

PLASMA SPRAYED CERAMIC COATINGS ON St 37 STEEL SUBSTRATES

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Inherent porosity of air plasma sprayed (APS) ceramic coatings strongly influences their corrosion resistance [1,2] with the density of connected pores apparently related to coating thickness. Insufficient adherence of APS obtained coatings being also a problem. Post-treatment techniques such as HIP and Laser are currently being used in order to achieved higher densification adherence and minimize penetration of corrosive agents.

This work reports on the electrochemical characterization of Al₂O₃ and Cr₂O₃ coatings projected on St 37 steel, without and with post-treatment. Long term exposure results are compared with those obtained by DC Electrochemistry in order to assess the representativity of the accelerated test.

Table 1 provides the references regarding systems, coatings and treatments for the systems studied throughout this work.

Table 1 - References for the coatings produced using a 80 KW air plasma torch

Ceramic Coating	Bond Coating	Treatment	Reference
----	NiAl	As projected	NA-BP
----	NiCr	As projected	NC-BP
Al ₂ O ₃	NiAl	As projected	A+NA-BP
Al ₂ O ₃	NiCr	As projected	A+NC-BP
Cr ₂ O ₃	NiAl	As projected	C+NA-BP
Al ₂ O ₃	NiAl	HIP	A+NA-HIP
Al ₂ O ₃	NiCr	HIP	A+NC-HIP
Cr ₂ O ₃	NiAl	HIP	C+NA-HIP
Al ₂ O ₃	NiAl	LASER	A+NA-Las
Cr ₂ O ₃	NiAl	LASER	C+NA-Las
Al ₂ O ₃	NiAl	Sealant	A+NA-Seal
Al ₂ O ₃	NiAl	As projected	AlcPE
Al ₂ O ₃	NiAl	As projected	AlcPB
		Low porosity	
Al ₂ O ₃	----	As projected	AlsPE
Al ₂ O ₃	----	As projected	AlsPB
		Low porosity	

A carbonate/bicarbonate solution with added chloride ions was prepared to pH 8.3. A conventional electrochemical cell was used with a Luggin Harper capilar used as a bridge to an external saturated calomel electrode (SCE). Measurements were carried out at room temperature in normally aerated solutions.

Fig. 1a shows for the system A+NA-BP the E vs t profile when immersed in a $\text{HCO}_3^-/\text{CO}_3^{2-}/\text{Cl}^-$ solution. In ≈ 60 hours a plateau is reached at -500 mV(SCE) followed by a continuous displacement of the potential up to -200 mV where there is no further variation in the next 400 hours.

Horizontal dashed lines correspond to the open circuit value attained by St37 steel and the bond layer as indicated.

When using NiCr as a bond layer potential, the profile follows the same tendency as for NiAl but with no further increase from $\approx -500 \text{ mV(SCE)}$ onwards up to the end of the test, 500 hours later. This fact was taken as an indication of the substrate being unattacked (see Fig. 1b). Passivation by a Cr_2O_3 film might be responsible for the observed behaviour. Cross sections for Alumina coatings with bond layers of NiAl and NiCr support these findings.

The behaviour of Cr_2O_3 as a coating was similar to that reported for Al_2O_3 . Nevertheless, the electrolyte seems to penetrate at a faster rate as indicated by the slope of E-t profile having induced simultaneous attack to bond layer (NiAl) and substrate.

The system A+NC-HIP offers a better performance when compared with A+NA-HIP. According to E vs t profile, bond layer and substrate are simultaneously attacked in the latter case. This is adjudicated to the formation of cracks due to volume variation associated to Al_2O_3 phase transformation from γ to α . The delay in reaching the substrate, for A+NC-HIP system, is probably the result of Cr_2O_3 formation as referred for A+NC-BP system.

Fig. 2 shows results with NiAl bond coating for both Al_2O_3 and Cr_2O_3 .

Fig. 3 shows the profile E vs t for the system C+NA-Las. The treatment provides superficial compactation so determining that penetration of the solution is verified only through cracks originated by thermal shock. Surface densification was evident.

The potential is found to slowly increase towards the bond layer potential after showing, for 250 hours, stable behaviour at a value of -600 mV(SCE) . Cracks due to thermal shock did not reach the bond layer. Attack to bond layer was superficial.

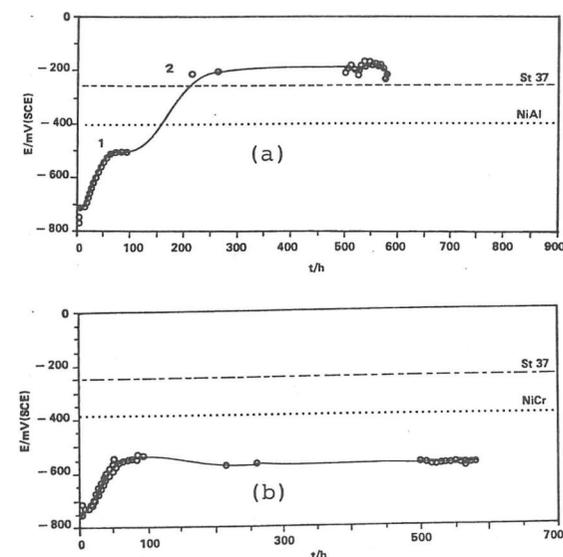


Fig. 1 - The open circuit potential as a function of exposure time for the Al_2O_3 coatings in a $\text{HCO}_3^-/\text{CO}_3^{2-}/\text{Cl}^-$. System A+NA-BP (a) System A+NC-PB (b)

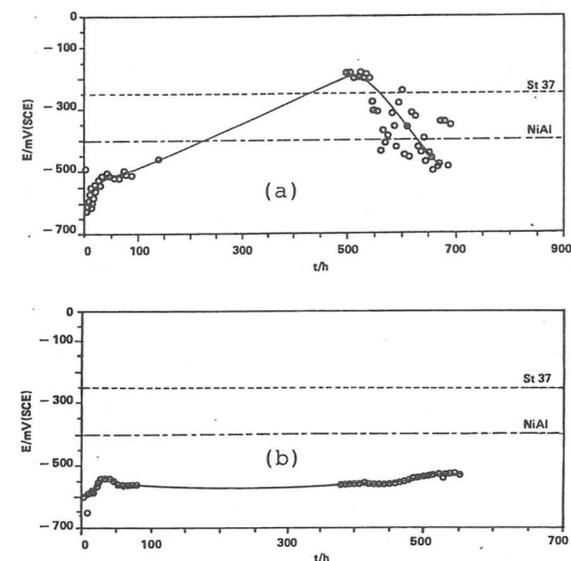


Fig. 2 - The open circuit potential as a function of time for coatings submitted to HIP treatment. System A+NA-HIP (a) System C+NA-HIP (b)

The potentiodynamic polarization curves for NiAl and NiCr coatings are characterized by an active region corresponding to Ni dissolution as Ni^{2+} being identified, with lower currents associated to NiCr on St37 steel.

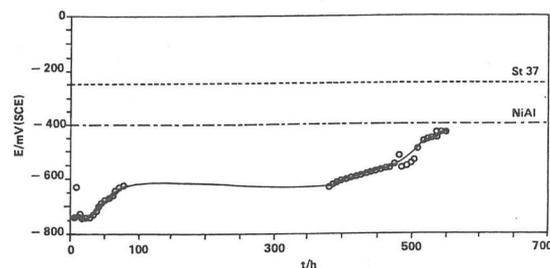


Fig. 3 - The effect of Laser refusion on the behaviour of a Cr_2O_3 coating using NiAl bond coating E vs t profile.

DC tests were also in agreement with results obtained for long term testing regarding the porosity of the coating and its direct influence in the type and extension of corrosion attack to bond layer and substrate. Higher porosity was related to higher current density associated to localized corrosion of either pitting or crevice type. It is to be noticeable that HIP and Laser treated systems revealed, generally, polarization characteristics corresponding to the bond layer.

Fig. 4 compares for Cr_2O_3 coatings, the behaviour for as projected, HIP and Laser treated samples. For the system A+NA-HIP the treatment introduced a slight changes in current density eventhough the existence of perpendicular cracks together with an increase in microcracking, and even porosity due to Alumina phase transformation, accompanied of volume variation that contributed to the attack propagation towards the substrate. In the case of Cr_2O_3 the cracking created by the HIP treatment was counteract by the densification of the ceramic coating bringing a reduction of porosity.

The porosity, as expected, was a key factor in the degradation of tested coatings allowing penetration of electrolyte contaminated with Cl^- ions and also oxygen, which is identified as acting in the cathodic reaction.

Oxides formed from Fe^{2+} or Fe^{3+} species were observed to diffused out after accumulation in the interior of porosities. Fe_2O_3 and Fe_3O_4 formed according to oxygen availability [4].

Localized corrosion of the pitting and crevice type is promoted due to a mechanism that allows dissolution to occur at the regions neighboring with connected pores.

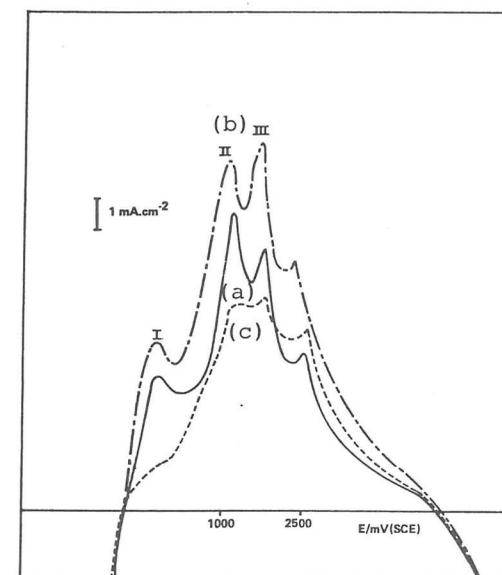


Fig. 4 - DC Polarization curves for Cr_2O_3 coatings C+NA-BP (a) C+Na-HIP (b) C+NA-Las (c).

REFERENCES

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