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THE INFLUENCE OF MULTILAYER Al_2O_3 AND CeO_2-DOPED ZrO_2 COATINGS ON 316L AUSTENITIC STEEL CORROSION IN 1N H_2SO_4 SOLUTIONS

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Ceramic materials are a class of inorganic materials with a wide variety of origins, structures and processing techniques, leading to a wide range of properties (physical, mechanical, thermal, electrical, magnetic, chemical, tribological), which can be developed accordingly. with specific requirements and uses. In order to improve the resistance to corrosion but also to other extreme conditions (temperature, erosion, radiation, etc.), of metals and alloys, new coating methods with different ceramic materials have been developed.

In this paper the results of experimental works that were performed for the physical deposition of electron vapor (EB-PVD) layers of Al_2O_3 oxide and ZrO_2 doped with CeO_2 on 316L stainless steel are presented. The samples were corroded in 1N sulfuric acid solution. The adhesion of the coatings was assessed by scratch test. Study performed by SEM scanning electron microscopy (SEM) and qualitative elementary chemical analysis of the surface by electron scattering (EDS). highlights structural, morphological and chemical composition changes produced by local pitting corrosion of the coatings.

Keywords: stainless steel, ceramic materials, EB-PVD, improve corrosion resistance, characterization

1. Introduction

316L stainless steel has a low carbon content and has very good properties of both thermal and corrosion resistance~~,~~ which makes it possible to be used in harsh environments where the metal is slightly corroded [1]. 316L stainless steel is widely used in the manufacture of products and equipment for work in high corrosion conditions in the chemical, energy, food, etc. industries. Recently 316L powdered steel is used to obtain products through additive manufacturing (AM) technology, which offers a high degree of freedom in geometry, the design of high value-added materials and the dimensions and

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shapes of high-grade components. complexity and finishing compared to traditional processes. [2-3].

Coatings obtained by physical vapor deposition (PVD) methods are one of the most common methods of improving the protection against corrosion of steels [3]. In aggressive environments, corrosion protection is limited, as these coatings usually incorporate a large number of defective pores through which the steel material is attacked. 4-5] In these areas, high-density electric currents may occur on small surfaces on the surface of the steel substrate, causing strong localized corrosion. [6-9]. Recent investigations have focused on the application of the deposition of atomic layers from different oxide materials to form a multilayer protection complex on steel [10-19]. Ceramic coatings have been widely used in the field of surface modification in recent decades due to their unique property. Modifying metal surfaces using a thin layer of ceramic coating provides an ideal way to improve the mechanical performance of metal substrates. Alumina having different crystalline forms of which the most common are θ-Al_2O_3, γ- Al_2O_3 and α- Al_2O_3 [20-23]. Once applied to metal substrates, it can improve surface functionality for applications such as corrosion and wear [24], electrical insulation coatings, environmental protection coatings [25], oxidation at high temperatures and high hardness.

Due to the complex of electrical, mechanical, opto-electronic properties (photoluminescence and high optic refractive index), chemical stability, and high thermal stability, ZrO_2 can be used to make coatings. with multiple uses [1, 26, 27]. Alumina or aluminum oxide (Al_2O_3) is a material commonly used to make ceramic coatings due to its high hardness, high melting point and erosion resistance. Alumina was deposited either as a single layer, multilayer or composite, comprising other compounds such as titanium oxide [28], zirconium oxide (zirconia), yttrium doped zirconium oxide and other oxide materials on various substrates such as stainless steel, steel carbon, metal alloys and superalloys [29]. In order for the layers to be resistant to wear, it has been proven that thin layers of alumina with a thickness of 0.5-10 μm are sufficient to resist wear and corrosion [30]. The EB-PVD technique allows the realization of coatings that can be used in a series of state-of-the-art applications with high values of adhesive strength and uniform thickness.

The aim of this study is to evaluate the properties and reliability of the multilayer oxide layer based on aluminum and doped zirconium obtained by EB-PVD on corrosion of 316L stainless steel substrate with potential applications in the piping system through which sulfuric acid used in the textile industry passes and nuclear reactors.For this purpose, surface roughness, adhesion and resistance to electrochemical corrosion were studied. The corrosion of the multilayer oxide samples was investigated in a corrosion cell, the samples being immersed in 1N H_2SO_4 acid solution, at room temperature, for about 60 minutes.

2. Materials and methods

The 316L steel substrate in the form of plates with dimensions of 55x55mm and thickness of 2 mm, were previously cleaned and degreased in organic solutions using an ultrasonic bath thermostat (model PRO150). The raw materials for the deposition of multilayer coatings were commercial Al_2O_3 powder (Amperit 740.002, max 99, 5 wt% Al_2O_3) and ZrO_2 powder doped with 8 wt% CeO_2 obtained by a hydrothermal process at moderate temperatures and pressures (max. 250 ° C) and 40 atm). The deposition was performed on a 316L stainless steel substrate, in a fully automatic EB-PVD advanced vacuum deposition system (Torr Inc, USA).

The controlled electron beam evaporation system consists of a stainless-steel vacuum chamber, with a size of 1500 x 1500 x 1650 mm (chamber volume 3m3), with several viewing ports on the front door used for introducing materials and visiting all other accessories, such as thickness sensors, as well as easy cleaning and maintenance of the room. The chamber and the front door are permanently water-cooled. The water-cooled crucibles were loaded with the afore-mentioned materials to be evaporated and continued to be positioned so that all surfaces were exposed to the vapor flow.

The deposition of the multilayered film was done using 4 electron guns of 10kW each placed inside the vacuum chamber. The thickness of the deposition was continuously controlled by means of a quartz balance. The substrate was heated to min. 500 °C by a radiant heater located behind the substrates, to ensure a good adhesion to the deposited films, the working vacuum inside the enclosure being (approx. 10-6 Towers), and the deposition rate being approx. 0.8-1A / s.

Corrosion tests were performed in a 1L ASTL type flat corrosion cell The electrolyte solution used was 1N H2SO4, according to ASTM A262 standard. To characterize the obtained layers, the pre- and post-deposition samples as well as the 1N H_2SO_4 corroded samples were analyzed using a high-resolution, fully digitized Quanta 250 (FEI) scanning electron microscope, equipped with XT Microscope server software and an energy dispersive X-ray spectrometer. Thus, in order to determine the metallographic structure, the samples were prepared metallographically being embedded in resin, sanded and polished. The scratch test was performed with a NANOVEA Scratch Test device on EB-PVD oxide layers.

The multilayer deposits were made on a 316L stainless steel support, on which was initially deposited a bonding layer (Ni-Cr alloy), an intermediate layer from ZrO2 doped with 8% gr. cerium oxide (CeO2), and Al2O3 as outer layer., The estimated thicknesses with the help of the quartz balance were 1µm for the bonding layer of NiCrAlY alloy, 1.5µm for the outer layer of ZrO2 doped with 8% gr. CeO2 and 5.5µm for the Al2O3 layer.

The samples were studied by scanning electron microscopy using the fully digitized, high-resolution Quanta 250 scanning electron microscope (FEI) equipped with XT Microscope server software and an energy dispersion X-ray spectrometer consisting of a fixed ELEMENT Silicon detector. Drift Fix and ELEMENT EDS Analysis Software. The elementary cross-section distribution of the coatings was performed using elementary X-ray mapping in Low Vacuum and High Vacuum modes, respectively, using the backscattered secondary electron detector (CBS) and the dispersive energy spectroscopy (EDS) detector. The analyzes were performed both on the surface of the samples for the study of the microstructure of the multilayer deposits and in the section for the study of the deposited layers. In the case of surface analyzes, the samples were fixed directly on the C-band, and for the analyzes performed in section, the samples were embedded in epoxy resin, then sanded and polished.

3. Results and discussion

The investigation in Fig. 1 shows 316L stainless steel low magnification surface micrographs to be coated with oxides. The surface micrograph of the 316L steel sample used as a substrate shows a structure with grains of irregular dimensions and areas with some structural defects produced as a result of surface preparation by polishing.

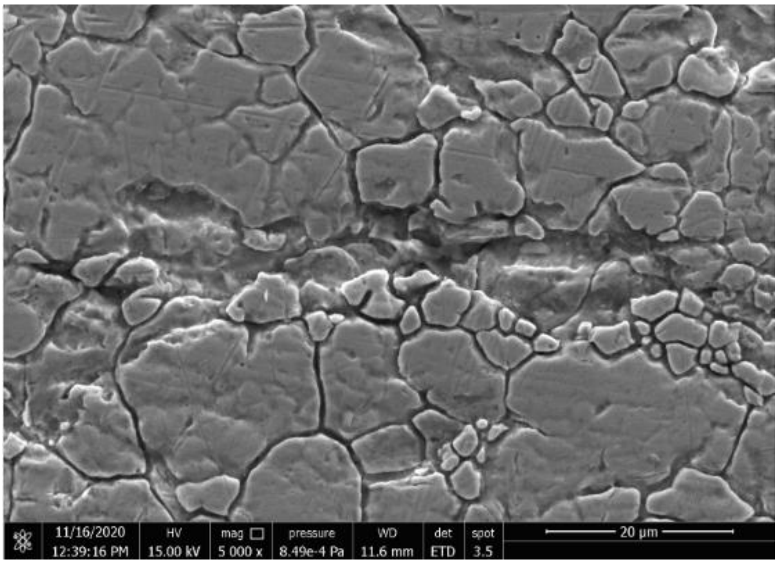

Fig. 1. SEM image of the 316L sample before deposition

The analyzes performed on the surface of the samples indicate a uniform deposition of the surface layer, being formed, from a granular mass with different structures and dimensions. Fig. 2 shows the typical SEM image of the sample coated with ZrO_2 doped with 8% gr. CeO_2 and Al_2O_3 which highlight the structure of the surface covered with corresponding growths that follow the initial morphology of the substrate.

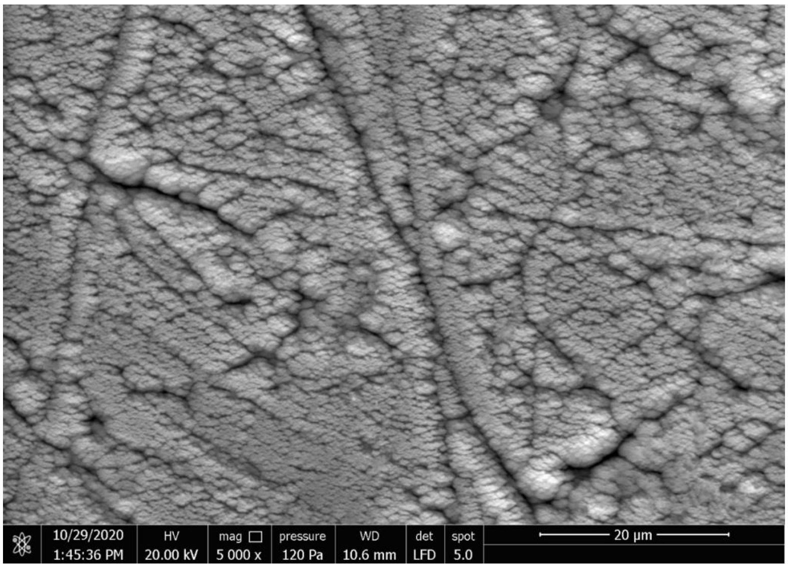

Fig.2. SEM image of sample coated with ZrO_2 doped with CeO_2 and Al_2O_3

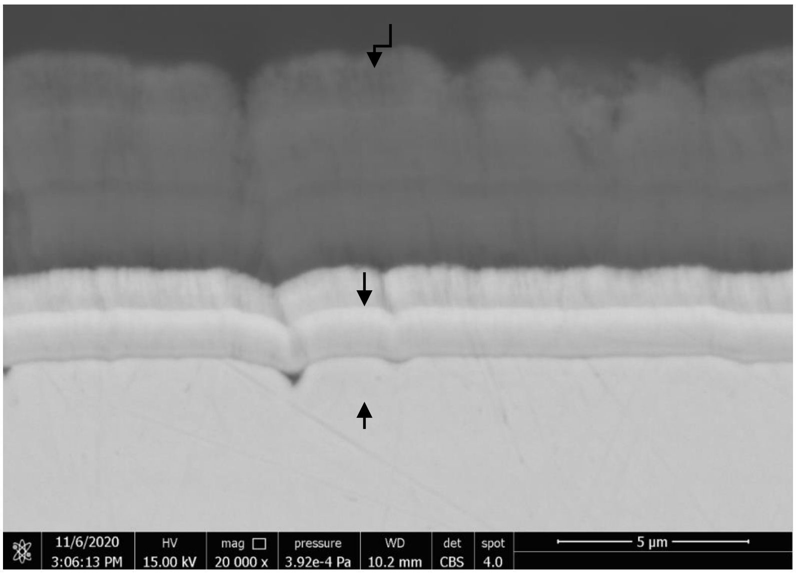

Fig.3. SEM microstructural aspect of the cross section on the test of deposits by EB-PVD of films (layers) of: acros + ZrO_2 -CeO_2 + Al_2O_3 on stainless steel substrate

The SEM micrograph from Fig.3 shows the morphology of the layers deposited in cross section. The three substrates can be observed, namely: the bonding layer (NiCrAlY), ZrO_2 doped with CeO_2 and Al_2O_3. The deposited layers are continuous, without the appearance of pores or micro-cracks.

The chemical composition of each layer was estimated by EDS analysis on the selected areas highlighted in Fig. 4.1. The results presented in Fig. 4.2 show that the majority of the elements contained in the powder evaporated by the EB-PVD process are found on the deposition made on the stainless-steel substrate.

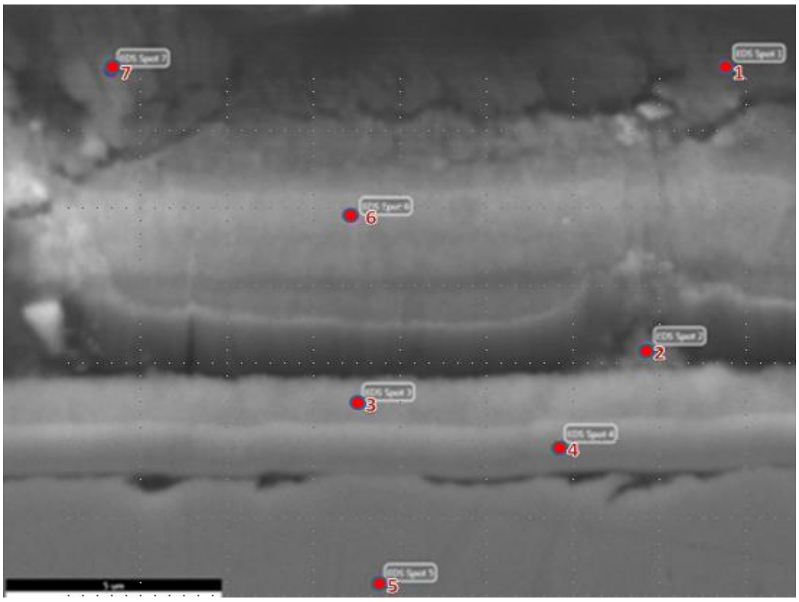

Fig.4.1. Qualitative EDAX analysis on the surface of the cross section of the oxide multilayer sample: acros + rare earth oxides-OPR (ZrO_2 - CeO_2) + Al_2O_3 on austenitic stainless-steel substrate

The semi-quantitative chemical composition of each layer deposited and of the stainless-steel support used was highlighted by point EDS analyzes, the results obtained being the following:

- Stainless steel support, contains: Fe, Cr and Ni;
- Across layer, contains mostly Ni, Cr and in smaller quantities: Al, Y, Zr, O, Ce;
- The Ce-doped ZrO2 layer contains Zr, Ce, O and in smaller quantities: Al, Y, Fe, Cr;
- Al2O3 layer, contains: Al, O.

The EDAX analysis performed confirms the presence of the deposited elements. The atomic and mass percentages of point 3 are shown in Table 1.

Table 1

EDS Spot 3 analysis on the surface of the samples before corrosion experiments

	Element	**Weigh%**	**Atomic%**
316L_ZrO_2 doped with CeO_2_Al_2O_3	CK	6.44	16.6
	OK	26.08	50.44
	ALK	8.26	9.47

	YL	0.99	0.34
	ZrL	35.76	12.13
	CeL	4.86	1.07
	CrK	9.29	5.53
	FeK	1.39	0.77
	NiK	6.93	3.63

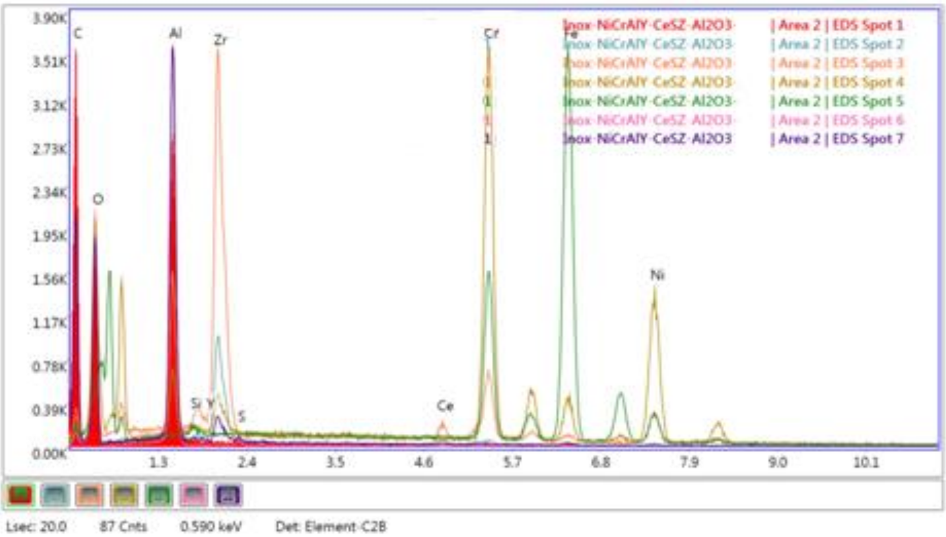

Fig.4.2. Qualitative EDAX analysis on the sample surface - EB-PVD deposition of films (layers): across+ OPR (ZrO_2 - CeO_2) and Al_2O_3 on stainless steel substrate

adhesive

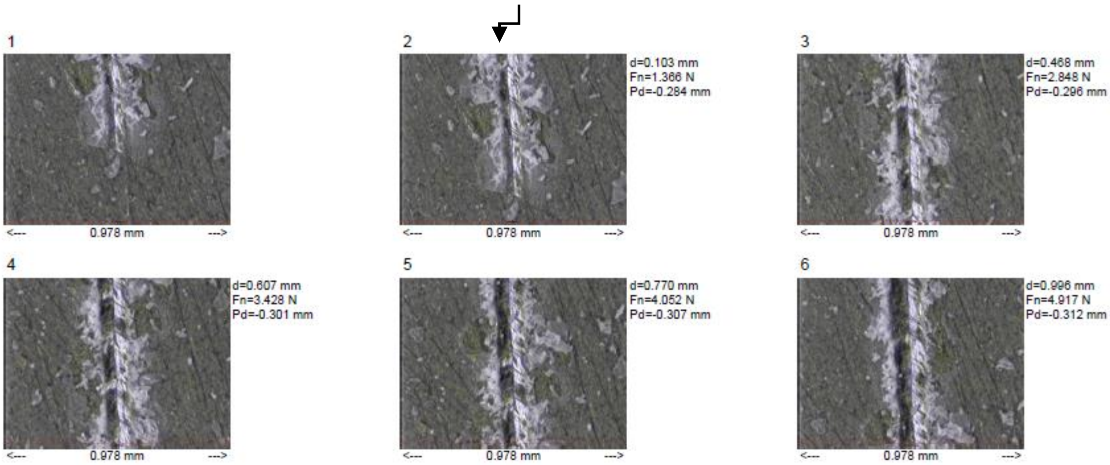

Fig.5. Scratch image resulting from the Linear scratch coating with multilayer oxide test

The presence of C in the EDS analysis is due either to the carbon strip on which the sample is fixed or can be explained by its presence in the embedding resin.

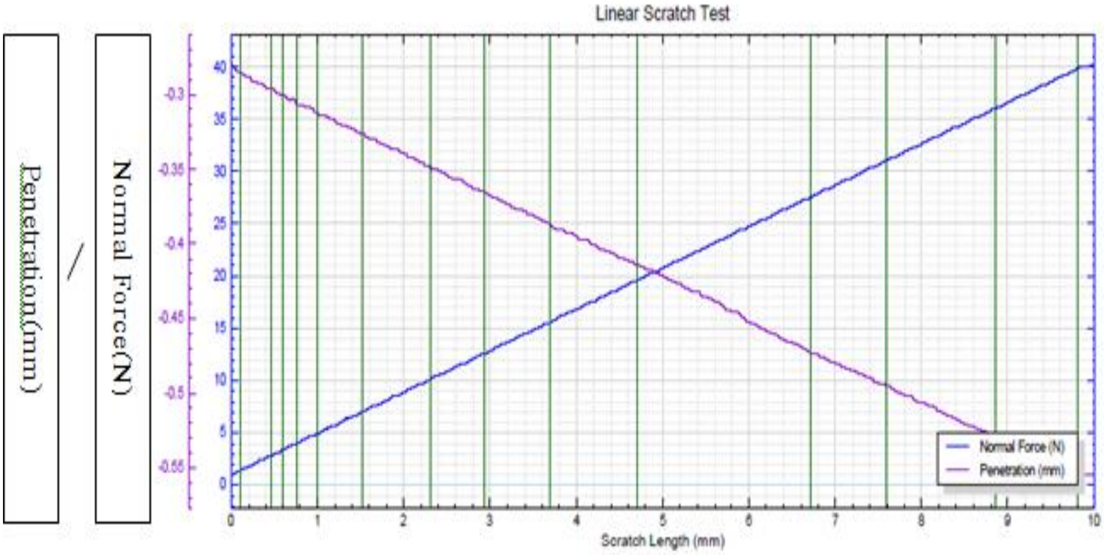

Fig.6. Linear scratch test of the multi-layer oxide coating scratch

Adhesion tests performed using the scratch test method and proved to be a simple and reliable method for assessing the mechanical / adhesion properties of multilayer oxide coatings. The scratch test was performed on coatings with several layers of Al_2O_3 oxide and CeO_2-doped ZrO_2 deposited by EB-PVD, on 316L austenitic stainless-steel substrate (Fig. 5). The adhesion proved to be directly proportional to the thickness of the coating; even at high loads (4.97N), as seen in the image in fig.6, it is observed that, with the increase of the normal force, the adhesion of the coatings decreases first in cohesive mode, then in an adhesive mode.

The SEM micrograph from Fig. 7 shows the microstructure of the samples obtained following the corrosion experiments performed in the electrochemical cell, in 1N H_2SO_4 sulfuric acid solution. It is observed that the samples show local degradations of the deposited coatings with pitting local corrosion appearance. This is demonstrated by the analysis of sediments with a composition modified by the action of 1 N H_2SO_4 acid medium. The EDS analyzes performed in the samples section, presented in table 1, highlighted the presence of the following elements: Al, Fe, Cr, Zr, Ni, Mn, Si, O, C.

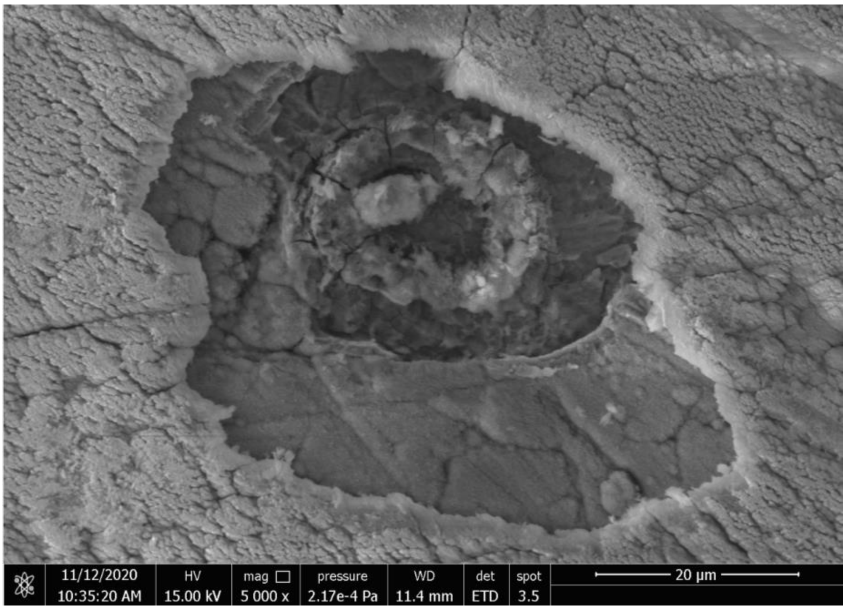

Fig.7. SEM Cross-sectional images of samples after corrosion experiments: across + OPR (ZrO_2 - CeO_2) and Al_2O_3, in 1N H_2SO_4 acid solution

Table 2

EDS analysis on the surface of the samples after corrosion experiments

	Element	**Weigh%**	**Atomic%**
316L_ZrO_2 doped with CeO_2_Al_2O_3	C K	0.00	0.00
	O K	29.13	49.00
	AlK	35.80	35.71
	SiK	0.07	0.07
	ZrL	9.05	2.67
	SK	0.53	0.44
	CeK	1.61	0.52
	CrK	6.65	3.39
	FeK	13.80	6.65
	NiK	3.36	1.54

4. Conclusion

The corrosion behavior of deposits based on ZrO_2 doped with CeO_2 and Al_2O_3 on austenitic 316L stainless steel was studied, using the evaporation technique EB-PVD. The deposited layers were chemically and structurally analyzed by SEM and EDX microscopy. The estimated thickness of the deposits was 1µm for the bonding layer of NiCrALY alloy, 1.5µm for the ZrO_2 layer doped with CeO_2 and 5.5µm for the Al_2O_3 layer, respectively. The deposited layers are continuous and adherent, without the appearance of pores and micro-cracks. The ceramic layers have a columnar growth specific to the coatings obtained by the EB-PVD method and the morphology of the surface follows the morphology of the stainless-steel substrate.

Corrosion tests were performed in an electrochemical corrosion cell in 1N H_2SO_4 sulfuric acid solution. The corrosion test was performed at room temperature by linear polarization. The microstructural characterizations were performed after 60 minutes of immersion of the electrodes in the studied electrolyte solution. The results obtained by comparing the samples before and after the corrosion tests highlight the appearance of some areas showing local degradations of the deposited coatings with pitting corrosion appearance. Further work is underway to study the mechanism for improving corrosion and to assess the potential use of these coatings.

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