Reaction products of Sm2Zr2O7 with calcium-magnesium-aluminum-silicate (CMAS) and their evolution

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Abstract

During flight, many silicates (sand, dust, debris, fly ash, etc.) are ingested by an engine. They melt at high operating temperatures on the surface of Thermal barrier coatings (TBCs) to form calcium-magnesium-aluminum-silicate (CMAS) amorphous settling. CMAS erodes TBCs and causes many problems, such as composition segregation, degradation, cracking, and disbanding. As a new generation of TBC candidate materials, rare-earth zirconates (Sm$_2$Zr$_2$O$_7$) have good CMAS resistance properties. The reaction products of Sm$_2$Zr$_2$O$_7$ and CMAS and their subsequent changes were studied by the reaction of Sm$_2$Zr$_2$O$_7$ and excess CMAS at 1350°C. After 1 h of reaction, Sm$_2$Zr$_2$O$_7$ powders were not completely eroded. The reaction products were Sm-apatite and c-ZrO$_2$ solutions. After 4 h of reaction, all Sm$_2$Zr$_2$O$_7$ powders were completely eroded. After 24 h of reaction, Sm-apatite disappeared, and the c-ZrO$_2$ solution remained.

Introduction

TBCs are used to limit the heat transfer through coatings and protect vital engine components from hot corrosion. However, high operating temperatures result in the melting of any silicate (sand, dust, runway, debris, fly ash, volcanic ash, etc.) that may be ingested by an engine. These molten silicates, commonly referred to as CMAS (calcium-magnesium-aluminum-silicate), cause severe degradation of TBCs and premature delamination, exposing the metallic components to dangerous hot gases$^{[1,2,3]}$.

The most commonly used TBC composition is 7 wt.% yttria-stabilized zirconia (7YSZ). However, 7YSZ shows poor resistance to CMAS infiltration. Therefore, significant research has been performed on searching for new TBC materials with good CMAS resistance. As a new generation of thermal barrier coating candidate materials, rare-earth zirconates (such as Sm$_2$Zr$_2$O$_7$) not only have low thermal conductivity, appropriate thermal expansion coefficients and high thermal stability but also have better CMAS resistance properties than 7YSZ. The results studied by Krause show that rare earth zirconates can resist CMAS erosion in the early stage of the reaction$^{[4,5,6]}$.

Therefore, the reactions of rare-earth zirconates and CMAS have been studied extensively. Most of these studies are devoted to studying the reaction products of rare-earth zirconates and CMAS, such as the study of Hengbei Zhao$^{[7]}$. The results studied by Julie M. Drexler showed that Sm$_2$Zr$_2$O$_7$ and CMAS react to form Sm-apatite$^{[8]}$. However, little attention has been given to the element proportion and crystal structure of Sm-apatite. Furthermore, evidence from previous research showed that Sm$_2$Zr$_2$O$_7$ also deteriorated slowly by CMAS with increasing penetration time. This phenomenon may be related to subsequent changes in reaction products in excess CMAS. Therefore, the reaction products of CMAS and Sm$_2$Zr$_2$O$_7$ were accurately determined in this paper, and subsequent changes in the reaction products were also studied.

Experimental Procedures
Sm$_2$O$_3$ (99.9%, Forsman, Beijing, China) and ZrOCl$_2$·8H$_2$O (99.5%, Forsman, Beijing, China) were employed as raw materials to produce Sm$_2$Zr$_2$O$_7$ powders by chemical coprecipitation. Sm$_2$O$_3$ powders and ZrOCl$_2$·8H$_2$O were dissolved in nitric acid (mass fraction 65%~68%, Sinopharm Chemical Reagent Co, Shanghai, China) and deionized water, respectively. The obtained solution was mixed and stirred to generate a homogeneous solution, followed by cautious addition to ammonia water (mass fraction 25%~28%, Sinopharm Chemical Reagent Co, Shanghai, China) until a gel-like precipitate was obtained. The precipitate was filtered with distilled water repeatedly. After drying at 100°C for 24 h and calcination at 1250°C for 5 h for crystallization, the resultant powders were ground and sieved to remove the coarse agglomerates. Then, the required Sm$_2$Zr$_2$O$_7$ powders for this study were obtained.

CMAS with a composition of 38CaO-5MgO-8Al$_2$O$_3$-49SiO$_2$ in mole ratio was used in this study. CaO (≥99.7%, Aladdin, Shanghai, China), MgO (≥99.7%, Aladdin, Shanghai, China), Al$_2$O$_3$ (≥99.7%, Aladdin, Shanghai, China), SiO$_2$ (≥99.7%, Aladdin, Shanghai, China) were weighed in molar ratios and suspended in alcohol. The mixture was fully mixed by planetary ball milling with absolute alcohol for 72 h at a speed of 350 rpm. The suspension was dried, and the mixed powders were then calcined at 1550°C for 4 h and quenched in water. By repeating the above steps once, CMAS glass for this study was obtained. The Sm$_2$Zr$_2$O$_7$ powders were uniformly placed on the top surface of the CMAS glass, and then the samples were heat-treated at 1350 °C for 1 h, 4 h and 24 h before quenching in air at room temperature.

The phase composition of Sm$_2$Zr$_2$O$_7$ powders after reaction with CMAS was characterized by X-ray diffraction (XRD, X’Pert PRO MPD, PANalytical) using CuKα radiation. Data were digitally recorded in a continuous scan in the range of angles (2θ) from 10° to 80° with a scanning rate of 4°/min. The microstructure and composition of Sm$_2$Zr$_2$O$_7$ powders after reaction with CMAS were examined by scanning electron microscopy (SEM, Philips S-4800, Hitachi Ltd., Yokohama, Japan) equipped with an energy spectrum analyzer (EDS). The reaction product analysis and elemental mapping of Sm$_2$Zr$_2$O$_7$ powders with CMAS after reaction were performed using transmission electron microscopy (TEM, TECNAI G20, FEI, USA) with an energy dispersive spectrometer (EDS). The specimen used in TEM was prepared by a focused ion beam instrument (FIB, Crossbeam 540, Carl Zeiss, German).

### Results And Discussion

Fig. 1 shows the XRD pattern of the powders after reacting with Sm$_2$Zr$_2$O$_7$ and CMAS. Compared with the standard peak PDF card, two kinds of peaks of reaction products can be found in Fig. 1. One is basically the same as the standard peak of Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ (PDF#29-0365). The peaks of Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ offset to high angles because the Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ from the reaction has lattice distortion. The other peak is basically the same as the standard peak of c-ZrO$_2$ (PDF#26-0341). Therefore, there are only Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ and c-ZrO$_2$ in the reaction products. No Sm$_2$Zr$_2$O$_7$ remains in the powders.

The images and the EDS patterns of Sm$_2$Zr$_2$O$_7$ powders eroded for 1 h at 1350°C are shown in Fig. 2. As seen in Fig. 2(a), the powders after reacting from Sm$_2$Zr$_2$O$_7$ and CMAS have two morphological
characteristics. One is the partly eroded powder (P1), and the other is the completely eroded powder (P2). Fig. 2(b) is an enlarged view of the partly eroded powder. As seen in Fig. 2(b), the partly eroded powder includes the light center area (Z1) and the dark shell area (Z2). There is a dividing line between the light center area and the dark shell area. According to the EDS pattern, the dark shell area has Ca, Si, Zr, and Sm elements. The light center area has Zr and Sm but no Ca or Si elements. Ca and Si elements only exist in the dark shell area.

To determine the composition of the light center area, TEM was used to analyze the sample. The transmission electron microscope bright field image of the light center area is shown in Fig. 3(a). Fig. 3 (b) shows the electron diffraction pattern of area S1. As shown in Fig. 3 (b), the space group is Fm-3m. Combined with the elemental proportion of S1, it can be determined that S1 is Sm$_2$Zr$_2$O$_7$. Other areas in Fig. 3(a) are tested in the same way; they are all Sm$_2$Zr$_2$O$_7$. This suggests that the light center area with Ca and Si free area is not eroded by CMAS. This dividing line is the boundary of the reaction zone and unreactive zone. This proves that the reaction product protects the Sm$_2$Zr$_2$O$_7$ ceramic from CMAS erosion.

To study the effect of reaction products on erosion, the boundary areas of the reaction zone and unreactive zone are analyzed by TEM, and the results are shown in Fig. 4. Fig. 4 (a) is a transmission electron microscope bright field image of the reaction boundary areas close to Sm$_2$Zr$_2$O$_7$. As shown in Fig. 4 (a), there is an obvious boundary between two different micromorphologies. As shown in the dotted line in the figure. The energy spectrum of the S2 and S3 areas on both sides of the dotted line was analyzed. The results are shown in Table 1. No element of CMAS is found in area S2. Ca and Si elements of CMAS are found in area S3. S3 is SAED analyzed, and the results are shown in Fig. 4 (c). The space group is Fm-3m. However, the lattice constant and the included angle are different from the standard value. This suggests that Ca and Si enter the lattice of Sm$_2$Zr$_2$O$_7$ and cause lattice distortion. Therefore, S2 is Sm$_2$Zr$_2$O$_7$, and S3 is an erosion product. Fig. 4 (b) is a transmission electron microscope bright field image of the reaction boundary areas close to CMAS. As shown in Fig. 4 (b), there are some small grains with different sizes, which include some spherical crystal grains (S4) and some rod crystal grains (S5). The energy spectra of areas S4 and S5 are analyzed, and the results are shown in Table 1. S4 and S5 are SAED analyzed, and the results are shown in Fig. 4 (d) and Fig. 4 (e). The space group of S4 is P6$_3$/m, and the space group of S5 is Fm-3m. Combining the XRD results and elemental proportions of S4 and S5, it can be determined that the spherical crystal grain (S4) is Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ and the rod crystal grain (S5) is a c-ZrO$_2$ solution. The light color area of S6 is SAEDP analyzed, and the results are shown in Fig. 4 (f). The electron diffraction pattern of S6 is diffuse scattering, which infers that S6 is amorphous. The results of the energy spectrum of S6 are shown in Table 1. Ca, Si, Mg and Al elements of CMAS are found in area S6. Therefore, S6 is CMAS. Compared with the elemental proportions of C$_{38}$M$_5$A$_8$S$_{49}$ and S6, the contents of Ca in S6 decreased significantly. From 38 at.% to 5 at.%. The contents of Al and Si in S6 increased. S6 is surrounded by Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ and c-ZrO$_2$ solutions, which dissolve part of Ca from S6. This leads to the content of Ca in S6 decreasing significantly.
In addition, there are loose areas after the reaction in Fig. 2(b). To study why protection against CMAS fails, the loose areas after reaction are analyzed by TEM, and the results are shown in Fig. 5. Fig. 5(a) is a TEM bright field image of the loose area after the reaction. As shown in Fig. 5(a), unlike the reaction boundary areas, the grains in this area are relatively loose. There is a large amount of residual CMAS. The closer to the CMAS direction, the larger the grain size. Fig. 5(c) is a TEM high-power bright field image of the loose area after the reaction. The rod crystal grains (S7) are larger than those in Fig. 4. Areas S8 are spherical crystal grains, and S9 is CMAS. The results of the energy spectra of S4 and S5 are shown in Table 1. Zr, Sm and Ca are found in area S7. Sm and Ca, Si and Zr elements are found in area S8. S7 and S8 are SAEDP analyzed, and the results are shown in Fig. 5 (b) and Fig. 5 (d). Combined with the elemental proportions of S7 and S8, it can be determined that S7 is a c-ZrO$_2$ solution (the space group is Fm-3m) and S8 is Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ (the space group is P6$_3$/m). S9 is residual CMAS. Compared with the elemental proportions of C$_{38}$M$_{5}$A$_{8}$S$_{49}$ and S6, the content of Ca in S9 decreased significantly. This is consistent with S6. In addition, the content of Si in S9 Decreased from 49 at.% to 40.67 at.%. This is because Ca$_2$Sm$_8$(SiO$_4$)$_6$O$_2$ grain growth requires more Si from CMAS.

The usual apatite crystal (space group is P6$_3$/m) formula is $A_{I}^{x}A_{II}^{6}(SiO_4)_6O_x$. $A_{I}$ and $A_{II}$ are alkali metal ions ($A_{I}^{+}$), alkali earth metal ions ($A_{II}^{2+}$) or rare earth ions ($A_{III}^{3+}$). $X$ is determined by the ionic valence of $A$. The coordination numbers of $A_{I}$ and $A_{II}$ are 9 and 7, respectively. In Sm-apatite, $A_{I}$ tends to be occupied by Ca$^{2+}$ with a larger ion radius. $A_{II}$ tends to be occupied by Sm$^{3+}$ with a smaller ion radius. Because the radii of Ca$^{2+}$ (118 pm) and Sm$^{3+}$ (113 pm) are similar, Sm$^{3+}$ may account for up to half the seat of $A_{I}$. Therefore, it forms $A_{I}^{1.2}A_{II}^{6}(SiO_4)_6O_2$ Sm-apatite, and the formula is (Ca$_2$Sm$_2$)Sm$_6$(SiO$_4$)$_6$O$_2$. According to the energy spectrum, the content of Sm in apatite is high. There is a small amount of Zr in the Sm-apatite. This is because Zr$^{4+}$ may account for the seat of $A_{I}$ or $A_{II}$. The radius of Zr$^{4+}$ (72 pm) is smaller than those of Ca$^{2+}$ and Sm$^{3+}$. Therefore, Zr$^{4+}$ tends to occupy $A_{II}$. Due to the introduction of Zr$^{4+}$, to achieve charge conservation, the low valence cation should increase, and the high valence cation should decrease in $A_{I}$. Therefore, Ca$^{2+}$ in $A_{I}$ increases and Sm$^{3+}$ decreases in $A_{I}$. The change in the number of cations causes vacancies to appear in $A_{I}$. It can be inferred that the chemical formula of Sm-apatite is $(Ca_{1+x}Sm_{1-y}E_y)_6(SiO_4)_6O_2$, where E is the vacancy. In the following, it is called Sm-apatite for short.

The image of Sm$_2$Zr$_2$O$_7$ powders eroded for 4 h at 1350°C is shown in Fig. 6(a). As shown in Fig. 6(a), all Sm$_2$Zr$_2$O$_7$ powders are eroded by CMAS. There are no partly eroded powders with core-shell structures. Fig. 6(b) shows only rod crystal grains (Z5) and spherical crystal grains (Z6). The elements of Z5 and Z6 are shown in Table 2. According to the reaction results for 1 h, rod crystal grains (Z5) are c-ZrO$_2$ solution, and spherical crystal grains (Z6) are Sm-apatite. This suggests that all Sm$_2$Zr$_2$O$_7$ powders are completely eroded by CMAS after a 4 h reaction. In addition, compared with the results of reaction for 1 h, it can be found that the contents of Sm, Ca and Si in c-ZrO$_2$ solution decrease.

The image of Sm$_2$Zr$_2$O$_7$ powders eroded for 24 h at 1350°C is shown in Fig. 6(c). It can be found that there are only rod crystal grains in CMAS. No spherical crystal grains exist in this situation. The elements
of the spherical crystal grain (Z7 in Fig. 6(d)) are also shown in Table 2. Based on the previous results, the rod crystal grains are still c-ZrO$_2$ solutions. Compared with the results of the contents of elements in Z6, there is no Si in the c-ZrO$_2$ solution. The contents of Sm and Ca are reduced.

CMAS and Sm$_2$Zr$_2$O$_7$ react to form Sm-apatite and c-ZrO$_2$ solutions, which can block the diffusion of elements in CMAS at the beginning of the reaction. With increasing reaction time from 1 h to 4 h, the Sm$_2$Zr$_2$O$_7$ powders are completely eroded by CMAS. This is because of the excess CMAS in the reaction. Excessive CMAS makes the barrier fail. Compared with 1 h, the grains of the Sm-apatite and c-ZrO$_2$ solutions grew. However, from 4 h to 24 h, Sm-apatite gradually disappeared until it was gone completely. It is speculated that Sm-apatite is completely dissolved in excessive CMAS. The c-ZrO$_2$ solution remains.

According to the above process, the erosion model of excessive CMAS to Sm$_2$Zr$_2$O$_7$ material is established and shown in Fig. 7. First, CMAS melts at approximately 1200°C. Liquid CMAS spreads on the surface of Sm$_2$Zr$_2$O$_7$. Then, Ca and Si in CMAS mainly diffuse into Sm$_2$Zr$_2$O$_7$, which results in lattice distortion of Sm$_2$Zr$_2$O$_7$. Zr and Sm in Sm$_2$Zr$_2$O$_7$ also diffuse into CMAS at the same time. When the content of Zr in CMAS is greater than its solubility, Zr will reprecipitate from CMAS to form c-ZrO$_2$. A small amount of Sm and Ca dissolve in c-ZrO$_2$. A c-ZrO$_2$ solution is formed. Meanwhile, Sm, which diffuses from Sm$_2$Zr$_2$O$_7$, reacts with Ca and Si to form Sm-apatite. Because c-ZrO$_2$ solution grains are close to Sm-apatite grains, these grains constitute a dense barrier layer that can block the diffusion of the elements in CMAS. During the reaction, some small grains are devoured by large grains following Ostwald's rule. The c-ZrO$_2$ solution and Sm-apatite grains will grow. However, as the reaction time further increased, Sm-apatite gradually dissolved in CMAS. This may be because the solubility of Sm is higher than Zr in CMAS. Sm in Sm-apatite can diffuse into CMAS completely. However, Zr in c-ZrO$_2$ solution cannot. Therefore, only the c-ZrO$_2$ solution remains. The disappearance of Sm-apatite breaks the tight bond between the c-ZrO$_2$ solution and Sm-apatite. Therefore, the barrier layer will fail. CMAS will follow the above process and continue to erode Sm$_2$Zr$_2$O$_7$. It can be inferred that Sm$_2$Zr$_2$O$_7$ will be completely eroded if the reaction is long enough time. In the end, only some c-ZrO$_2$ solution grains remain.

**Conclusion**

The Sm$_2$Zr$_2$O$_7$ powders were uniformly placed on the top surface of the CMAS glass and heat-treated at 1350 °C for 1 h, 4 h and 24 h. After 1 h of reaction, Sm$_2$Zr$_2$O$_7$ powders were not completely eroded. Completely eroded powders and partly eroded powders with core-shell structures were formed. The reaction products were Sm-apatite and c-ZrO$_2$ solutions. Furthermore, because c-ZrO$_2$ solution grains were close to Sm-apatite grains, these grains constituted a dense barrier layer that can block the diffusion of the elements in CMAS. After 4 h of reaction, partly eroded powders disappeared, and all Sm$_2$Zr$_2$O$_7$ was eroded. The content of Sm-apatite in the reaction product decreased. The grains of Sm-apatite and c-ZrO$_2$ solution grew. After 24 h of reaction, Sm-apatite disappeared, and the c-ZrO$_2$ solution remained. The
disappearance of Sm-apatite broke the tight bond between the c-ZrO$_2$ solution and Sm-apatite, which is the main reason for barrier layer failure.

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Tables
Table 1

| at.% | Ca | Si | Sm    | Zr    | Mg | Al |
|------|----|----|-------|-------|----|----|
| S1   | -  | -  | 51.21 | 48.79 | -  | -  |
| S2   | -  | -  | 50.75 | 49.25 | -  | -  |
| S3   | 5.17 | 7.66 | 47.69 | 39.48 | -  | -  |
| S4   | 15.32 | 40.06 | 42.82 | 1.80 | -  | -  |
| S5   | 5.77 | - | 22.86 | 71.37 | -  | -  |
| S6   | 13.50 | 60.16 | -    | -    | 6.27 | 20.07 |
| S7   | 5.77 | - | 20.92 | 73.31 | -  | -  |
| S8   | 16.28 | 40.78 | 40.26 | 2.66 | -  | -  |
| S9   | 28.75 | 40.67 | 3.36 | -    | 7.34 | 19.88 |

Table 2

| at.% | Ca | Si | Sm    | Zr    | Mg | Al |
|------|----|----|-------|-------|----|----|
| Z1   | -  | -  | 51.11 | 48.89 | -  | -  |
| Z2   | 15.88 | 25.41 | 20.91 | 36.01 | -  | 1.79 |
| Z3   | 23.38 | 40.11 | 15.27 | 11.29 | 2.67 | 7.27 |
| Z4   | 12.61 | 11.43 | 9.41  | 62.10 | 1.81 | 2.64 |
| Z5   | 22.72 | 46.20 | 12.35 | 10.88 | 1.98 | 5.87 |
| Z6   | 8.77 | 3.53 | 7.63  | 80.06 | -  | -  |
| Z7   | 6.16 | -  | 4.78  | 89.06 | -  | -  |