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A study on the oxidation resistance of electrodeposited and nanostructured YSZ thermal barrier ceramic coatings

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Abstract

A method is developed to electrodeposit nanostructured yttria-stabilized zirconia (YSZ) as thermal barrier ceramic coating on In.738LC Ni base superalloy substrate. The microstructure of the deposit and its oxidation resistance were investigated in detail in the present study. The first step was to applying an incipient conversion coating from an acidic solution in order to improve the coating adhesion. The deposition was performed in an aqueous solution containing yttrium and zirconium soluble salts as well as potassium chloride. Oxidation resistance of the specimens was tested at 1000 °C through a cyclic voltammetry method. The surface morphology and cross section of specimens were examined by a scanning electron microscope. According to the obtained results, it was concluded that nanostructured YSZ coating can obtained by electrochemical synthesis with better oxidation resistance compared to the conventional coatings. This was attributed to the formation of the ultrafine and compact structures. Meanwhile, homogenous distribution of micro-pores which was observed within the coating might have also affected the oxidation phenomenon.

Keywords: Yttria stabilized zirconia (YSZ); Oxidation resistance; Nanostructured ceramic; Thermal barrier coatings; SEM

1. Introduction

Thermal barrier coatings (TBCs) are being used in air and land based gas turbines for propulsion and power generation systems. They are utilized not only to reduce heat transfer through the coating but also to protect metal components from oxidation and hot corrosion. The currently used TBCs are yttria stabilized zirconia (YSZ) produced through air plasma spray (APS) and electron beam assisted physical vapor deposition (EB-PVD) techniques as the two main processing methods [1–3]. Recently some efforts has been developed to fabricate ceramic coatings by the electrodeposition method due to its advantages of producing both thin and thick coatings on the complex-shaped substrates, controllable microstructure, simplicity of the process and low-cost equipment, as well as, its high deposition rate over the prevalent methods [4–6].

The feasibility of cathodic electrodeposition of various ceramic materials including individual oxides, complex oxide compounds and composites has been demonstrated in the literature [7,8]. In the cathodic electrodeposition process, metal ions and/or complexes are hydrolyzed by electro-generated base to form oxide, hydroxide and peroxide deposits on the cathode surface. While, hydroxide and peroxide deposits can be converted to corresponding oxides through external thermal treatment.

According to literature, it has been reported that nanostructured coatings with improved mechanical properties showed better thermal resistance and lower thermal conductivity compared to the similar coarse-grained coatings [9]. Liang and Ding [10] evaluated the thermal shock resistance of nano and conventional YSZ coatings at 1000–1300 °C range and demonstrated that the number of cycles to failure of the nano YSZ coatings was 2–3 times greater than that for the conventional ones. Wang et al. [11] also evaluated the thermal

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shock resistance of the both nano and conventional ceramic coatings to 1200 °C and found similar results. Lima and Marple [5] demonstrated that the nanostructured YSZ coatings could be engineered to counteract sintering effects and to exhibit significantly lower increases in their thermal diffusivity and elastic modulus values at high temperature compared to those of conventional ones.

In the present work, nanostructured YSZ thermal barrier coating was deposited on Inconel 738LC by utilizing special electrodeposition technique. In normal cathodic electrodeposition, due to the high negative applied potential, water electrolysis occurs and hydrogen gas evolves and consequently an alkaline media forms on the surface. The metallic cations present in solution deposit as hydroxides on the alkaline surface and can be converting to oxides by an external heat treatment. The fast H2 evolution interferes with deposition process and necessitates a potential control and balance over the two processes. This potential control affects the nucleation and crystal growth of the deposits which can also be used to control the microstructure of the deposit that can affect oxidation resistance as well.

The aim of this work is to use cyclic voltammetry for controlling the two processes of H2 evolution and crystal growth of the deposits which affects its properties.

Table 1
Chemical composition of the examined Inconel 738LC in the present study.

Element	Mass percentage (wt%)
Al	3.58
Ti	4.08
Co	17.85
Cr	9.90
Ni	64.58

2. Experimental procedures

2.1. Conversion coating

A controlled conversion treatment in acidic solution was carried out in order to functionalize the substrate surface. The obtained particular morphology of the conversion coating presented micro-pores having high specific area which made it suitable for the subsequent deposition. Highly porous conversion coating with strong interfacial adhesion to the substrate facilitates the electrochemical deposition of further ceramic layers and enhances its adhesion [12-14]. In the present study, Inconel 738LC, an ultra low-carbon nickel-based superalloy, specimens with exposed surface dimensions of 20 mm × 30 mm were utilized as substrates. Table 1 lists the examined substrate chemical composition. The specimen surfaces were mechanically polished with 60 grit SiC abrasive paper before

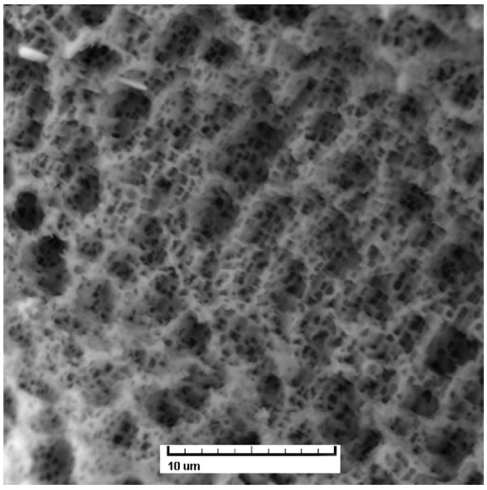

Fig. 1. SEM image showing the porous and rough surface morphology of the conversion coating.

Table 2
Bath composition and condition utilized for the conversion treatment.

H_2SO_4 (vol%)	HCl (vol%)	$Na_2S_2O_3 \cdot 5H_2O$ (Mole)	Inhibitor content (mL L^{-1})	Temperature (°C)	Cycle time (s)	Treatment time (min)
15	7	0.005	1	60	30	10

Table 3
Galvanostatic deposition parameters for the conventional YSZ coating.

$ZrO(NO_3)_2 \cdot nH_2O$ (Mole)	$YCl_3 \cdot 6H_2O$ (Mole)		KCl (Mole)	pH	Current density (mA cm^{-2})	Deposition time (min)
0.05	0.05	M	0.01	1.8	5	15

Table 4
Optimum cyclic voltammetry deposition parameters for the nanostructured YSZ coating.

$ZrO(NO_3)_2 \cdot nH_2O$ (Mole)	$YCl_3 \cdot 6H_2O$ (Mole)	KCl (Mole)	$ZrO(NO_3)_2 \cdot nH_2O/YCl_3 \cdot 6H_2O$ ratio (vol%)	pH	Potential range (V)	Scan rate (v s^{-1})
0.05	0.05	0.01	80/20	1.8	(−2)–0	50

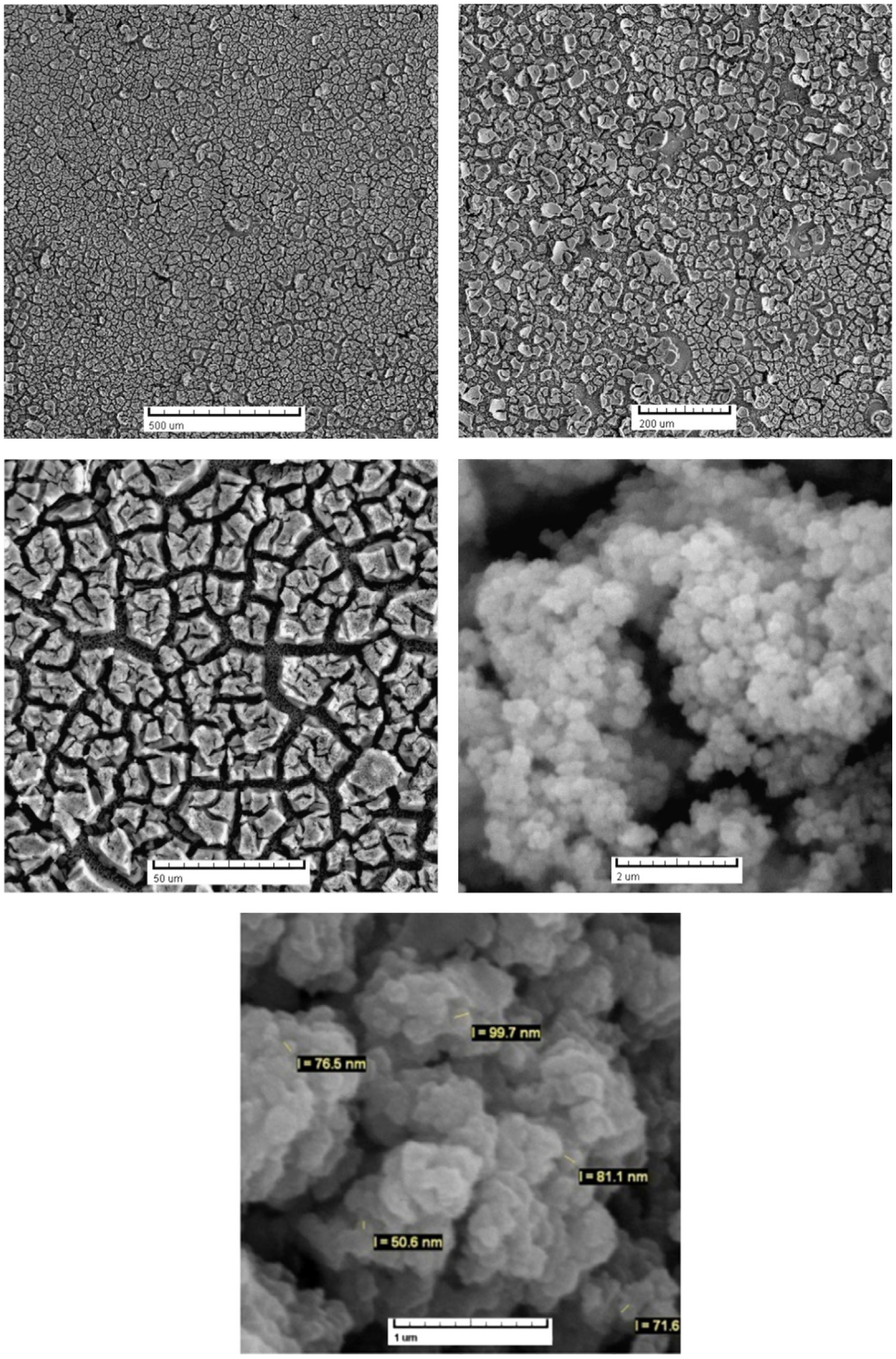

Fig. 2. A college of SEM micrographs acquired from the as-deposited nanostructured YSZ coating.

applying the coating and then washed with distilled water, rinsed with ethanol and finally dried in air.

Conversion coatings were obtained by chemical oxidation of the substrate in an acidic solution under periodic cathodic and anodic potentials that contained additives of sodium thiosulphate in order to control the growth rate of the deposition and also to obtain micro-porous morphology. Sample treatment was followed by rinsing in the demineralized water and drying at 60 °C for 15 min. The conditions of the conversion treatment are summarized at Table 2.

2.2. Electropdeposition of conventional YSZ coating

The direct current electrochemical deposition of ceramic compounds was performed in aqueous solution containing yttrium chloride ($YCl_3 \cdot 6H_2o$) and zirconyl nitrate (Zro

$(No_3)_2 \cdot nH_2o$) salts. The electrochemical cell in a galvanostatic regime included a substrate as working electrode and a platinum counter electrode. Electrodeposition was carried out at current density of 5 mA/cm^2. The coating morphology and its composition were characterized using Oxford CAMSCAN-MV2300 SEM equipped with energy dispersive spectroscopy (EDS) detector. The details of the conversion treatment are presented in Table 3.

2.3. Electropdeposition of nanostructured YSZ coating

Cyclic voltammetric mode is the most widely used technique for acquiring qualitative information about electrochemical reactions while it was used as the electrochemical method to deposit nanostructured/nano-layered coating in this study. Using Amel System 5000 electrochemical system, the electrodeposition was carried out in a cell having Pt wire as the counter electrode, saturated calomel as the reference and the Inconel 738 as the working electrodes. All experiments were conducted at ambient temperature of 25 ± 1 °C. It must be mentioned that in cyclic voltammetry mode the voltage was swept between 0 to −2 V at a fixed rate several times to get a dense deposit. As the formation of a nanostructured layer is attributed to combined effects of various parameters comprising potential range, scan rate and the number of cycles, all have been investigated ultimately. Table 4 presents the optimum electodeposition condition to obtain a nanostructured and layered YSZ coating.

2.4. Oxidation test

The oxidation resistance of nano and conventional YSZ coatings were examined in an air furnace at 1000 °C in cyclic mode of 1 h heating and 30 min of cooling in forced air in 15 progressive cycles.

3. Results and discussion

3.1. Coating

Fig. 1 illustrates the surface morphology of the sample after conversion treatment which produced a highly porous and rough surface. This was attained through cathodic potential which solved the passive layer on substrate followed by subsequent anodic potential which provided a rough surface.

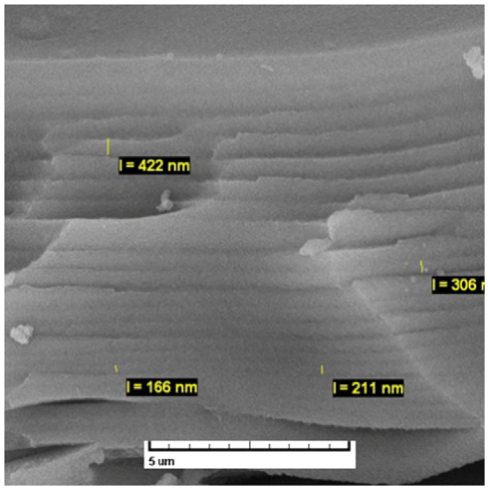

Fig. 3. SEM micrograph acquired from cross-section of as-deposited nanostructured YSZ coating showing the formation of individual layers within deposition.

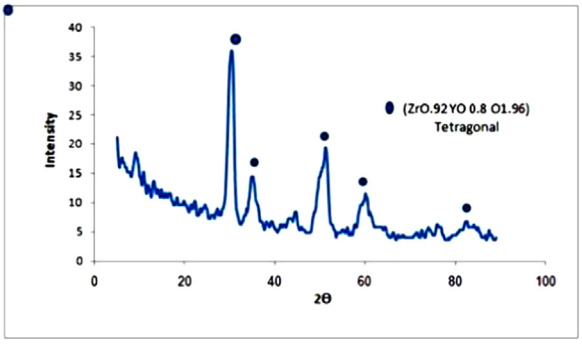

Fig. 5. XRD pattern acquired from the nanostructured coating after heat treatment at 800 °C for 2 h.

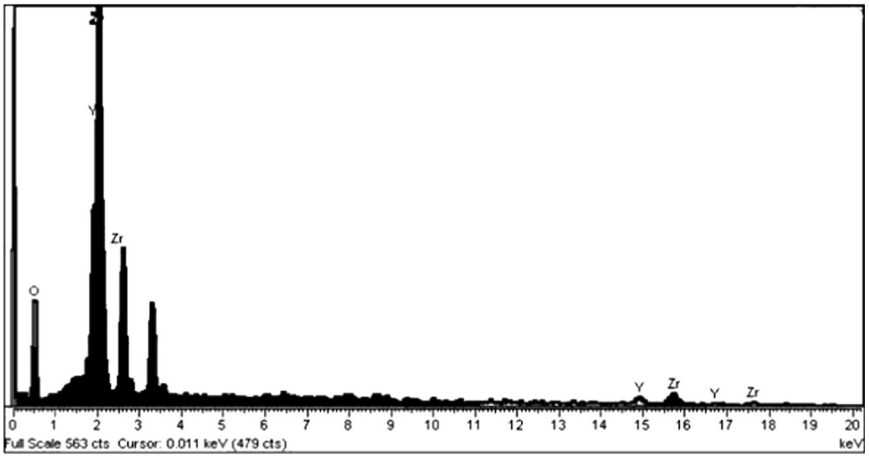

Fig. 4. SEM–EDS micro-chemical analysis of nanostructured YSZ coating.

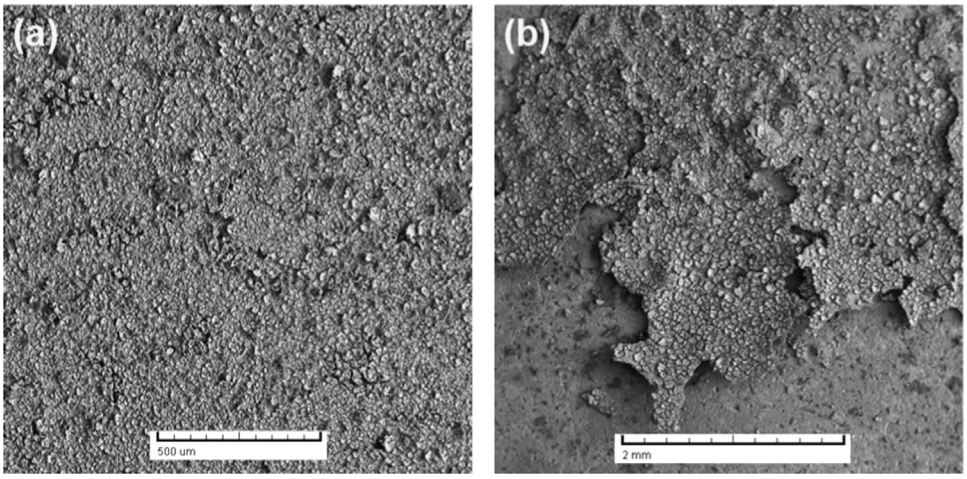

Fig. 6. The SEM micrographs showing the surface of different coatings after oxidation cycles: (a) nanostructured coating and (b) conventional coating.

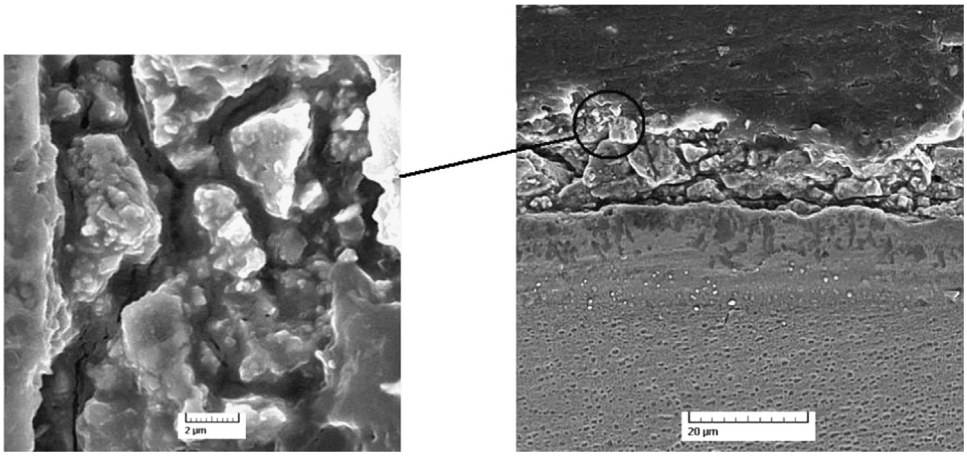

Fig. 7. The cross-sectional SEM images of the conventional coating after 15 cycles of oxidation at 1000 °C.

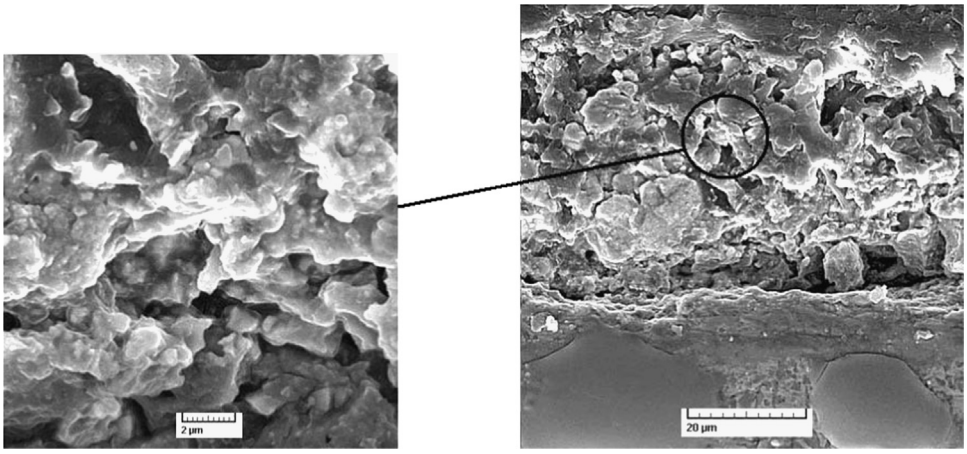

Fig. 8. The cross-sectional SEM images of the nanostructured coating after 15 cycles of oxidation at 1000 °C.

This morphology is desirable for electrodeposition of YSZ layer due to its rough and high surface area. Fig. 2 shows SEM micrographs of the nanostructured YSZ coating produced by cyclic voltammetric mode, under the condition explained in Table 3, at different magnifications. It could be seen that the formed particles are spherical and agglomerated from nano-size particles with diameters of 50–100 nm. It is shown that the coating is deposited uniformly and dense but a few numbers of voids and micro-cracks are formed within the YSZ layer. The layer seems to be adhered properly to the surface.

It is proven that the thermal conductivity of YSZ layer is strongly relied on the micro-structural characteristics of the deposit [15]. By using cyclic voltammetric mode, the multi-layered coating provided diverse properties compared with

conventional coatings. Fig. 3 shows SEM micrograph acquired from cross-section of nano-multilayered YSZ deposited after 30 deposition cycles wherein the properties of multilayer coating was controlled by the voltammetric sequences. The figure also illustrates individual YSZ layers that each one has been formed in each cycle while the thickness of each layer is 200–500 nm. Furthermore, Fig. 4 depicts the SEM–EDS micro-chemical analysis of the coating which shows the presence of 6–8 wt% of Y_2O_3 needed to be YSZ.

3.2. Phase stability

The cathodic electrodeposition was achieved via hydrolysis of metal ions or complexes through electro-generated hydroxide which can be converted into corresponding oxides by performing thermal treatment [16]. Based on the formed oxide, hydroxide and/or peroxide deposits, Fig. 5 presents the acquired XRD pattern from the nanostructured coating after heat treatment at 800 °C for 2 h. Only peaks of the tetragonal phase in the XRD pattern could be found. This revealed that upon cooling to room temperature the tetragonal to monoclinic transformation did not occur in the YSZ coating, so the partially stabilized zirconia was formed and the only existing phase was yttrium zirconium oxide ($ZrO_{0.92}YO_{0.8}O_{1.96}$).

3.3. Oxidation

Fig. 6 shows the surface morphology of the two different coatings (nano and conventional) after performing 15 oxidation cycles. The coating is separated from the surface in conventional coating while the nano-coating is adhered without major break or separation. Therefore the nano-coating is more resistant in oxidation in terms of coating integrity, homogeneity, crack size, morphology and distribution. The specimen's bond strength was attained based on ASTM C633-79 standard [17].

This behavior can also be observed in cross sectional SEM images of the two coatings as shown in Fig.7. After 15 cycles of oxidation at 1000 °C. Wide cracks appeared throughout the surface of the coating towards the substrate that makes oxygen diffusion easier to the base metal. For comparison, Fig. 8 presents the cross-sectional SEM images of the nanostructured coating after under similar condition while it could be found that the thickness of cracks in the nanostructured specimen was smaller than that for the conventional coating since no obvious cracks between the coating and base metal were originated in the nanostructured sample. The stability of this coating would be explained under oxidation mechanism and process. Oxygen diffuses from the pores and/or cracks in molecular from but it can also diffuse as O^{2-} through zirconia crystal layer which is transparent to the O^{2-} at above 1200 °C [17].

The formation of ultrafine grains and dense nanostructure of YSZ layer played effective role in reducing the oxygen permeation within the ceramic zirconia layer [18]. The rate of oxygen diffusion through micro-cracks and linked porosities was rather than compacted particles [19]. The open pores and micro-cracks of conventional YSZ coatings provided easy penetration path for oxygen resulted in more oxidation; however, voids acted as suppressers of crack propagation. As the compact specimen had large number of interfaces of nano-multilayered structure and the grain boundaries, micro-porosity within the nanostructured coating improved its oxidation resistance. From Fig. 8, the nano-multilayers provided a compact structure after oxidation cycles. As layer structure would not be explained by the microstructure developed within the coatings after oxidation, it was concluded that the nano-layers of YSZ were quite preventive for oxygen access to the coated metal interface.

The thermal stresses and elastic modulus were the two important factors affected the thermal cycling life. The conventional YSZ coating had both relatively larger residual stresses and larger elastic modulus than the nanostructured coating. So, it could be concluded that the difference in the stress levels of the coatings was a fundamental reason resulted in the highlight difference of thermal cycling life of the deposited layers [19].

4. Conclusions

Based on the acquired results, it is possible to electrodeposit the conventional and nanostructured YSZ coatings using cyclic voltammetric mode as reversible reaction. The nanostructured YSZ layer deposited by cyclic voltammetric mode provided homogenous grain distribution with lamellar structure which promoted the oxidation resistance. Results obtained from the oxidation test suggested that pores and also micro-cracks existed within the nanostructured layer played an important role in the oxidation resistance improvement in comparison with conventional YSZ coating. The formation of wide cracks at the surface of the conventional coating made a contribution to the better oxidation.

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