Na$_2$SO$_4$ + V$_2$O$_5$ Corrosion Behavior of BaNd$_2$Ti$_3$O$_{10}$ for Thermal Barrier Coating Applications

Yajuan She, Yiwen Guo, Zanxian Tan and Kai Liao *

School of Mechanical and Electrical Engineering, Hunan Applied Technology University, Changde 415000, China; sheyajuan94@163.com (Y.S.); yiwen123qwe@163.com (Y.G.); Tzx888UT@163.com (Z.T.)

* Correspondence: liaokai102@csuft.edu.cn

Received: 15 August 2020; Accepted: 16 September 2020; Published: 20 September 2020

Abstract: BaNd$_2$Ti$_3$O$_{10}$ has been considered as a promising thermal barrier coating (TBC) candidate material, which reveals many advantages over the widely used TBC material of yttria partially stabilized zirconia, such as lower thermal conductivity, better high-temperature capability, and higher resistance to environmental deposits corrosion. In this study, the hot corrosion behavior of BaNd$_2$Ti$_3$O$_{10}$ in Na$_2$SO$_4$ + V$_2$O$_5$ molten salt at 900 °C and 1000 °C is investigated. Exposed to the salt for 4 h at 900 °C, BaNd$_2$Ti$_3$O$_{10}$ pellets had an obvious reaction with the salt, forming corrosion products of NdVO$_4$, TiO$_2$, and BaSO$_4$, and the reaction layer was ~30 µm, beneath which no salt trace could be found. Prolonging the corrosion time to 20 h, the type of the corrosion products had no change. At an elevated corrosion temperature of 1000 °C for 4 h, the corrosion products were still NdVO$_4$, TiO$_2$, and BaSO$_4$, but NdVO$_4$ revealed a significant growth, which fully covered the pellet surface. The mechanisms by which the corrosion reaction between BaNd$_2$Ti$_3$O$_{10}$ and the molten salt occurred were discussed.

Keywords: thermal barrier coating; BaNd$_2$Ti$_3$O$_{10}$; hot corrosion; Na$_2$SO$_4$ + V$_2$O$_5$; Corrosion mechanism

1. Introduction

Thermal barrier coatings (TBCs) are extensively used onto the hot-components (blades, vanes, and combustion chamber) of turbine engines, which give rise to thermal insulation and protect metallic parts from corrosion, increasing the efficiency and performance of turbines [1–3]. A typical TBC system usually consists of a ceramic topcoat and a bond coat, the latter of which is designed to enhance the oxidation and corrosion resistance, as well as to improve the adhesion between the ceramic top coat and the substrate. The ceramic top coat is commonly made of yttria partially stabilized zirconia (YSZ), and is usually fabricated by air plasma spraying (APS) and electron beam physical vapor deposition (EB-PVD) [4–6]. YSZ TBCs have revealed many advantages, such as low thermal conductivity, excellent toughness, and good thermal expansion match with the substrate [1,7–9].

In marine environments or for the usage of low-quality fuel, TBCs face problems of molten salt attack, which caused by vanadium, sulfur, and phosphorous from fuel impurities or corrosive environments condensing the coating surfaces [10–15]. At 600–1000 °C, molten salt corrosion to YSZ TBCs is rather severe. The salt melts at high temperatures and infiltrates into the coating, during which a reaction between molten salt and YSZ occurs, decreasing the stabilizer in the TBC. As a result, the coating would undergo an undesirable phase transformation, causing failure much more quickly than if no molten salt is present [16–19]. Although the degradation mechanism by which molten salt attacks YSZ TBCs has been clear, measurements to solve the corrosion issue still need large studies, and some researchers have made some attempts [15,20–25], such as introducing Al$_2$O$_3$, CeO$_2$, Ta$_2$O$_5$, and RE$_2$O$_5$ (RE = rare earth) into the ZrO$_2$-based system as a new stabilizer or co-dopants.
In order to further improve engine efficiency, there are great motivations for increasing the engine-operating temperature. However, YSZ TBCs have an operation temperature limitation (1200 °C), above which they suffer from phase transformation and thermal conductivity increasing. Moreover, a practical requirement for TBCs is that the thermal conductivity should be as low as possible for better thermal insulation. Therefore, alternative TBC materials are largely required with even better phase stability, improved thermo-physical and mechanical properties, and superior high-temperature capability. However, for these novel TBCs operated at higher temperatures, threats resulting from molten salts still exist. Hence, it is necessary to understand the hot corrosion behavior of newly developed TBC materials in molten salts.

Recently, the hot corrosion behavior of some TBC candidate materials exposed to molten salt has been evaluated. Ouyang et al. reported the hot corrosion behavior of Gd$_2$Zr$_2$O$_7$ and Yb$_2$Zr$_2$O$_7$ ceramics in V$_2$O$_5$ molten salt, and investigated the associated mechanisms [13,26]. Guo et al. indicated that (Sm$_{0.5}$Sc$_{0.5}$)$_2$Zr$_2$O$_7$ has a better corrosion resistance to Na$_2$SO$_4$ + V$_2$O$_5$ molten salt than Sm$_2$Zr$_2$O$_7$ [27]. Cao et al. studied the corrosion products of LaTi$_2$Al$_6$O$_{19}$ ceramic resulting from V$_2$O$_5$ salt attack, and discussed their formation mechanisms [14]. Chen et al. investigated the corrosion behavior of plasma sprayed LaMg$_2$Al$_6$O$_{19}$ coatings in V$_2$O$_5$ molten salt [28]. BaNd$_2$Ti$_3$O$_{10}$ belongs to BaLa$_2$Ti$_3$O$_{10}$ (Ln: La, Nd, Sm) series, which is a perovskite derivative. It has been reported that BaLa$_2$Ti$_3$O$_{10}$ has low thermal conductivities, good high-temperature capability, and excellent resistance to environmental deposits corrosion, giving rise to be promising TBC candidate materials [29,30]. Additionally, BaLa$_2$Ti$_3$O$_{10}$ TBCs have been successfully produced by Guo et al., which have better thermal cycling performance than YSZ TBCs [31]. However, how BaNd$_2$Ti$_3$O$_{10}$ performs in molten salt is still unclear, and no report on the hot corrosion behavior of BaNd$_2$Ti$_3$O$_{10}$ exposed to molten salt exists in open literature.

In this study, the Na$_2$SO$_4$ + V$_2$O$_5$ corrosion behavior of BaNd$_2$Ti$_3$O$_{10}$ for possible use as a novel TBC material is investigated at 900 °C for 4 h and 20 h, and 1000 °C for 4 h. The emphasis is analyzing the corrosion products of BaNd$_2$Ti$_3$O$_{10}$ due to molten salt exposure by using dense pellets, based on which the related corrosion mechanisms are discussed.

2. Experimental Procedure

BaCO$_3$, TiO$_2$, and Nd$_2$O$_3$ powders are used as raw materials to produce BaNd$_2$Ti$_3$O$_{10}$ powder by a solid-state reaction method. The raw materials mixed with an appropriate quantity were ball milled in ionized water at a speed of 400 rpm for 10 h, followed by drying at 160 °C for 10 h and calcination at 1500 °C for 24 h. The process was repeated until pure BaNd$_2$Ti$_3$O$_{10}$ powder was fabricated. BaNd$_2$Ti$_3$O$_{10}$ pellets for hot corrosion tests were prepared by cold pressing at ~250 MPa, followed by sintering at 1500 °C for 10 h.

Hot corrosion tests were conducted using Na$_2$SO$_4$ + V$_2$O$_5$ salt (50 mol% Na$_2$SO$_4$ and 50 mol% V$_2$O$_5$) in a furnace. Prior to the tests, pellets were ground by 800# SiC papers, followed by ultrasonic cleaning in ethanol and drying at 120 °C. Na$_2$SO$_4$ + V$_2$O$_5$ salt was uniformly spread on the pellet surface by using a very fine glass rod. The salt content on the pellet surface was ~10 mg/cm$^2$, which was determined by calculating the weight difference between the samples before and after the salt coverage. BaNd$_2$Ti$_3$O$_{10}$ pellets covered with Na$_2$SO$_4$ + V$_2$O$_5$ salt were isothermally heated in a furnace, followed by cooling down to room temperature with the furnace. The heat treatment conditions were as follows: 900 °C for 4 h and 20 h, and 1000 °C for 4 h.

X-ray diffraction (XRD; Rigaku Diffractometer, CuKa radiation, Tokyo, Japan) was employed to conduct phase composition analysis, and the scanning angle (2θ) range was 10°–80° with a scanning rate of 0.1°/s. The peak identification was carried out using MDI Jade 6.0 software. Surface morphologies and composition analysis were conducted by a scanning electron microscope (SEM; TDCL54800, Hitachi Ltd., Tokyo, Japan) equipped with energy dispersive spectroscopy (EDS, IE 350), and cross-sectional microstructure was analyzed using a scanning electron microscope (SEM; TDCLSU1510, Hitachi Ltd., Tokyo, Japan).
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Japan). For cross-section observations, the samples were cold mounted in epoxy resin, and then grinded by 150#, 400#, 800#, 1200#, and 2000# SiC papers, following by polishing with diamond pastes (5 µm size).

3. Results and Discussion

Figure 1a shows the surface microstructure of BaNd₂Ti₃O₁₀ bulk. It has inhomogeneous grains, with an average size of 5–10 µm. The cross-sectional microstructure is shown in Figure 1b. The fabricated pellet reveals a dense microstructure, and few pores could be found, the relative density of which is above 95%. According to the surface and cross-section observations, it could be considered that in the following corrosion experiments, the salt penetration might be limited due to the dense microstructure of the pellet, and the corrosion may occur at the surface regions resulting from the reaction between molten salt and BaNd₂Ti₃O₁₀.

![Surface (a) and cross-section (b) microstructures of BaNd₂Ti₃O₁₀ pellet.](image)

Figure 2 shows the XRD patterns of BaNd₂Ti₃O₁₀ pellets after hot corrosion tests in Na₂SO₄ + V₂O₅ salt, and that of the as-fabricated pellet is also presented for comparison. Exposed to 900 °C for 4 h and 20 h, the sample surfaces have similar XRD patterns, consisting of diffraction peaks ascribed to NdVO₄, TiO₂, and BaSO₄. This suggests that the corrosion leads to the formation of these products, the types of which are corrosion time independent at 900 °C. Additionally, the substrate phase (BaNd₂Ti₃O₁₀) is detected, which indicates that the corrosion on the surface is uneven causing
some regions are uncorroded, or the reaction layer on the surface is thin. After corrosion at 1000 °C for 4 h, only NdVO$_4$ and some TiO$_2$ could be detected by XRD, which might be because that the corrosion product of NdVO$_4$ largely grows covering the pellet surface. This will be further confirmed by SEM observations in the following sections.

Figure 2. XRD patterns of the as-fabricated BaNd$_2$Ti$_3$O$_{10}$ pellet and the pellets after hot corrosion in Na$_2$SO$_4$ + V$_2$O$_5$ salt at 900 °C for 4 h and 20 h, and 1000 °C for 4 h.

Figure 3 shows typical surface morphologies of BaNd$_2$Ti$_3$O$_{10}$ sample after hot corrosion at 900 °C for 4 h. It is evident that many corrosion products are formed on the sample surface, as shown in Figure 3a. In Figure 3b showing these products at a higher magnification, it could be found that they have three different shapes, i.e., rod shaped (marked as A) particle shaped (marked as B), and plate shaped (marked as C), and their chemical compositions are listed in Table 1. Compound A consists of Nd, V, and O, compound B has Ti and O, while compound C is composed of Ba, S, and O. Based on the above XRD results, one could determine that compounds A, B, and C are NdVO$_4$, TiO$_2$, and BaSO$_4$, respectively.
Figure 3. Surface morphologies of BaNd$_2$Ti$_3$O$_{10}$ pellet after hot corrosion in Na$_2$SO$_4$ + V$_2$O$_5$ molten salt at 900 °C for 4 h. (a) and (b) show the images with different magnifications.

Table 1. Chemical compositions of compounds A–C in Figure 3 (in at.%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ba</th>
<th>Nd</th>
<th>Ti</th>
<th>V</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>17.1</td>
<td>-</td>
<td>18.3</td>
<td>-</td>
<td>64.6</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>33.4</td>
<td>-</td>
<td>-</td>
<td>66.6</td>
</tr>
<tr>
<td>C</td>
<td>16.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.8</td>
<td>65.4</td>
</tr>
</tbody>
</table>

The cross-sectional microstructure of the sample after corrosion at 900 °C for 4 h is shown in Figure 4a. A significantly different layer with a thickness of ~30 µm can be observed on the sample surface, in which some parts are dense and other regions are rather loose. Beneath this reaction layer, the pellet keeps structure integrity, and has no molten salt trace. In an enlarged image as shown in Figure 4b, the dense parts could be identified as the original substrate, which could provide the explanation for the detection of BaNd$_2$Ti$_3$O$_{10}$ phase by XRD, and the loose regions are composed of corrosion products, which are composed of rod shaped NdVO$_4$ and particle shaped TiO$_2$. One could find that, at the interface of the reaction layer and the original substrate, there are some pores, which might be attributed to the thermal expansion mismatch between the newly formed layer and the original BaNd$_2$Ti$_3$O$_{10}$ pellet.
Figure 4. Cross-sectional microstructures of BaNd\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} pellet after Na\textsubscript{2}SO\textsubscript{4} + V\textsubscript{2}O\textsubscript{5} molten salt corrosion at 900 °C for 4 h. (a) and (b) show the images with different magnifications.

Figure 5 shows the SEM images of the BaNd\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} sample exposed to corrosion at 900 °C for 20 h. This is similar to the case of 4 h corrosion; corrosion products are also evident in this case, as shown in Figure 5a. Enlarging this image, one could clearly observe these differently shaped corrosion products, i.e., rod shaped (D), particle shaped (E) and plate shaped (F), as presented in Figure 5b. EDS was employed to analyze the chemical composition of these products, and the results are also listed in Table 2. Compound D contains Nd, V, and O, compound E is composed of Ti and O, while crystal F consists of Ba, S, and O. According to the above XRD results, it could be confirmed that D, E, and F are NdVO\textsubscript{4}, TiO\textsubscript{2}, and BaSO\textsubscript{4}, respectively.
BaNd$_2$Ti$_3$O$_{10}$ sample was subjected to hot corrosion in Na$_2$SO$_4$ + V$_2$O$_5$ salt at 1000 °C for 4 h, and its surface morphologies are shown in Figure 6. The sample surface is almost completely covered by corrosion products, as shown Figure 6a. In the enlarged image (Figure 6b), the corrosion product with a rod shape could be clearly observed, but other shaped products are rare, only presenting a few particle shaped compounds. EDS analysis of the rod-shaped compound indicates that it is composed of Nd, V, and O, and could be identified as NdVO$_4$ in combination with the XRD result. The particle shaped corrosion products are TiO$_2$ based on EDS and XRD analysis. BaSO$_4$ and BaNd$_2$Ti$_3$O$_{10}$ are
not detected by SEM, mainly attributed to the significant growth of NdVO₄ which covers the whole surface of the sample.

**Figure 6.** Surface morphologies of BaNd₂Ti₃O₁₀ pellet after Na₂SO₄ + V₂O₅ molten salt corrosion at 1000 °C for 4 h. (a) and (b) show the images with different magnifications.

Based on the aforementioned observations, it could find that in the presence of Na₂SO₄ + V₂O₅ molten salt, BaNd₂Ti₃O₁₀ undergoes evident corrosion, and the type of corrosion products are temperature and time independent, which consists of NdVO₄, TiO₂, and BaSO₄. However, an elevated temperature causes significant growth of NdVO₄, which can cover the whole surface of the sample.

The mechanism for the formation of these corrosion products could be understood in terms of the breakdown of the chemical bonds of BaNd₂Ti₃O₁₀ by molten salt [14,32]. From the viewpoint of crystallography, BaNd₂Ti₃O₁₀ crystal has a lattice consisting of a tri-perovskite [Nd₂Ti₃O₁₀] layer separated by a Ba layer along c-axis [29,30]. In the lattice, the Ba insertion layers are weakly bonded, which are easy to be destroyed by molten salt. As a result, Ba-O bonds in BaNd₂Ti₃O₁₀ lattice is expected to first break due to molten salt attack, giving rise to the formation of Ba contained corrosion products.
products. Then, Nd and Ti are enriched in the crystal due to the consumption of Ba, which provides a greater chance for the salt to destroy Nd-O and Ti-O bonds. Thus, other corrosion products containing Nd and Ti are expected to be generated.

For the mixture of Na$_2$SO$_4$ and V$_2$O$_5$ salts, a reaction occurs above 900 °C by the following expression [11,18,27,33]:

$$Na_2SO_4(l) + V_2O_5(l) \rightarrow 2NaVO_3(l) + SO_3(g)$$ (1)

In this study, the formed products resulting from Equation (1) react with BaNd$_2$Ti$_3$O$_{10}$ pellets. Based on the reaction products analysis by XRD and SEM, the reaction between BaNd$_2$Ti$_3$O$_{10}$ and the molten salt could be expressed by the following equation:

$$BaNd2Ti3O10(s) + 2NaVO3(l) + SO3(g) \rightarrow BaSO4(s) + 2NdVO4(s) + 3TiO2(s) + Na2O(s)$$ (2)

It has been reported that for YSZ pellets or coatings, molten salt has a large tendency to penetrate inside, reacting with YSZ to form YVO$_4$ and m-ZrO$_2$, which causes a large and deep reaction region, where the phase composition and microstructure are largely destroyed [17–19,21]. By comparison, in the presence of Na$_2$SO$_4$ + V$_2$O$_5$ molten salt, there is only a ~30 µm thickness destroyed region/layer on the BaNd$_2$Ti$_3$O$_{10}$ pellet surface, beneath which no molten salt trace could be found (Figure 4). Although EDS line scans or maps of this layer is not provided here, based on the identified reaction products on the pellet surface and cross-section observations, one could confirm that the destroyed region is composed of reaction products. The formation of these corrosion products has largely consumed the salt; as a result, very limited molten salt can infiltrate the deep regions of the pellets. In other words, the reaction layer could be considered as a sacrificial layer, the formation of which can protect the pellet or coating from severe damage. Hence, BaNd$_2$Ti$_3$O$_{10}$ is resistant to Na$_2$SO$_4$ + V$_2$O$_5$ salt corrosion to a certain extent; especially, its resistance to molten salt corrosion is better than YSZ.

4. Conclusions

BaNd$_2$Ti$_3$O$_{10}$, a promising TBC candidate material, was exposed to Na$_2$SO$_4$ + V$_2$O$_5$ molten salt at 900 °C and 1000 °C to evaluate its hot corrosion resistance. After exposure to Na$_2$SO$_4$ + V$_2$O$_5$ salt for 4 h at 900 °C, there was an obvious reaction between BaNd$_2$Ti$_3$O$_{10}$ and the salt, producing NdVO$_4$, TiO$_2$, and BaSO$_4$ as the corrosion products, which formed a reaction layer with a thickness of ~30 µm, and the regions beneath the reaction layer were not destroyed by the molten salt. At 900 °C for 20 h in the salt, the type of corrosion products of BaNd$_2$Ti$_3$O$_{10}$ pellet had no change. At an elevated corrosion temperature of 1000 °C for 4 h, although the corrosion products were still NdVO$_4$, TiO$_2$, and BaSO$_4$, NdVO$_4$ crystals grew significantly and fully covered the pellet surface. Based on the research results, BaNd$_2$Ti$_3$O$_{10}$ is found to have a good resistance to Na$_2$SO$_4$ + V$_2$O$_5$ salt corrosion, and due to the excellent high-temperature capability and thermo-physical properties, it has a potential application for TBCs, especially under the corrosive environments containing vanadium and sulfur.

Author Contributions: Conceptualization, Y.S. and K.L.; methodology, Y.S. and Y.G.; validation, Z.T. and K.L.; formal analysis, Y.S.; investigation, Y.S. and Y.G.; resources, Z.T. and K.L.; writing—original draft preparation, Y.S.; writing—review and editing, K.L.; supervision, K.L.; project administration, K.L.; funding acquisition, K.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the National Natural Science Foundation of China (Grant Nos. 51475483).

Conflicts of Interest: The authors declare no conflict of interest.
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