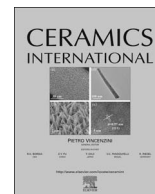




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## Hot corrosion behavior of $(\text{Gd}_{0.9}\text{Sc}_{0.1})_2\text{Zr}_2\text{O}_7$ in $\text{V}_2\text{O}_5$ molten salt at 700–1000 °C

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### ABSTRACT

Hot corrosion behavior of  $(\text{Gd}_{0.9}\text{Sc}_{0.1})_2\text{Zr}_2\text{O}_7$  ceramic exposed to  $\text{V}_2\text{O}_5$  molten salt at 700–1000 °C was investigated, providing better understanding of its corrosion resistance as a promising thermal barrier coating. Obvious corrosion reaction occurred between  $(\text{Gd}_{0.9}\text{Sc}_{0.1})_2\text{Zr}_2\text{O}_7$  and  $\text{V}_2\text{O}_5$  molten salt after 4 h heat treatment, corrosion products being temperature dependent. At 700 °C, large amount of  $\text{Sc}_2\text{O}_3$  doped  $\text{ZrV}_2\text{O}_7$  and  $\text{GdVO}_4$ , together with a minor amount of  $\text{Sc}_2\text{O}_3$ -stabilized tetragonal  $\text{ZrO}_2$  (*t*- $\text{ZrO}_2$ ), formed on the sample surfaces. With the increase of the test temperature,  $\text{Sc}_2\text{O}_3$  doped  $\text{ZrV}_2\text{O}_7$  turned to decompose, leading to the formation of more *t*- $\text{ZrO}_2$ . At 900 °C and 1000 °C, the corrosion products were composed of  $\text{GdVO}_4$  and *t*- $\text{ZrO}_2$ . The mechanism by which the corrosion reaction occurs is proposed based on phase diagrams and Lewis acid-base rule.

### 1. Introduction

Thermal barrier coatings (TBCs) are extensively applied to hot-section metallic components in gas-turbine engines to provide insulation and corrosion protection, improving engine efficiency and performance [1,2]. A typical TBC system usually consists of a ceramic topcoat as thermal insulation layer and a metallic bond coat. The bond coat is designed to provide oxidation and corrosion resistance as well as to improve the bonding between the topcoat and the substrate [3,4]. The widely used top coat is made of 7 wt%  $\text{Y}_2\text{O}_3$ -stabilized metastable tetragonal  $\text{ZrO}_2$  (*t*'-YSZ). However, the accepted upper limit for YSZ TBC use is 1200 °C. Higher temperatures cause the destabilization of *t*' phase into Y-lean and Y-rich phases. The former transforms to monoclinic (*m*) phase on cooling accompanied with a large volume increase [1,5–8].

When low grade fuels are used, hot corrosion becomes a life-limiting factor for TBCs application. The impurities in low quality fuels commonly contain vanadium and sodium. In a temperature range of 600–1050 °C, molten sodium salts of vanadium and sulfur condensed onto the TBCs are extremely corrosive [9–11]. They can leach out the stabilizer yttria in YSZ and destabilize the *t*' structure, which causes the spallation of the coating much more quickly than if the molten salts are

absent. Extensive efforts have been conducted to enhance the hot corrosion resistance of YSZ against sulfate-vanadate molten salts. Research has indicated that titania stabilized zirconia coating reveals superior hot corrosion resistance compared with YSZ coating [12]. Omar et al. have enhanced the corrosion resistance of YSZ coating by doping MgO [13]. Loghman-Estarki and Liu et al. have found that the addition of  $\text{Sc}_2\text{O}_3$  in YSZ can improve its hot corrosion resistance [14–16]. It has been reported that nanostructured coatings exhibit better hot corrosion resistance than their conventional counterparts [15–17].

The power output and efficiency of gas engines scale with their maximum operation temperature. Hence, there is a great need to increase engine-operating temperature. However, YSZ TBCs are unlikely to meet the long-term requirements for advanced engines even when the molten salt is not a concern. Additionally, in anticipation of better thermal insulation, there is a practical requirement for TBCs with even lower thermal conductivity. The search is thus underway for TBC materials that have even better phase stability, higher sintering resistance and lower thermal conductivity. Several high-temperature ceramics with lower thermal conductivity (for example,  $\text{Gd}_2\text{Zr}_2\text{O}_7$ ,  $\text{LaPO}_4$ ,  $\text{La}_2\text{Ce}_2\text{O}_7$  and  $\text{LaMgAl}_{11}\text{O}_{19}$ ) are being pursued, some of which have been proposed as novel TBC candidates [1,18–23]. Many reports indicate enormous threat imposed to high-temperature ceramics by

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molten salts [11,12,23–26]. Thus, investigation on the hot corrosion behavior of new TBC materials in molten slats is essential for developing alternative TBCs that have the potential capability operating above 1200 °C.

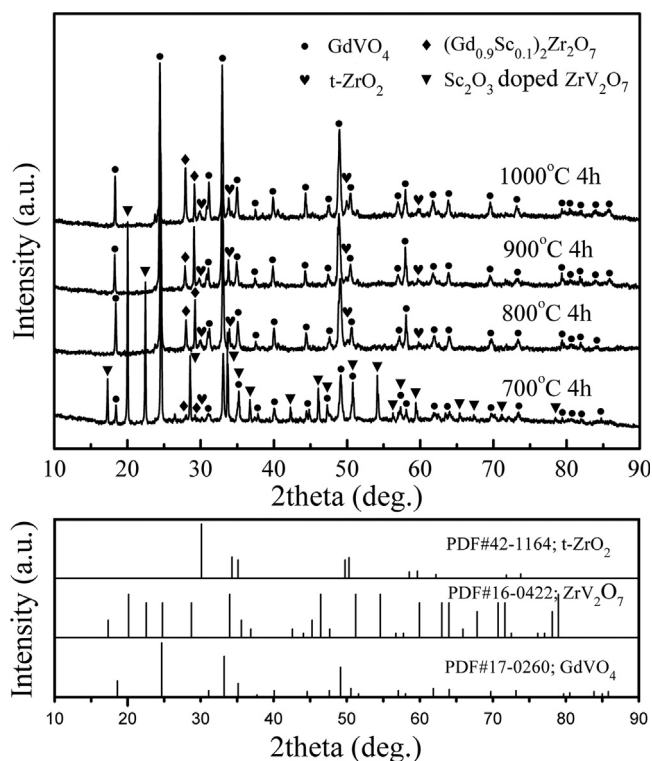
(Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> keeps phase stability up to 1600 °C, has thermal expansion coefficient comparable to YSZ and reveals much lower thermal conductivity than YSZ [27,28]. Specially, compared with Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, a widely investigated TBC material, its toughness is significantly improved [27,28]. Thus, (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> has been considered as a promising TBC material. However, its phase and microstructure evolution upon high temperature exposure to molten vanadium oxide is limited in open literature. In this study, the hot corrosion behavior of (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> ceramic in V<sub>2</sub>O<sub>5</sub> salt at 700 °C, 800 °C, 900 °C and 1000 °C is investigated. The emphasis of this work is placed on analyzing the corrosion products resulted from the reaction between (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and V<sub>2</sub>O<sub>5</sub> salt by using dense pellets and identifying the corrosion mechanisms.

## 2. Experimental procedure

(Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> powders were produced by a chemical co-precipitation and calcination method, using RE<sub>2</sub>O<sub>3</sub> (RE=Gd and Sc, purity 99.99%) and ZrOCl<sub>2</sub>·8H<sub>2</sub>O (purity 99.95%) as raw materials. Before fabrication process, Gd<sub>2</sub>O<sub>3</sub> and Sc<sub>2</sub>O<sub>3</sub> powders were calcined at 900 °C for 4 h to remove moisture and other volatile impurities. Appropriate amounts of RE<sub>2</sub>O<sub>3</sub> and ZrOCl<sub>2</sub>·8H<sub>2</sub>O were dissolved in nitric acid and deionized water, respectively. The obtained solutions were mixed and stirred to yield homogeneous solution. Then, the mixed solution was slowly added to excess ammonia water (pH > 12) to get precipitate, followed by filtering and washing with deionized water and alcohol several times until a pH 7 was reached. The resultant precipitate was dried at 120 °C for 10 h and then calcined at 900 °C for 5 h for crystallization. In order to obtain bulks for hot corrosion tests, the powders were cold pressed at ~250 MPa and then sintered at 1600 °C for 15 h.

Theoretical density of (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> was calculated by using its lattice parameter available in the literature [27], and the bulk density was measured by Archimedes method. The theoretical density and the measured bulk density are 6.62 g/cm<sup>3</sup> and 5.08 g/cm<sup>3</sup>, respectively. Thus, the relative density of the sintered samples are ~76.7% and the porosity is ~23.3%, which is close to that of the coating produced by air plasma spraying (APS). Hot corrosion tests were conducted according to our previous study and other researchers' experiments [12,14,16,17,26]. Prior to the tests, the sintered samples were ground by 800 grit sandpaper, followed by ultrasonic cleaning in ethanol and drying at 120 °C. Subsequently, V<sub>2</sub>O<sub>5</sub> powders with average particle size of ~10 μm were uniformly spread on the sample surfaces by using a very fine glass rod. An analytical balance was used to determine the weight of the specimens before and after V<sub>2</sub>O<sub>5</sub> coverage. Finally, 0.0178 ± 0.005 g of V<sub>2</sub>O<sub>5</sub> powders were coated on the sample surfaces, and the salt concentration was calculated to be ~10 mg/cm<sup>2</sup>. Then, the specimens were isothermally heated at 700 °C, 800 °C, 900 °C and 1000 °C for 4 h, followed by cooling down to room temperature with furnace.

Phase constitution of the samples was characterized by X-ray diffraction (XRD; Rigaku Diffractometer, Tokyo, Japan). Raman spectrum was recorded by a microscopic confocal Raman spectrometer (RM2000; Renishaw, Gloucestershire, UK) using 532 nm excitation from an argon ion laser. The spectral resolution was ~1 cm<sup>-1</sup>, and the signal was collected at a rate of 600 cm<sup>-1</sup>/30 s. Microstructure and composition analysis were carried out using a scanning electron microscope (SEM; FEI, Eindhoven, Holland) equipped with energy dispersive spectroscopy (EDS, IE 350).



**Fig. 1.** XRD patterns of (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> ceramics after hot corrosion tests in V<sub>2</sub>O<sub>5</sub> salt at 700–1000 °C for 4 h. The standard PDF cards of GdVO<sub>4</sub>, ZrV<sub>2</sub>O<sub>7</sub> and t-ZrO<sub>2</sub> are also presented.

## 3. Results and discussion

XRD measurements were carried out on the corroded surfaces of (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> samples, and the results are presented in Fig. 1. In the XRD pattern of the sample after 4 h hot corrosion at 700 °C, strong peaks ascribed to GdVO<sub>4</sub> (PDF#17-0260) and close to ZrV<sub>2</sub>O<sub>7</sub> (PDF#16-0422) can be clearly observed. The detection of weak (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> peaks indicates that the reaction layer on the sample surface is quite thin, thus X ray can penetrate through it. It is worthwhile to note that there is a weak peak appearing at 2θ ≈ 30.5°, suggesting the presence of another phase. However, only based on this single diffraction peak, the phase cannot be determined.

In order to investigate the influence of temperature on the corrosion products, (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> bulks were exposed to 800 °C, 900 °C and 1000 °C for 4 h in V<sub>2</sub>O<sub>5</sub> salt, and their XRD patterns are also included in Fig. 1. GdVO<sub>4</sub> (PDF#17-0260) and (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> peaks are evident in all the patterns. Notice that the peak at 2θ ≈ 30.5° still exists, the intensity of which increases with the increase of the corrosion temperature. Meanwhile, another two peaks appear at 2θ ≈ 34° and 50°. Comparing with the standard PDF card of t-ZrO<sub>2</sub> (PDF#42-1164) shown in Fig. 1, one could ascribe these unidentified peaks to t-ZrO<sub>2</sub> phase. Based on the aforementioned XRD analysis, it is possible to find that the corrosion products of (Gd<sub>0.9</sub>Sc<sub>0.1</sub>)<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in V<sub>2</sub>O<sub>5</sub> molten salt are temperature dependent. At 700 °C, they contain GdVO<sub>4</sub> and a phase close to ZrV<sub>2</sub>O<sub>7</sub>, together with a minor amount of t-ZrO<sub>2</sub> phase, while those at 800 °C, 900 °C and 1000 °C mainly consist of GdVO<sub>4</sub> and t-ZrO<sub>2</sub>.

Raman spectroscopy is an extremely valuable tool for characterizing the crystal structure of compounds [29,30]. To confirm the above conclusions and further analyze the structure of the corrosion products, Raman spectrum measurements were conducted. As shown in Fig. 2a, Raman modes appearing at ~434 cm<sup>-1</sup>, ~474 cm<sup>-1</sup>, ~570 cm<sup>-1</sup>, ~690 cm<sup>-1</sup>, ~720 cm<sup>-1</sup> and ~885 cm<sup>-1</sup> could be ascribed to GdVO<sub>4</sub>. To confirm this argument and exclude the presence of ScVO<sub>4</sub>, we produced GdVO<sub>4</sub> and ScVO<sub>4</sub> bulks and measured their Raman spectra.

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