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Phase Analysis and Microstructural Investigations of $\text{Ce}_2\text{Zr}_2\text{O}_7$ for High-Temperature Coatings on Ni-Base Superalloy Substrates

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Abstract: Crystalline cerium-zirconate (CZ) powders were synthesized via solution-assisted combustion synthesis route and calcined at 850°C for 8 h to obtain coarse crystalline powders. SEM (scanning electron microscopy) characterization studies were done to evaluate the morphology of the powders. XRD analysis of the resulting powder confirmed the presence of crystalline $\alpha\text{-Ce}_2\text{Zr}_2\text{O}_7$ along with a $\text{Ce}_2\text{Zr}_2\text{O}_8$ phase having a disordered fluorite cubic lattice. Phase composition, lattice parameters, and the atomic positions were also investigated. Refinement of XRD data was done to quantify the amount of $\alpha\text{-Ce}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_8$ phases. Ni-base superalloy Inconel 625 was chosen as the coating substrate, and the powders were coated using an air plasma spraying (APS). A thermally grown oxide (TGO)/ Al_2O_3 layer was observed owing to the high temperature of the substrate as well as the diffusion of bond coat material into the substrate. Coated samples were characterized by SEM to study the surface morphology, coating thickness, and interface microstructures. The thickness of the coated sample was found to be 400 μm . Thermal cycling test of the coated sample was carried out at 750°C for 50 h to evaluate the thermal shock resistance of the coating as well as the spalling behavior of the coating. Preliminary oxidation tests were carried out for 50 h at 750°C to evaluate the oxide growth by measuring weight gain of the oxide layers formed. Oxide growth signifies the gradual increment of layers over a period with a parabolic rate constant of about $K_p = 1.18 \times 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$.

Keywords: thermal barrier coatings; combustion synthesis; cerium zirconate; Air Plasma Spraying (APS); NiCrAlY; TGO and oxidation resistance

Introduction

Coatings on superalloy substrates are well known for various intrinsic and extrinsic applications that were governed by the influence of temperatures. An extremely oxidative environment requires protective coatings that do not spall easily. Ceramic coatings having high hardness and wear resistance exposed to thermal and corrosive conditions coupled with relatively low densities offer several advantages over metallic materials. A ceramic top coat has significantly lower thermal conductivity than the metallic substrate, and by applying an internal coating of the components, it is possible to establish a significant temperature drop (several 100 K) across the ceramic layer by suitably selecting materials for Thermal Barrier Coatings (TBCs). During past decades, Yttria Stabilized Zirconia (YSZ) was identified as one of the essential ceramic topcoat material developed in the last 30 years [1]. Role of the ceramic top coat is to reduce the effect of temperature by insulating, while the metallic bond coat decreases coefficient of thermal expansion (CTE) mismatch between the top coat and the substrate, thus enhancing the efficiency and service life of gas turbines. Among the potential ceramic candidates for TBCs Fluorites, Perovskites, YSZ, Mullites, Lanthanide orthophosphates as well as pyrochlore structures which shows, promising thermophysical properties [1–3]. The linear Thermal Expansion Coefficient of Lanthanum Cerium Zirconate (LCZ) is higher than that of 8 mol% YSZ when the temperature is above 400°C, but the thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ was much lower than that of YSZ. With an increase in temperature, the Thermal Expansion Coefficient of these ceramics increases, while the thermal conductivity decreases [4–6]. The endurance of the coatings against thermal cycle/shock and its degradation depends on adherence of coating layers as well oxide layer growth on coating surface during service [7, 8]. Though LaAlO_3 (LA) is being

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claimed as a potential oxide metal which can replace YSZ. Not much literatures has been on LaAlO_3 coatings. LA has been synthesized and characterized, for their flow-related characteristics, and the capability to deliver stoichiometric perovskite structures [8]. Microstructural studies of layered TBCs showed three coating layers such as an Interfacial layer, bond, and top coats, respectively and the mechanical properties were compared with the common TBCs with a single layer of each coat. The porosities in the top coats of the single structure (TBC-1 and TBC-2) were 19.6% and 10.2%, respectively, and those of the layered structure (TBC-3 and TBC-4) changed from 8.2% to 18.9% [9]. Longer dwell times and higher particle temperatures increase the thickness of the oxide layer and a high concentration of oxide stringers within the bond coat [10]. Growth of the TGO layer is more related to the bond coat properties and chemistry since ZrO_2 is stable at high temperature [11]. Thermal Spalling tests were performed for two TBCs samples based on zirconia with different thicknesses in the top and bond coats [12]. Atmospheric plasma spraying (APS) and high-velocity oxy-fuel (HVOF) were commonly used techniques for bond coated oxides that are seen as dark, elongated phases that appear in the microstructure, parallel to the interface. Interface roughness of the bond coat was found as one of the likely factors that affect the lifetime of TBC systems [12–14]. Two types of the bond coat were prepared by different methods namely, APS and HVOF [14]. Hardness and fracture toughness values of TBCs increased due to densification of the top coat during cyclic thermal exposure, and the bond coat prepared by the HVOF process showed higher values than that by APS process. At high temperatures, tensile stresses occur as a result of differences in thermal expansion coefficient and those Stresses driven surface diffusion was proposed as a plausible mechanism of the bond coat rumpling observed in TBCs upon thermal cycling [15, 16]. Some important characteristics of the top coat are high melting temperature, low thermal conductivity, the thermal expansion coefficient by underlying super-alloy, resistance to oxidation and corrosion, strain tolerance [16]. At high temperatures, tensile stresses result from differences in thermal expansion coefficient and temperature gradients during rapid thermal cycling are stabilized between the substrate and ceramic layer [16]. The fracture resistance and adhesion behavior of the interfacial Al_2O_3 scale may also be important issues although these topics have received relatively little attention about plasma-sprayed TBCs [17].

With an increase in temperature, the thermal expansion coefficient of $\text{La}_2\text{Zr}_2\text{O}_7$ ceramics was enhanced. The corresponding reduction in thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ can be attributed to the significantly higher

concentration of oxygen vacancies and the larger atomic weight of the solute cations in this material [6]. The misfits between the bond coat and substrate are more subtle such that they occur not only from thermal expansion but also from phase transformations and void swelling. Understanding these misfits, ascertaining their importance to system durability, and finding means to control them, has been an important area of research focus. Actual spall formation is preceded by smaller cracks that extend and coalesce along delamination planes, located either within the oxide layer or at the interface between the TGO and the bond coat [18]. Composite powders of Al_2O_3 and $\text{Ce}_2\text{Zr}_2\text{O}_7$ prepared as the top coat material shows the highest values of K_{IC} ($6.5 \text{ MPa m}^{-1/2}$) and (620 MPa) were achieved in 10 vol% $\text{Ce}_2\text{Zr}_2\text{O}_7$ composites, sintered more than theoretical density [19].

The phase diagram of CeO_2 - ZrO_2 from Figure 1 shows that cubic solid solution forms CeO_2 at ZrO_2 (<10 mol%) below 900°C [20]. High-temperature coating using $\text{Ce}_2\text{Zr}_2\text{O}_7$ (CZ) has been investigated for oxidation resistance and spalling behavior of the thermally sprayed coatings. Microstructural analysis of coatings shows the formations of the dense compound with a low porosity level of the coatings. This primary investigation generally talks about the improvement of oxidation resistance and how the oxide layer affects the compound stability. The first attempt in developing cerium zirconate (CZ) as a

Figure 1: Phase diagram of CeO_2 - ZrO_2 reproduced from Saha and D.C Agarwal [21].

candidate material for the top coat and structural correlations of the phases obtained from the solid solution of $\text{CeO}_2\text{-ZrO}_2$ were made.

Experimental work

Experimentation part consists of the preparation of CZ with a pyrochlore phase and thermal spraying of the powders onto an Inconel 625 substrate followed by the characterization of the coated samples for microstructure, thermal cycling, and oxidation behavior.

Materials and preparation

High purity compounds Cerium nitrate, 98% pure ($\text{Ce}(\text{NO}_3)_2$), Zirconyl Nitrate powder, 99% pure ($\text{ZrO}(\text{NO}_3)_2$), Glycine, 99% pure ($\text{CH}_2\text{NH}_2\text{COOH}$), Nitric acid, 10N (HNO_3) of analytical grade were used as a precursor for $\text{Ce}_2\text{Zr}_2\text{O}_7$ powders. The synthesis technique used here is solution assisted combustion technique with precursors of Cerium Nitrate Hexahydrate ($\text{Ce}(\text{NO}_3)_2$) and Zirconyl Nitrate ($\text{ZrO}(\text{NO}_3)_2$) along with Glycine ($\text{C}_2\text{H}_5\text{NO}_2$) as fuel. The stoichiometric property of reactant was prepared based on the reaction.

The stoichiometric reaction is presented below

The synthesis was carried out by dissolving each of the reactants in nitric acid, and the complete mixing of the powders into the solution was ensured. Zirconyl nitrate solution was treated with cerium nitrate solution initially. Glycine was dissolved in distilled water and then added in drops to the mixture with the slow stirring rate. The whole mixture was stirred for about 45 min with mild heating until a clear solution was obtained. This solution mixture was transferred to an alumina crucible and was

kept in a muffle furnace at 923 K (650°C) for 10 to 15 min per batch to obtain the powders. Finally, the powders were sintered at 1100°C for the formation of a complete $\text{Ce}_2\text{Zr}_2\text{O}_7$ pyrochlore phase as were seen in the phase diagram of the $\text{CeO}_2\text{-ZrO}_2$ system [15, 16]. The agglomerate was crushed and sieved, which yielded powders of size 25 μm and above.

Substrate preparation

Inconel 625 samples of dimensions 3 cm $\times$ 3.8 cm were taken and sandblasted to get a 100 μm surface roughness to improve coating adherence. Samples surface was then degreased and cleaned with acetone to remove any entrapped silica particles and other foreign particles. Optical emission spectroscopy (OES) was carried out before coating to obtain the composition of the substrate (Table 1).

Thermal spray coating of Inconel sample

A most conventional form of thermal spraying is air plasma spraying (APS) where argon and hydrogen gasses are used as primary and secondary gasses, respectively. Thermal plasma spray (TPS) is a molten droplet deposition technology in which micrometer-sized particles of metals and ceramic powders are introduced into an arc plasma jet, entrained therein and propelled onto a polished substrate. The particles acquire thermal energy and momentum from the thermal plasma; undergo melting, followed by impact on the substrate surface and rapid solidification. Typically, for oxides and even most metallic alloys, plasma spraying is conducted under ambient conditions and hence the term APS (spraying of oxidation-sensitive metals in a low-pressure environment). The resultant deposited materials comprise of an assemblage of “splats” of rapidly solidified materials assembled to form a brick wall structure. Typical powder

Table 1: Composition of Inconel 625.

Element	C	Mn	Si	P	S	Ni	Co	Nb
Percentage (%)	0.08	0.35	0.35	0.015	0.015	53.50	1.00	4.5
Element	Cr	Fe	Al	Mo	Ti	B	Cu	
Percentage (%)	19.5	15.6	0.8	3.00	1.1	0.006	0.15	

particle sizes range from 10 to 100 μm with resultant splats of the order of a few microns in thickness and 100–150 μm in diameter. Parameters used for APS coated top coat and bond coat are shown in Table 2.

Table 2: Coating parameters used in preparation of APS bond and top COATS.

Parameters	Bond Coat (NiCrAlY)	Top Coat ($\text{Ce}_2\text{Zr}_2\text{O}_7$)
Feed rate (mg/mm)	90	100
Powder Carrier Gas (l/min)	3	3
Gun to work distance (mm)	180	150
Current/Voltage (A/V)	450/90	550/100
Gun speed (mm/s)	10	10
Primary and secondary gas (Ar/He)	30/20	45/5
Step distance (mm)	8	5

Characterization of powders and coated samples

XRD analysis is a rapid analytical technique used for phase identification of a crystalline material and can provide useful information such as crystal structure, unit cell dimensions, and crystallite size. Identification and characterization of compounds can be carried out from the diffraction pattern. In the present work, X'pert High Score plus software, an indigenously developed software with ICDD database, which was used to analyze the crystallographic information on phase formations and their lattice parameters. Also, Structure Prediction Diagnostic Software (SPuDS Version is 2.12.12.20. The software was developed by Michael Lufaso from university of north Florida and Pat Woodward from Ohio state university, United States of America.) was used for analyzing the atomic lattice positions and the bond distance between various atoms. The microstructural study was carried out using a JEOL 600 make Scanning Electron Microscopy. Secondary electron (SE) imaging mode was used to analyze the morphology and size of the powder particles. The coated layers, thickness, and morphology of coating were also analyzed using SEM. Thermal cycling tests were performed using a muffle furnace to check the stability of the coatings, involving repeated heating and cooling cycles for about 10 min duration. Thermal cycling was carried out for 50 cycles, and the microstructural results were analyzed. High-temperature isothermal oxidation studies were conducted to evaluate the coating performance at high temperature and

stability. Isothermal oxidations were carried out at 750°C for 50 h to determine the onset of oxide growth relate the ease with which a material develops an oxide layer as well as the stability of the oxides grown. Evaluation of oxide growth was done by taking the rate constant of the oxide layers. By measuring the weight gain of the oxide layer with increasing oxidation times and plotting the weight gain against the oxidation time, the rate constant for the oxidation process was obtained.

Results and discussion

Results of characterization of the CZ powders initially and as well as microstructural analysis and thermal behavior of coated samples are discussed in detail in the following section.

XRD analysis

XRD pattern confirmed the presence of $\alpha\text{-Ce}_2\text{Zr}_2\text{O}_7$ phase and due to the oxidation of Ce^{3+} to Ce^{4+} in the $\text{Ce}_2\text{Zr}_2\text{O}_7$ phase converts the resultant phase as $\beta\text{-Ce}_2\text{Zr}_2\text{O}_8$ as very well agreed with the previous literature results [22]. A sharp color change during the calcination process exhibits a distinct light yellowish color after the final transformation. It has a stable structure up to 1600°C similar to $\text{Ce}_2\text{Zr}_2\text{O}_7$ as well agreed with a phase diagram. Identification of the $\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_8$ phases are primarily understood concerning the change in lattice parameters. From the XRD pattern shown in Figure 2, the CZ has formed with a different phase composition $\beta\text{-Ce}_2\text{Zr}_2\text{O}_8$ along with traces of $\text{Ce}_2\text{Zr}_2\text{O}_7$, indicating the incomplete transformations of the powders during calcinations. Structure of $\beta\text{-Ce}_2\text{Zr}_2\text{O}_8$ reveals the presence of disordered cubic fluorite structure with a pyrochlore form. Pyrochlore generally possesses a structure of cations occupying seven-eighths of the tetrahedral sites with Wyckoff positions (special atomic sites) 48f and 8a sites between the cations. Peaks corresponding to 29.18°, 33.82°, 48.59° and 57.67° shows the existence of $\alpha\text{-Ce}_2\text{Zr}_2\text{O}_8$ peaks matching with the intensities of the cubic phase of (222), (400), (440), (622) and (444) planes, while the peak at 70.7° showed the presence of $\text{Ce}_2\text{Zr}_2\text{O}_7$ and the reference pattern correctly matched with JCPDF no 052–1104.

The lattice parameter calculated using above crystallographic data was found to be 10.589 Å and interfacial angles were 90° each, the volume of the unit cell was found to be 1187.31 Å³. (Table 3)

Figure 2: XRD analysis of synthesized $\text{Ce}_2\text{Zr}_2\text{O}_8$ powders.

Table 3: Parameters of $\text{Ce}_2\text{Zr}_2\text{O}_8$ powders calculated from XRD pattern.

S.no	2Theta[°]	(hkl) Values	d-spacing[Å]
1	29.180	(222)	3.058
2	33.824	(400)	2.640
3	48.596	(440)	1.872
4	57.677	(622)	1.597
5	70.702	(444)	1.526

The fractional amount of $\text{Ce}_2\text{Zr}_2\text{O}_8$ (CZ) formed was estimated from the relative intensities ratio of the primary phase with the secondary phase compounds using the equation given below [20],

$$\%X_{\text{CZ}} = \frac{I_{(222)}}{I_{(222)} + I_{(444)}} \quad (2)$$

The above equation can be modified depending on the Miller indices of the specific phases present. The presence of $\text{Ce}_2\text{Zr}_2\text{O}_8$ phase was estimated using eq. (2). Increasing the sintering temperature to 1200°C improved the phase purity of the compound to 100% with an accompanying increase in grain size of the calcined powders. Lattice parameters and interplanar spacings are calculated as per the standard procedures used in X'Pert High Score plus software.

From the precursors, of $\text{ZrO}_2\text{-CeO}_2$ few other phases were observed along with primary CZ phase. Ceria (CeO_2) substitution into the ZrO_2 solid solution affects the untransformed $\text{Ce}_2\text{Zr}_2\text{O}_7$ associated with some lattice strain and has good agreement with the previous literature [22]. Hence the $\text{Ce}_2\text{Zr}_2\text{O}_7$ phase was analyzed at the peak positions 58.02, 71.01 and 43.62 respectively and found to exactly match the tetragonal structure of CZ as strongly agreed with previous findings [20, 22]. These untransformed tetragonal crystals give rise to the small amount of peak shift as well as peak broadening in the XRD pattern of the CZ powders. Peak broadening associated with the FWHM is a significant factor, and it is found to vary for each peak position. Hence the values of each FWHM determined by using the high score plus software are shown in Table 5. Debye-Scherrer formulae (eq. 5) use the FWHM values obtained from the broadening effect of each peak in order to calculate the average crystallite size [19].

$$D = 0.9\lambda / \beta \cos\theta \quad (3)$$

D – Crystallite size (nm)

λ – Wavelength source

β – FWHM (°)

Crystallite sizes calculated using the above equation (Table 4), shows the presence of fine crystalline CZ phase (Figure 2) with minimum peak broadening,

Table 4: Crystallite size for $\text{Ce}_2\text{Zr}_2\text{O}_8$ calculated (using Debye-Scherrer equation).

S.no	Peak Position [°]	FWHM [°]	Crystallite size (nm)
1	29.180	0.207	6.91
2	33.824	0.310	4.67
3	48.496	0.392	3.87
4	57.677	0.400	3.95
5	60.502	0.410	3.90

Table 5: FWHM values corresponding to the peak positions.

S.no	2 theta [°]	FWHM[°]
1	29.180	0.207
2	33.824	0.310
3	48.496	0.392
4	57.677	0.400
5	60.502	0.410

indicating a small amount of lattice strain during phase transformations. Phase quantification shows more broadened peaks that are observed predominantly for $\text{Ce}_2\text{Zr}_2\text{O}_8$ phases, which indicates a small crystallite size with an average value of 4.66 nm.

The structural refinement of the unit cell data was done using the SPuDS. The primary purpose of using this software is to predict the cell parameters, atomic structural positions along with the bond valence strength calculation of each atom present in the unit cell. Results of SPuDS analysis of pyrochlore structure are presented in Table 6.

Table 6: Summary of results for unit cell refinements [22].

Atom	Band valence	Oxidation states	Occupancy	Atomic sites
Ce	2.959	3	1.00	16d
Zr	3.998	4	1.00	16c
O1	1.893	2	1.00	48f
O2	2.555	2	0.08	8b
O3	2.354	2	0.92	8a

Space group analysis of the phases formed was carried out and found to be the Fd-3 m group for $\text{Ce}_2\text{Zr}_2\text{O}_7$ and P213 group for $\text{Ce}_2\text{Zr}_2\text{O}_8$ corresponding to the space group number 227, which confirms the ideal pyrochlore structure. Unit cell parameters obtained from structural

analysis were found to be 10.707 Å, and the volume of unit cell was 1225.387 Å³, respectively. The secondary phase observed in the XRD analysis has a space group of P42/nmc with the space group number 137 thereby confirming the presence of primitive tetragonal lattices. The oxygen vacancies occupy 1/8th of the tetrahedral sites (8b) sites and found to have an ordered $\text{Ce}_2\text{Zr}_2\text{O}_7$ structure. Before oxidation, the oxygen ions initially occupied 8b sites while Ce and Zr ions occupied 16c and 16d sites, respectively. Oxygen atoms remain the same positions before and after oxidation. The site 8a coordinates with four Ce ions and the 8b sites coordinated with 4Ce ions, the 8b sites with 4 Zr ions and the 48f sites coordinated with 2 Ce and 2 Zr ions. Earlier refinement results show that the 48f and oxygen sites have full occupancies, and also the 48f site always occupies as 1 [22].

Details of the occupancy state of various atoms with the atomic coordinates (Table 7) along with the calculated bond distance and valence states are tabulated Table 8.

Table 7: Occupancy state with the atomic coordinates for various atoms.

Atoms	Sites	X	Y	Z	Occupancy
Ce	16d	0.5000	0.5000	0.5000	1.00
Zr	16c	0.000	0.0000	0.0000	1.00
O1	48f	0.3304	0.1250	0.1250	1.00
O2	8b	0.1250	0.1250	0.1250	0.08
O3	8a	0	0	0	0.92

Table 8: Bond distance and valencies data.

A sites	X sites	Multiplication factor	Distance	Valency	Occupancy
Ce(16d)	O(48f)	x6	2.621	0.2936	1.000
Ce(16d)	O(8b)	x2	2.316	0.2434	1.000
B Sites	X sites	Multiplication factor	Distance	Valency	Occupancy
Zr(16c)	O(48f)	x6	2.078	0.1093	1.000

Tables 7 and 8 relate the atomic positions by the distance between the cations to anions (both A & B sites) together with their occupancies shall be used for the further refinements using the Rietveld method.

Microstructural analysis of coated specimens

Observations of thermally grown oxide (TGO)

SEM investigations provided useful information on microstructural features such as phases present, pores, micro-crack formations as well as the formation of TGO. SEM characterization of TBC of as-coated specimens was used to analyze the total coating thickness consisting of both topcoat and bond coat. SEM images of the cross-section in the vicinity of the $\text{Ce}_2\text{Zr}_2\text{O}_8/\text{NiCrAlY}$ interface are shown in Figure 3(a) and (b).

SEM micrograph (Figure 3(a) and (b)) confirms the presence of a thin TGO layer at the $\text{Ce}_2\text{Zr}_2\text{O}_8/\text{NiCrAlY}$ interface with an increased thickness of about $16\text{ }\mu\text{m}$ due to inward diffusion phenomenon of oxygen. Micrograph of the TGO layer also reveals that nonuniform variations in thickness at the $\text{Ce}_2\text{Zr}_2\text{O}_8/\text{NiCrAlY}$ interface. This TGO layer is primarily a composite consisting of two layers observed with the contrasting colors one with black layer closer to the bond coat layer, and the gray layer near the CZ phase.

SEM micrograph (Figure 4) of the TGO layer at higher magnification shows the presence of pores and nonuniformly sized particles, especially in the gray layer. Consequently, the TGO layer was identified as Al_2O_3 (alumina) that usually appears gray (Figure 3) which is in agreement with the previous literature [16, 17].

In air plasma sprayed (APS) samples, inter-splat pores result from the impingement of molten droplets

Figure 4: SEM micrograph of TGO at higher magnification.

onto micro-cracks and fine grain boundaries. These pores provide a high impedance to heat flow along the thickness of the coating resulting in a TBC with low thermal conductivity. It was observed that the ideal $\alpha\text{-Al}_2\text{O}_3$ (TGO) layer grows on the bond coat both during top coat depositions as well as during component service. Interconnected porosity exists in the coating allows easy diffusion of oxygen from the service environment to the bond coats as illustrated by J.A Haynes et al., during the investigations of the various MCrAlX bond, coats have reported similar observations [17]. The growth rate of the TGO usually follows parabolic growth law given by eq. (4) [7],

Figure 3: (a) Cross section of $\text{Ce}_2\text{Zr}_2\text{O}_8$, (b) NiCrAlY interface.

$$h^2 = 2 K_p \cdot t \quad (4)$$

where,

h is the thickness, (μm)

t is the time (sec) and

K_p is the parabolic rate constant ($\text{mg}^2\text{cm}^{-4}\text{hour}^{-1}$)

Thermal cycling studies on coated samples

Thermal stability of the coating was carried out by thermal cycling to check the coating adherence along with the coating shock resistance behavior during the operating temperatures. During the operation of aero gas turbine engines, the coating system is subjected to thermal cycles that increase the bond coat surface temperature close to 1000°C [17, 23]. Under this condition, the temperature difference between the top coat and bond coat may exceed 100°C or more. In the present research, coated samples were subjected to thermal cycling at 850°C with each cycle involving 10 min of alternate heating and cooling.

SEM micrograph (Figure 5) of thermal cycled samples showed that the coating exhibits a strong adherence to the substrate up to 50 cycles with the very minimal amount of distortion. Thermal spalling was not observed until the 20th cycles, and from the micrograph, coating is found to be strongly adherent thereby lowering the coating distortion rate. At this temperature, significant densification of the CZO (sintering) as well as creep of the bond

coat occurs and is found to be accompanied by temperature dependent TGO layer growth. However, as the number of thermal cycles increased, the thermal stresses developed by these processes eventually cause spallation of the TBCs, which usually occurs at the $\text{Ce}_2\text{Zr}_2\text{O}_8/\text{NiCrAlY}$ interface due to the thermal stress developed. The spallation results from the linkage of the cracks formed in the TBC layer above the TGO.

From Figure 5, the failure observed during the thermal cycling might have occurred due to the following reasons and is consistent with the previous literature findings. Abdullah Cahit et al. have reported similar results. [7],

- a) Large in-plane compressive stresses in TGO, especially during cooling, leading to rumpling of the coating.
- b) During the TGO growth, imperfections exist (or developed) around the TGO. Tensile stresses are induced normal to the TGO/Bond Coat interface, which facilitates crack initiation during early stages at the interface.

Investigation of high-temperature oxidation behavior of coated samples

Isothermal oxidation behavior varies non linearly with the weight gain of the oxide with respect to time in hours. This formed oxide layer was observed to have a mixed type of oxide layer growth, which is again a predominant factor in predicting the lifetime of CZ coatings. Variation in thickness of alumina and mixed oxide

Figure 5: Thermal cycled at 50th cycle.

layer increases as a function of aging time and the relationship between the average thickness of each layer and aging time was also established to explain the oxidation kinetics of the material.

A plot of weight gain of the oxide layers concerning time (Figure 6) and the slope value gives the rate constant K_p as $1.18 \times 10^{-3} \text{ mg}^2 \text{ cm}^{-4} \text{ hour}^{-1}$, indicating a parabolic growth rate of oxide layers with respect to time. Mohamed Morsi et al. [16] have reported a similar parabolic growth rate in the case of TBCs.

Towards observing CZO layer as the top coat that has a little thickness variation despite an increase in aging time. Further, the thickness of the TGO layer gradually increases with aging time. The relationship between TGO thickness and the square root of time shows that the growth of mixed oxide obeys the parabolic law. Hence, the mixed oxide is protective despite the presence of porosity in the coating.

Influence of defects on the coating

SEM micrograph of the oxidized sample shows (Figure 7), the presence of microcracks and porosity in the coating both in CZ and TGO layers of aged specimens. The amount of porosity, as well as the micro cracks in each layer, increased with aging time. In particular, the micro cracks in the CZ top layer increased notably, while the porosities present in the mixed oxide also showed an

Figure 7: SEM micrograph showing the formation of cracks in the mixed oxide layers.

increase in micro-cracks formations in the alumina layer (TGO). The reason because the porosity and microcrack in the CZO layer are formed due to thermal expansion mismatch accompanying the formation and growth of TGO which is in agreement with the result of a previous study [7]. Further, the formation of various porosities in the mixed oxide is caused by Kirkendall porosity caused by the difference in diffusion rate between the top coat and TGO layer [11].

Figure 6: Plot of weight gain as a function of time during oxidation of coated samples.

Formation of defects such as micro crack or porosity in the coated specimens increases the stress in the vicinity of the crack tip. Accordingly, a macro-crack or delamination could initiate from the tip of the defects. Hence, the presence of porosities both at the top coat and at the interface zone improves the conductivity by facilitating the inward diffusion of oxygen. Thus it is evident that the thermal conductivity of the top coat gets reduced Sang-Won Myoung et al. [9] have reported a similar result during an investigation on YSZ coatings over a nickel base superalloy substrate.

Conclusions

Major conclusions from the present work are:

- Synthesis of CZ by solution assisted combustion synthesis was carried out.
- XRD analysis confirmed the presence of nearly pure Cerium zirconate ($\text{Ce}_2\text{Zr}_2\text{O}_7$) compound along with a minimal amount of secondary phase constituents.
- SEM micrograph and the crystallite size obtained from XRD confirmed the nanocrystalline nature of CZ.
- SEM micrographs before and after coating show the presence of various layers (Topcoat, Bond coat with CZO/NiCrAl interface zone).
- SEM investigations on thermal cycled confirmed that the coating exhibits excellent adherence to the substrate.
- Limited porosity and microcracks were observed after the thermal cycling of specimens, which indicated that the coating has better compatibility along with lower thermal conductivity.
- Results of studies on weight gain as a function of time during oxidation studies indicated a parabolic growth with a constant of $K_p = 1.18 \times 10^{-3} \text{ mg}^2\text{cm}^{-4}\text{hour}^{-1}$, indicating the protective nature of coatings.

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