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Research Article

Electrochemical Behavior of Yttria Stabilized Thermal Barrier Coating on Mild Steel in Artificial Sea Water

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Abstract: The plasma sprayed Yttria stabilized thermal barrier coating electrochemical behavior was investigated in artificial sea water by Linear Polarization Resistance (LPR), Open Circuit Potential, and Electrochemical Impedance Spectroscopy (EIS) methods at room temperature. Thermal properties of applied coating after 600 hours exposure in 3.5% NaCl solution demonstrated 0.5% weight loss at about constant heat flow rate of 1 watt/gm upto 400ºC followed by regain in weight at 600ºC due to endothermic reaction. The initial weight loss at constant heat flow was attributed to stabilization of coating. The electrochemical analysis revealed that the open circuit potential became positive after 600 hours compared to 0 hour with decrease in polarization resistance. The 28% decrease in charge density after 600 hours exposure in 3.5% NaCl solution was in support to decrease in polarization resistance. The decrease in charge transfer resistance was attributed to the ingress of chloride ions at the coating metal interface and localized corrosion reactions at the oxide film.

Keywords: Thermal barrier coating, plasma spray, corrosion resistance, electrochemical

1. INTRODUCTION

Thermal-barrier coatings (TBCs) have great importance for insulation of components operating at higher temperatures rather than protecting base from oxidation. The TBCs have markedly increased the efficiency and life of gas turbines operating at elevated temperatures [1]. The TBC is usually a multilayer composite coating system consists on metallic bond coat and ceramic top coat. The metallic bond coat is multifunctional interlayer which provides oxidation resistance to substrate and promotes strong bonding between top coat and base alloy [2–4].

A typical TBCs top coat is yttria-stabilized zirconia (YSZ) with a metallic bond coat. The bond coat may have different recipes such as Ni-Cr-Al-Y super alloy, Ni-Al, and Cr-Ni-Al, etc. YSZ top coat is considered best as it has low thermal conductivity and high temperature stability [5]. During operation at high temperature the hot gases diffuse through the pores in the top coat and oxidize the bond coat. Long term thermal exposure results in the growth of oxide layer between the bond and top coat and hence cracking of TBCs.

At room temperature the diffusion of electrolyte through micro-pores within the top coat will facilitate growth of oxide layer at bond and top coat interface and, eventually, failure of coating would become certain. To evaluate degradation mechanism of TBCs in artificial sea water, the electrochemical

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impedance spectroscopy (EIS) is a reliable method. The porosity within topcoat and diffusion of electrolyte can be evaluated by Equivalent Electrical Circuit Model (ECM) simulated to the physical system at room temperature [6–9].

The objective of this study was to assess the corrosion tendency of TBCs when exposed to sea water at room temperature. The physical absorption of electrolyte in the coating and structural changes were estimated by thermal analysis. Additionally, the mechanism of electrochemical reactions at the coating/metal interface was investigated by electrochemical impedance spectroscopy.

2. MATERIALS AND METHODS

2.1. Substrate Coating

Coupons of carbon steel (0.08% C, 2.0% Mn, 1.09 % Si, 0.045% P and 0.03% S) of 12.5x 25mm size were grit blasted with steel grit # 29 to attain approximate surface roughness of 9µm. The coupons were cleaned in distilled water and then by acetone followed by ultrasonic cleaning at 60°C. Coupons were again rinsed in distilled water and dried with compressed air to ensure removal of aqueous medium.

Table 1. Operating parameters of air plasma spray coating.

Parameter	Value
Torch current intensity	500 Amp
Pressure & composition of gas	50psi (Ar/H_2)
Pressure of carrier gas (Ar)	60 psi
Powder feed rate	6 lbs/hr
Spray distance & angle	6 inches at 90^0
Preheating temperature	150 ^{0}C
Substrate cooling temperature	Normalizing

The Sulzer Metco Air Plasma Spray (APS) coating system was used for TBC to deposit over the surface. Before coating the powder was heated at 105°C in an oven for about 30 minutes to remove moisture. Ni_5Al (Metco 450 NS powder) was deposited at the substrate by APS as a bond coat and YSZ (ZrO_2–8 wt% Y_2O_3) top coat was applied over bond coat similarly. The operating parameters of APS are given in Table 1. The thermal analysis such as Differential Scanning Calorimeter (DSC) and Thermo-gravimetric Analysis (TGA) of the top coat after 600 hours immersion in 3.5% NaCl solution was carried out to evaluate its physical absorption of electrolyte characteristics.

2.2 Electrochemical Testing

The electrochemical characteristics of applied Thermal Barrier Coating (TBC) were evaluated by Open Circuit Potential (OCP) measurements, Linear Polarization Method (LPR) and Electrochemical Impedance Spectroscopy (EIS).The coated surface was exposed to 3.5% NaCl solution in a three electrode cell system while other sides of the samples were covered with polyester resin. In this cell Saturated Calomel Electrode (SCE) was a reference, graphite as an auxiliary and coated sample acted as a working electrode. The electrical contact was made with the sample by soldering a wire at the back. The OCP and LPR scan (within potential range -200 to +200mV Vs. SCE) were taken after every 72hours upto 600 hours providing an initial stabilization delay of 24hours. Similarly EIS spectrums were obtained with 10mV AC perturbation at the open circuit potential and frequency range of 100 KHz–10 mHz. The whole electrochemical investigation was exercised by using Gamry Potentiostat (PC14-750).

3. RESULTS AND DISCUSSION

3.1 Thermal Analysis of Thermal Barrier Coating (TBC)

The results of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of YSZ top coat when exposed to 3.5% NaCl solution after 600 hours are shown in Fig. 1a & b, respectively. It was evaluated that loss in mass of coating when

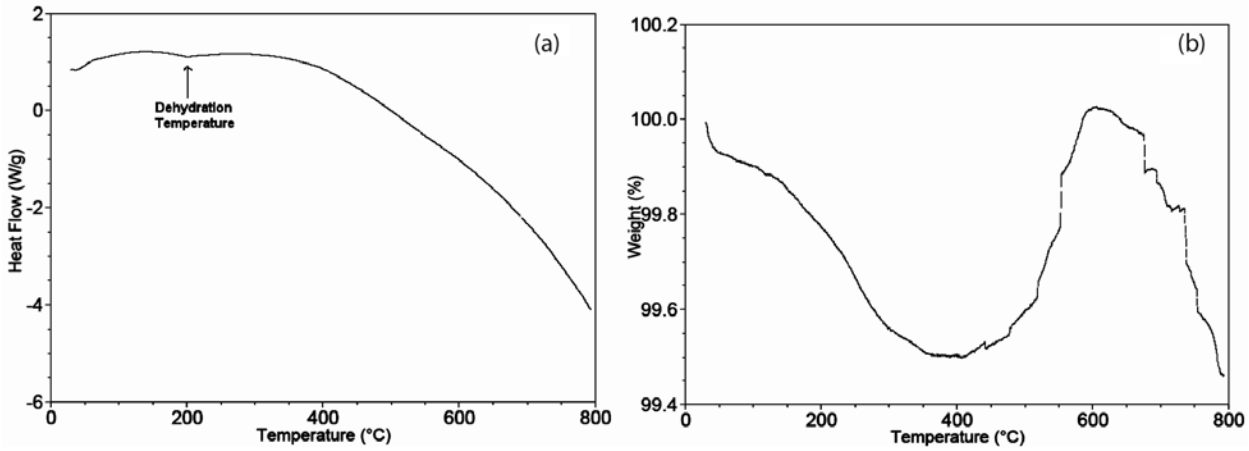

Fig. 1. Thermal analysis of TBC (a); DSC (b); TGA.

heated at the rate of 5ºC/min, there was an exothermic regime of DSC below 400ºC. This exothermic behavior with continuous decrease in 0.5% weight in TGA was attributed to the stabilization of YSZ. The endothermic peak in the DSC curve at 180ºC was due to the dehydration process with about 0.2% weight loss which demonstrated the actual ability of physical absorption of water in the coating upto this temperature. The endothermic behavior of YSZ coating above 400ºC with regain of weight upto 590ºC corresponded to crystallization of YSZ and diffusion of anions (oxygen, chlorides) within the cubic lattice of ZrO_2 after stabilization with Y_2O_3 from the electrolyte. The addition of 'Y ions' in Zirconia occupies lattice positions which produce oxygen vacancies. With the addition of Yttria in Zirconia promote oxygen ions to ingress within the YSZ lattice (oxidation) with increase in temperature [10].

3.2 Open Circuit Potential (OCP)

The open circuit potential (E_{ocp}) is a predictive parameter to estimate corrosion tendency of a system. The E_{ocp} of TBC samples with respect to Saturated Calomel Electrode (SCE) was determined for 600 hours when immersed in 3.5% NaCl solution. The values of E_{ocp} were determined after every 72 hours after initial stabilization for 24 hours. The potential trend was extrapolated at 0 hour to evaluate corrosion tendency of unexposed coated sample. The potential at 0 hour was -594 mV and gradually increased to noble potential (-345.2 mV) after 600 hours (Fig. 2). The tendency to shift potential in noble direction (positive direction) was attributed to the formation of oxide film at the bond coat surface but still active (-345.2 mV) potential was related to the presence of chloride ions in the electrolyte which may damage the oxide film. The shift of potential at the rate of 0.297 mV/hour towards noble direction indicated development of passive film hindering electrochemical reactions.

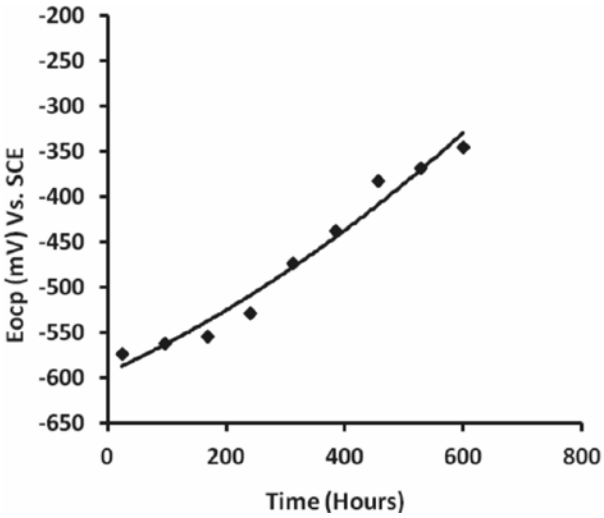

Fig. 2. Change in open circuit potential (OCP) with time.

3.3 Linear Polarization Resistance (LPR)

Linear polarization is an efficient method to evaluate corrosion rates and to understand kinetically

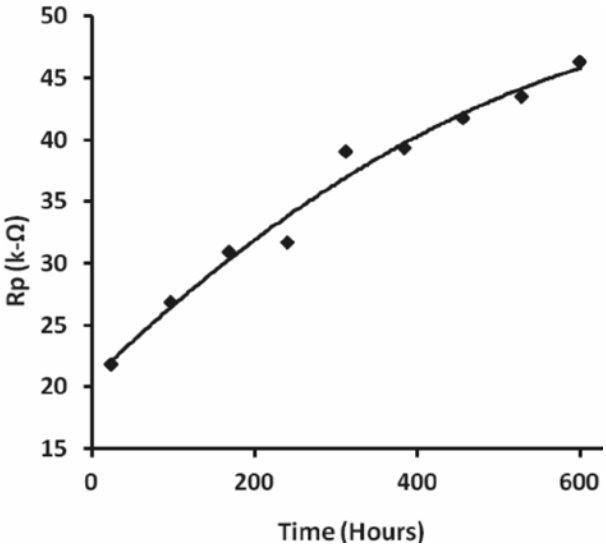

Fig. 3. Variation in Polarization Resistance (R_p).

controlled electrochemical reactions. The LPR curves were fitted by using Echem Analyst software and polarization resistance (R_p) and current density (i_d) values after each 72 hour interval were determined. The trend of change in R_p value with time (Fig. 3). The increase in R_p and decrease in i_d values in 600 hours of exposure was observed and this tendency was considered due to the formation and accumulation of corrosion product within the pores of coating after 600 hours at the interface of top ceramic coat and bond coat. The initial R_p and i_d values after 24hours exposure were 21.80 k-Ω and 1.195 µA, respectively. These quantities with respect to initial values reached to 46.31 k-Ω and 0.5626 µA in 600 hours. This shows the independence of Yittria stabalized Ziconia (YSZ) top coat to hinder the diffusion of electrolyte. The charge density of YSZ coating when immersed in 3.5% NaCl solution was calculated by integrating the current potential values of LPR curves. It was deduced that initial charge density (160.6 µC/cm^2) of coating was deteriorated to 114.6 µC/cm^2 as presented in Fig. 4. This decrease of 46 µC/cm^2 in charge density and increase in polarization resistance suggested the formation of corrosion product and accumulation within the pores in the coating after 600 hours exposure. This was also responsible for the reduction in the active sites for electrochemical reactions.

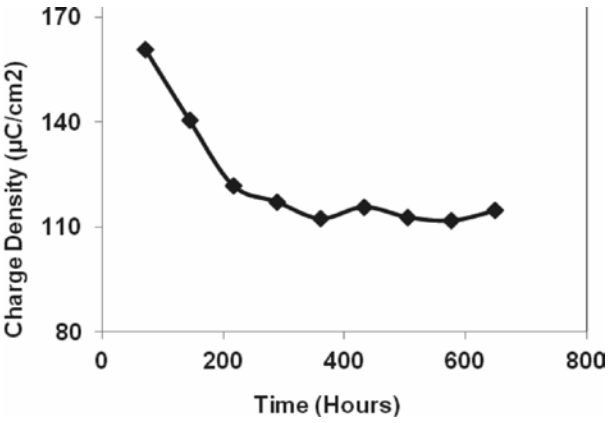

Fig. 4. Decrease in charge density measured by LPR.

3.4 Electrochemical Impedance Spectroscopy (EIS) of TBC

The EIS Nyquist plots for coated samples were obtained at room temperature as shown in Fig. 5. These plots were modeled and simulated with equivalent electrical circuit which was investigated by fitting the curves having goodness of fit upto 95%. It was apparent from the EIS investigation that there were three time constants in the spectrums. The solution resistance and YSZ coating resistance at higher frequency and in the second time constant depicted kinetically controlled reactions at the interface of top coat and bond coat by developing charge transfer resistance of 1.950 k-Ω at 0 hour which further decreased to 1.734 k-Ω after 600 hour. This decrease in R_{ct} was due chloride ingress at the interface and localized reactions with oxide film at the bond coat surface and by hydrolyzing of corrosion products. YSZ top coat resistance was very low due to free penetration of electrolyte through inherent micro-pores in the YSZ. The EIS study evaluated kinetic and mass transport controlled behavior of YSZ top coat and capacitative behavior of bond coat at low frequency in a third time constant was related with the formation of unstablized oxide film at the bond coat. This behavior of bond coat was attributed to the formation of oxide film at the interface of bond coat and top coat. This result for YSZ demonstrates typical behavior of TBC that mass transport controlled reactions transformed to kinetically controlled reactions at low frequency regime of impedance spectrum.

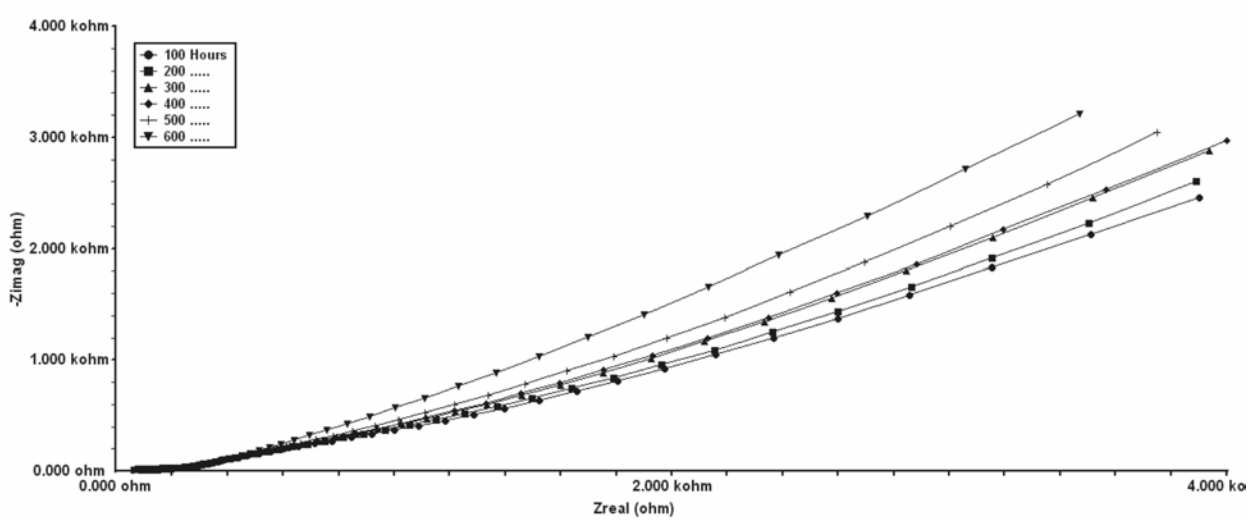

Fig. 5. Electrochemical impedance spectroscopy (EIS) Nyquist plots.

In TBC the kinetics of electrochemical reactions depend on the ionic resistance of electrolyte, microstructure of top, oxide film and bond coat, thickness, porosity and intrinsic defects within the coating [7].

4. CONCLUSIONS

The thermal analysis of coating after exposure to 3.5% NaCl solution revealed the absorption of electrolyte within the coating and exothermic behavior of top coat YSZ upto 400ºC temperature regime and a sharp dip for endothermic reactions corresponded to the stabilization of YSZ and dehydration of electrolyte, respectively. The initial loss in weight as revealed by thermal analysis was related to desorption of electrolyte while further increase in temperature and exothermic behavior of top coat and heat evolution corresponded to the stabilization of top coat. The shift of open circuit potential in positive direction and increase in polarization resistance with exposure time were related to the oxide film formation at the interface of top and bond coat. But the decrease in charge transfer resistance (R_{ct}) as determined by EIS was due chloride ingress at the interface and localized reactions on oxide film at the bond coat surface since their greater capability of hydrolyzing the corrosion product.

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