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Thermal Spray Spinel Coatings on Steel Substrates: Influence of the Substrate Composition and Temperature

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Abstract

Spinel coatings on steel substrates have been obtained by a thermal spraying process. The projection has been done on cold or hot substrates. A further thermal treatment has been performed on some coatings formed on cold substrates. A good adhesion has been observed only on steels rich in oxidizable elements (Z38 CDV5). These coatings have been characterized and tested in a foundry. Adhesion tests have been done by the pulling method and by indentation. The concentration profiles of the most important elements from the metal/oxide interface to the bulk have been determined by EPMA analysis. This set of results has allowed us to show the importance of the coating microstructure and of the diffusion processes on the metal/ceramic bond strength and of the coating stability in contact to Al/Si melted alloys. Such coatings are then good candidates to be used in a foundry to protect the casting tools, mainly when they are performed on heated surfaces.

1 Introduction

Due to the high chemical inertness of ceramics and to the possibility of connecting them to metals, they are increasingly being used as coatings to protect metals in corrosive environments. Some ceramic coatings can also act as thermal barrier. They can both insulate and protect the metal which can then endure extreme thermal cycling under hostile environments. The requirement that the coating must fulfil is dictated by the functions of the device. Nevertheless, its limitations are not due generally to the coating itself but rather by the adhesion quality which is reflected by the fracture resistance of the metal/ceramic interface. Of course, the strength of the metal–ceramic bond is directly linked to the way of formation of the metal/ceramic bonding and to the nature of the material couples but it is also linked to the presence of active species which influence the thermodynamic properties of the interfacial region. Calculating bond strengths is theoretically possible, but at present, results are not available for complex metal/ceramic interfaces. To optimize the metal/ceramic bonding it is then important to have a complete characterization of the interfacial region and to understand as much as possible the correlations between the atomistic configurations and the macroscopic properties.

In the present work, a melted ceramic oxide (Al_2O_3, MgO 70/30 in wt) has been projected in air, using an oxyacetylene flame wire gun fed by a flexible cord, onto previously sanded chromium/molybdenum steels. The spraying has been done on a cold substrate, or on a cold substrate followed by a thermal treatment, or on a hot substrate. Different tests have been performed to characterize these coatings. The adhesion has been controlled by adherence and indentation tests. The metal/ceramic interface has been characterized by EPMA analysis. Furthermore, the coating behavior in contact with Al/Si melted alloys has been studied because such coatings could be used in foundry to protect the casting tools. The set of data obtained has allowed us to identify the main parameters that govern the adhesion and the properties of the coatings.

2 Materials and Coating Procedures

The substrates considered are chromium and molybdenum steels containing different amounts of oxidizible elements (Table 1). They have been coated by the spinel $MgAl_2O_4$ (Al_2O_3/MgO $\approx$70/30 in wt). The samples for the adhesion tests

Table 1. Composition of the XC38 and Z38 CDV5 steels

		Steel XC38							
Al	C	Cr	Cu	Mn	Mo	Ni	P	S	Si
0·06	0·38	0·21	0·22	0·66	0·02	0·02	0·02	0·016	0·27
				Steel Z38 CDV5					
		C	Cr	Mn	Mo	Si	V		
		0·34–0·42	4·5–5·5	0·2–0·5	1·2–1·5	0·8–1·2	0·4–0·6		

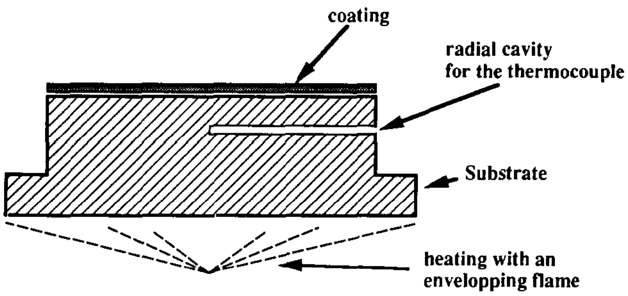

Fig. 1. Sample for the foundry tests.

and EPMA analysis were disks of 50 mm diameter and 3 mm thickness. Those for the foundry tests were cylinders of approximately 50 mm thickness and 50 mm diameter, in order to be able to insert them at the bottom of a casting mould (Fig. 1). All the samples were sandblasted immediately before coating. This allows both cleaning of the substrate surface and creation of surface irregularities giving better adhesion of the coating during the projection (mechanical adhesion).

The projections were performed in air with an oxyacetylene thermal spray flame gun (CYBERJET model) on which was fitted a ceramic supple string 'SFECORD'. The coating material is melted in the flame and then thrown with a high velocity onto the previously cleaned surface of the substrate. During spraying, the samples were maintained by a steel support. The thickness of the coatings was between 0·1 and 0·2 mm, according to the spraying conditions.

The spinel coatings have been performed on XC 38 and Z38 CDV5 steels, which contain different amounts of oxidizible elements. Three types of coatings have been performed:

- — coatings on cold substrates — samples called IS
- — coatings on cold substrates followed by a thermal treatment under a vacuum of $0{\cdot}5 \times 10^{-2}$ Torr at 800°C, for 100 h — samples called IIS.
- — coatings on a substrate heated at a controlled temperature close to 650–700°C — samples called IIIS

For the coatings IIIS, the temperature of the substrate was controlled with a chromel/alumel thermocouple placed in a radial cavity, as shown in Fig. 1. The heating was performed with an enveloping flame and was maintained during the projection. For the smaller samples an assisted cooling was performed up to 300°C, i.e. for 8 min, in order to prevent thermal shocks. The samples for the foundry (Fig. 1) have a higher calorific capacity. Their temperature decreases naturally from 700 to 300°C, in approximately 17 min.

3 Results

Whatever the type of projection, the coatings on the XC 38 steels crumbled after the projection, during the cooling of the sample. The concentration of oxidizible elements is one of the main differences between the XC38 and the Z38 CDV5 steels. These elements seem to be active species during the projection, performed in air. They can lead to the formation of oxides on the metal surface, in an oxidising atmosphere. These oxides can then react with the coating and create chemical bridges between the metal and the ceramic. The beneficial effect caused by such reactions, due both to the dissolution and to the diffusion of the active species near the metal/ceramic interface, are known in the literature.[1,2] McDonald and Eberhart[1] have found that impurities that are highly oxygen-active can make a major contribution to the adhesion at the interface. Characterizations of the coatings performed on the Z38 CDV5 steel have then been done, in order to establish the main parameters responsible of the adhesion and to check the influence of the oxidizible elements.

3.1 Adhesion tests

The coating adherence is often taken as a criterion which allows definition of the best coating conditions.[3] In the following, two adherence testing methods have been used, in order to compare the adhesion resistance of the spinel coatings on the Z38 CDV5 steels.

3.1.1 Pulling out tests

The adhesion resistance is measured with a traction machine, INSTRON model 1185. The pull

Table 2. Pulling out tests

Sample	Pull out strength (N)	Pull out surface (mm^2)	Adherence (MPa)	Observations
IS	2050	41	50·0	Detachment between the coating and the substrate, in the middle of the sample
	2150	138	15·6	Detachment between the coating and the substrate, from a corner
	2250	103	21·8	Detachment between the coating and the substrate, from an edge
IIS	2550	166	15·4	Coating pulling out
	2750	10	275	The pulling out occurs in the coating thickness
	2850	120	23·8	Coating pulling out
IIIS	3400	130	26·2	The pulling out occurs in the coating thickness
	3950	25	158	Detachment between the coating and the substrate from a corner and partial pulling out of the coating
	4750	20	238	Detachment between the coating and the substrate from a corner and partial pulling out of the coating

rate is equal to 0·5 mm/min. The strength leading to the break at the metal/oxide interface allows the adhesion quality to be known. It is a critical value generally called 'adherence' of the ceramic coating. The results reported in Table 2 show that the adherence is higher for the coatings thermally treated and the best results are obtained for the coatings performed on heated metal substrate (coatings IIIS). Nevertheless, a break sometimes occurs in the thickness of the coatings IIIS. This may be due to changes in temperature during the projection, leading to thermal stresses in the ceramic.[4] Indeed, it is difficult to keep exactly the same experimental conditions from one experiment to the other, with our experimental arrangement. An improvement of the thermal treatment conditions with a better control of the temperature of both the substrate and the coating during the projection can then give promising results. Nevertheless, it may be pointed out that the main use of these coating is to protect steel against corrosion. Therefore, the break inside some coatings observed during the tests does not change the corrosion-preventing performances of the ceramic in service conditions.

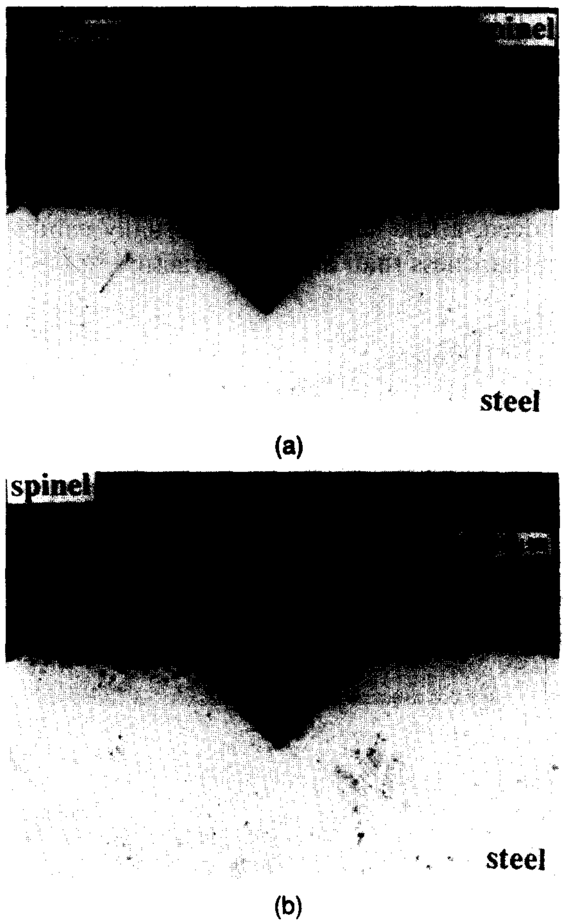

Fig. 2. Spinel coated steel (Z38 CDV5) indented in the interface region (indenter load 5 kg during t = 15 s). (a) Spinel sprayed on an unheated substrate. Note that cracks propagate along the metal/ceramic interface. (b) Spinel sprayed on a heated substrate. Note that the indentation zone is smaller.

3.1.2 Vickers indentation tests

Vickers indentation tests have been performed with a micro-durometer Leitz (HPO-250) at the interface zone of the coatings IS and IIIS. Different loads have been applied on the indenter and the results are in agreement with the pulling out tests. Indeed, we have observed that cracks start to appear for an indenter load of 2 kg for the coatings IS and of 10 kg for the coatings IIIS. Figure 2 shows micrographs of indented samples under a load of 5 kg, applied for 15 s. It illustrates clearly the strong dependence of the coating processing conditions on the mechanical properties of the samples. Indeed, the indentation zone is smaller when the coating is performed on a heated surface (coatings IIIS) and a crack, propagating along the metal/oxide interface, is observed only for the coating IS.

3.2 Optical microscopy

Typical cross sections of coatings IS and IIIS on Z38 CDV5 steel are reported in Fig. 3. These micrographs show that the coatings IIIS have a fine microstructure while those performed on an unheated surface (coatings IS) are less dense and microcracks are observed between the particles. Similar observations have been done by Claes and Helgesson[4] who have studied the appearance of alumina droplets sprayed onto cold (20°C) or preheated (600°C) metal substrates. When a droplet hits a cold substrate, it scatters leading to the formation of irregular shape droplets.[4] Indeed, the temperature being too low, the surface tension does not allow them to coalesce and to have a spherical shape. Consequently, they are less mobile and cannot flow into the irregularities of the substrate or of the previous layers. This leads to a porous coating with many interfaces and therefore to a coarse microstructure (Fig. 3(a)). On the contrary, when the droplets hit a preheated substrate they can come together and have time to flow into the irregularities. A more dense coating is then obtained, as shown in Fig. 3(b). It may be pointed out that these microstructural observations are consistent with the indentation tests (Fig. 2). Indeed, a fine microstructure usually exhibits a higher hardness than a coarse structure.[5]

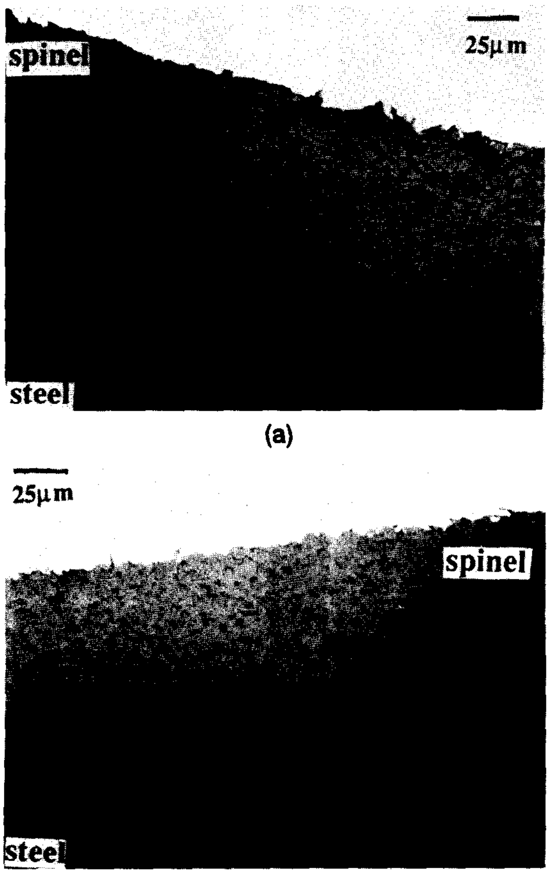

Fig. 3. Cross section micrographs: (a) spinel sprayed on an unheated substrate, (b) spinel sprayed on a heated substrate. Note the perturbation of the metal/oxide interface and the fine microstructure of the coating performed on a heated substrate.

Furthermore, we have observed that the coating IS interface stays planar, whereas at the coating IIIS interface (Fig. 3) perturbations occur in places. Of course, such instabilities have a beneficial effect on the coating adhesion. The initial surface perturbations increase in amplitude when a diffusion process takes place.[6] Consequently, such interface morphologies are consistent with the formation of a 'diffusive coating' when the ceramic is sprayed on heated surfaces.

3.3 Electron probe microanalysis

The concentration profiles of the most important elements from the metal/oxide interface to the bulk have been determined by EPMA analysis, in samples IS and IIIS. Typical concentration profiles of Fe, Cr and Si in the oxide and of Al and Mg in the substrate, are reported in Fig. 4. They show clearly the increase of the diffusion zones in the heated coatings. The amount of Fe and Cr close to the interface are nearly the same in samples IS and IIIS. These values seem to be controlled by the solubility limit of these elements in the oxide. The Fe and Cr profiles are very steep in samples IS, whereas they are more extended when the coating is performed on a heated surface (samples IIIS). For silicon, the concentration in the metal seems not to be affected near the interface when the coating is deposited on an unheated substrate and the amount in the oxide is close to the limit of detectability (Fig. 4(a)). In the heated substrate, the silicon concentration increases near the interface both in the metal and in the oxide, due probably to an interfacial reaction between Si and $MgAl_2O_4$ (Fig. 4(b)). For V, Mn and Mo, their amount in the oxide is generally below the limit of detectability.

3.4 Behaviour of the coatings in foundry in contact with an Al/Si melted alloy

The three types of coatings have been studied. The samples (Fig. 1) have been inserted at the bottom of the mould which receives the Al/Si melted alloy, at 700°C. The coating is then subjected to different simultaneous degradations: liquid alloy impact, erosion by the liquid current, thermal shock, thermal stresses and liquid alloy corrosion. The behaviour of the coatings after several casting cycles are described in Table 3. Only the 'diffusive coatings', performed on heated substrate, are very stable. After several casting cycles we have not observed a surface degradation of the ceramic while a scaling is detected, from the first casting cycles, for the coatings performed on unheated substrates. These results are consistent with both the fine microstructure of the coatings IIIS and the strong adherence. Nevertheless, an increase of the quality of the coatings IS is observed after a thermal treat-

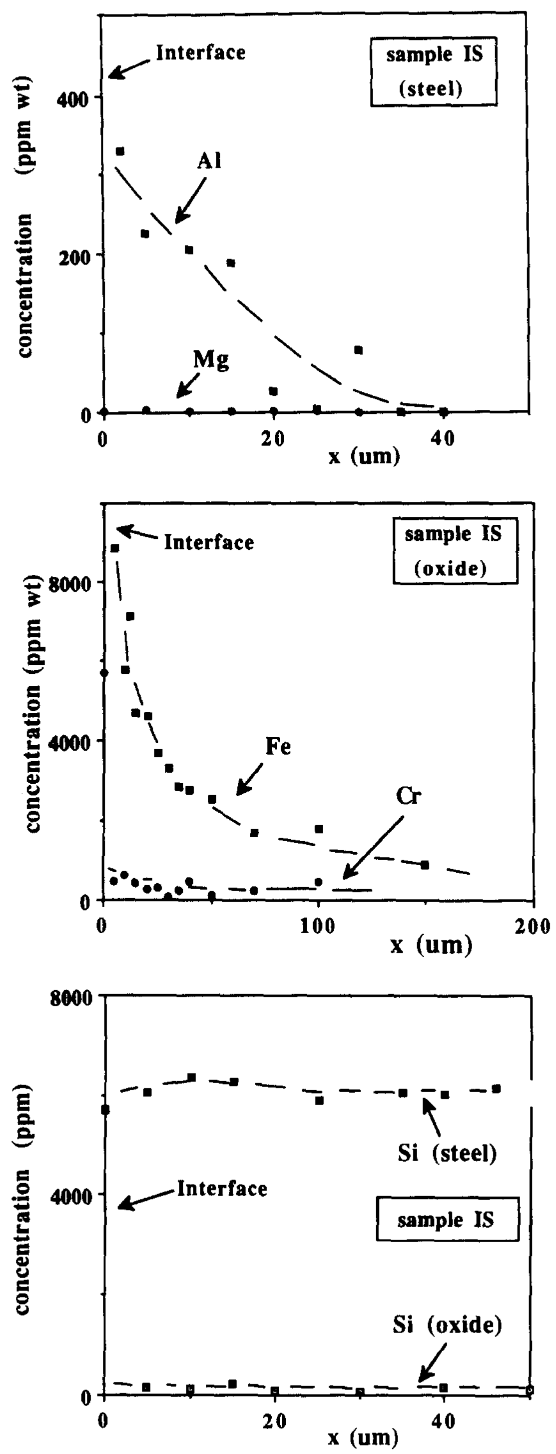

Fig. 4(a). Concentration profiles from the steel/spinel interface of Fe, Cr and Si in the oxide and Al, Mg and Si in the unheated steel.

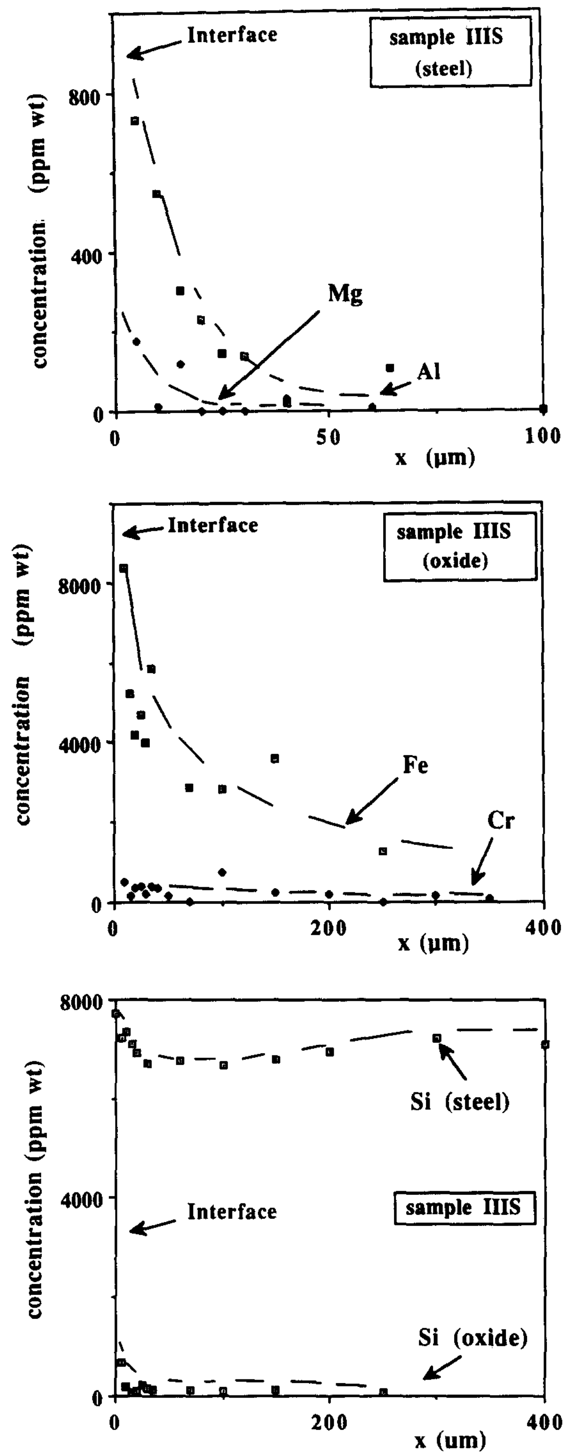

Fig. 4(b). Concentration profiles from the steel/spinel interface of Fe, Cr and Si in the oxide and of Al, Mg and Si in the heated steel.

ment at 700°C (samples IIS). These results show that the degradation of the coating IIS, while continuous, is low (Table 3). An improvement of the coating IS can then be expected by changing the thermal treatment conditions (Section 2).

4 Conclusion

In this work we have first shown the importance of the steel composition on the metal/ceramic bond strength of thermal sprayed coatings. Spinel coatings deposited on XC38 steels crumbled after the projection while spinel coatings on Z38 CDV5 steels are stable. This behaviour has been attributed to the higher amount of oxidizible elements in the Z38 CDV5 steels. Optimization of the properties of the spinel coatings deposited on Z38 CDV5 steel substrates, for use in foundry to protect casting tools against the severe erosion–corrosion conditions encountered when the mould receives the melted alloy, have been performed. The lifetime of the coating deposited on cold substrates increases

Table 3. Coating behaviour in contact with Al/Si melted alloys, after several casting cycles

Spinel coating type	IS	IIS	IIIS
Casting cycles	50	50	730
Observations	Coating scaling from the beginning of the test The interfacial adhesion seems correct	Low and continuous degradation of the coating The interfacial adhesion seems correct	The coating quality widely satisfied the purpose of the test
Coating quality conclusions	Medium	Medium	Satisfactory

when it has been thermally treated at 700°C after deposition, while more promising results have been obtained with coating deposited on heated substrates. Adherence tests, EPMA analysis and microscopical observations have identified the main parameters responsible of the protective properties of the coatings. The fine microstructure, which increases the toughness against the erosion by the melted alloy impact, and the strong metal/ceramic bond contribute to the protective performances of the coatings performed on heated substrates. These properties are in part due to the diffusion processes at the metal/oxide interface as well as the surface instabilities which have a beneficial effect on coating adherence.

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