Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 30 (2010) 2707–2713

www.elsevier.com/locate/jeurceramsoc

Technical note

High-temperature hot corrosion behavior of gadolinium zirconate by vanadium pentoxide and sodium sulfate in air

Zhan-Guo Liu, Jia-Hu Ouyang *, Yu Zhou, Sa Li

Institute for Advanced Ceramics, Department of Materials Science, Harbin Institute of Technology, No. 92, West Da-Zhi Street, Harbin 150001, China

Received 5 November 2009; received in revised form 23 April 2010; accepted 4 May 2010

Abstract

Gadolinium zirconate ($Gd_2Zr_2O_7$) prepared by solid state reaction exhibited a defect fluorite-type structure. Reactions between $Gd_2Zr_2O_7$ ceramic and vanadium pentoxide (V_2O_5), sodium sulfate (Na_2SO_4), and $V_2O_5 + Na_2SO_4$ mixture were investigated from 700 to 1000 °C in air using an X-ray diffractometer (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). V_2O_5 reacts with $Gd_2Zr_2O_7$ to form gadolinium vanadate ($GdVO_4$) and monoclinic zirconia (m-ZrO_2) at 900 and 1000 °C in air. However, no chemical reaction product between Na_2SO_4 and $Gd_2Zr_2O_7$ is found at 900 and 1000 °C in air. V_2O_5 reacts with equal molar Na_2SO_4 to form sodium vanadate ($NaVO_3$) at 610 °C. In the temperature range of 700–1000 °C, $Na_2SO_4 + V_2O_5$ mixture reacts with $Gd_2Zr_2O_7$ in air to form the final reaction products of $GdVO_4$ and m-ZrO_2.

Keywords: $Gd_2Zr_2O_7$; Hot corrosion; V_2O_5; Na_2SO_4

1. Introduction

Thermal barrier coatings (TBCs) are extensively used to insulate metallic components against hot gas stream, and have become a critical technology for improving performance of gas-turbine engines.[1–3] TBCs systems typically consist of a metallic oxidation protection layer and a thermally insulative ceramic topcoat. The state of the art topcoat material is 6–8 wt.% yttria-stabilized zirconia (YSZ), which is generally produced by plasma spraying (PS) or electron beam physical vapor deposition (EB-PVD).[4] However, YSZ is limited to applications below 1200 °C.[5] Above 1200 °C, the t'-phase zirconia transforms into cubic and tetragonal phases. During cooling the tetragonal phase will further transform into the monoclinic phase, which is accompanied with a volume change of 3–5% and a severe damage of TBCs.[4–7]

In recent years, there is an increasing demand for developing new design strategies or new materials for TBCs in order to address the challenges of more demanding operating environments. Among high-melting ceramic materials, rare-earth zirconates with the general formula $Ln_2Zr_2O_7$ (Ln = lanthanide) have been shown to posses some very important properties for TBCs application. The thermal conductivities of rare-earth zirconates varied from 1.1 to 2.0 $W\,m^{-1}\,K^{-1}$ in the temperature range of room temperature to 1400 °C.[8–12] In addition, the phase transition temperatures of rare-earth zirconates are clearly higher than the t-m phase transformation temperature of YSZ, such as 2300 °C for $Nd_2Zr_2O_7$, 2000 °C for $Sm_2Zr_2O_7$, and 1530 °C for $Gd_2Zr_2O_7$, respectively.[13] $Gd_2Zr_2O_7$-based zirconates are a class of potential candidate materials for high-temperature TBCs applications (temperature above 1150 °C) instead of currently used YSZ TBCs, where both hot corrosion and oxidation reaction are a great concern.[10] When TBCs are operated with low-quality fuels containing appreciable levels of vanadium, sodium, sulfur, etc, the hot corrosion of ceramic topcoat becomes significant at elevated temperatures.[14] Mohan et al. tested the degradation of YSZ coatings by molten Na_2SO_4 at a temperature range from 900 to 1200 °C.[15] Chen et al. found that the penetration of molten V_2O_5 into YSZ coatings were quite deleterious to ceramic topcoat and lead to the formation of $LaVO_4$ and m-ZrO_2 from 800 to 1200 °C.[16,17] In our previous work, V_2O_5 reacted with $Gd_2Zr_2O_7$ at 700–850 °C.[18] Molten V_2O_5 reacted

---

* Corresponding author at: Harbin Institute of Technology, Dept. Materials Science, PO Box 433, 92 Westdazhi Street, Nangang Dist., Harbin, Heilongjiang 150001, China. Tel.: +86 451 86414291; fax: +86 451 86414291.

E-mail address: ouyangjh@hit.edu.cn (J.-H. Ouyang).

0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.05.002

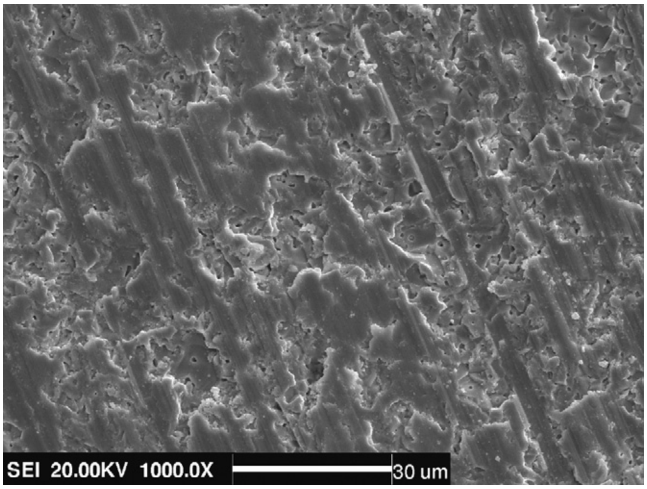

Fig. 1. Surface morphology of unpolished $Gd_2Zr_2O_7$ ceramic sintered at 1650 °C for 10 h in air.

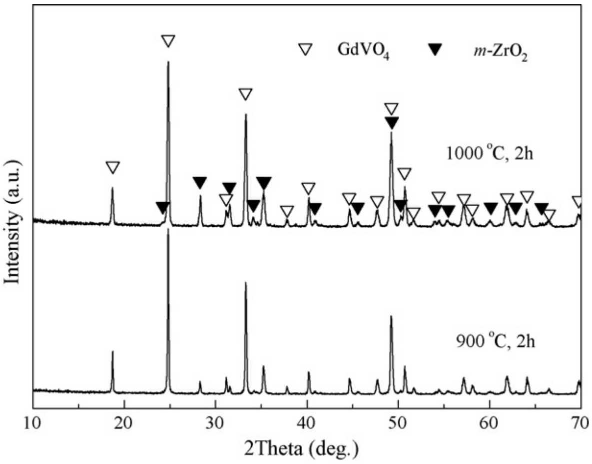

Fig. 2. X-ray diffraction patterns of V_2O_5-coated $Gd_2Zr_2O_7$ specimen heat-treated at 900 °C and 1000 °C for 2 h in air.

with $Gd_2Zr_2O_7$ to form ZrV_2O_7 and $GdVO_4$ at 700 °C; however, in a temperature range of 750–850 °C, molten V_2O_5 reacted with $Gd_2Zr_2O_7$ to form $GdVO_4$ and m-ZrO_2. For a comparative study, Marple et al. investigated the hot corrosion behavior of $La_2Zr_2O_7$ and YSZ coatings to vanadium- and sulfur-containing compounds at 900 and 1000 °C, respectively.[19] $La_2Zr_2O_7$ coatings had a relatively high corrosion resistance to the attack by molten V_2O_5. $La_2Zr_2O_7$ coatings remained well bonded to the substrate after exposure to V_2O_5, and formed only minor amounts of $LaVO_4$. However, $La_2Zr_2O_7$ coatings in contact with sulfate salts ($3Na_2SO_4$:$2MgSO_4$) at 900 °C exhibited a very rapid disintegration of coatings to form $La_2O_2SO_4$, MgO and m-ZrO_2 under a gas flow consisting of 2000 mL/min of dried air and 5 mL/min of SO_2.[19] The YSZ coatings after thermal exposure to vanadia formed a mixture of YVO_4 and monoclinic ZrO_2, which resulted in increased microcracking and spallation of ceramic topcoat. However, YSZ coatings exhibited an excellent resistance to the attack by sulfate salts. When $La_2Zr_2O_7$ and YSZ coatings were exposed to a mixture of vanadia and sulfate salts, both coatings were degraded, the YSZ by vanadia and the $La_2Zr_2O_7$ by the sulfate.[19] In the present study, in order to investigate the hot corrosion behavior of $Gd_2Zr_2O_7$ ceramic by V_2O_5 at elevated temperatures, Na_2SO_4 and $V_2O_5 + Na_2SO_4$ mixture, hot corrosion experiments were performed at different temperature up to 1000 °C for 2 h in air.

2. Experimental procedure

In the present study, $Gd_2Zr_2O_7$ was prepared by a solid state reaction process. Details of the sample preparation can be found in our previous work.[18] XRD measurement shows that $Gd_2Zr_2O_7$ has a single phase of defect fluorite-type structure. The specimens with dimensions of 10 mm × 10 mm × 2 mm were ultrasonically degreased in acetone, and dried at 100 °C in oven. These specimens, in contact with three kinds of different salts, namely V_2O_5, Na_2SO_4, and $Na_2SO_4 + V_2O_5$ mixture (50–50 mol.%), were isothermally heat-treated at different temperatures ranging from 700 to 1000 °C for 2 h in air. During hot corrosion test, the salts were spread uniformly over the surface of $Gd_2Zr_2O_7$ specimen at a concentration of 15 mg/cm^2 by using a very fine glass rod cleaned and dried ultrasonically.

Crystal structures of hot corrosion specimens were identified by an X-ray diffractometer (XRD, D/Max-2200VPC, Rigaku Co. Ltd., Japan) with Cu $K\alpha$ radiation at a scan rate of 3°/min. The microstructural analysis of hot corrosion specimens was carried out with a scanning electron microscope (SEM, CamScan MX 2600FE, UK) equipped with energy-dispersive X-ray

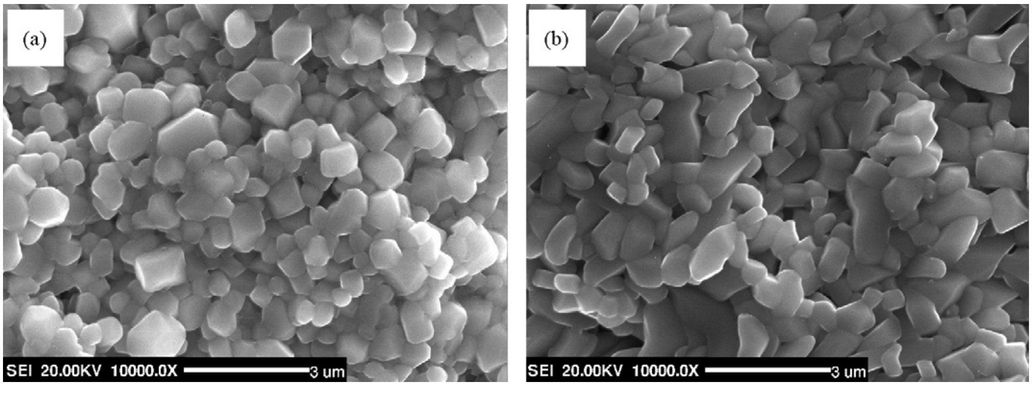

Fig. 3. Microstructure of V_2O_5-coated $Gd_2Zr_2O_7$ specimens heat-treated at different temperatures for 2 h in air: (a) 900 °C; (b) 1000 °C.