



ELSEVIER

Contents lists available at ScienceDirect

Ceramics International

journal homepage: [www.elsevier.com/locate/ceramint](http://www.elsevier.com/locate/ceramint)

# Hot corrosion behavior of TiO<sub>2</sub> doped, Yb<sub>2</sub>O<sub>3</sub> stabilized zirconia exposed to V<sub>2</sub>O<sub>5</sub> + Na<sub>2</sub>SO<sub>4</sub> molten salt at 700–1000 °C

Lei Guo<sup>a,b,\*</sup>, Zheng Yan<sup>a</sup>, Jianxing Yu<sup>b</sup>, Chenglong Zhang<sup>a</sup>, Mingzhu Li<sup>a</sup>, Fuxing Ye<sup>a</sup>, Vincent Ji<sup>c</sup>

<sup>a</sup> School of Materials Science and Engineering, Tianjin University, Tianjin Key Laboratory of Advanced Joining Technology, Key Lab of Advanced Ceramics and Machining Technology of Ministry of Education, No. 92, Weijin Road, Tianjin 300072, China

<sup>b</sup> Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration, Shanghai 200240, China

<sup>c</sup> CMMO/SP2M, UMR CNRS 8182, Université Paris-Sud, 91405 Orsay Cédex, France

## ARTICLE INFO

### Keywords:

Thermal barrier coatings  
Yb<sub>2</sub>O<sub>3</sub>-stabilized zirconia  
Hot corrosion  
V<sub>2</sub>O<sub>5</sub> + Na<sub>2</sub>SO<sub>4</sub>

## ABSTRACT

3.5 mol% Yb<sub>2</sub>O<sub>3</sub> stabilized zirconia (YbSZ) doped with 10 mol% TiO<sub>2</sub> (Ti-YbSZ) was produced, and its hot corrosion behavior exposed to Na<sub>2</sub>SO<sub>4</sub> + V<sub>2</sub>O<sub>5</sub> molten salt was investigated. The as-fabricated ceramic mainly consists of metastable tetragonal (t') phase. When exposed to the molten salt at 700 °C, 800 °C, 900 °C and 1000 °C for 2 h and 10 h, YbVO<sub>4</sub> and m-ZrO<sub>2</sub> formed as corrosion products due to chemical reactions between the ceramics and the salt. Ti<sup>4+</sup> in Ti-YbSZ solid solution keeps stable during the hot corrosion tests, which acts as a stabilizer for ZrO<sub>2</sub>, preventing total decomposition of the t' phase. After the hot corrosion tests, Ti-YbSZ has an apparently lower m phase content than Y<sub>2</sub>O<sub>3</sub> doped Zirconia and YbSZ, indicative of better corrosion resistance. The hot corrosion mechanism of Ti-YbSZ is proposed based on Lewis acid-base rule, phase diagrams and thermodynamics.

## 1. Introduction

Thermal barrier coatings (TBCs), which are extensively employed onto hot-section metallic components in gas-turbine engines, can significantly enhance the performance and efficiency of engines [1–3]. A TBC system is typically comprised of a metallic bond coat and a ceramic top coat. The former is designed to protect the underlying substrate from oxidation and corrosion and to strengthen the bond between the top coat and the substrate [4,5]. A typical top coat is the 7 wt% Y<sub>2</sub>O<sub>3</sub>-stabilized metastable tetragonal ZrO<sub>2</sub> (t'-YSZ) type, which is usually prepared by air plasma spraying, electron beam physical vapor deposition, or plasma spray physical vapor deposition [6–9]. A major disadvantage of YSZ is that it has a limited operating temperature (lower than 1200 °C) for long-term applications [1–3,10,11]. At higher temperatures, the t' phase decomposes into Y-lean and Y-rich phases. Upon cooling, the former transforms to a monoclinic (m) phase with large volume expansion, causing cracks in the coating.

When low-grade fuels with certain amounts of impurity elements are used or TBCs are employed in engines for marine applications, hot corrosion resistance becomes a key durability issue for TBCs. At 600–1050 °C, molten sodium salts of vanadium and sulfur condensed onto TBCs exhibit extreme corrosion [12–15]. Molten salts penetrate into the coating microstructure and react with the coating, leaching out

the stabilizer yttria in YSZ. Consequently, the t' phase becomes unstable, promoting the formation of large amounts of m phase during cooling. Studies have shown that YSZ TBCs spall much more quickly with than without molten salts.

Extensive efforts have been directed toward enhancing the phase stability and corrosion resistance of TBCs in the presence of molten salts. Research has indicated that tailoring the coating microstructure can mitigate hot corrosion degradation of TBCs. Ghasemi et al. reported that functionally graded TBCs have better hot corrosion resistance than double-layer coatings [16]. Compared with conventional coatings, nanostructured coatings have proved to be more resistant to corrosion [14,17,18]. Composition optimization of ZrO<sub>2</sub>-based solid solution provides an alternative technique to improve the corrosion resistance. ZrO<sub>2</sub> doped with Sc<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub> and co-doped with Gd<sub>2</sub>O<sub>3</sub>-Yb<sub>2</sub>O<sub>3</sub> have been found to be more resistant than YSZ to hot corrosion [15,19–24]. Guo et al. have found that compared with YSZ coatings, zirconia–18titanium–10yttria (TiSZ) coatings in V<sub>2</sub>O<sub>5</sub> + Na<sub>2</sub>SO<sub>4</sub> molten salt at 1050 °C exhibit higher hot corrosion resistance [13].

Our previous study on the ZrO<sub>2</sub>-Yb<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system [25] found a composition exhibiting comprehensive properties superior to those of YSZ for TBC applications, i.e., 10 mol% TiO<sub>2</sub>-doped, 3.5 mol% Yb<sub>2</sub>O<sub>3</sub>-stabilized zirconia (Ti-YbSZ). These properties include phase stability, thermal conductivity, thermal expansion coefficient, and toughness. For

\* Corresponding author at: School of Materials Science and Engineering, Tianjin University, No. 92, Weijin Road, Tianjin 300072, China.  
E-mail address: [glei028@tju.edu.cn](mailto:glei028@tju.edu.cn) (L. Guo).

<http://dx.doi.org/10.1016/j.ceramint.2017.09.167>

Received 28 August 2017; Received in revised form 20 September 2017; Accepted 20 September 2017  
0272-8842/ © 2017 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

the application of Ti–YbSZ in an aggressive combustion environment, its hot corrosion properties need to be investigated. In this study, Ti–YbSZ bulk samples are produced and exposed to  $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$  molten salt at 700 °C, 800 °C, 900 °C and 1000 °C for 2 h and 10 h. Emphasis is placed on analyzing the phase constitution, composition and structural evolution of the corrosion products. The effects of  $\text{TiO}_2$  doping on the hot corrosion behavior are assessed by comparing the hot corrosion resistance of Ti–YbSZ and YbSZ. The corrosion mechanism of Ti–YbSZ in  $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$  molten salt is determined on the basis of the Lewis acid–base rule, phase diagrams, and thermodynamics.

## 2. Experimental procedures

By chemical co-precipitation, 3.5 mol%  $\text{Yb}_2\text{O}_3$  stabilized zirconia (YbSZ) powders were produced using  $\text{Yb}_2\text{O}_3$  (purity: 99.99%) and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (purity: 99.95%) as raw materials, following the procedure described in our previous study [25]. Ti–YbSZ powders were fabricated by a solid state reaction method, using  $\text{TiO}_2$  and the YbSZ powders as raw materials. 10 mol%  $\text{TiO}_2$  and 90 mol% YbSZ powders were mixed mechanically with deionized water by a planetary ball mill (QM-3SP4, China) at a speed of 400 rpm for 8 h. During the ball-milling procedure,  $\text{ZrO}_2$  balls with diameters of 5 mm and 10 mm were used, and the ball-to-powder mass ratio is 2:1. The suspension was then dried at 150 °C for 12 h and calcined at 1400 °C for 10 h. The obtained powders were cold-pressed at  $\sim 250$  MPa and sintered at 1500 °C for 10 h to obtain bulk samples [25].

Hot corrosion tests were performed in a furnace. Prior to testing, the bulk samples were ground using an 800 grit sandpaper, ultrasonically cleaned in ethanol, and dried at 120 °C. 50 mol%  $\text{Na}_2\text{SO}_4 + 50$  mol%  $\text{V}_2\text{O}_5$  ( $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ ) salt was selected as the corrosion medium for the tests. To perform accelerated hot corrosion, the salt with a content of 10  $\text{mg}/\text{cm}^2$  was spread onto the center of sample surfaces. An analytical balance was employed to determine the weight of the specimens before and after the salt coverage. Finally,  $0.0090 \pm 0.005$  g of  $\text{V}_2\text{O}_5$  and  $0.0070 \pm 0.005$  g of  $\text{Na}_2\text{SO}_4$  powders were covered on the surface of each sample. The salt-covered samples were then set in a furnace with an ambient atmosphere at 700 °C, 800 °C, 900 °C, and 1000 °C for 2 h and 10 h. After heat treatments, the samples were allowed to cool down to room temperature with the furnace.

The phase constitution of corrosion products was analyzed by X-ray diffraction (XRD; Rigaku Diffractometer, Tokyo, Japan). After hot corrosion tests, the surface morphologies and chemical composition of the samples were analyzed by scanning electron microscopy (SEM; TDCLS4800, Hitachi Ltd., Japan) with energy dispersive X-ray spectroscopy (EDS, IE 350). The cross-sectional microstructure of the samples was also observed by SEM (TDCLSU1510, Hitachi Ltd., Japan).

## 3. Results

Fig. 1 shows the XRD patterns of the as-fabricated Ti–YbSZ and the samples after the hot corrosion tests in  $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$  molten salt for 2 h and 10 h at varying temperatures. The as-fabricated ceramic mainly consists of a  $t'$  phase with minor amounts of m phase, which is consistent with our previous study [25]. When exposed to the molten salt, Ti–YbSZ chemically reacts with the salt. After the hot corrosion test at 700 °C for 2 h, the diffraction peaks representing the  $t'$  phase (PDF#79-1769) become weaker, whereas the m phase peaks become stronger, as shown in Fig. 1a. This finding indicates that the hot corrosion test leads to  $t'$  phase decomposition, increasing the amount of m phase. Another corrosion product is  $\text{YbVO}_4$  (PDF#72-0271), detected by XRD. Notably, several  $\text{Na}_2\text{SO}_4$  diffraction peaks are detected, indicating the presence of residual  $\text{Na}_2\text{SO}_4$  salt on the sample surface. With increased corrosion temperature, the peak intensity ratio of m- $\text{ZrO}_2$  to  $t'$ - $\text{ZrO}_2$  increases, suggesting the formation of m phase in larger amounts.  $\text{Na}_2\text{SO}_4$  salt is still detected by XRD after the hot corrosion test at 800 °C for 2 h but not at higher temperatures.

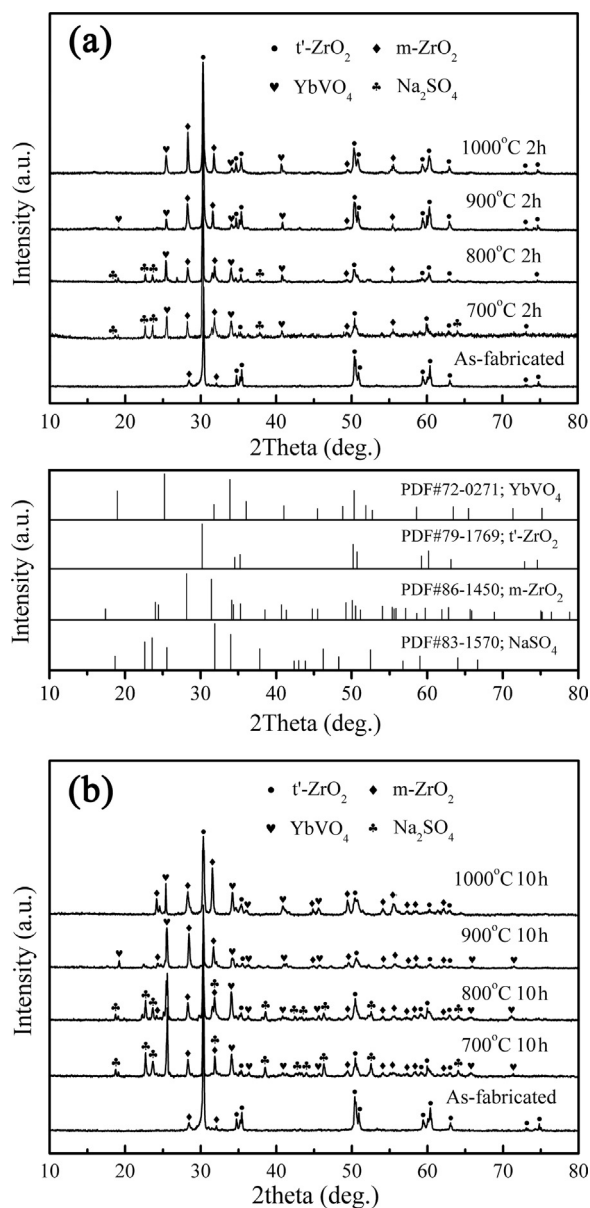


Fig. 1. XRD patterns of the as-fabricated Ti–YbSZ ceramic and samples after hot corrosion tests in  $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$  molten salt at 700–1000 °C for 2 h (a) and 10 h (b). The standard spectra of  $\text{YbVO}_4$ ,  $t'$ - $\text{ZrO}_2$ , m- $\text{ZrO}_2$ , and  $\text{Na}_2\text{SO}_4$  are also presented.

The XRD patterns of the samples after the hot corrosion tests for 10 h are presented in Fig. 1b. Exposure to the molten salt at 700–1000 °C for 10 h promotes the formation of m- $\text{ZrO}_2$  and  $\text{YbVO}_4$  as corrosion products. The same occurrence is observed in the hot corrosion tests for 2 h.  $\text{Na}_2\text{SO}_4$  is detected on the sample surfaces when the corrosion temperature is not higher than 800 °C. With an increase in temperature, a larger amount of m phase is formed, owing to  $t'$  phase decomposition. XRD analysis indicates that chemical reactions occur between Ti–YbSZ and  $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$  molten salt, prompting the formation of corrosion products. These products, found to be independent of temperature and heat duration in this study, consist of m- $\text{ZrO}_2$  and  $\text{YbVO}_4$ .

For  $\text{ZrO}_2$ -based ceramics for TBC applications,  $t'$  phase is desirable due to its high toughness. However, when exposed to high temperatures (above 1200 °C) or molten salt, the  $t'$  phase loses its stability and undergoes disastrous phase partitioning to cubic and equilibrium t phases [3,7,13,26,27]. The latter transforms to the m phase during cooling, together with excessive volume expansion, negatively affecting the

Download English Version:

<https://daneshyari.com/en/article/7888910>

Download Persian Version:

<https://daneshyari.com/article/7888910>

[Daneshyari.com](https://daneshyari.com)