Creep strength of $\text{Al}_2\text{O}_3 + \text{ZrO}_2 \cdot 5\text{CaO}$ subjected to thermal cyclic test

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Abstract

The present paper examines the failure mechanism of the coating system of $\text{Al}_2\text{O}_3\text{--ZrO}_2 \cdot 5\text{CaO}$ applied on a Cast iron substrate. The atmospheric plasma spray coating technique was used for coating. A muffle furnace was used to heat the sample to $600 \pm 2^\circ\text{C}$ followed by ambient cooling. Both the heating and cooling cycles were maintained for 30 min. Results were compared between the as-sprayed coated specimen and the post thermal cyclic test specimen. It has been noticed that normal stresses developed due to the formation of thermally grown oxide at the interface of the top/bond coat and constitutes the weakest link in the coating system. Also, differential porosity at the interface led the moisture to penetrate from the top coat to the bottom coat. Thus, a thermochemical process occurred below the bond coat, leading to the formation of oxides and made the top coat gradually more brittle during the thermal cyclic process.

Keywords $\text{Al}_2\text{O}_3\text{--ZrO}_2 \cdot 5\text{CaO}$ · Muffle furnace · Thermal barrier coatings · Thermally grown oxide · Thermochemical

1 Introduction

Thermal barrier coatings (TBCs) are often used to protect the components subjected to high-temperature applications viz. gas turbine engines, internal combustion parts, etc. [1]. In the previous studies it has been found that yttria stabilized zirconia failed due to the phase transformation from tetra, $t\text{-ZrO}_2$ to monoclinic, $m\text{-ZrO}_2$ [2]. It is required to improve the thermal cyclic behavior by appropriate material composition. Fracture response and thermal resistance of yttria-stabilized zirconia (YSZ)–NiCoCrAlY bond coat (BC) under thermomechanical loads were investigated by Rangaraj and Kokini [3], and it has been reported that thermal shock resistance is low in brittle materials like ceramics [3]. It has been found that failure mainly governed by the thermos-mechanic failures, chemical failures, erosion failures, oxidation of bond coat, hot erosion effect, CMAS ($\text{CaO}\text{--MgO}\text{--Al}_2\text{O}_3\text{--SiO}_2$) attack, inconsistency in the thermal expansion, and due to changes in the thermal conductivity, etc. [4–9]. Thermal shock resistance changes with many properties such as fracture toughness, elastic

modulus, Poisson's ratio, thermal expansion coefficient, and thermal conductivity. It has been investigated that thermal stresses do occur due to the temperature difference at the interface of the bond coat and surface of the specimen when cooled with water [10]. Few basic properties such as toughness, low thermal conductivity, stability at high temperature, high thermal expansion coefficient and low elastic modulus values are required to resist the thermal shock failure [11, 12]. Ceramic materials have the high-temperature resistant capacity so that they can be used in TBC systems to reduce the thermal shock failures. They satisfy basic properties such as toughness, low thermal conductivity, low coefficient of thermal expansion and low elastic moduli. Studies found that the elastic modulus value changes with the closing or growth of cracks and plays a crucial role in the determination of TBC life. If crack growth increases, the value of the elastic modulus will change and that will hamper the TBC life period under service conditions [13–15]. The failure of the coatings depends on cracks, show when they propagate and result in failure [16–18].

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In the present investigation, an effort has been made to investigate the causes and mechanisms behind the spallation of composite coating $\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--}5\text{CaO}$ applied to a cast iron (CI) substrate of particular thickness. The muffle furnace was used to heat and cool the coated sample uniformly during the thermal cyclic test. It is believed that the above studies are valuable for material scientists for the design of thermal-shock-resistant materials.

2 Experimental methodology

2.1 Selection of material and powder trade names

Cast iron (CI) was selected as a substrate material. The selection of powder was based on the thermal coefficient of expansion provided by Sulzer Metco. The trade names of different powders are shown in Table 1.

2.2 Coating methodology

The Atmospheric plasma spray technique was used to coat on the cast iron substrate. Before the coating process, the mixture of Al_2O_3 and $\text{ZrO}_2\text{--}5\text{CaO}$ in 50:50 was prepared using the ball mill technique. The substrates were chemically cleaned using tetra chloride-ethylene followed by preheating to the temperature of $250 \pm 50^\circ\text{C}$. This process was done to minimize the thermal mismatch between the substrate and the bond coat. The schematic of a coating system is shown in Table 2. The top coat thicknesses were about $100\ \mu\text{m}$. The plasma spray machine specification and spray parameters for bond coat and top coat are given in Tables 3 and 4 respectively.

2.3 Thermal cyclic test procedure

The thermal cyclic test was conducted in a Muffle furnace. The temperature of the furnace was maintained at a temperature of $600 \pm 2^\circ\text{C}$. The coated substrate was kept on silica ceramic cups to ensure uniform heating all-around. The heating and cooling cycle time of 30 min was maintained throughout the experiment. The cooling was done under ambient conditions.

Table 1 Trade name and composition of the powder

Trade Name	Composition by wt%
Metco 105 SFP	99% Al_2O_3
Metco 201 NS	$\text{ZrO}_2\text{--}5\text{CaO}$ (45% ZrO_2 and 5% CaO)
Metco 452	Fe38Ni10Al (52% Fe, 38% Ni and 10% Al)

Table 2 Schematic of the coating system applied on CI substrate

Topcoat ($100\ \mu\text{m}$)
Pure ceramic
$\text{Al}_2\text{O}_3 + \text{ZrO}_2\text{--}5\text{CaO}$
Bond coat ($50\ \mu\text{m}$)
(Metallic powder)
Fe38Ni10Al
Substrate (gray cast iron)

2.4 Coating characterization

Evaluation of the coating thickness, surface morphology, and determination of elemental composition was carried out using Zeiss Evo 18 special edition machine, and the machine specifications are given in Table 5. XRD analysis was carried out on Bruker, and its specifications are given in Table 6.

3 Results and discussion

The morphology of the as-sprayed and after thermal cyclic test is shown in Fig. 1a, b respectively. The composite mixture applied as the top coat was found to be homogeneous with localized agglomeration, uneven micro voids, and localized pin holes. At a higher magnification of $1500\times$, noticeable hair cracks were observed in the case of post-thermal cyclic test samples (Fig. 1b). Cracks were formed in the alloyed mixture, mainly at the interfaces of the adjoining splats of the two different phases, alumina, and calcia stabilized zirconia. Hair crack impressions were seen, mostly on the grains of the Zirconia phase. The coefficient of thermal expansion values for alumina and zirconia dioxide are, $9.6 \times 10^{-6}\ \text{K}^{-1}$ and $15.3 \times 10^{-6}\ \text{K}^{-1}$ respectively [19]. The nucleation of these cracks are often attributed to the inconsistency in thermal coefficient of expansion between the two phases [20]. Also, due to the repeated thermal cyclic loading, i.e., heating and cooling, residual compressive stresses are initiated in the composite mixture [21]. It is also evident from the micrograph, that the network of cracks is more or less same in both the phases, Zirconia

Table 3 Air plasma machine specification

Specifications	Parameters
Plasma gun	3 nylon brush
Nozzle temperature	$10,000^\circ\text{C}$
Current	500 amps
Voltage	65–70 V
Powder feed	45–50 g/min
Spray distance	50–78 mm

Table 4 Plasma spray parameters for different coating materials

Materials	Primary gas (argon) pressure (bar)	Secondary gas (hydrogen) pressure (bar)	Carrier gas argon flow (lpm)	Current (Amps)	Voltage (V)	Spray distance (mm)
$\text{Al}_2\text{O}_3 + \text{ZrO}_2 \cdot 5\text{CaO}$	3.7	3.45	35	500	65	65–76
Fe38Ni10Al	6.9	3.30	35	500	65	50–76

Table 5 Machine specifications of Zeiss Evo 18

Parameters	
Filament	Tungsten
Secondary e-image resolution	50 nm
Tilt	0°–60°
Rotation	360°
EHT	200 V–30 kV
Magnification	50–100 K (depends on sample)

Table 6 X-ray diffractometer specifications

Parameters	
Make	Bruker
Model	D8 advance
Measuring circle diameter	435,500,600
Smallest addressable increment	0.0001°
Reproducibility	0.0001°
Anode	Cu
Detector	Scintillation and Lynxeye

phase/grains (white color) and Alumina phase (dark gray color), identified as shown in Fig. 1b. The bulk stresses present in the bond coat decide the life of the coating, and

the residual stresses present at the interface may interact with the micro defects and promote crack growth [22].

It is also evident that the top coat delaminated from the bond coat. The bond coat didn't spall from the substrate, and excellent metallurgical bonding was manifested. The reason of spallation of the top coat, $\text{Al}_2\text{O}_3\text{--ZrO}_2 \cdot 5\text{CaO}$ from the bond coat, Fe38Ni10Al can be attributed to the thermal inconsistency at the interface and the effect got amplified during the prolonged heating and cooling cycle. It is also understood that it is the weakest link formed at the top/bond coat interface. Another reason for failure at the interface can be attributed to the differential porosity between the interfaces and to the roughness. The roughness at the interfaces act as stress concentrators and to a certain extent decides the lifespan of the coatings [23]. The average porosity for as-sprayed coatings in case of the top coat and bottom coat was found to be 1.90 and 2.75%, (Fig. 2a, b) respectively. The life of the coatings was also found to depend on the porosity, horizontal and vertical cracks at the interface of the top/bond coat. Lu et al. [24] had found that the presence of porosity is generally beneficial if a pre-existing crack dominates the failure. However, in the present work, the porosity difference at the interface and the moisture present in the atmosphere, causes oxidation and can be visualized as dark black spots at the top coat (Fig. 3a). A crack developed on the surface after 312 thermal cyclic tests, is shown in Fig. 3b. EDX analysis has also confirmed the oxidation phenomenon. No trace of any iron element was found in

Fig. 1 Morphology of the top coat. **a** As-sprayed coating. **b** After thermal cyclic test

Fig. 2 Micrograph of as-sprayed average porosity. **a** 1.90% topcoat and **b** 2.75% bond coat

Fig. 3 Micrograph of the topcoat post thermal cyclic test. **a** Oxidation status after 295 cycle, **b** crack propagation after 312 thermal cycles test

case of as-sprayed coatings (Fig. 4a). The abundance of the individual elements, traces of iron content 1.51 wt% along with oxygenated element 50.85 wt% has been confirmed after thermal cyclic tests (Fig. 4b, c). The oxidation at the top manifests due to the thermochemical reaction between the iron (Fe) elements present in the bond coat with the moisture present when exposed to ambient temperature during the thermal cyclic test [25]. The byproduct, rust, formed at the surface can also be identified with the help of thermochemical, redox reaction, given in Eq. 1.

During the test, it was noticed that the thermally grown oxide layer (TGO) developed at the junction of the bond coat and top coat resulting in weakening of the top coat/bond coat interface (Fig. 5a, b). The growth of the TGO layer was found to increase with increase in time. At the end of 312 cycles, the top coat started delaminating from the edges shown in Fig. 5b. The failure of the coating in

the present work is in agreement with results obtained by Osorio et al. [1].

4 Conclusion

The thermochemical effect was found to be crucial and had a detrimental impact on the life of the coating systems. No failure of the coating was observed during constant heating, as long as the specimen remained in the Muffle furnace. Bond coat shows excellent metallurgical bonding with the substrate. During a prolonged heating and cooling cycle it is speculated that TGO, a brittle byproduct formed at the bond (Fe38Ni10Al)/top coat ($\text{Al}_2\text{O}_3\text{--ZrO}_2\text{--5CaO}$) interfaces. Thermochemical and differential porosity at the interface was found to develop the weakest link in the coating system also found governing mechanism behind spallation of the top coat. After 312 cycles the visible crack observed and considered as the failure of the top coat.

Fig. 4 EDX and elemental composition of the topcoat. **a** As-sprayed coatings, **b** and **c** after the thermal cyclic test

Compliance with ethical standards

Conflict of interest The authors acknowledge that there is no financial or personal relationship with a third party whose interests could be positively or negatively influenced by the article's content.

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Fig. 5 **a** SEM micrograph ($\times 200$) at the cross section with no TGO layer between top coat/bond coat. **b** SEM micrograph ($\times 500$) at the cross section with TGO layer between top coat/bond coat

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