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THERMALLY OXIDIZED ZIRCONIUM NANOCRYSTALLINE THERMAL BARRIER COATING DEPOSITED BY EB-PVD

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ABSTRACT

Zirconium oxide nanocrystalline deposited on the bound coat of thermal barrier coating TBC by an electron beam physical vapour deposition EB-PVD was thermally oxidized at oxygen ambient after deposition process within 1073 K resulting in Zirconium oxide top layer with various stoichiometries. Intermetallic alloys based on γ -TiAl due to offer low density over conventional Ni supper alloy was used as substrate. Field emission scanning electron microscopy FESEM observation of the deposited specimens at three different oxygen partial pressure during coating indicate the appropriate adhesion of ZrO_2 when thermally grown oxide TGO had been taken place as buffer layer between top coat and bound coat which are contain 8mol% Yttria Stabilized Zirconia (YSZ) and MCrAlY respectively. Energy dispersive spectrometer EDS to determine the composition of present element after deposition was employed. XRD analysis of the ex situ TBC components revealed the phases formed at different oxygen partial pressure. The present of this intermediate TGO layer was confirmed by observation of $AL2O_3$ and yttrium aluminates ($YAlO_3$ and/or $Y3Al_5O_{12}$) phases in the XRD patterns. $Al2O_3$ provides an effective diffusion barrier that protects the underlying metal from deleterious oxidation during thermally oxidizing the zirconium. Using rapid thermal processing RTP analysis data, the effective oxidation temperature on the stoichiometry of zirconium oxide and thickness of grown were investigated therewith, the crystallization of zirconium oxide films was initiated at about 480 K and was almost completed at 525 K. Micro indentation test was accomplished to qualifying the adhesion of Zirconium oxide nanocrystalline and the interfacial of bond coat.

Keywords : *zirconium oxide, nanocrystalline, EB-PVD,TBC*

1.0 INTRODUCTION

Thermal barrier coating (TBC) systems are commonly used in gas turbines to reduce thermal effect and increase turbine efficiency. Today the most durable TBCs on rotated turbine parts are yttria stabilized zirconia (YSZ) coatings that are applied by electron beam physical vapor deposition (EB-PVD) [1-2]. Intermetallic alloys based on γ -TiAl have the potential to be important structural materials for high temperature aerospace and automotive applications. The major advantage γ -TiAl based materials offer over conventional materials is their low density (3.7±3.9 g/cm^3). In the case of oxidation resistance, the scales on γ -TiAl generally consist primarily of alumina (a-Al_2O_3) and rutile (TiO_2), whereas both of these oxides are

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thermodynamically stable proper oxidation resistance might be achieved Figure 1 shown the schematic cross section through the oxide layers and the oxygen diffusion zone in titanium and titanium aluminide [3-4].

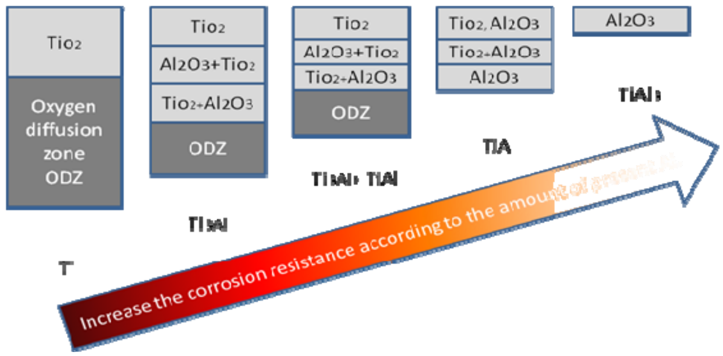

Figure 1 : Schematic cross section through the oxide layers and the oxygen diffusion zone in titanium and titanium aluminide (Smialek et al. 1985)

The TBCs are typically composed of an underlying metallic bond coat which known as MCrAlY (M = Ni,Co) as an oxidation resistant layer and yttria-stabilized zirconia (YSZ) as ceramic top coat that provides thermal insulation toward metallic substrate [5-6]. The ceramic layer creates a temperature drop between the operating atmosphere and the metal surface, thus allowing the component to operate at higher temperatures, so that higher efficiency and lower emissions can be achieved [7]. The common characteristic of bond coats applied between the top coat and the superalloy substrate is provide slow growing continuous and protective oxide scale (Al_2O_3) which form thermally grown oxide TGO layer on the topcoat/bond coat interface during high temperature oxidation [8-10]. Yttria stabilized zirconia coating systems are widely used as ceramic top coat for the thermal, oxidation and hot corrosion protection of high-temperature components used in turbine engines and gas turbine [7]. TBC's, usually applied by either air plasma spraying (APS) or electron beam-physical vapor deposition (EB-PVD), is most often stabilized zirconia with Y_2O_3 as the stabilizer [11-12]. The EB-PVD process offers the advantage of a superior strain and thermo shock tolerant behavior of the coatings due to their columnar microstructure in addition it had been reported that, low modulus zirconia structures applied by EBPVD had thermal cyclic lives of the order of a factor of 10 over the best plasma-sprayed coatings [1, 5, 12]. In the present paper FESEM and X-ray diffraction XRD investigations on thermally oxidized zirconium oxide nanocrystalline deposited on TBC by an EB-PVD at three different partial pressure of oxygen are performed in order to get a deeper insight into the correlation between microstructure and process parameters.

2.0 EXPERIMENTS

The investigation was performed on a first-stage by cutting the two millimeter thick plate of γ –TiAl to specimens of rectangular shape 10 x10 mm dimension by employing wire cute CNC, the chemical composition of the substrate studied is reported in Table 1.

Table 1: Composition of γ –TiAl substrate (wt. %)

Element	Ti	Al	Nb	Cr
Wight percent	48	48	2	2

Specimens before deposition were abraded with SiC paper up to 1200 grade, polished and ultrasonically cleaned in ethanol prior to achieve a fresh metal surface. After that, the clean specimens were immersed in 2% hydrofluoric acid (HF) solution for 1minit subsequently washed by distilled water and dried with nitrogen gas. Roughness before deposition was measured as tabulated on Table 2.

Table 2 : Surface roughness measurement

Roughness parameter	**Roughness value**
Ry	1.22 μm
Rz	0.92 μm
Ra	0.18 μm

The pellet-type evaporation bond coat used in the study was made of a MCrAlY alloy, whose chemical composition has been presented in Table 3 obtained by SEM-EDX analysis as in Figure 2. EB-PVD single source coater was used with the 1.6kW beam power, an acceleration voltage of 3kV and the vacuum level was kept at 2x10-6 Torr at 400°C to accomplish 3μm thick deposition. To obtain distinctive stoichiometry of zirconium and zirconium oxide different partial pressures of oxygen was introduced while deposition of top coat by employing EB-PVD with the 2.5kW beam power, an acceleration voltage of 5kV and three vacuum levels 4x10-4, 2x10-5, 1.2x10-6 Torr was used respectively on previous coated specimen.

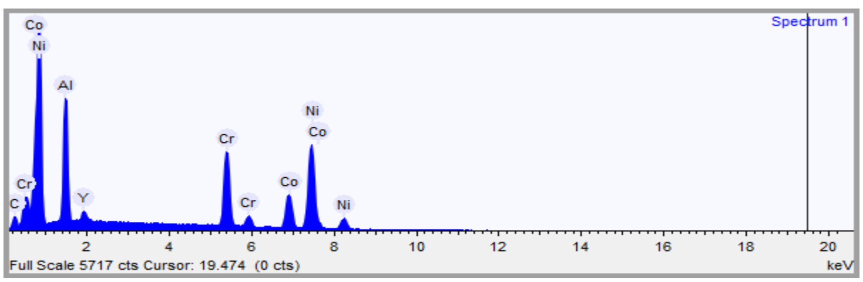

Figure 2 : SEM-EDX analysis

Table 3 : Composition of bound coat obtained by SEM-EDX analysis

Elements	**Co**	**Cr**	**Al**	**Y**	**Ni**
percentage	20-30	18-22	11-13	0.4-0.6	base

In addition, rapid thermal processing, RTP was used at pressure of 2 bar oxygen to further oxidizing stoichiometry of Zirconium nanocrystalline deposited by EB-PVD at three differences oxygen partial pressure on the bound coat of thermal barrier coating TBC the partial schematic diagram of thermally oxidizing cycle is shown at Figure 3 that cycle was continued for 30 min. Thermally oxidizing at pressure of 2 bar oxygen and rapid heating up to1123 K was applied after deposition process. Resulting in ZrO_2 top layer obtain from various Zirconium stoichiometries.

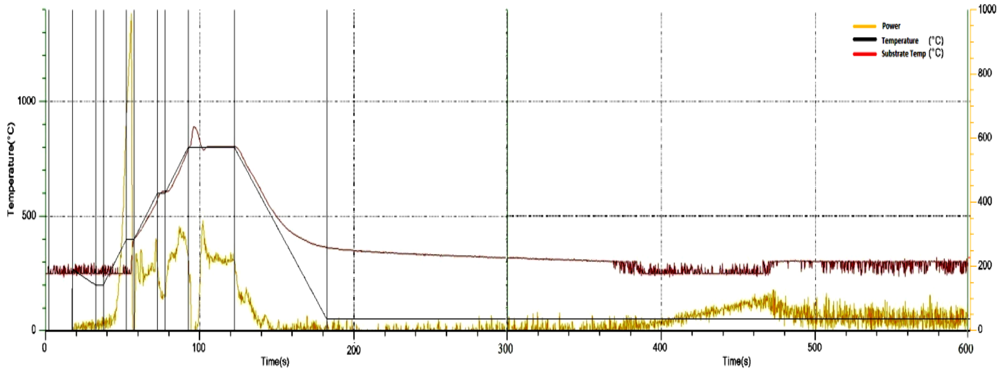

Figure 3 Partial schematic diagram of thermally oxidizing cycle with RTP

Micro indentation test was accomplished to qualifying the adhesion of Zirconium oxide nanocrystalline top coat at interfacial of bond coat by employing Vickers micro hardness. On each sample three indentations were produced. After indentation an SEM with a magnification of 100X was used to evaluate indentation effects. The damage to the coating surface in terms of delamination at applied load was defined adhesion strength quality shown in Figure 4.

(a) (b) (c)

Figure 4 : Indentation effect at surface of top coat deposited at three difference load for sample a,b,c with 5 kg, 10 kg and 20 kg respectively

Moreover, three Vickers micro hardness test were produced on the cross section close to the coated verge of specimens shown as Figure 5. Each indicated point on the Figure 5 is an average of three indentations at difference position.

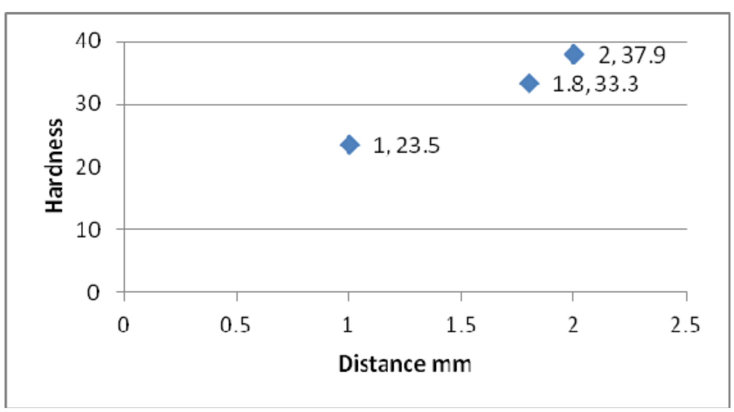

Figure 5: Vickers micro hardness value vs. distance for each sample.

The microstructure, morphology and chemical composition of the surface and the cross-section of the coatings were examined by scanning electron microscopy (SEM) equipped with energy dispersive spectrometer (EDS).The phase composition of the coatings was determined using the X'Pert Philphs diffractometer, using the X-ray radiation with the CuKα . The measurements were made in the 2θ angle ranging from 25 to 100°.

3.0 RESULTS AND DISCUSSION

The investigated Zirconium oxide nanocrystalline deposited on the bound coat of thermal barrier coating TBC by an electron beam physical vapour deposition EB-PVD deposited onto γ -TiAl type are characterised by a uniform thickness. The YSZ coating shown a compacted, adherent structure while the partial pressure of Oxygen is 4x10-4 Torr coating has a compacted nanocrystalline structure after thermally oxidized at oxygen ambient as mentioned condition compare to those specimen which were deposited at lower partial pressure of Oxygen 2x10-5, 1.2x10-6 Torr individually. Figure 6 illustrated the coating adhesion at difference partial pressure of Oxygen after Rapid Thermal Processing RTP.

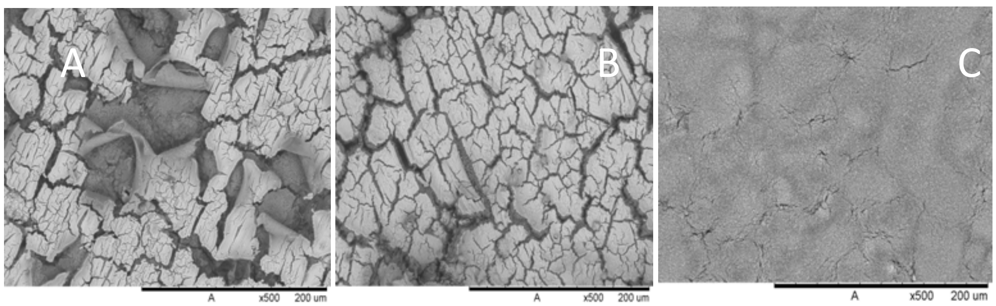

Figure 6 : FESEM analysis of deposited bond coat 2x10-6 torr , top coat A,B,C respectively $4x10^{-4}$Torr , $2x10^{-5}$ Torr and $1.2x10^{-6}$ Torr and thermally oxidize (2 barr, up to 1123K) respectively. A,B,C respectively 5 Kg $4x10^{-4}$Torr , 10 Kg $2x10^{-5}$ Torr and 20 Kg $1.2x10^{-6}$ Torr

3.1 FESEM image analysis

Higher magnification also is evidence of condense and crack free structure of Zirconium oxide nanocrystalline. It can be conclude adhesive top layer was formed by increase the partial pressure of Oxygen during deposition and increase proportion of Zr/ZrO_2 (stoichiometry).

Two hypotheses may explain this phenomenon:

i. Formation of TGO layer by introduce Oxygen
ii. Just increase in ratio of ZrO_2 is responsible of good adhesion.

After the thermally oxidizing process, hardness of the cross verge to the coated surface of specimen shown increasing of hardness volue.According to the Fick's law at the high temperature diffusion can take place thus, increasing in the hardness occurred due to the diffusion of bond coat and substrate. By compression of XRD patterns before and after thermally oxidized of 2 samples, reveals that deposition on 2x10-5 torr will cause formation of Al_2O_3 and TiO_2 during thermally oxidizing process due to insufficient adhesion of top layer and bond coat. In counterpart, the sample coated at $4x10^{-4}$ indicates the best prevention against formation of Al_2O_3 and TiO_2 during thermally oxidizing process.

4.0 CONCLUSIONS

i. By increase the partial pressure of oxygen to 4x10-4 during deposition reduction of target could be prevented.

ii. According to XRD pattern temperature of substrate during deposition is not sufficient to form TGO even at high partial pressure of oxygen.

iii. Coating at higher pressure of O_2 promotes outstanding adhesion up to 20 Kg load.

iv. Formation phases such as $(Al0.76Hf0.24)Ni_3$, Ni_4Ti_3 are the evidence of diffusion of bond coat to substrate which caused increasing in hardness as well.

v. Exist of AlZr and $(Al0.76Hf0.24)Ni_3$ phases are base on the stoichiometry of those element in metallic condition while regarding to EXD pattern Zr and Hf are the elements present in the top layer.

vi. Different nanocrystalline formed by thermally oxidized Zr could be nobility of this work.

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