IMPROVEMENT OF CORROSION BY MOLTEN SALTS IN COATING POWDERS MIXED IN DIFFERENT COMPOSITIONS OF YSZ- Al_2O_3

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ABSTRACT

The improvement of corrosion performance at high temperatures of coatings in which the alumina composition in Yttria-stabilized zirconia (YSZ- Al_2O_3) was varied in 3 different percentages was studied. These systems were deposited on AISI 304L stainless steel substrates using plasma spraying. The determination of the corrosion rate was performed in a corrosive environment containing 20 % Na_2SO_4 and 80 % V_2O_5 , at temperatures ranging from 800 °C to 900 °C. The structural characterization was determined by X-ray diffraction (XRD), and the analysis of the surface after exposure at 900°C was performed by scanning electron microscopy (SEM). The best performing system was the one containing 40% alumina, due to the morphology and structural change.

Keywords: Alumina (Al_2O_3), Zirconia stabilized with Ittria, Coatings, Corrosion.

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INTRODUCTION

Thermal barrier coatings have been the main solution to protect metal components subject to thermal cycling conditions at high temperatures and in corrosive environments. This type of coating protects metal components working in the hottest areas such as gas turbines and diesel engines.^{1,2} The insulating properties of these coatings lead to an improvement in performance, through the increase in working temperatures, and in the average life of the components, by reducing the temperature of the metal, in addition to a reduction in the cooling system.³ A thermal barrier generally consists of a coating, such as thermal insulation, and a metal-bonding coating between the substrate and the insulating coating, which is used to provide good adhesion, and an oxide layer which yields strong corrosion protection for the substrate.^{3,4} A variety of techniques have been used to commercially lay the thermal barrier system, including thermal spraying via the plasma spray process (PS).⁴

For high-temperature applications, Al_2O_3 , ZrO_2 , and Yttria-Stabilized Zirconia (YSZ) coatings have been proposed to be designed as coating systems and mixed to reduce the heat transfer rate without affecting corrosion resistance.⁵

The thermal projection has been developed as a surface coating technology, consisting of the deposition of molten material. The main objective of this technique is to provide an increase in the useful life of the elements by offering an extensive list of materials to be deposited and substrates to be coated.⁶ The speed and temperature at which the particles impact the substrate define the properties of adhesion, porosity, hardness, roughness and resistance to wear and corrosion of the coating being deposited.⁷⁻¹¹

The most important technique of thermal projection is that of plasma spraying, two wires of the material to be deposited, electrically charged with opposite polarity, are brought simultaneously to a contact point where a plasma spraying that melts the wires jumps, and high-pressure gas projects the molten metal in

the form of drops towards the substrate.¹² This technique has the advantage of being economical and can be applied to metal coatings, resistant to corrosion, wear, and good adhesion.^{13,14}

In this research, the plasma spraying system was used to produce YSZ and Al₂O₃ coatings to form a structure and evaluate its performance to provide a replacement for high-strength coatings. The characterization of the coatings was done by optical microscopy, scanning electron microscope (SEM), and X-ray diffraction (XRD). Additionally, the rate of deterioration was determined using potentiodynamic polarization curves to determine the behavior of the different systems according to temperature.

EXPERIMENTAL

Material and Methods

The coatings were deposited on AISI 304 stainless steel substrates. Before the deposition, the specimens were prepared superficially obtaining the appropriate roughness and improving the adhesiveness of the system. To produce the coating, the plasma spraying was used with a 0.16 cm diameter tubular wire. The composition of the wire and the powder used in the conformation of the coatings is a zirconium compound stabilized with yttria and alumina (Al₂O₃-YSZ).

After depositing the coatings, the characterization of the electrochemical properties according to temperature was developed at temperatures ranging from 800 °C to 900 °C using anodic polarization curves. An EG&G PARC 27A potentiostat and a cell composed of three electrodes were used: working electrode samples from the different systems [100 YSZ], [80% YSZ - 20% Al₂O₃], [60% YSZ - 40% Al₂O₃] and [40% YSZ - 60% Al₂O₃], platinum as counter electrode and Ag/AgCl reference electrode.

The corrosive agent used in the test is a mixture of 20% sodium sulfate - 80% vanadium pentoxide (% by weight) obtained from analytical grade reagents. The mixture was established based on the general weight (150 g), adding 20% sodium sulfate (30 g) with 80% vanadium pentoxide (120 g) macerated and homogenized for 45 minutes in mortar. It was then placed in a 30 g porcelain crucible fixed inside a vertical furnace. The electrochemical cell was placed in the furnace and the heating started from the ambient temperature up to the 900 °C - temperature necessary to conduct the electrochemical tests. The assembly diagram used in the laboratory is shown in Fig. 1.¹⁵ The internal temperature was controlled using a type k thermocouple connected to a temperature controller. To simulate an industrial boiler environment, a mixture of oxidizing gas 1% SO₂ -99% O₂ was used.

The coatings were characterized structurally by X-ray diffraction with a Philips X-ray diffractometer, with Bragg-Brentano configuration ($\theta/2\theta$) in the ground beam mode, Cu K α radiation (1.540998Å) working at 45 kV and 40 mA.

Coatings after exposure to high temperatures were studied superficially by scanning electron microscopy with an FEI Tecani F20 FEG-TEM electron microscope operating at 15 kV.

The polarization curves were obtained by applying a potential difference of ± 300 mV at a scanning speed of 0.125 mV s⁻¹ in potentiodynamic form. The corrosion rate and potential corrosion potential were obtained by the extrapolation of Tafel. An EG&G PARC 273A potentiostat was used, the potential corrosion values (*E*_{corr}) and the corrosion current density (*i*_{corr}) are determined after 3 hours of exposure to the corrosive medium, the time necessary to stabilize the corrosion potential. To obtain meaningful information from the analysis, 3 measurements per sample were performed.

RESULTS AND DISCUSSION

Figure-2 shows the results of the potentiodynamic tests using Tafel for the systems [80% YSZ – 20% Al₂O₃], [60% YSZ – 40% Al₂O₃], [40% YSZ – 60% Al₂O₃] and [100% YSZ]. Their comparison with the [100 % YSZ] coating and the alumina variations of 20 %, 40 % and 60 % depending on the study temperatures 800 °C, 850 °C, and 900 °C. For the coatings in a combination of YSZ and Al₂O₃, the parameters of corrosion velocity, current density and corrosion potential were obtained by the intersection of the extrapolation of the anodic and cathodic Tafel curves. Each of the systems was evaluated at temperatures ranging from 800 °C to 900 °C.^{15,16} For the system [100% YSZ] the current density of the coatings and the corrosion rate was the highest, this is observed in the displacement of the potentiodynamic curves to the right, on the X-axis. For the sample evaluated at 900 °C, the highest corrosion current density values of all evaluated systems are evident. This protective capacity of the film

decreases due to the decrease of the polarization resistance value.^{17,18} The values of corrosion potential, current density and corrosion rate for all systems studied are recorded in Table-1.

Fig.-1: Diagram of the Furnace and the Adaptation of the Corrosion Cell.

Fig.-2: Potentiodynamic Polarization Curves of Systems As A Function of Temperature, a) [80 YSZ - 20 Al₂O₃], b) [60 YSZ - 40 Al₂O₃], c) [40 YSZ - 60 Al₂O₃] and d) [100 YSZ].

About the potentiodynamic curves and the respective data, it is evident that the corrosion current density shows a decrease in the coating [80 YSZ - 20 Al₂O₃]. It is also observed that systems with the Al₂O₃ component have a lower current density compared to the coating [100% YSZ] without alumina addition.

As this measure is directly proportional to the corrosion rate of the sample, it was found that adding Al_2O_3 systems improves corrosion resistance to coatings. This result is explained by the high-temperature stability in harsh chemical environments offered by alumina. Also, the low coefficient of thermal expansion of alumina makes it possible to reduce thermal stresses in coatings, giving them good resistance to thermal shock and dimensional changes influenced by temperature changes.¹⁹

Table-1: Values of the Tafel Parameters for the Coatings Studied.

Temperature	Corrosion Potential mV	Corrosion Current Density $\mu\text{A}/\text{cm}^2$	Rate of Corrosion $\mu\text{m/y}$
[80 YSZ – 20 Al_2O_3]			
800	-0.09	82.1	738
850	-0.114	346	3084.5
900	-1.12	1001	8940.8
[60 YSZ – 40 Al_2O_3]			
800	-0.50	77.47	692.65
850	-0.20	23.41	209.04
900	-0.45	6.02	53.59
[40 YSZ – 60 Al_2O_3]			
800	-0.091	3.46	31.83
850	-0.209	20.03	178.84
900	-0.747	142.3	1268.5
[100 YSZ]			
800	-0.31	457	11607
850	-0.85	598	15189
900	-0.56	1725	43815

The study shows that the coatings resist very well at temperatures of 800 °C. However, a proportional increase was found between the corrosion density and the temperature increase. These results enable us to infer the potential field of application of these coatings in parts subjected to operating temperatures above 800 °C.²⁰ The system coatings [60% YSZ – 40% Al_2O_3] show an opposite behavior to the system previously analyzed. At temperatures above 800 °C there is a decrease in the corrosion rate due to the porosity of the coating and the flow of heat through the film. The result is low thermal conductivity. For coatings studied at temperatures of 850 °C and 900 °C the result is the emergence of metastable phases with anticorrosive resistance due to the content of Al_2O_3 .²¹ It can, therefore, be concluded that most of the agglomerates in the film have had enough time to melt and solidify, resulting in homogeneous and stable systems.

The system [40% YSZ – 60% Al_2O_3] shows the lowest corrosion velocity values at 800 °C of all coating systems studied, due to their homogenization. The best anticorrosive performance is related to the final grain size when Al_2O_3 is added. However, as the temperature increases to 900 °C the corrosion current density increases due to the increased porosity of the coating. Additionally, the increase of Al_2O_3 in the coatings allows greater densification, a decrease of the porosity and compaction of the films. These characteristics allow a better anticorrosive performance by increasing the corrosion resistance values.²² The explanation lies in the formation of a passive layer of Al_2O_3 during immersion in the molten salts, this would prevent the coating from corrosive attacks at elevated temperatures.²³

Figure-3 shows the X-ray diffractogram of the yttrium oxide stabilized zirconia (YSZ) coating. A high proportion, of crystalline phases, is evident. The size of the peaks determines the existence of large and spaced crystals. These characteristics would indicate a favoring to the entrance of the corrosive solution generating an increase of corrosion speed. The evaluated behaviors correspond to the thermodynamic results obtained at the three temperatures studied. This corroborates that at 900 °C the corrosion current density is high due to thermal expansion processes originated by the greater spacing between the crystals that make up the coating.²⁴

Figure-4 shows the X-ray diffractograms corresponding to the system coatings [60% YSZ – 40% Al_2O_3] and [40% YSZ – 60% Al_2O_3]. The formation of peaks in the graphs indicates that they are mostly

crystalline systems. However, it is observed that the coatings have fewer crystalline phases related to YSZ compounds when substituted by Al_2O_3 structures. The increase in the intensity of the peaks related to the crystalline phase is to be expected for the case of the system [40% YSZ – 60% Al_2O_3] due to the higher weight content of alumina in the compound. However, the greater intensity of the peaks allows establishing that the crystallization processes are controlled by the compound YSZ.²⁵ The peak width is more significant for the system with 60% Al_2O_3 , associated with the presence of an intermediate phase between YSZ and Al_2O_3 due to the superposition of the diffraction peaks of the phases. The relative width of the peaks indicates that the crystal sizes are smaller for the system [60% YSZ – 40% Al_2O_3] which correlates with the information obtained from potentiodynamic curve tests where the greater anticorrosive efficiency in high-temperature processes is related to the homogeneous distribution of the grains that make up the film.²⁶ The diffraction spectra for system coatings [80% YSZ – 20% Al_2O_3] is similar to [60% YSZ – 40% Al_2O_3] so they are not reported, as are the diffractograms of the YSZ system.

Fig.-3: X-ray Diffractogram Corresponding to the YSZ Coating.

Figure-5 shows the surface analysis following the potentiostat tests at a temperature of 900 °C. Figure-5a shows an image of the 100% yttria-stabilized zirconia surface with a loss of coating on the lower left side. This result is explained by the higher corrosion velocity and corrosion density values of all evaluated systems. Also, the shape of the polarization curves determines a high dilution due to the rupture of passivity in the presence of the corrosive agent. The heterogeneity linked to the different grain sizes on the coated surface causes a progressive accumulation of condensed salt due to the melting temperature of sodium sulfate, 884 °C, inducing a higher corrosion velocity value at 900 °C.^{27,28}

Fig.-4: X-ray Diffraction Spectra of the Coatings of [40 YSZ - 60 Al_2O_3] and [60 YSZ - 40 Al_2O_3].

Concerning the micro-chemical analysis, in the micrographics the dilution is observed in greater proportion due to the unleashing of accelerated corrosion processes when the system is submitted to temperatures close to 900 °C.²⁹ The addition of alumina to the YSZ compound affects the final structure of the system producing a partial stabilization of the zirconia by the presence of Al_2O_3 . As a result of the partial stabilization process, the grain size is affected, which leads to a modification of the surface morphology of the coating, improving its density and resistance to corrosion. The variation in the surface topography of the coatings is associated with the increase in alumina in the systems as evidenced in Fig.-5b, Fig.-5c and Fig.-5d. For system coatings [80% YSZ – 20% Al_2O_3] there is a loss of film related to the increase in the current density of corrosion associated, as well as the [100% YSZ] system, to the liquid state of the corrosive solution.³⁰ In the system [60% YSZ – 40% Al_2O_3] (Fig.-5c), the superficial growth of an oxide layer is evidenced as well as detachments in several zones as a result of the mixture of the compounds. Therefore, increasing the amount of alumina in the systems results in a decrease in crystal size as corroborated by the diffraction spectrum. Figure-5d shows a detachment in coatings with composition [40% YSZ – 60% Al_2O_3] due to the amount of alumina present in the film. With the results obtained, higher efficiency and lower corrosion current density, it is possible to affirm that the optimal system for this type of test is that of coatings with a maximum of 40% Al_2O_3 .³¹

Fig.-5: Micrographics of the Coatings after Exposure to 900°C, a) [100 YSZ], b) [80 YSZ - 20 Al_2O_3], c) [40 YSZ - 60 Al_2O_3] and d) [60 YSZ - 40 Al_2O_3].

CONCLUSION

The potentiodynamic polarization curves indicate that the behavior of the corrosion current and the corrosion rate depends in most cases on the temperature. If the temperature increases the corrosion rate also increases. However, for the case of system coatings [60% YSZ – 40% Al₂O₃] the corrosion rate shows an opposite trend as the corrosion current density decreases to 850 °C and increases to 900 °C indicating stabilization at higher temperatures.

The increased corrosion resistance of the coating is generated when alumina is stabilized at temperatures between 800 °C and 850 °C. At these temperatures, the grain size is smaller, and the films are more compact resulting in lower current densities. Therefore, this type of system is recommended to work at temperatures close to and above 900 °C.

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