Hot corrosion behavior of Yb$_2$Si$_2$O$_7$ ceramic by NaVO$_3$ and V$_2$O$_5$ at 700°C to 900°C

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Abstract. To better understand the hot corrosion behavior of Yb$_2$Si$_2$O$_7$ ceramic in molten NaVO$_3$ and V$_2$O$_5$ coatings at temperature range of 700°C to 900°C in air. Corrosion products of YbVO$_4$ and SiO$_2$ were identified under NaVO$_3$ corrosion. But only YbVO$_4$ was found under V$_2$O$_5$ corrosion with some residual corrosion agent. In above two conditions, the corrosion products of YbVO$_4$ have the same crystallographic structural characteristic, but morphology has significant difference. In the first case, YbVO$_4$ is rod-like with a tetrahedral cone at each end because of NaVO$_3$ being weak acid to lead to lower driving force for the corrosion reactions. Thus corrosion products of YbVO$_4$ grew with less nuclei and large elongation. However, V$_2$O$_5$ showed strong acid with strong driving force bringing higher nucleation rate and suppressing the growth of YbVO$_4$, which resulted in granular YbVO$_4$. And the size of granular YbVO$_4$ crystals increased slightly with test temperature rising.

1. Introduction

Si-based ceramics, such as SiC and Si$_3$N$_4$, can be used as high temperature structural components for aeroengine. Under dry oxygen conditions, a layer of SiO$_2$ protective layer will be formed on the surface of Si-based ceramics, showing good oxidation resistance \cite{1}. However, the water vapor in the high temperature gas reacts with the SiO$_2$ protective layer to form the gaseous product Si (OH)$_4$, which results in the decrease of the high temperature performance of the ceramic components. Therefore, environmental barrier coatings (EBCs) are often used to prevent the formation of Si (OH)$_4$ and improve their service life \cite{2-4}. Rare earth silicates have good chemical stability, oxidation resistance, chemical compatibility with Si-based ceramics and water-oxygen corrosion resistance \cite{5-7}. They are the most promising candidate materials for EBCs.

Among rare earth silicates, Yb$_2$Si$_2$O$_7$ has good phase stability from room temperature to high temperature, matching thermal expansion coefficient with SiC and better resistance to water-oxygen corrosion \cite{5,8}. However, in addition to a large amount of water vapor, oxygen and siliceous minerals, there are also various molten salt impurities (such as Na, S, V, Cl, etc.) in the exhaust gas of aeroengine, which can cause corrosion of substrates and EBCs of high temperature components \cite{9,12}. It is necessary to study the corrosion behavior of NaVO$_3$ and V$_2$O$_5$ molten salts on Yb$_2$Si$_2$O$_7$ ceramic.
2. Materials and methods
In order to simulate the molten salt corrosion condition of EBCs, \( \text{Yb}_2\text{Si}_2\text{O}_7 \) sintered bulk ceramics were used as corrosion specimen. Its powders were synthesized by using commercial \( \text{Yb}_2\text{O}_3 \) and \( \text{SiO}_2 \) powders (purities > 99%) at 1500\(^\circ\)C. The chemical reaction formula is shown in chemical equation (1). \( \text{Yb}_2\text{Si}_2\text{O}_7 \) powders were weighed 5 g and put into a press die. And its compacts with the size of 15 mm \( \times \) 15 mm \( \times \) 6.5 mm were prepared by using a single-axis hydraulic press under 20 MPa pressure for 5 min. When sintered in a box furnace at 1500\(^\circ\)C for 12 hours, the size of the sintered bulk ceramics is 12.2 mm \( \times \) 12.2 mm \( \times \) 4.5 mm. Their macroscopic surface is relatively smooth. The \( \text{Yb}_2\text{Si}_2\text{O}_7 \) equiaxed grains are compactly accumulated and the grain boundary is clear\(^{[13]}\), but there are a few small pores at the grain boundary. The surface morphology is shown in Fig. 1. The results of XRD showed that both \( \text{Yb}_2\text{Si}_2\text{O}_7 \) powders and the sintered bulk ceramics were pure \( \text{Yb}_2\text{Si}_2\text{O}_7 \) phase.

\[
\text{Yb}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow \text{Yb}_2\text{Si}_2\text{O}_7
\]  

(1)

The temperature range of gas emitted by aeroengine is large. In this paper, the temperature range of 700\(^\circ\)C - 900\(^\circ\)C was chosen as the test condition with holding time of 2 hours. The corrosive media of \( \text{NaVO}_3 \) and \( \text{V}_2\text{O}_5 \) powders were uniformly coated on the upper surface of the \( \text{Yb}_2\text{Si}_2\text{O}_7 \) ceramic specimens at a concentration of about 20 mg/cm\(^2\). Then hot corrosion tests were carried out by putting these corrosive samples into the box furnace at a set temperature of 700\(^\circ\)C, 800\(^\circ\)C or 900\(^\circ\)C. After corrosion test, the corroded samples were taken out and naturally cooled to room temperature.

The corroded samples were cleaned with deionized water and their phase components were identified by X-ray diffraction (XRD, Bruker D8 Advance diffractometer, Cu K radiation) at a scanning rate of 6\(^\circ\)/min. The microstructures were observed by scanning electron microscopy (SEM, JSM-5310, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS, Link-ISIS, England) operating at 20 KV.

3. Results
Fig. 2 shows XRD analysis results of \( \text{Yb}_2\text{Si}_2\text{O}_7 \) bulk ceramics. As can be seen from Fig. 2a, the samples coated \( \text{NaVO}_3 \) powders have diffraction peaks of yttrium vanadate (\( \text{YbVO}_4 \)) and silicon dioxide (\( \text{SiO}_2 \)) in addition to \( \text{Yb}_2\text{Si}_2\text{O}_7 \) after corrosion, but \( \text{NaVO}_3 \) phase is not detected, and the influence of temperature change on XRD diffraction peaks is not evident. Fig. 2b is the XRD analysis results after the samples were corroded by \( \text{V}_2\text{O}_5 \) coating. \( \text{YbVO}_4 \) diffraction peaks appeared at all test temperatures. \( \text{V}_2\text{O}_5 \) phase remained in samples at 700\(^\circ\)C and 800\(^\circ\)C, while it was not detected after 900\(^\circ\)C corrosion, indicating that corrosive agent was consumed.
Fig. 2. XRD patterns of Yb₂Si₂O₇ corroded samples with NaVO₃ coating (a) and V₂O₅ coating (b) before hot corrosion

The SEM images of the corroded sample surfaces are shown in Fig. 3(a), (b) and (c) which were obtained at 700 °C, 800 °C and 900 °C respectively by coating NaVO₃ before hot corrosion. Two kinds of corroded products are observed with different morphology marked A and B in Fig. 3(a). The shape of the product A is rod with a tetrahedral cone at each end, while the product B is lamellar agglomeration. Also, the elemental compositions of A and B corroded products are different by EDS analyses and they were mainly composed by Yb, V and O at point A and Si and O at point B. After comprehensively analyzing with XRD results, the corroded products at A and B were identified as YbVO₄ and SiO₂ respectively.

Fig. 3 The SEM images of the corroded sample surfaces obtained at 700 °C (a), 800 °C (b) and 900 °C (c) respectively by coating NaVO₃ before hot corrosion and the EDS analysis results at point A (d) and B (e)
Fig. 4 The SEM images of the corroded sample surfaces obtained at 700°C (a), 800°C (b) and 900°C (c) respectively by coating V$_2$O$_5$ before hot corrosion and the EDS analysis results at point C (d) and D (e).

From the SEM images in Fig. 3(a), (b) and (c), the morphology changes of the corroded products YbVO$_4$ and SiO$_2$ are clearly different. The shape and size of YbVO$_4$ hardly changed with hot corrosion temperatures. While the morphology of SiO$_2$ agglomeration changed from lamellar at 700°C to bigger axiolitic at 800°C and then much bigger at 900°C.

Unlike the analysis results in Fig. 3, only YbVO$_4$ was obtained by coating V$_2$O$_5$ on Yb$_2$Si$_2$O$_7$ bulk ceramics at 700°C to 900°C and its shape was granular. From the images of Fig. 4 (a), (b) and (c), it can be seen that the size of YbVO$_4$ grains increased slightly with increasing test temperatures. Moreover, the V$_2$O$_5$ on the surface of the samples left more and thicker at 700°C, and the less residual V$_2$O$_5$ was in the form of a thin fluid after corrosion at 800°C and 900°C.

4. Discussion

The hot corrosion mechanism mainly includes the vulcanization and dilution processes [14]. The chemical reaction of vanadium compounds with metal oxides follows a Lewis acid-base dilution mechanism and the acid-base properties of metal oxides depend on the acidity and alkalinity of the reactants [15]. The acid-base dilution mechanism is widely used in ceramic materials. For example, the reaction of YSZ and T$_1$SiC$_2$ can be explained by this theory [16, 17]. According to this theory, Yb$_2$Si$_2$O$_7$ can be regarded as composed of Yb$_2$O$_3$ and SiO$_2$ in a ratio of 2:1, wherein SiO$_2$ is an acidic oxide, and the acidity or alkalinity of the metal oxide Yb$_2$O$_3$ mainly depends on the acid-base property of the molten salt.

For the weakly acidic NaVO$_3$, the corrosion product of YbVO$_4$ composed at 700°C to 900°C, is due to the reaction of acidic salt with Yb$_2$O$_3$. Therefore, the corrosion mechanism in that case can be described by the chemical equation (2).

$$\text{Yb}_2\text{Si}_2\text{O}_7 (s) + 2\text{NaVO}_3 (l) \rightarrow 2\text{YbVO}_4(s) + 2\text{SiO}_2(s) + \text{Na}_2\text{O}(s) \quad (2)$$

For strong acidic V$_2$O$_5$, the corrosion mechanism at 700°C to 900°C can be described by the chemical equation (3).

$$\text{Yb}_2\text{Si}_2\text{O}_7 (s) + 2\text{V}_2\text{O}_5 (l) \rightarrow 2\text{YbVO}_4(s) + 2\text{SiO}_2(s) + \text{Na}_2\text{O}(s) \quad (3)$$

As shown in Fig. 3 and Fig. 4, the corrosion product of YbVO$_4$ exhibited significant different
morphology. The crystal structure of YbVO$_4$ was reported to be similar to that of ZrO$_2$ [18, 19]. The growth mode of the YbVO$_4$ crystal having the ZrO$_2$ structure is a tetragonal prism and a tetragonal double-cone type, it is the reason why the YbVO$_4$ generated by the NaVO$_3$ corrosion reaction is a rod shape with pyramids at both ends. The crystal of YbVO$_4$ preferentially grows in the c-axis (0 0 1) direction as shown in Fig.5. However, according to research reports, the main driving force for crystal growth and morphological change is the reduction of surface energy. The order of the free energy of the ZrO$_2$ crystal plane is (0 0 1) < (1 1 0) < (1 1 2) [20]. At the same time, Chen and Rosenflanz [21] pointed out that driving force is essential for crystal elongation. Lower driving force leads to less nucleation rate and the possibility of crystal elongation is greater. Conversely, the greater the driving force, the higher the nucleation rate. So the possibility of crystal elongation is less. Under experimental conditions, the acidity of V$_2$O$_5$ is stronger than that of NaVO$_3$ and the driving force of the reaction is greater. Thus a large amount of crystallization nuclei will occur and a high nucleation rate will inhibit the growth of YbVO$_4$ crystal. Finally, granular YbVO$_4$ crystal are obtained. For the latter, only rod-like corrosion product of YbVO$_4$ can be obtained.

![Fig.5. Schematic diagram of the morphology of YbVO$_4$ crystal obtained on surface of Yb$_2$Si$_2$O$_7$ bulk ceramics coated by NaVO$_3$ [20]](image)

5. Conclusions

(1) The corrosion reaction at 700°C to 900°C for Yb$_2$Si$_2$O$_7$ bulk ceramics coated with NaVO$_3$ led to products of YbVO$_4$ and SiO$_2$ and their morphology were rod-shaped with tetrahedral pyramid at both ends and lamellar to axiolitic agglomeration, respectively.

(2) When Yb$_2$Si$_2$O$_7$ bulk ceramics were corroded by V$_2$O$_5$ at 700°C to 900°C, the morphology of corrosion product YbVO$_4$ was granular and its crystal size increased with the temperature rising. There was some V$_2$O$_5$ left on the surface of the Yb$_2$Si$_2$O$_7$ bulk ceramics.

(3) Under the experimental conditions, less crystal growth driving force resulted in lower nucleation rate for corrosion product YbVO$_4$ because the corrosion agent NaVO$_3$ shows weak acidic. So rod-like YbVO$_4$ was obtained and its size hardly changed. But strong acidic V$_2$O$_5$ led to greater crystal growth driving force. The nucleation rate of corrosion product YbVO$_4$ was higher and its shape changed to granular. The size of granular YbVO$_4$ increased with temperature rising, but the number decreased.

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