

Research Article

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Isothermal Oxidation Behavior of Gadolinium Zirconate ($Gd_2Zr_2O_7$) Thermal Barrier Coatings (TBCs) produced by Electron Beam Physical Vapor Deposition (EB-PVD) technique

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Abstract: Thermal Barrier Coatings (TBCs) provide thermal insulation for gas turbine components operating at high temperatures. Generally, TBCs were produced on a MCrAlY bond coat with 7-8% Ytria Stabilized Zirconia (YSZ) using Atmospheric Plasma Spray (APS) technique. In this study, Inconel 718 substrate material was coated with CoNiCrAlY bond coat using high velocity oxygen fuel (HVOF) technique. Afterward, $Gd_2Zr_2O_7$ was deposited on samples using Electron Beam Physical Vapor Deposition (EB-PVD) technique. Produced TBCs were exposed to isothermal oxidation tests at 1000°C for 8 h, 24 h, 50 h and 100 h in muffle furnace. Scanning electron microscopy-energy distribution X-ray (SEM-EDX) spectroscopy was used to investigate thermally grown oxide (TGO) layer and TGO growth behavior of TBCs. In addition, X-ray Diffractometer (XRD) analysis was performed to TBCs to understand whether phase transformation occurs or not before and after oxidation.

Keywords: Thermal barrier coatings (TBCs); Isothermal oxidation; thermally grown oxide (TGO); $Gd_2Zr_2O_7$

1 Introduction

TBCs are widely used in groups of materials such as gas turbine components operating under high temperature

conditions. TBCs are exposed to oxidation due to the high temperature [1,2]. Standard TBC system consists of Ni based superalloy substrate, MCrAlY contented bond coat, TGO layer formed during the oxidation and ceramic top coat layer. In TBCs, failure generally starts from TGO layer due to new oxide formations and thermal expansion mismatch. Bond coat can be produced using thermal spray techniques such as atmospheric plasma spray (APS), cold gas dynamic spray (CGDS) or high velocity oxygen fuel (HVOF) techniques. Top coat can be deposited only plasma spray (PS) techniques or electron beam physical vapor deposition (EB-PVD) due to its high melting point. HVOF and CGDS techniques provide dense and low oxide contented metallic bond coat layer in contrast to APS technique [3-5]. Laminar structured coatings with high porosity and oxide content can be obtained using APS technique [6]. Columnar structured and dense top coats can be produced using EB-PVD technique which provide high strain tolerance [7].

YSZ is a state of art top coat material for TBC systems due to its superior properties. However, it has some limitations such as low sintering resistance and its phase transformation stability up to 1200°C [8,9]. Rare earth zirconates ($Re_2Zr_2O_7$) exhibit attractive properties such as lower thermal conductivity, higher operating temperature and higher sintering resistance compared to YSZ [10]. $Re_2Zr_2O_7$ are stable up to 1500°C. Rare earth (Re: Gd, La, Sm, etc.)⁺³ elements are replaced with Zr^{+4} . This substitution causes formation of oxygen vacancy in crystal structure. Thus, phonon scattering increase and thermal conductivity decrease. Atomic weight of Gd is higher than Y [11]. This also contributes for lower thermal conductivity. Wu et. al. [12] reported that thermal conductivity value of $Gd_2Zr_2O_7$ is 1.6 W(m.K)^{-1} while YSZ has 2.3 W(m.K)^{-1} at 700°C. $Gd_2Zr_2O_7$ has an ionic conductivity due to presence of oxygen vacancy in its crystal structure. However, $Gd_2Zr_2O_7$ has better resistance against oxygen penetration compared to YSZ [13]. Because it has stable

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anion Frenkel pair defect and therefore, higher activation energy is required for the diffusion of oxygen [1,10].

In the present study, HVOF CoNiCrAlY bond-coated $Gd_2Zr_2O_7$ TBCs produced by EB-PVD are subjected to 1000°C with different time periods isothermally to investigate their oxidation behavior and TGO growth.

2 Experimental Procedure

2.1 Substrate, Bond and Top Coating Production and Preparation

Grit blasted and ultrasonically cleaned disc shaped 5 mm Inconel 718 was used as substrate material. CoNiCrAlY powders (Sulzer Metco Amdry 9951, $-38+5.5 \mu\text{m}$ particle size) were sprayed on substrate using HVOF technique with Table 1 parameters. $Gd_2Zr_2O_7$ ingot was deposited on bond coated substrates using EB-PVD technique based on Table 1 parameters.

2.2 Oxidation Tests and Characterization

Substrate, as-deposited bond and top coats roughness values were calculated taking from average of 5 different measurements by SJ-310, Mitutoyo instrument. Average hardness were obtained using Micro-Duromat 400E tester under 50 g load taking 5 measurements from different regions of each layers of as-deposited TBC. Image J software program was used to calculate average porosity as percentage. Average porosity measurements were obtained from 5 different cross-sectional SEM images at 1000x magnification. Table 2 shows roughness, hardness and porosity values of TBC layers.

Before the oxidation tests, TBCs were exposed to vacuum annealing at 1080°C with 2 h. Isothermal oxidation tests were performed at 1000°C with 8 h, 24 h, 50 h and 100 h in Protherm high temperature furnace (PLF 130/12). After oxidation tests, samples were cold mounted and prepared metallographically to investigate in SEM (Tescan, Maia3). Before and after oxidation tests, XRD analysis was performed to TBCs to detect phase changes.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

Figure 1 shows cross-sectional SEM and elemental mapping images of as-deposited TBCs. According to Figure

Table 1: Bond and top coating working parameters.

HVOF CoNiCrAlY Working Parameters				
Combustion Gases	Powder feed	Powder carrier gas	Spray distance	Gun speed
O_2 (250 slpm), C_3H_8 (80 slpm), Air (700 slpm)	25 g/sec	N_2 (6,5 slpm)	200 mm	20 mm/s
EB-PVD $Gd_2Zr_2O_7$ Working Parameters				
Temperature	Rotation Speed	Vacuum	Condensation ratio	
800±20°C	25 rpm	5×10^{-5} - 1×10^{-4} Torr	3,7 $\mu\text{m}/\text{min}$	

Table 2: Roughness, hardness and porosity values of substrate and coatings.

Substrate and Coatings	R_a (μm)	Hardness (GPa)	Porosity (%)
Inconel-718	5.38	3.09	-
CoNiCrAlY Bond Coat	5.91	4.38	2.5 ± 0.5
$Gd_2Zr_2O_7$ Top Coat	6.37	4.26	1.9 ± 0.3

1a, top coat has a columnar structure as characteristic property of EB-PVD technique. It includes low porosity and it has columnar gaps due to surface roughness of bond coat. Surface roughness of bond coating is particularly related to unmelted particles. The thickness of top coat is approximately 200 μm . 100 μm thick bond coating has very low oxide and porosity due to the advantage of HVOF technique. Bond coat porosity content is about $2.5 \pm 0.5\%$. Top coat porosity content is about $1.9 \pm 0.3\%$. Vacuum heat treatment of bond coat at 1080°C for 2h prior the oxidation test was provided formation of β -NiAl phases, stabilization of coating and thin α - Al_2O_3 layer which act as oxygen barrier. Similar processes have been applied in the literature [14-16]. Elemental mapping image in Figure 1b shows the formation of Al rich β -NiAl phases, γ phases rich in Co, Ni, Cr and thin Al_2O_3 layer due to the vacuum heat treatment as well as elemental distribution of bond and top coat.

In TBCs, oxidation occurs through penetration of oxygen from top coat to bond coat due to the ionic conductivity of top coat and existing porosity or voids in its structure. In addition, bond coat and interfaces can include voids and porosities. The oxygen in contact with the bond coat causes oxidation at high temperatures. Figure 2 shows the SEM cross-sectional images of oxidation periods of $Gd_2Zr_2O_7$ TBC at 1000°C. In the first stage, interface only consists of Al_2O_3 because Al has highest affinity to oxygen compared to other bond coat elements.

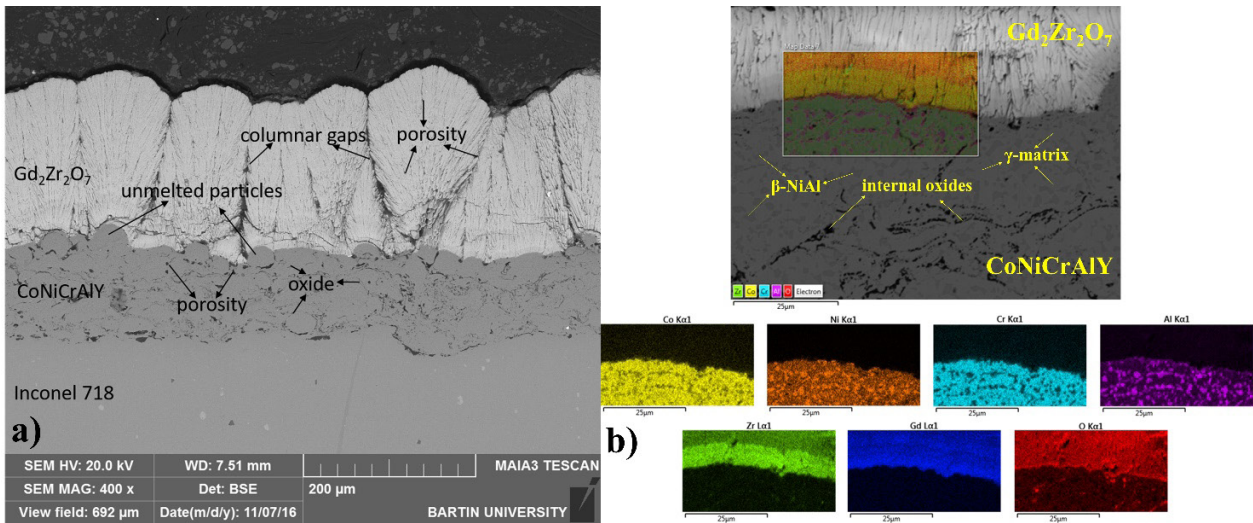


Figure 1: Cross-sectional a) SEM and b) elemental mapping images of as-deposited TBC.

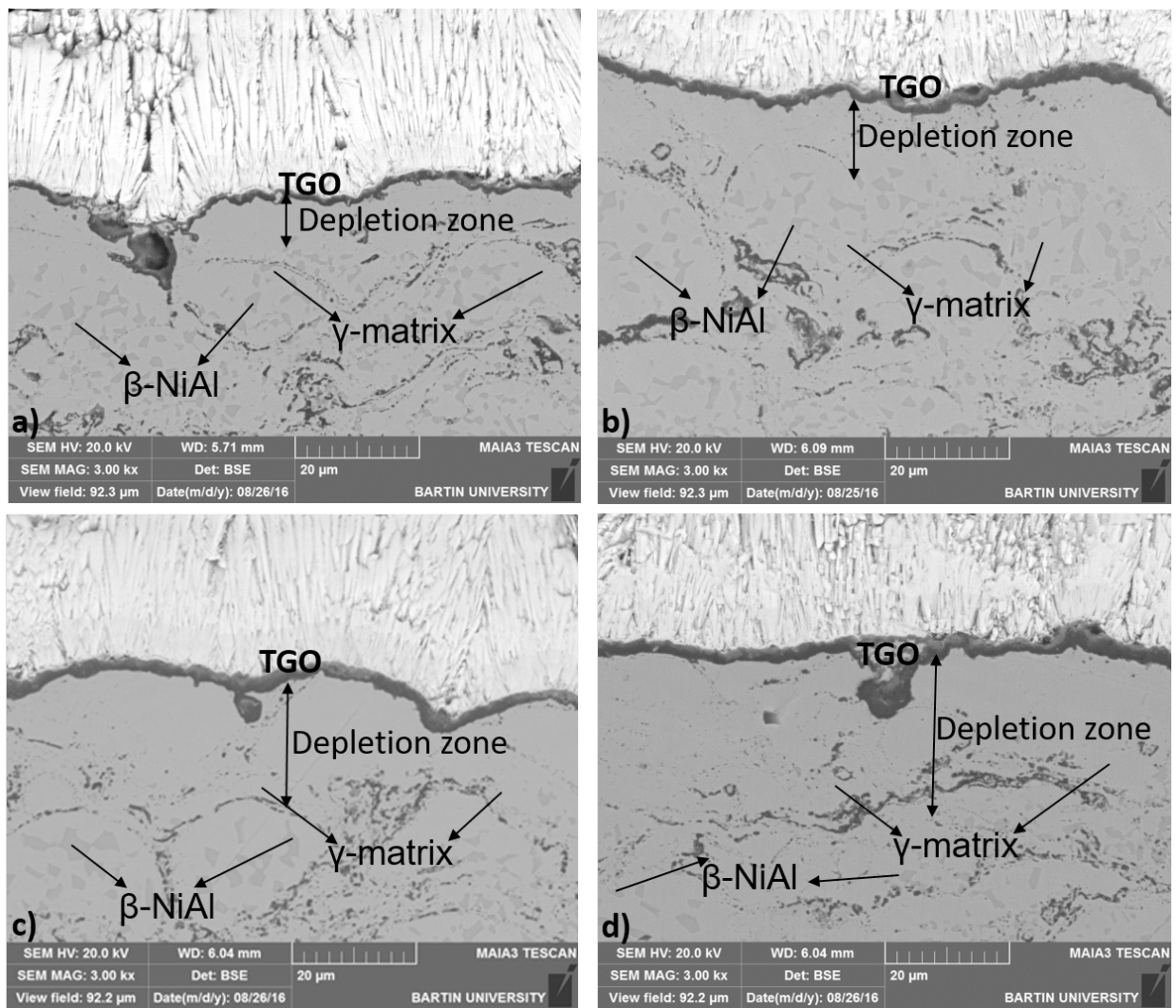


Figure 2: Cross-sectional images of a) 8 h, b) 24 h, c) 50 h and d) 100 h oxidized TBCs at 1000.°C.

Al₂O₃ which act as oxygen barrier is the most desired phase at the interface. TGO layer thickness increase depending on time and this causes the stress increase at the interface. The thicknesses of TGO layers for each oxidation time was given in Figure 3. Dark gray phases (β-NiAl) provide diffusion of Al to interface and as a result β-NiAl phases deplete and depletion zone distance increases depending on time. When β-NiAl phases deplete or drop under a critical value, other elements diffuse to interface and mixed oxides or spinel phases which are undesired phases due to their high growth rate can form such as (Co, Ni)(Cr, Al)₂O₄ spinels, (Co, Ni)O or Cr₂O₃ [16].

At the end of the oxidation tests, TGO layer preserved its uniformity and spallation was not observed although top coat includes visible crack formation starting from

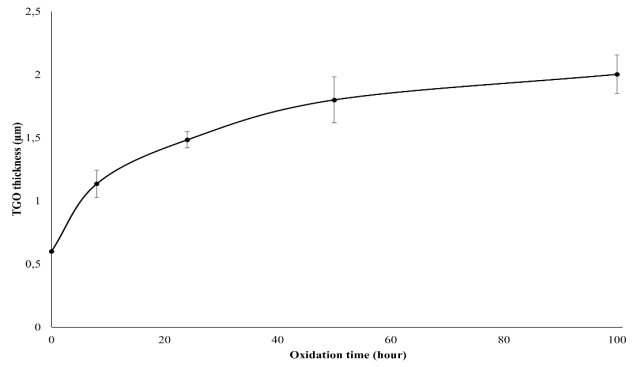


Figure 3: Variation of TGO layer thicknesses depending on the increasing time.

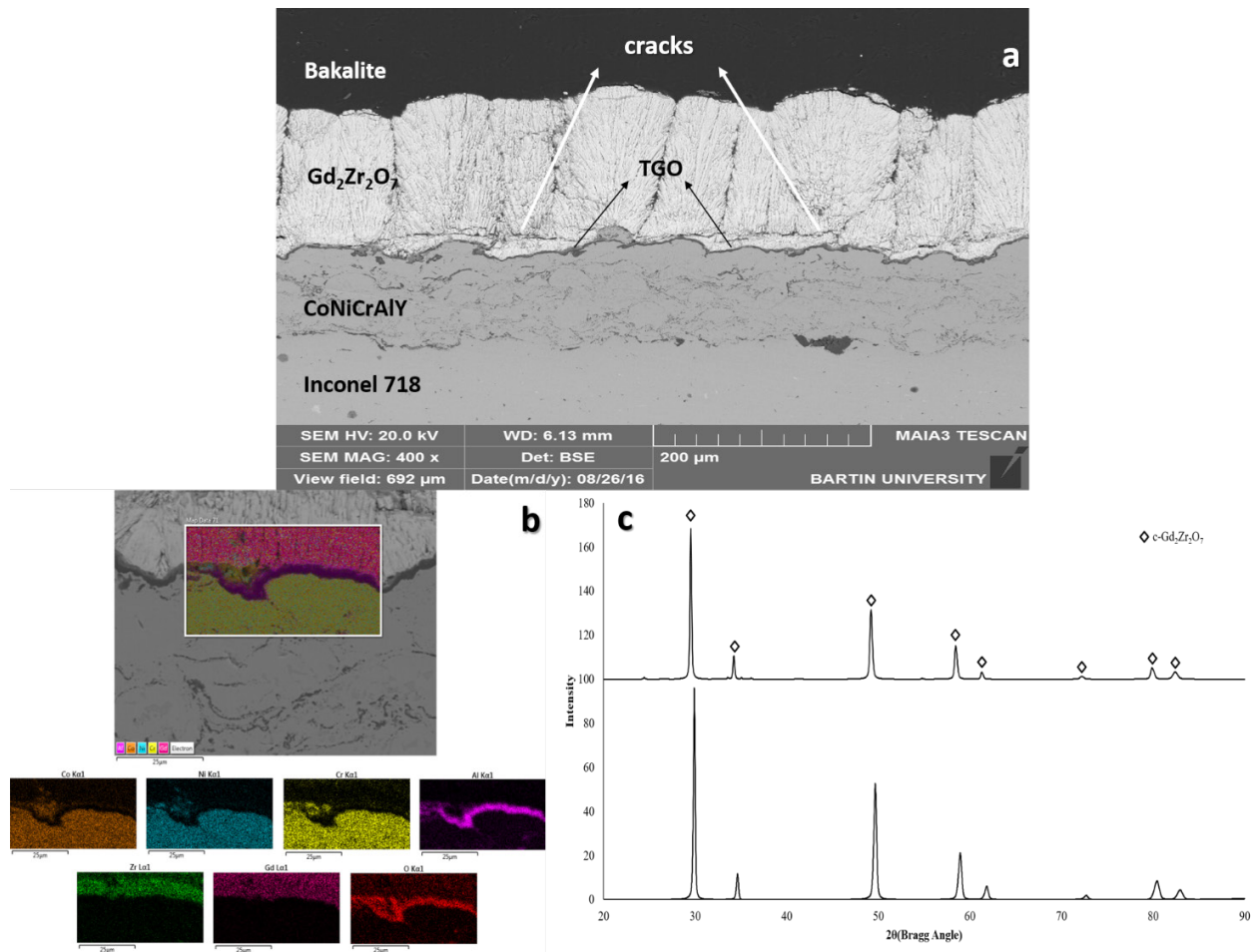


Figure 4: a) 400x SEM and b) 3000x elemental mapping image of 100 h oxidized TBC c) XRD graph of as-deposited and 100 h oxidized TBCs.

TGO layer. In Figure 4a), cracks and TGO layer can be seen. In Figure 4b), the elemental distribution of TGO layer can be seen at higher magnification. According to this elemental mapping analysis, TGO layer dominantly consists of Al_2O_3 and some traces of spinel or mixed oxide phases. The formation of mixed oxide phases may have been due to the initial oxidation stage or the rapid oxygen penetration that occurs with the cracking of the top coat. Crack formation can be occurred due to thermal expansion mismatch as well as growth of TGO layer. Especially, new oxides like spinel or mixed oxides can cause higher stress formation. Besides, $\text{Gd}_2\text{Zr}_2\text{O}_7$ have low fracture toughness thus crack formation in high TGO thicknesses is easier than YSZ [16]. To minimize the fracture toughness and thermal expansion mismatch, double layered TBCs can be used in TBC systems [1].

According to XRD analysis in Figure 4c, as-deposited TBC system only consists of c- $\text{Gd}_2\text{Zr}_2\text{O}_7$. Phase transformation was not observed at the end of the isothermal oxidation test. The absence of phase transformation has a vital importance in the TBCs because it prevents the formation of more stress in the system.

4 Conclusion

CoNiCrAlY bond coated Inconel 718 was successfully deposited using EB-PVD technique with $\text{Gd}_2\text{Zr}_2\text{O}_7$. According to oxidation tests, TGO thickness increases depending on time and TGO layer is mainly composed of Al_2O_3 phase and very little other oxides. After the oxidation tests, TBCs still remains intact and spallation was not observed although formation of cracks occurs in 100 h. Mixed oxides or spinel phase traces were detected in 100 h oxidation test. In top coat structure, phase transformation was not detected at the end of the oxidation tests according to XRD results. An alternative top coat material to YSZ, $\text{Gd}_2\text{Zr}_2\text{O}_7$, is suitable for use in TBCs because of its low thermal conductivity, high phase stability, and low oxygen penetration. However, it should be made more reliable by improving fracture toughness and thermal expansion coefficients. In the future work, $\text{Gd}_2\text{Zr}_2\text{O}_7$ will be produced as composite and functionally graded, and the oxidation performances will be examined.

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Conflict of interest: Authors state no conflict of interest.

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