Improved hot corrosion resistance of plasma sprayed YSZ/Gd₂Zr₂O₇ thermal barrier coating over single layer YSZ

P.G. Lashmi, Sumil Majithia, V. Shwetha, N. Balaji, S.T. Aruna*

Surface Engineering Division, Council of Scientific and Industrial Research, National Aerospace Laboratories, Bangalore 560 017, Karnataka, India

ARTICLE INFO

Keywords:

Gadolinium zirconate (GZO)
Bilayer
Plasma spraying
Hot corrosion
Thermal cycling

ABSTRACT

In recent years, research is focused on the development of rare earth zirconates based thermal barrier coatings (TBC). In the present study, bilayered 8 wt% yttria stabilized zirconia (YSZ)/gadolinium zirconate (GZO) TBC system has been developed by atmospheric plasma spraying (APS) process from powders prepared by a single step co-precipitation technique. Hot corrosion behavior of all the coatings are tested in fused Na₂SO₄ + V₂O₅ mixture at the concentration of approximately 25 mg/cm² at 910 °C for 30 h. Formation of gadolinium vanadate (GdVO₄) is observed to be the corrosion product in YSZ/GZO bilayer coatings from Energy Dispersive X-ray analysis (EDAX) and is further confirmed by X-ray diffractometry (XRD) analysis. FESEM cross-section analysis of the YSZ/GZO bilayer coating after corrosion test affirms the effectiveness of the bilayer design in preventing the penetration of corrosive salts to the YSZ layer. Also, YSZ/GZO bilayer TBC exhibited a higher thermal cyclic life (300 cycles) than the single layer 8YSZ (175 cycles) coatings at 1100 °C.

1. Introduction

Thermal barrier coatings (TBCs) are ceramic materials that remarkably assist in increasing the efficiency of advanced gas turbines and protect components from severe thermal loads [1]. The conventional architecture of TBCs comprises of a bond coat (MCrAlY) followed by a ceramic top coat. The prevailing industrial standard ceramic top coat material is 7–8 wt% yttria stabilized zirconia (YSZ) by virtue of its notable thermo-mechanical properties [2]. But the application of YSZ is limited as it undergoes a phase transformation from tetragonal (t') to monoclinic zirconia (ZrO₂) phases at temperatures > 1200 °C, leading to 3–5% volume expansion, resulting in cracking damage and coating failure [3].

With the escalating demands for efficient gas turbines it is inevitable to explore new ceramic materials possessing better properties like higher thermal stability, good thermo-cyclic efficiency, low thermal conductivity etc. Amongst the evolving TBC topcoat candidates, gadolinium zirconate (GZO) with defect fluorite structure possesses better thermal properties. Unlike YSZ, GZO does not undergo phase transformation from tetragonal to monoclinic structure at higher temperatures (> 1200 °C). Instead, an order-disorder transition has been observed at 1530–1550 °C from defect fluorite structure to pyrochlore structure without any detrimental effects. From the literature, it is evident that the order-disorder transition has no significant effect on

the integrity of coating. This phase transformation in GZO does not involve any significant volume change as the cubic crystal structure remains unchanged. In accordance with the phase diagram, the solidification basically starts from fluorite and transforms completely to pyrochlore during cooling below ~1530 °C. But, due to the rapid solidification on the substrate during plasma spraying, the formation of pyrochlore phase is suppressed resulting in the formation of metastable defect fluorite phase. The defect fluorite phase possess oxygen vacancies and anions at random positions in the cubic crystal structure, whereas the pyrochlore has cations and oxygen vacancies that occupy a specific position in the crystal structure [4–6]. The thermal expansion coefficient (9–11 × 10^{−6}/K) of GZO which determines the magnitude of thermal stress in the coating is comparable to YSZ. In addition to this, the lower thermal conductivities (1.2–1.7 (W/mK) at 1000 °C) also reduce the bond coat oxidation thereby diminishing the coating failure [7,8]. However, by scrutinizing the literature it has been observed that GZO as a single layer do holds up few limitations when used as single layer TBC [9,10]. It is prone to react with thermally grown oxide (TGO) grown at the interface between bond coat and ceramic top coat at high temperatures and forms porous layer of GdAlO₃ perovskite structure which is not favourable for TBC applications [11]. Hence, recent studies have been focused on the development of bilayered YSZ/Gd₂Zr₂O₇ coating system [12,13].

Another prevailing threat to TBC life is the attack of corrosive

* Corresponding author.

E-mail address: aruna_reddy@nal.res.in (S.T. Aruna).

<https://doi.org/10.1016/j.matchar.2018.11.007>

Received 6 June 2018; Received in revised form 11 September 2018; Accepted 4 November 2018

Available online 06 November 2018

1044-5803/ © 2018 Elsevier Inc. All rights reserved.

species such as vanadium, sodium and sulphur from low-grade fuels used in land based gas turbines. Firstly, when YSZ coatings are exposed to such attacks vanadia readily reacts with yttria to form yttrium vanadate. Thus the destabilization of zirconia takes place leading to the formation of monoclinic zirconia (m-ZrO₂). On the other hand, NaVO₃ which is one of the corrosive reactants elevates the atomic mobility and promotes the depletion of yttria from YSZ. As the reaction time increases, complete exhaustion of Y₂O₃ from zirconia lattice takes place. In the course of cooling, transformation of t'-ZrO₂ to m-ZrO₂ takes place accompanied by 3–5% of volume expansion resulting in the spallation and failure of YSZ TBCs [14–16]. The phase transformation is immensely accelerated reducing the coating life further. It has also been ascertained from the reports that gadolinium zirconate has better resistance to sodium sulphate and vanadium pentoxide corrosive elements than YSZ [17,18]. There are limited reports illustrating the behavior of bilayered YSZ/GZO TBCs subjected to hot corrosion. The corrosion properties of suspension plasma sprayed (SPS) YSZ, YSZ/GZO and dense GZO/GZO/YSZ coatings at 900 °C have been studied and the bilayer coating exhibited lower hot corrosion resistance due to the infiltration of the molten salts through the columnar gaps [19]. Habibi et al. have reported the hot corrosion behavior of plasma sprayed YSZ, 50 wt% YSZ + 50 wt% Gd₂Zr₂O₇, and Gd₂Zr₂O₇ fabricated using agglomerated powders. It has been observed that amongst all the coatings, Gd₂Zr₂O₇ exhibited better corrosion resistance [20]. Plasma sprayed LaPO₄ doped GZO nanostructured coatings subjected to hot corrosion were examined in the presence of Na₂SO₄ + V₂O₅ and V₂O₅ corrosive salts. Formation of a continuous dense reaction layer on the coating surface inhibited further salt penetration across the coating thickness which in turn deteriorated the corrosion rate thereby manifesting better corrosion resistant properties for LaPO₄ doped GZO coatings [21]. There is a very recent paper on hot corrosion and thermal cycling of LaPO₄/YSZ double ceramic layer TBC [22]. The bilayer coating exhibited better hot corrosion resistance. However, it showed poor thermal cycling behavior due to lower toughness of LaPO₄ coating.

Solution precursor plasma sprayed double layered YSZ/GZO coating with improved phase stability, cyclic durability and increased surface temperature capabilities has been reported [23]. Bakan et al. have studied the microstructure and thermal cycling behavior of plasma sprayed YSZ/GZO coatings fabricated from commercial powders. The plasma sprayed bilayer YSZ/GZO coatings exhibited longer thermal cycling life than standard YSZ coatings [24]. Failure analysis of bilayer and triple layer GZO-YSZ based suspension plasma sprayed coatings subjected to thermal cycling has been reported [25]. The triple layer TBC exhibited higher thermal cycling life than the single and bilayer coatings and the failure of the coatings were attributed to the spallation at TGO/bond coat interface [25].

However, the hot corrosion behavior of plasma sprayed bilayered YSZ/GZO coatings using feedstock powders prepared from chemical routes has not yet been explored in the literature. Moreover, as the properties of feedstock powders such as chemical composition, crystallite phases, particle size, morphology and distribution determine the coating microstructure, the current study is committed towards the synthesis of plasma grade GZO powders by co-precipitation method. Unlike several other multi-step agglomeration processes like spray-drying, co-precipitation method is simple and cost-effective and hence it is employed for the preparation of feedstock powders. In this work, single layered YSZ and bilayered YSZ/GZO TBCs were deposited by APS technique using laboratory synthesized feedstock powders and were subjected to 45 wt% V₂O₅ + 55 wt% Na₂SO₄ corrosive salts at 900 °C for 30 h. The hot corrosion properties of coatings were studied along with their thermal cycling behavior.

2. Materials and Methods

2.1. Synthesis of Plasma Grade Powders

Plasma grade flowable 8 wt% YSZ and GZO powders were prepared by a single step co-precipitation technique. The detailed experimental procedure for the synthesis of flowable 8 wt% YSZ powders has already been described in our previous work [26]. The steps involved in the preparation of GZO powders are as follows: gadolinium nitrate solution was prepared by adding dilute nitric acid to 50 g of Gd₂O₃ powder (99.9% purity, Mincometsal). Subsequently, 83.03 g of zirconium oxychloride (ZrOCl₂·8H₂O) (98% extra pure, Loba Chemie) was dissolved in distilled water and added to gadolinium nitrate solution followed by stirring. Then ammonium bicarbonate (98.5% extra pure, Loba Chemie) solution of known concentration was added to the solution mixture to get a white precipitate (pH ~9). The obtained precipitate was then washed, filtered, dried and calcined for 4 h at 900 °C. The calcined powder was then sieved to segregate the fine and coarse particles. The coarse flowable powders were then used for plasma spraying.

2.2. Atmospheric Plasma Spraying

Fabrication of single layer YSZ as well as bilayer YSZ/GZO TBCs were carried out using synthesized powders by atmospheric plasma spraying (APS) using Sulzer Metco 9MB plasma spray gun on the substrates coated with metallic bond coat layer. The bond coat material used is AMDRY 962 (Sulzer Metco) with the composition Al-9.07 wt%, Cr-23.22 wt%, Ni-67.39 wt% and Y-0.33 wt%. Details of the substrates used for the fabrication of all the coatings has been reported in our previous work [26]. Table 1 shows the optimized plasma spray parameters employed for the fabrication of all the coatings. As synthesized GZO powders and plasma sprayed GZO coatings including the post hot corrosion tested coatings were characterized for phase using X-ray diffractometer (Bruker D-8 Advance, Cu-Kα radiation, 1.5405 Å). The particle size of as prepared GZO powders were analysed using laser light scattering method (Mastersizer 2000, Malvern Instruments).

2.3. Hot Corrosion Test

Hot corrosion tests on the fabricated coatings (4 samples each of YSZ and YSZ/GZO) were conducted using mixture of 55 wt% of sodium sulphate (Na₂SO₄, Loba chemie, 99% purity) and 45 wt% vanadium pentoxide (V₂O₅, Loba chemie, 99% purity) salts. The surface of the coatings was coated manually by the corrosive salt mixture such that the concentration of salt is 25 mg/cm² [26]. The samples were kept in a muffle furnace at 910 °C in air atmosphere. The samples were soaked for 30 h in the furnace and were taken out after cooling for further characterization. The as sprayed coatings and the coatings after hot corrosion tests were examined for microstructure and elemental analysis by Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss) and Energy Dispersive X-ray Analysis (EDAX).

The porosity level of the coatings was calculated by the Archimedes' principle. First, the density of the free forms of 8YSZ and GZO coatings

Table 1
Plasma spray parameters employed for coating fabrication.

Parameters	NiCrAlY	YSZ	GZO	YSZ/GZO
Voltage (V)	40	60	50	60/50
Current (A)	500	600	500	600/500
Primary gas, Ar (nlpm)	40	40	40	40
Secondary gas, H ₂ (nlpm)	7	9	7	9/7
Carrier gas pressure, Ar (bar)	2	2	2	2
Powder feed rate (g/min)	15	15	15	15
Spray distance (cm)	20	10	10	10
Spray gun speed (mm/min)	800	800	800	800

with $200 \pm 30 \mu\text{m}$ thickness were measured by water immersion method. Three independent measurements were taken for each coating and their mean value with standard deviation were calculated. The density of the coatings was estimated by the following equation:

$$\text{Coating density} = \frac{D}{W - S}$$

where D, W and S are dry, saturated and suspended weights of the free forms respectively.

The % porosity of the coatings was estimated by the following equation [27]:

$$\text{Porosity (\%)} = 100 - \frac{\text{Coating density}}{\text{Bulk density}} \times 100$$

2.4. Thermal Cycling Test

High temperature thermal cycling test was carried out on the fabricated coatings (4 samples each of YSZ and YSZ/GZO) by isothermal heating and air quenching. YSZ single layer as well as YSZ/GZO bilayer coatings were plasma sprayed over the metallic bond coat on Ni superalloy substrate (composition from EDAX analysis: Al-0.40 wt%, Cr-11.53 wt%, Fe-19.90 wt%, Ni-5.43 wt% and Mo-10.775 wt%) of 25 mm diameter and 3 mm thick. The same plasma spraying parameters in Table 1 were employed for the coating fabrication. The edges of these disk shaped samples were bevelled prior spraying in order to minimize the development of stress from the free edges. Thermal cycling (TC) of the plasma sprayed samples were conducted in the laboratory TC furnace facility (Thermal cycling furnace, Parikshan Furnace, India). The isothermal cyclic oxidation test was carried out at 1100°C with a ramp of 5 mins to 1100°C ($\pm 5^\circ\text{C}$) followed by 60 min soaking at 1100°C and forced air quenching for 15 min to $\sim 30^\circ\text{C}$. The samples were visually inspected and All the bare, bond coated and top coated samples were periodically weighed before and after every 10 cycles using an electronic balance. The cycling was continued until visible spallation and cracking of the samples occurred and the lifetime of the coatings has been defined as the number of thermal cycles until the failure of TBCs ($\sim 30\%$ visible delamination).

3. Results

The optical micrograph of as prepared GZO powder is shown in Fig. 1. The particles are angular blocky in shape. From the particle size analysis, the average agglomerated particle size (d_{50}) was found to be $75 \mu\text{m}$. Fig. 2(a) and (b) shows the XRD patterns of the synthesized GZO powder and as sprayed coating respectively. The as prepared GZO powder and the coating exhibited $\text{Gd}_2\text{Zr}_2\text{O}_7$ phase with defect fluorite

Fig. 1. FESEM micrograph of as prepared GZO powder.

Fig. 2. XRD analysis of (a) as prepared GZO powder (b) Plasma sprayed GZO coating.

structure (PDF-ICDD 01-078-4784) [19]. In addition to the major peaks of defect fluorite structure, some unknown minor peaks were observed in the case of as prepared GZO powder. Interestingly, these unknown phases vanished in the plasma sprayed coating.

The surface morphology of as sprayed GZO coatings is shown in Fig. 3. Typical features of plasma sprayed coatings such as fully melted and partially melted zones were observed on the surface of the coatings. Fig. 4(a) shows the cross-sectional micrographs of GZO coatings ($\sim 120 \mu\text{m}$) on NiCrAlY bond coat over the superalloy substrate. The elemental analysis of the coating in Fig. 4(b) affirmed the composition of GZO.

Fig. 5 shows the cross-sectional images of bilayer YSZ/GZO TBC along with the EDS mapping. It is evident that the bond coat is of thickness $100 \mu\text{m}$ followed by YSZ ($130 \pm 20 \mu\text{m}$) and GZO ($100 \pm 20 \mu\text{m}$). The surface and cross-sectional images of YSZ has already been reported [25].

The surface morphology and EDS analysis of single layer YSZ TBC post corrosion shown in Fig. 6(a) and (b) confirms the formation of corrosive products. Whereas the surface morphology of YSZ/GZO coating reveals the presence of GdVO_4 , m-ZrO_2 besides the unreacted Na_2SO_4 molten salt shown in Fig. 7(a), (b) and (c).

Fig. 8 (a–c) shows the cross-section of YSZ/GZO TBC subjected to hot corrosion along with EDS analysis. It is evident from the images that even after 30 h of hot corrosion treatment, the interfaces are very much intact with good adhesion.

Fig. 9(a) and (b) shows the XRD analysis of YSZ and YSZ/GZO coatings after hot corrosion test at 910°C for 30 h in 45% $\text{Na}_2\text{SO}_4 + 55\% \text{V}_2\text{O}_5$ respectively. In single layer YSZ coating, YVO_4 and monoclinic zirconia were formed as the product of hot corrosion test. Formation of YVO_4 phases can be explained based on Eq. (4). Whereas in YSZ/GZO bilayer coatings, the formed corrosion products are assigned to GdVO_4 , monoclinic and tetragonal zirconia phases in

Fig. 3. Surface morphology of as sprayed GZO coating at $2\text{K} \times$ magnification.

Fig. 4. (a) Cross-sectional micrographs of GZO coating at 500 × magnification (b) EDS analysis of as sprayed coating.

Fig. 5. Cross-sectional micrographs of as sprayed YSZ/GZO coating at 500 × magnification.

accordance with the literature [28].

Results of thermal cycling test at 1100 °C are shown in Fig. 10. From the thermal cycling results, it is clear that the double layered YSZ/GZO system exhibited improved thermal cycling life than the single layer YSZ coatings. The enhanced lifetime of bilayer coatings can also be substantiated from the rate of oxidation weight gain as shown in Fig. 11. From the Table 2 it is obvious that the rate of oxidation weight gain of YSZ/GZO bilayer coatings is lower than that of YSZ single layer TBCs at 1100 °C.

SEM micrographs and photographs of YSZ and YSZ/GZO samples subjected to thermal cycling are shown in Fig. 12(a) and (b) respectively. It is apparent from the results the YSZ single layer TBC has undergone visible spallation than the bilayer coatings. The failure of YSZ TBC can be associated with the evolution of thermally grown oxide (TGO) layer due to bond coat oxidation by the oxygen transport through the interconnected pores of ceramic. Whereas, the bilayer spallation occurs at the sample edges after thermal cycling test.

Fig. 6. (a) Surface micrograph and (b) EDS analysis of YSZ TBC after hot corrosion test at 910 °C in the presence of 45% Na₂SO₄ + 55% V₂O₅ for 30 h at 4K × magnification.

Fig. 7. Surface micrographs and EDS analysis of YSZ/GDZ bilayer coatings after hot corrosion test at $910\ ^\circ\text{C}$ in the presence of $45\% \text{Na}_2\text{SO}_4 + 55\% \text{V}_2\text{O}_5$ for 30 h at $4K\times$ magnification.

4. Discussion

The equation for the formation of GZO powder can be written as follows:

According to ASTM B213-97 standard the co-precipitation synthesized GZO powders exhibited flowability of 33 s/50 g and the particle

size distribution was as follows: $d_{10} - 28$, $d_{50} - 74$, $d_{90} - 136\ \mu\text{m}$ respectively. From the XRD patterns, presence of a very low intensity secondary phase peak was found in the case of GZO powder, which could be due to the existence of some intermediate phase. But the secondary phase peak (indicated by * in Fig. 2) disappeared in the plasma sprayed GZO coatings demonstrating the formation of phase pure GZO due to the subjection under high temperature plasma flame. Moreover, the peaks of GZO powder pattern are relatively broader indicating smaller crystallite size (15 nm from Scherrer's formula). This shows that the GZO powder is an agglomerate of nanosize crystallites.

Fig. 8. Cross-sectional micrographs of YSZ/GZO coating at $500\times$ magnification after hot corrosion test at $910\ ^\circ\text{C}$ in the presence of $45\% \text{Na}_2\text{SO}_4 + 55\% \text{V}_2\text{O}_5$ for 30 h at $4K\times$ magnification.

Fig. 9. XRD patterns of (a) YSZ (b) YSZ/GZO coatings after hot corrosion test at 910 °C in the presence of 45% Na₂SO₄ + 55% V₂O₅ for 30 h.

Fig. 10. Weight change curves from cyclic oxidation testing at 1100 °C of YSZ and YSZ/GZO TBCs.

Fig. 11. Fitting curve of rate of weight gain during thermal cycling test at 1100 °C.

Table 2

The calculated K_p for thermally cycled coatings at 1100 °C.

Coatings	K _p (mg ² ·cm ⁻⁴ ·h ⁻¹)
8YSZ	1.8351
8YSZ/GZO	0.4874

The porosity of the GZO and YSZ coatings was around ~17–20%. From the surface analysis presence of cracks were observed on the surface of the coating due to the generation of residual stress at the grain boundaries.

In the case of post corrosion test at 910 °C for 30 h, the probable reaction between GZO and the corrosive salts may be written as in Eqs. (2) and (3). In both the cases, Na₂SO₄ does not readily react with GZO according to Na₂SO₄-V₂O₅ binary phase diagram [20]. It reacts with V₂O₅ to form sodium metavanadate (NaVO₃) with melting point of 610 °C. Further Na₂O readily reacts with V₂O₅ forming NaVO₃ which in turn reacts with the coating to form YVO₄ in YSZ TBC and GdVO₄ in YSZ/GZO TBCs as major corrosion products besides m-ZrO₂ and t-ZrO₂ phases. Traces of unreacted Na₂SO₄ phases were also detected from X-ray analysis of YSZ/GZO bilayer coatings.

The surface micrographs of single layer YSZ TBCs reveals the formation of rod-like YVO₄ crystals along with m-ZrO₂ covering the entire surface post corrosion. The highly reactive Na₂VO₃ increases the atomic mobility and destabilize the zirconia by depleting yttria. The depleted Y³⁺ from YSZ lattice tends to migrate towards the V species to grow as YVO₄ rods at the grain boundaries. As the duration of corrosion increases the Y³⁺ is consumed resulting in the growth of YVO₄ rods. In addition to this, yttria deficient destabilized ZrO₂ endures tetragonal to monoclinic transformation resulting in 3–5% volume expansion eventually the coating failure through cracking and spallation during cooling.

On the other hand, the corrosion products of YSZ/GZO coating were recognized to be GdVO₄, m-ZrO₂ besides the unreacted Na₂SO₄ molten salt. The higher durability of GZO/YSZ TBCs against hot corrosion attack can be attributed to the bilayer design. The corrosion reaction initiates from the top GZO surface where the molten salts such as V₂O₅ and Na₂VO₃ penetrate through the coating porosity and react to form GdVO₄ phases. The penetration of corrosive species reaches the bottom YSZ layer provided that the top GZO layer is completely depleted. Also, in the single layer system the molten salts directly react with YSZ whereas, it reacts with GZO layer first in the bilayer coatings prolonging the reaction to deplete YSZ. The depletion of the top GZO transpires only with the presence of sufficient amount of corrosive species. In the present conditions, the molten corrosive salts available have completely reacted with GZO layer forming GdVO₄ as corrosive products thereby preventing the underlying YSZ from damage. Also, the presence of unreacted Na₂SO₄ on the surface of the coating and as confirmed by EDS analysis could be due to the fact that the melting point and boiling point of Na₂SO₄ is 884 °C and 1404 °C respectively, some of the molten sodium sulphate may evaporate after higher temperature thermal exposure > 1000 °C [29,30]. Whereas, from the cross-sectional images of YSZ/GZO TBCs after 30 h of hot corrosion treatment, it is noticeable that the interfaces are very much intact with good adhesion. The corrosive salts at the exposure temperature did not infiltrate through the coating thickness illustrating the potentiality of the bilayer design. Due to the prolonged reactivity at the top GZO layer, the propagation of corrosive phases has been hindered. As a result of incomplete reaction the unreacted Na₂SO₄ remained on the top GZO surface. Thus the underlying YSZ layer has been effectively protected by the top GZO from the corrosion attack, enabling better corrosion resistance than single layer YSZ TBCs. Additionally, the concentration of YVO₄ rods in YSZ coating were higher than that of GdVO₄ rods on the coating surface. This also explains the reason behind the lower volume fraction of monoclinic ZrO₂ in YSZ/GZO TBCs than that of YSZ TBCs. Unlike the SPS GZO/YSZ TBCs [12], the present study illustrates that the plasma sprayed bilayer coating without columnar microstructure is

Fig. 12. Photographs and cross-section micrographs of samples after thermal cycling at 1100 °C (a) single layer YSZ (b) bilayer YSZ/GZO TBCs at 200× magnifications.

a better option to design a TBC with improved hot corrosion resistance. Furthermore, the hot corrosion properties of YSZ/La₂Ce₂O₇ (LCO) bilayer TBCs have been studied in our previous work [26]. In comparison to YSZ/LCO bilayer TBCs, the YSZ/GZO coatings exhibited better corrosion resistance properties.

The weight gain results of YSZ and bilayer YSZ/GDZ coatings exposed to 1100 °C thermal cycling revealed higher weight gain for YSZ single layer TBCs. Unlike the YSZ/GZO bilayer coatings, the YSZ coatings failed after 175 cycles. This failure mechanism in YSZ based coatings are commonly attributed to the defects in thermally grown oxide layer. Also the less cycling life could be due to the inner oxidation bond coat causing coating failure [20]. An improved thermal cycling life (300 cycles) was observed for bilayer YSZ/GZO coatings.

The high temperature oxidation behavior of the thermally cycled YSZ and YSZ/GZO coatings is expected to follow the equation shown below [30]:

$$\left(\frac{\Delta m}{S}\right)^2 = K_p t \quad (5)$$

where Δm is the oxidation weight gain (mg); S is the coated surface area (cm²); K_p is the parabolic rate constant (mg²·cm⁻⁴·h⁻¹); t is the oxidation time.

The rate constant of oxidation weight gain can be attained by linear fitting with respect to Eq. (5). The parabolic rate constant shown in Table 2 is obtained from the slope of the fitted line. From the rate constant values, it is prominent that the YSZ/GZO bilayer coatings have the lowest parabolic constant denoting the effectiveness of the top GZO layer in preventing the oxidation penetration thereby delaying the oxidation process. The investigated results can be further validated from the SEM micrographs and photographs of 8YSZ and 8YSZ/GZO TBCs in Fig. 12. Reason for the spallation of single layer YSZ can be correlated to the formation of thin TGO layer shown in the EDS-line spectra Fig. 12(a). This well-known phenomenon is due to the

transformation of high density metallic bond coat to low density oxide with low coefficient of thermal expansion by the addition of oxygen within the coating volume [29]. The cross-section micrographs of YSZ/GZO TBCs after thermal cycling test in Fig. 12(b) indicates good adhesion of bottom YSZ ceramic layer to the bond coat. However, the top GZO layer experiences chipping, exhibiting variation in thickness across the length of the coating layer. This can be due to the lower fracture toughness of GZO than YSZ and hence propagation of cracks is relatively faster than in YSZ [30].

5. Conclusions

This study provides a simple, economical approach for the preparation of plasma sprayable GZO powders. The technique used for the powder preparation is a single step process and is advantageous over other agglomeration techniques like spray drying. The technique also enables to prepare considerable quantity of phase pure flowable powders in a short period of time and thus meets the standard of the commercial powders. Also, YSZ/GZO coatings with bilayer architecture fabricated from the synthesized powder could be effective TBC topcoat material suitable for harsh environment and the proposed design can considerably enhance the lifetime of TBC.

Acknowledgement

The authors acknowledge the encouragement received from Director, CSIR-NAL and Head, SED, CSIR-NAL for their encouragement. This work was supported by ARDB under GTMAP program (Sanction No. 2031800). The authors thank Mr. Siju and Mr. G. Sreenivas for FESEM and XRD data.

Data Availability Statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References

- [1] S. Bose, J. DeMasi-Marcin, Thermal barrier coating experience in gas turbine engines at Pratt & Whitney, *J. Therm. Spray Technol.* 6 (1997) 99–104, <https://doi.org/10.1007/BF02646318>.
- [2] X.Q. Cao, R. Vassen, D. Stöver, Ceramic materials for thermal barrier coatings, *J. Eur. Ceram. Soc.* 24 (2004) 1–10, [https://doi.org/10.1016/S0955-2219\(03\)00129-8](https://doi.org/10.1016/S0955-2219(03)00129-8).
- [3] R.A. Miller, Thermal barrier coatings for aircraft engines: history and directions, *J. Therm. Spray Technol.* 6 (1997) 35–42, <https://doi.org/10.1007/BF02646310>.
- [4] E. Bakan, D.E. Mack, G. Mauer, R. Vaßen, Gadolinium zirconate/YSZ thermal barrier coatings: plasma spraying, microstructure, and thermal cycling behavior, *J. Am. Ceram. Soc.* 97 (2014) 4045–4051, <https://doi.org/10.1111/jace.13204>.
- [5] P. Wilde, C.R. Catlow, Molecular dynamics study of the effect of doping and disorder on diffusion in gadolinium zirconate, *Solid State Ionics* 112 (1998) 185–195, [https://doi.org/10.1016/S0167-2738\(97\)00509-2](https://doi.org/10.1016/S0167-2738(97)00509-2).
- [6] G. Mauer, D. Sebold, R. Vaßen, D. Stöver, Improving atmospheric plasma spraying of zirconate thermal barrier coatings based on particle diagnostics, *J. Therm. Spray Technol.* 21 (2012) 363–371, <https://doi.org/10.1007/s11666-011-9706-1>.
- [7] S.R. Choi, N.P. Bansal, D. Zhu, Mechanical and thermal properties of advanced oxide materials for higher-temperature coatings applications, in: D. Zhu, K. Plucknett (Eds.), *Advances in Ceramic Coatings and Ceramic-Metal Systems: Ceramic Engineering and Science Proceedings*, vol. 26, Wiley-Blackwell, 2008, pp. 11–19, <https://doi.org/10.1002/9780470291238.ch2>.
- [8] Z.G. Liu, J.H. Ouyang, Y. Zhou, Structural evolution and thermophysical properties of $(\text{Sm}_x\text{Gd}_{1-x})_2\text{Zr}_2\text{O}_7$ ($0 \leq x \leq 1.0$) ceramics, *J. Alloys Compd.* 472 (2009) 319–324, <https://doi.org/10.1016/J.JALLCOM.2008.04.042>.
- [9] D. Lee, T.W. Kim, K.S. Lee, Design of thermal barrier coatings using gadolinium zirconate ceramics: a study on gadolinium zirconate/YSZ bilayers, *J. Ceram. Soc. Japan* 117 (2009) 550–554, <https://doi.org/10.2109/jcersj2.117.550>.
- [10] P.F. Mensah, R. Diwan, S. Nandikolla, O. Coker, Thermo-mechanical Study of the Role of $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZ) in Improving Life of YSZ and GZ Double Layered Thermal Barrier Coatings, *IMECE2012-88279*, vol. 7, (2016), pp. 1–6, <https://doi.org/10.1115/imece2012-88279>.
- [11] R.M. Leckie, S. Krämer, M. Rühle, C.G. Levi, Thermochemical compatibility between alumina and $\text{ZrO}_2\text{-Gd}_2\text{O}_3$ thermal barrier coatings, *Acta Mater.* 53 (2005) 3281–3292, <https://doi.org/10.1016/j.actamat.2005.03.035>.
- [12] K.S. Lee, D.H. Lee, T.W. Kim, Microstructure controls in Gadolinium Zirconate/YSZ double layers and their properties, *J. Ceram. Soc. Japan* 122 (2014) 668–673, <https://doi.org/10.2109/jcersj2.122.668>.
- [13] M. Frommherz, A. Scholz, M. Oechsner, E. Bakan, R. Vaßen, Gadolinium zirconate/YSZ thermal barrier coatings: mixed-mode interfacial fracture toughness and sintering behavior, *Surf. Coat. Technol.* 286 (2016) 119–128, <https://doi.org/10.1016/j.surfcoat.2015.12.012>.
- [14] S.Y. Park, J.H. Kim, M.C. Kim, H.S. Song, C.G. Park, Microscopic observation of degradation behavior in yttria and ceria stabilized zirconia thermal barrier coatings under hot corrosion, *Surf. Coat. Technol.* 190 (2005) 357–365, <https://doi.org/10.1016/J.SURFcoat.2004.04.065>.
- [15] Z. Chen, N. Wu, J. Singh, S. Mao, Effect of Al_2O_3 overlay on hot-corrosion behavior of yttria-stabilized zirconia coating in molten sulfate-vanadate salt, *Thin Solid Films* 443 (2003) 46–52, [https://doi.org/10.1016/S0040-6090\(03\)00670-9](https://doi.org/10.1016/S0040-6090(03)00670-9).
- [16] I.N. Qureshi, M. Shahid, A. Nusair Khan, Hot corrosion of yttria-stabilized zirconia coating, in a mixture of sodium sulfate and vanadium oxide at 950 °C, *J. Therm. Spray Technol.* 25 (2016) 567–579, <https://doi.org/10.1007/s11666-015-0374-4>.
- [17] Z. Chen, S. Speakman, J. Howe, H. Wang, W. Porter, R. Trice, Investigation of reactions between vanadium oxide and plasma-sprayed yttria-stabilized zirconia coatings, *J. Eur. Ceram. Soc.* 29 (2009) 1403–1411, <https://doi.org/10.1016/j.jeurceramsoc.2008.09.016>.
- [18] Y. Hui, S. Zhao, J. Xu, B. Zou, Y. Wang, X. Cai, L. Zhu, X. Cao, High-temperature corrosion behavior of zirconia ceramic in molten $\text{Na}_2\text{SO}_4 + \text{NaVO}_3$ salt mixture, *Ceram. Int.* 42 (2016) 341–350, <https://doi.org/10.1016/j.ceramint.2015.08.116>.
- [19] K. Praveen, J. Satyapal, M. Nicholas, S. Bjo, R.L. Peng, Hot Corrosion Mechanism in Multi-layer Suspension Plasma Sprayed $\text{Gd}_2\text{Zr}_2\text{O}_7$ /YSZ Thermal Barrier Coatings in the Presence of $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$, vol. 26, (2017), pp. 140–149, <https://doi.org/10.1007/s11666-016-0486-5>.
- [20] M.H. Habibi, L. Wang, S.M. Guo, Evolution of Hot Corrosion Resistance of YSZ, $\text{Gd}_2\text{Zr}_2\text{O}_7$, and $\text{Gd}_2\text{Zr}_2\text{O}_7 + \text{YSZ}$ Composite Thermal Barrier Coatings in $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ at, vol. 32, (2012), pp. 1635–1642, <https://doi.org/10.1016/j.jeurceramsoc.2012.01.006>.
- [21] L. Guo, M. Li, S. He, C. Zhang, Q. Wang, F. Ye, Preparation and hot corrosion behavior of plasma sprayed nanostructured $\text{Gd}_2\text{Zr}_2\text{O}_7\text{-LaPO}_4$ thermal barrier coatings, *J. Alloys Compd.* 698 (2017) 13–19, <https://doi.org/10.1016/j.jallcom.2016.12.241>.
- [22] C. Zhang, J. Fei, L. Guo, J. Yu, B. Zhang, Z. Yan, F. Ye, Thermal cycling and hot corrosion behavior of a novel LaPO_4 /YSZ double-ceramic-layer thermal barrier coating, *Ceram. Int.* 44 (2018) 8818–8826, <https://doi.org/10.1016/j.ceramint.2018.02.057>.
- [23] C. Jiang, E.H. Jordan, A.B. Harris, M. Gell, J. Roth, Double-layer gadolinium zirconate/yttria-stabilized zirconia thermal barrier coatings deposited by solution precursor plasma spray process, *J. Thermal Spray Technol.* 24 (2015) 895–906, <https://doi.org/10.1007/s11666-015-0283-6>.
- [24] S. Mahade, N. Curry, S. Björklund, N. Markocsan, P. Nylén, Failure analysis of $\text{Gd}_2\text{Zr}_2\text{O}_7$ /YSZ multi-layered thermal barrier coatings subjected to thermal cyclic fatigue, *J. Alloys Compd.* 689 (2016) 1011–1019, <https://doi.org/10.1016/j.jallcom.2016.07.333>.
- [25] S.T. Aruna, B. Arul Paligan, N. Balaji, V. Praveen Kumar, Properties of plasma sprayed yttria stabilized zirconia thermal barrier coating prepared from co-precipitation synthesized powder, *Ceram. Int.* 40 (2014) 11157–11162, <https://doi.org/10.1016/j.ceramint.2014.03.143>.
- [26] P.G. Lashmi, P.V. Ananthapadmanabhan, Y. Chakravarthy, G. Unnikrishnan, N. Balaji, S.T. Aruna, Hot corrosion studies on plasma sprayed bi-layered YSZ/ $\text{La}_2\text{Ce}_2\text{O}_7$ thermal barrier coating fabricated from synthesized powders, *J. Alloys Compd.* 711 (2017) 355–364, <https://doi.org/10.1016/j.jallcom.2017.04.022>.
- [27] Y. Ozgurluk, K.M. Doleker, A.C. Karagölanli, Hot corrosion behavior of YSZ, $\text{Gd}_2\text{Zr}_2\text{O}_7$ and YSZ/ $\text{Gd}_2\text{Zr}_2\text{O}_7$ thermal barrier coatings exposed to molten sulfate and vanadate salt, *Appl. Surf. Sci.* (2017), <https://doi.org/10.1016/j.apsusc.2017.09.047>.
- [28] F. Zhou, Y. Wang, L. Wang, Z. Cui, Z. Zhang, High temperature oxidation and insulation behavior of plasma-sprayed nanostructured thermal barrier coatings, *J. Alloys Compd.* 704 (2017) 614–623, <https://doi.org/10.1016/J.JALLCOM.2017.02.073>.
- [29] S. Mahade, R. Li, N. Curry, S. Björklund, N. Markocsan, P. Nylén, Isothermal oxidation behavior of $\text{Gd}_2\text{Zr}_2\text{O}_7$ /YSZ multilayered thermal barrier coatings, *Int. J. Appl. Ceram. Technol.* 13 (2016) 443–450, <https://doi.org/10.1111/ijac.12527>.
- [30] Z. Babiak, F.W. Bach, L. Bertamini, F. Hindryckx, J.P. Krugers, C. Mertens, B. Michel, S. Sturlese, W. Unterberg, Proceedings of the 6th Liège Conference: Materials for Advanced Power Engineering, ASM International, Materials Park, OH, USA, 1998, pp. 1611–1618.