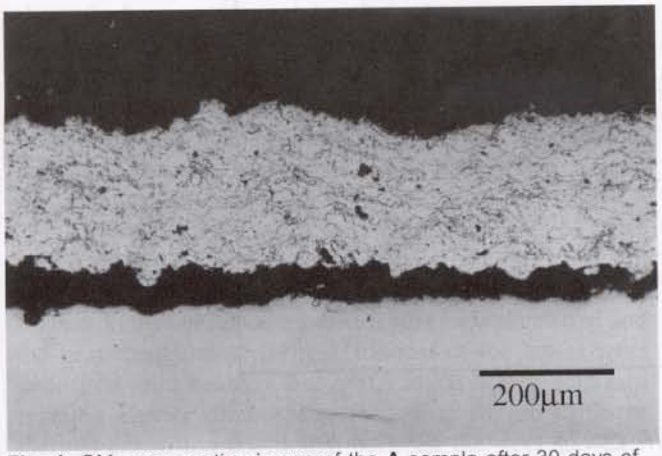


Fig. 4: OM cross-section image of the **A** sample after 30 days of immersion in aerated and unstirred H_2SO_4 solution.

The analysis of the samples after 1 month of immersion revealed a complete depleting of **A** and **B** coatings due to the steel substrate, while no attack to **Q3** sample was observed. Only for **Q3** sample an attack to the surface was detected, causing NiCr matrix and metallic oxides dissolution. The metallic matrix close to the carbides suffered preferential attack due to the nobler behaviour of the Cr_3C_2 phase.

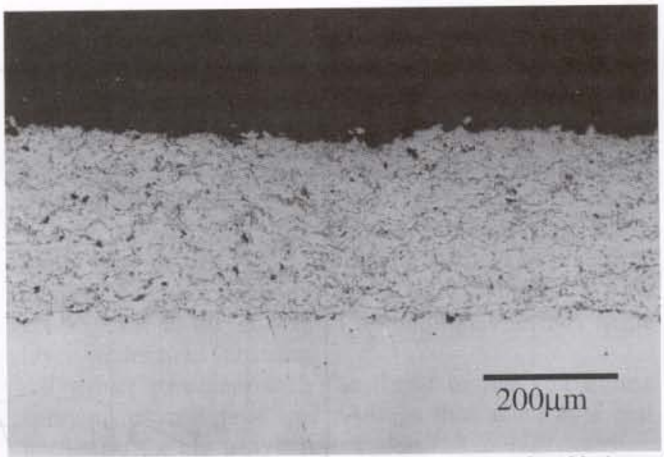
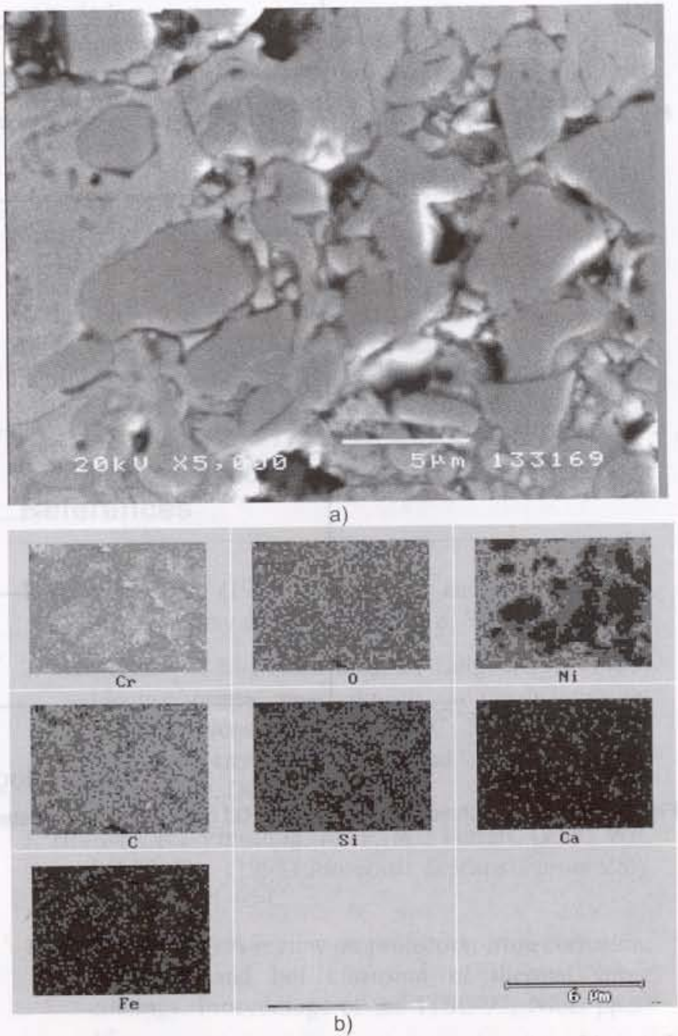


Fig. 5: OM cross-section image of the **Q3** sample after 30 days of immersion in aerated and unstirred H_2SO_4 solution.



a)

b)

Fig. 6: Preferential attack localised at the upper part of the **Q3** coated steel after 24 hours of immersion in 3.4% NaCl solution, a) SEM image and b) Elemental distribution obtained using EDS analysis.

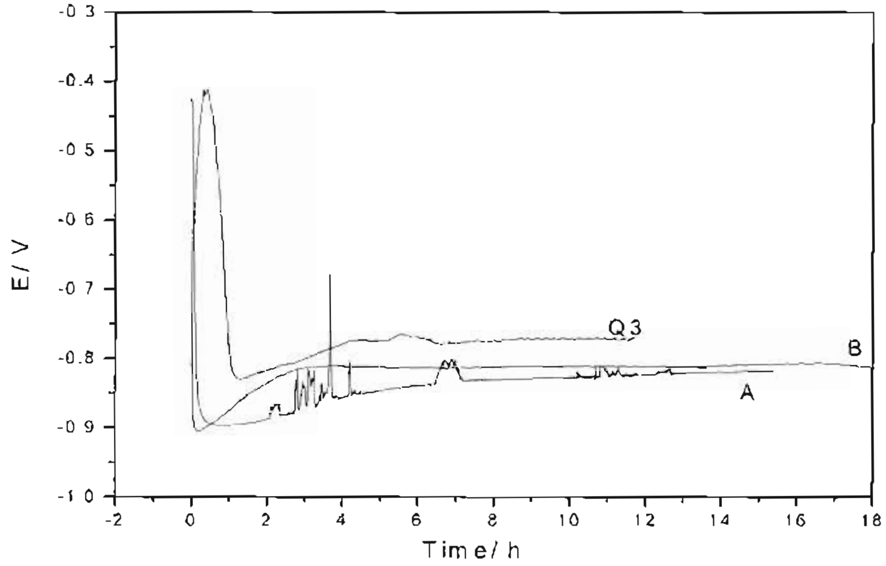


Fig. 7: E_{oc} (mV) vs. time (hours) for **A**, **B** and **Q3** coated steels in aerated and unstirred 0.5 M H_2SO_4 solution.

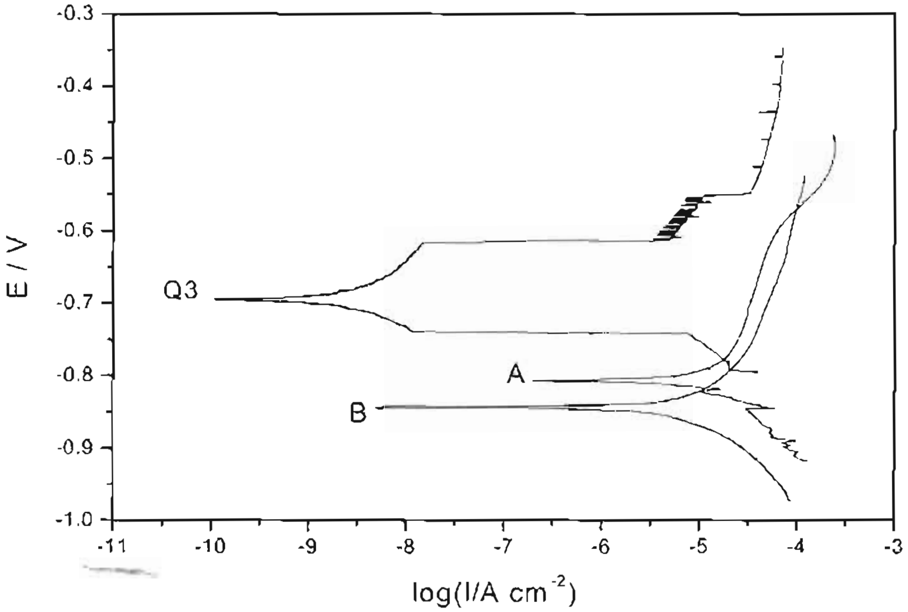


Fig. 8: Polarisation curves (CP) for **A**, **B** and **Q3** coated steels in aerated and unstirred 0.5 M H_2SO_4 solution.

Table 1. Composition of the steel used as substrate.

%wt	C	Si	Mn	P	S
steel	0.22	0.28	0.51	0.02	0.02

Table 2. Spraying parameters for the coated steels.

	O_2 L min^{-1}	C_3H_6 L min^{-1}	nº of layers	d_{proj}* mm	v** mm/s
A	420	60	15	300	500
B	483	69	15	200	500
Q3	483	69	30	200	1000

**Spraying distance, **velocity of gun displacement.*

The same behaviour was noticed when the Cr_3C_2-NiCr coating was studied in 3.4%NaCl solution and even with accelerated corrosion tests as cyclic polarization. To illustrate the Q3 coating behaviour in 3.4% NaCl solution **figure 6** shows the SEM cross-section image of the upper layers of this Q3 coating after 1 month of immersion and the elemental distribution EDS image in such region. Take note of the preferential attack of the matrix between the carbides with the consequent loss of mechanical properties of the upper layers of the coating.

Open circuit tests (E_{corr} vs. time) performed during 1 day of immersion showed a strong decrease in the corrosion potential of the three coated steels evaluated. The potential decay was greater for A and B samples than for Q3 one (**figure 7**), in agreement with the structural characterization, in which thermal treated Q3 sample showed a low corrosion in the steel substrate.

Figure 8 depicts the polarization curves for A, B and Q3 samples. Notice that a nobler behaviour and a low corrosion current density were observed for the Q3 sample, in agreement with the structural characterization, indicating that this coating showed a better protection of the steel against the electrolyte attack.

Although small cracks were detected, localized close to the steel substrate on the thermal treated Q3 sample, such cracks seem to be full of oxides and act as a stress relaxation barrier. Once the first layers were deposited and the heat treatment performed, the rest of the layers were deposited on a heated Cr_3C_2-NiCr layer, which acts as a relaxing barrier diminishing the effect of the different thermal expansion coefficient between the steel substrate and the coating itself. This is the reason why the rest of the coating (the upper layers in Q3 coating) is deposited with minor cracks and defects, leading to a coating that offers a better steel protection against the electrolyte penetration than A and B coatings.

When the electrolyte cannot reach the steel substrate, the coating itself is corroded via the NiCr matrix and oxides dissolution. This was only observed on the upper part of the Q3 coating.

In samples A and B, the steel substrate was preferentially corroded and the coating was completely depleted due to the fact that a ferrous oxide layer was formed between the coating and the steel.

Conclusions

- Changes in the spraying parameters used to prepare A and B coated steels produced only a low improvement in the corrosion resistance.
- Once the electrolyte reached the steel substrate, it was really corroded in the galvanic pair formed between the coating and the steel, causing a final depletion of the coating due to the growth of a continuous ferrous oxide layer on the steel substrate.
- Thermal treatment with the flame of the gun during spraying process produced coatings that acted as a real barrier for the electrolyte penetration.
- When the electrolyte did not reach the steel substrate, the metallic matrix in the upper layers of the coating was corroded.
- A good agreement between electrochemical results and the structural characterisation was found and the improvement of the corrosion resistance of the coating submitted to thermal treatment with the flame of the gun was clearly seen.

Acknowledgments

- The authors thank the financial support from FAPESP (Proc. 00/01893-9), CNPq (Proc. 521569/95-8) and the facilities of the S.C.T. of Universitat de Barcelona, Spain.
- The authors want to thank also the Generalitat de Catalunya and the CICYT for the 2001SGR145 Project.

References

1. Pawlowski, L. (1995) The science and engineering of thermal spray coatings. J.Wiley & Sons ed, 414p.

2. Guilemany, J. M.; Fernandez, J.; Delgado, J.; (1999) Electrochemical measurements and characterisation of a thermal sprayed HVOF Cr_3C_2-NiCr coating in a corrosive environment. United Thermal Spray Conference, Düsseldorf, p 474.

3. Hofman, R.; Vreijiling, M. P. W.; Ferrari, G.M.; Wit, J.H.W. De: (1998) *Materials Science Forum* 289-292, pp. 641-654.

4. Tobe, S. (1997) A review on protection from corrosion, oxidation and hot corrosion of thermal spray coatings. Proceedings of the ITSC'97, Nice. pp.3-12.

5. Calero, J. A. (1997) Caracterización de recubrimientos de cermets de Cr_3C_2-NiCr obtenidos por HVOF e interpretación fenomenológica del proceso mediante simulación matemática. Universitat de Barcelona, PhD, Barcelona, Spain.

6. Guilemany, J., Cabot, P., Fernández, J. (1998) *Materials Science Forum*, 289-292. pp. 667-678.

7. Guilemany, J., Fernández, J. Benedetti, A., Delgado, J. (2001) Influence of thermal treatments in the corrosion behaviour of HVOF Cr_3C_2-NiCr coatings in aqueous NaCl environment. Proceedigs of the UTSC'2001, Singapore, pp 1165-1171.

8. Guilemany, J., Fernández, J., Benedetti, A., Delgado, J. (2000) The use of electrochemical techniques to follow the behaviour of thermal spray coatings in aqueous agressive media. Proceedings of the MATERIALS WEEK 2000. Munich. CD.

9. D. Garreau, J. M. Saveant and E. S. K. Binh, (1978) *J. Electroanal. Chem.* 89 427.

10. Suegama, P. H.; Fugivara, C. S.; Benedetti, A. V.; Fernández, J.; Delgado J., Guilemany J. M.; (2002) *J. Appl. Electrochem.* 32, pp 1287-1295.