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Alumina plasma spraying on 304L stainless steel: Role of a wüstite interlayer

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Abstract

Excellent adhesion values (>70 MPa) of alumina coatings achieved by Atmospheric Plasma Spraying (APS) were obtained on pre-oxidized stainless steel (304L), covered with a continuous layer of wüstite ($Fe_{1-x}O$) surmounted by a very thin magnetite layer. This is due to epitaxial relationships between alumina, magnetite and wüstite, as shown by Transmission Electron Microscopy (TEM), giving a “crystallographic bonding”.

Keywords: Stainless steel; Alumina coatings; Atmospheric Plasma Spraying (APS); Transmission Electron Microscopy (TEM); Adhesion test

1. Introduction

In the field of the Atmospheric Plasma Spraying (APS), it is commonly accepted that poor adhesions of coatings are due to surface conditions of the substrates and presence of adsorbates and condensates on the substrates.[1] Consequently, in order to improve coatings adhesion, substrates are often

(i) grit blasted to ensure a strong mechanical bond between the impacting particles and the substrate and
(ii) pre-heated in air above around 600 K, in order to eliminate, from the surface, adsorbates and condensates.[2]

However the grit blasting is not always possible (e.g. on thin substrates) and may leave grit residues between the substrate and coating. Moreover, for APS processing on metals or alloys, pre-heating induces a superficial oxidation of the substrate, which is particularly noticeable for iron-based alloys. The characteristics of the formed oxide layers vary according to the pre-heating treatments, and the coatings on so-oxidized substrates present a very broad range of adhesion/cohesion values, with poor reproducibility.[3,4]

If oxidation is carried out in CO_2 instead of air,[5] the behaviour is very different: for instance, on low-carbon steels, pre-oxidations in CO_2 provide an excellent adhesion of alumina plasma sprayed coatings.[6] This result has been attributed to the presence of a wüstite phase $Fe_{1-x}O$ on the surface of the steel before alumina deposition. This new mode of adhesion has been called “crystallographic bonding”, because the high adherences observed were due to the progressive sliding between the successive crystalline lattices from the inner alloy to the α-Al_2O_3 outer splats: alloy/wüstite/magnetite/γ-Al_2O_3/α-Al_2O_3. The chain of structural relationships so constituted develops strong bonds across the interfaces, without any properties gap.[7] This process presents also the advantage of sparing the grit-blasting step.

Recently, a study devoted to the oxidation of austenitic low-carbon stainless steel 304L (72 wt.% Fe, 18 wt.% Cr and 10 wt.% Ni), in CO_2, identified wüstite as the superficial oxide phase.[8] Hence it appeared as very interesting to confirm that such a pre-oxidation treatment of this last alloy provides also a good adhesion of alumina plasma deposits, knowing that, contrary to what was observed on C40E, the growth of wüstite on the 304L alloy was preceded by the inner formation of chromia and of iron-chromium spinel.

Thus, the aim of the present study was to achieve alumina coatings on alloy 304L pre-oxidized in CO_2, in order to test the coating adhesion and to characterize the interfacial relationships.

2. Experimental

2.1. Raw materials

2.1.1. Pre-oxidized 304L alloy

The substrates used were 304L steel plates, provided by Chaumeil S.A. (Brive, France). Their composition is given in

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Table 1
Composition of the 304L stainless steel.

Element	C	Si	Mn	P	S	Cr	Ni	Co	Cu	N	Fe
wt.%	0.024	0.240	1.340	0.033	0.026	18.060	8.100	0.200	0.360	0.0830	71.534

Table 1. The disk-shaped samples were 25 mm in diameter and 7 mm in thickness. They were polished up to SiC papers grit 4000.

For the pre-oxidation treatment, they were dived during 1–60 min in the hot area of a furnace, heated by $MoSi_2$ resistors, and working in a controlled atmosphere of carbon dioxide (Air Liquide France, N27, purity of 99.7 vol.%). The gas pressure was 10^5 Pa and the temperature 1273 K. At the end of the treatment, the samples were rapidly removed out of the warm zone of the furnace.

The oxide scale has been studied exhaustively.[8] A schematic representation of its morphology is given in Fig. 1.

The outer oxide is constituted of wüstite (with traces of Fe_3O_4 at the extreme surface[9]) while the inner oxide is composed of a thin layer of chromia (at the interface substrate/oxide). A spinel phase type chromite is present inside the oxide layer, surrounding residual metallic nodules. The substrate, near the oxide, is depleted in chromium. Fig. 2a provides the XRD patterns of the surface of the oxide scale, for pre-oxidation times of 10 and 50 min, where the oxide phases wüstite and spinel are identified (Fe_3O_4, in very little quantity, is detected only by XPS).

For pre-oxidation times up to 25 min, i.e. for weight gains below 0.6 mg cm^{-2}, the roughness Ra of the surfaces increased evenly from 0.031 ± 0.001 μm (surface condition of the polished non-oxidized samples) to 0.3 ± 0.2 μm. For longer durations of pre-oxidations there was no change noticeable, Ra varying randomly between 0.3 and 0.6 μm.

2.1.2. Alumina

Alumina powders (from H. C. Starck GmbH) were only composed of the α phase corundum (JCPDS file no. 1-70-5679) and their major impurities were SiO_2, Fe_2O_3 and Na_2O (each content ≤0.01 wt.%). Two batches were used:

- AMPERIT® 740.0, which had a grain size between 5 and 22 μm (named powder [+5–22]), with a trimodal repartition of the grains around 1 μm, 8 μm and 20 μm (Fig. 3a). The micrograph of Fig. 4a shows that the grains were smooth and angular, which is characteristic of a powder obtained from a fused and crushed material;

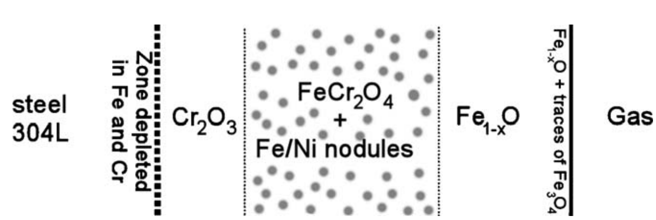

Fig. 1. Schematic cross section of the pre-oxidized stainless steel.

- AMPERIT® 740.1 with a grain size from 22 to 45 μm (named powder [+22–45]), was more homogeneous and centred around 40 μm (Fig. 3b) with some little grains around 1 μm. The aspect of the grains, seen in Fig. 4b, is the same that of the finest powder.

2.2. Plasma spraying

Thermal plasma deposition of alumina on pre-oxidized samples was carried out with a Sulzer Metco PTF4 type torch using an arc current of 600 A, with argon and dihydrogen flow rates of 33 and 10 NL min^{-1}, respectively.

Alumina powders were injected perpendicularly to the plasma jet by a powder feeder (Sulzer Metco 9MPE), through an injector of 1.5 mm diameter located at 6 mm from the nozzle exit and at 9 mm above the torch axis. Samples wheeling support (cylindrical, 120 mm in diameter) allowed 10 substrates to be treated simultaneously. In order to control the surface temperature of the substrates and eliminate particles with a too-low momentum (periphery of the jet), an air barrier was placed at

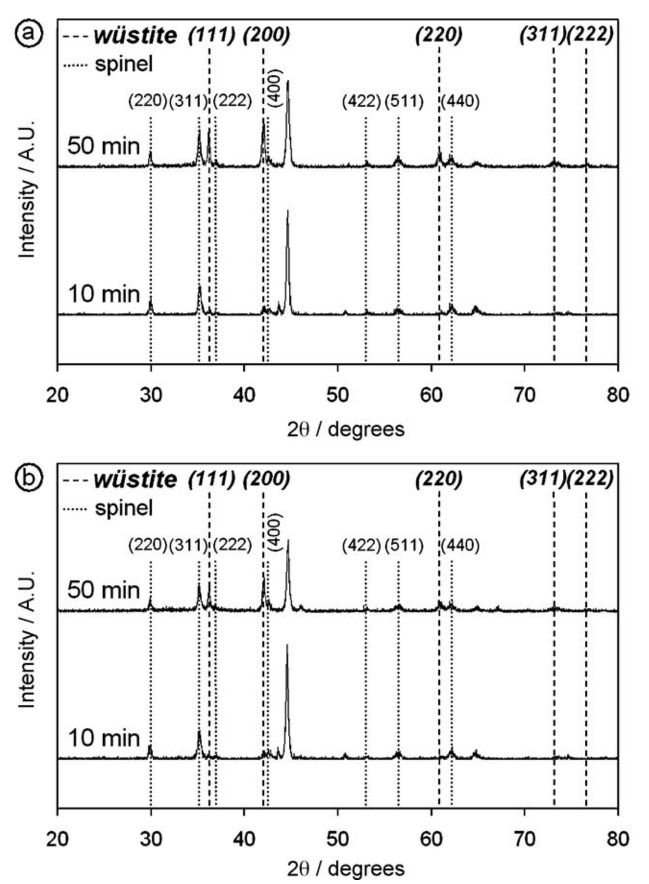

Fig. 2. XRD patterns of pre-oxidized samples before (a) and after (b) pre-heating around 600 K; the peaks not indexed are those of the substrate.