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Microstructural characterization of GZ/CYSZ thermal barrier coatings after thermal shock and CMAS+hot corrosion test

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ABSTRACT

In this study, first, $Gd_2Zr_2O_7$/ceria–yttria stabilized zirconia (GZ/CYSZ) TBCs having multilayered and functionally graded designs were subjected to thermal shock (TS) test. The GZ/CYSZ functionally graded coatings displayed better thermal shock resistance than multilayered and single layered $Gd_2Zr_2O_7$ coatings. Second, single layered YSZ and functionally graded eight layered GZ/CYSZ coating (FG8) having superior TS life time were selected for CMAS + hot corrosion test. CMAS + hot corrosion tests were carried out in the same experiment at once. Furthermore, to generate a thermal gradient, specimens were cooled from the back surface of the substrate while heating from the top surface of the TBC by a CO_2 laser beam. Microstructural characterizations showed that the reaction products were penetrated locally inside of the YSZ. On the other hand, a reaction layer having ~6 μm thickness between CMAS and $Gd_2Zr_2O_7$ was seen. This reaction layer inhibited to further penetration of the reaction products inside of the FG8.

1. Introduction

Generally thermal barrier coatings (TBCs) are used in aircraft and land based gas turbine engines [1–15]. The main purpose of TBCs is to ensure not only thermal insulation to the metallic components of gas turbines but also to protect them from harsh environmental effects such as oxidation, hot corrosion, wear and fly ash damage. A typical and commercial TBC system consists of (1) yttria-stabilized zirconia (YSZ) based ceramic top layer, (2) a metallic bond layer (typically MCrAlY) and (3) a thermally grown oxide (TGO, predominately alpha-alumina) layer [1–3]. However, this TBC system which is YSZ based suffers from a number of issues having destructive effects. Such as an undesirable phase transformation and sintering taking place above 1170 °C. Because of this phenomena, the highest operation temperature reached is about 1170 °C for YSZ based TBC systems [4]. Moreover, YSZ is vulnerable to the hot corrosion that is deterioration of the coating in the existence of $Na_2SO_4 + V_2O_5$ salts coming from low quality jet fuel especially used in military aircrafts, and Ca–Mg–Al–Silicate (CMAS) attack caused by flying ash.

In order to meet increasing demands for more efficient next generation gas turbines, it is necessary (a) to push the temperature limits of YSZ, and (b) to enhance CMAS and hot corrosion resistance of the TBC system. Therefore, an alternative ceramic top coat material having better thermal properties than YSZ and different coating architectures should be sought [1,4–7]. One of the possible alternative ceramic top coating material is gadolinium zirconate ($Gd_2Zr_2O_7$ or GZ) with pyrochlore or defect fluorite-type structure having high thermal stability at elevated temperatures (>1200 °C) and lower thermal conductivity (1.2–1.7 W/mK^{-1} and 2.1 W/mK^{-1} at 1000 °C for GZ and YSZ, respectively) compared to YSZ. Moreover, previous studies proved that GZ has more superior CMAS and hot corrosion attack resistance characteristics than YSZ. Although these attractive properties, GZ has lower coefficient of thermal expansion value (CTE, $10.4 \times 10^{-6}\,K^{-1}$ and $11 \times 10^{-6}\,K^{-1}$ for GZ and YSZ respectively) than YSZ and an undesirable phase formation ($GdAlO_3$) at the contact zone with TGO layer. These unfavorable features of the GZ reduce its thermal cycling or thermal shock life time [7–10].

In order to delay the thermal shock failure of single layered GZ TBC arising from thermal effect, multilayered (MLed) and functionally graded (FGed) topcoat designs are introduced as a solution. According to researches in the literature [11–16], MLed and FGed systems reduce the thermal conductivity and improve thermal strain tolerance of TBC. Furthermore, the reaction between coating layer and TGO will be prevented owing to a second coating material coated in between GZ and TGO layers. Therefore, better thermal cycling and thermal shock life time can be achieved by

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using MLed and FGed designs than single layered design. In the literature [9,11,13,14,16–24], thermal cycling and shock life time performance tests of TBCs have been carried out by using different methods. The main distinction between these test methods is only in the kind of heating (by using laser beam, furnace, gas burner etc.) and cooling (by using air jet, water quenching etc.) sources. As different from the other methods, oxidation of the bond coat has less importance in the thermal shock test which water quenching is applied for cooling [25]. In one of our previous work [17], CYSZ/Al_2O_3 TBCs having multilayered designs were produced by plasma spraying technique and their thermal cycling behaviour were tested by heating them via a CO_2 laser beam to 1150 °C and cooling by an air jet. However any cracks or pull outs were not observed on the coating surfaces. Hence, it was thought that either a dynamic gas flame or thermal shock test methods should be used to test the thermal life time performance of the coatings on more harsh conditions.

In this study, gadolinium zirconate/ceria-yttria stabilized zirconia (GZ/CYSZ) based MLed and FGed TBC systems having 2, 4, 8 and 12 layers were selected as coating samples. These coatings were produced by high-velocity oxy-fuel (HVOF) and air plasma spraying (APS) processes, and their microstructure, phase stability, laser remelting behaviour, thermal and mechanical properties were investigated in our previous studies [16,26]. Moreover, in the same study [16], thermal cycling life time of GZ/CYSZ MLed and FGed TBCs was evaluated by using a gas burner and air cooling system having a unique specimen holder design. However, their thermal shock behavior and CMAS + hot corrosion resistance have not been studied yet. Thus, main purpose of this study is to research the thermal shock behavior and CMAS + hot corrosion resistance of GZ/CYSZ TBCs having MLed and FGed designs. CYSZ was selected as second coating material due to its higher CTE ($13 \times 10^{-6}\ K^{-1}$) than YSZ. It was anticipated that CYSZ would reduce the thermal stress caused by thermal expansion mismatch in GZ/CYSZ multilayered and functionally graded TBC system. Therefore an improvement in thermal shock life time was expected. Thermal shock experiment was carried out in a tube furnace and specimens were directly thrown in a cold water. CMAS and hot corrosion resistance test was performed simultaneously and a laser beam was used as a heat source as distinct from the literature. In addition, the specimens concurrently with the heating were cooled from the back surface to create a thermal gradient on the TBC. Thus, it is believed that a harsh environment which may be close to the actual working conditions was created. There is no such research in the literature related to the thermal shock and CMAS resistance of MLed and FGed coatings which contain GZ and CYSZ. Furthermore, application of the CMAS + hot corrosion resistance test and assembly of the test system were unique in this research.

2. Experimental

The coating designs and procedure of the HVOF and APS processes were described elsewhere in detail [16]. Briefly, in the all designs, composition of the bottom and topmost layers were 100% CYSZ and GZ, respectively. TBC's containing only GZ or CYSZ in each layer were specified as MLed coatings. However, each layer had different ratio of mixture of CYSZ and GZ in the FGed coatings. The multilayered (ML2, ML4, ML8 and ML12) and functionally graded (FG4, FG8 and FG12) coatings were coded with the numbers indicating number of layers. Also, single layered GZ and YSZ (sample codes: GZ1 and YSZ1 respectively) coatings were produced as reference samples. Substrates were stainless steel (C 0.08%, Cr 18%, Fe 68%, Mn 2%, Ni 11%, Si 1%) with a diameter of 25 mm and 2 mm in thickness.

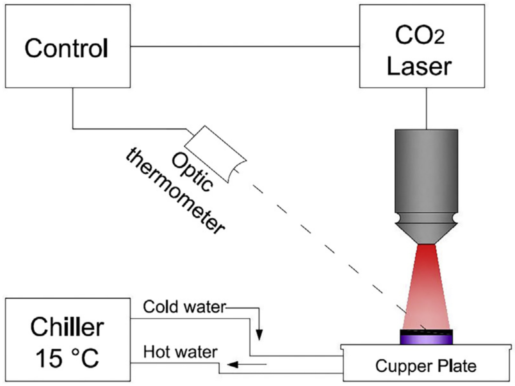

Fig. 1. Schematic explanation of CMAS + hot corrosion test system. Specimens were heated from the top surface of the TBC by using a CO_2 laser beam and simultaneously cooled from the back surface of the substrate to create a thermal gradient.

Thermal shock tests were carried out to evaluate the thermal shock life time of the MLed and FGed GZ/CYSZ TBCs. Each cycle of the thermal shock test were performed by directly placing TBCs to the tube-type resistance furnace (*Xinyu XY-1700*) at high temperature (1250 °C) in air and followed by 5 min. holding them in the furnace. Then TBCs were directly dropped (quenched) into cold water (10–15 °C). The failure criterion was defined as 50% spallation of the top coat in the thermal shock test.

In literature [12,22,27–31], CMAS and hot corrosion tests of TBCs have been conducted in a furnace under isothermal conditions. Moreover, these tests generally are performed separately as an independent process. However, CMAS and hot corrosion products may simultaneously affect the TBCs under real operating conditions, especially in military aircrafts. In this study, first time in literature, CMAS and hot corrosion (CMAS + hot corrosion) tests were carried out in the same experiment at once and a defocused CO_2 laser beam (PRC STS 3001 model, max 3.0 kW) was used as heat source. As seen in Fig. 1 which is schematic explanation of the CMAS + hot corrosion test system, the specimens were heated from the top surface of the TBC and simultaneously cooled from the back surface of the substrate to create a thermal gradient between the surface and substrate. The samples having best thermal shock performance were selected for CMAS + hot corrosion test. Also, single layered YSZ was chosen as a control sample. To perform an accelerated CMAS and hot corrosion test;

1. Hot corrosion powder was prepared by mixing Na_2SO_4 and V_2O_5 powders at a weight ratio of 1:1.
2. Simulated CMAS glass were made by mechanical milling. The chemical composition of CMAS glass which was obtained by the XRF (*Rigaku ZSX Primus-II*) analysis after milling was given in Table 1.
3. CMAS and hot corrosion powders were mixed in a turbula type mixer for 4 h by using zirconia balls. The mixing ratio of final powders was 60 wt% of CMAS and 40 wt% of hot corrosion.
4. The as-mixed powders were spread on the surface of TBCs at a concentration of 30 mg/cm^2.
5. The samples were heated by laser system (see Fig. 1) to 1250 °C in less than 10 seconds and held for 1 h.

Microstructural characterization of the TBCs was carried out with field emission (*JSM 7000F, JEOL*) scanning electron microscope (FESEM) equipped with back scattered electron (BSE) detector, secondary electron detector (SEI) and energy-dispersive spectrometer (EDS).

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