Reaction products of $\text{Sm}_2\text{Zr}_2\text{O}_7$ 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 corrodes TBCs and causes many problems, such as composition segregation, degradation, cracking, and disbanding. As a new generation of TBC candidate materials, rare-earth zirconates (such as $\text{Sm}_2\text{Zr}_2\text{O}_7$) have good CMAS resistance properties. The reaction products of $\text{Sm}_2\text{Zr}_2\text{O}_7$ and CMAS and their subsequent changes were studied by the reaction of $\text{Sm}_2\text{Zr}_2\text{O}_7$ and excess CMAS at 1350 °C. After 1 h of reaction, $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were not completely corroded. The reaction products were Sm–apatite and c-ZrO₂ solid solution. After 4 h of reaction, all $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were completely corroded. After 24 h of reaction, Sm–apatite disappeared, and the c-ZrO₂ solid solution remained.

Keywords: $\text{Sm}_2\text{Zr}_2\text{O}_7$ ceramic; calcium–magnesium–aluminum–silicate (CMAS); reaction product; corrosion

1 Introduction

Thermal barrier coatings (TBCs) are used to limit the heat transfer through coatings and protect vital engine components from hot corrosion [1,2]. 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 [3,4]. These molten silicates, commonly referred to as calcium–magnesium–aluminum–silicate (CMAS), cause severe degradation of TBCs and premature delamination, exposing the metallic components to dangerous hot gases [5–7].

The most commonly used TBC composition is 7 wt% yttria-stabilized zirconia (7YSZ). However, 7YSZ shows poor resistance to CMAS infiltration [8–10]. 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 $\text{Sm}_2\text{Zr}_2\text{O}_7$) not only have low thermal conductivity [11–13], appropriate thermal expansion coefficients, and high thermal stability, but also have better CMAS resistance properties than 7YSZ [14,15]. The results studied by Li *et al.* [14] show that rare-earth zirconates can resist CMAS corrosion in the early stage of the reaction.

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

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rare-earth zirconates and CMAS, such as the study of Gok and Goller [15]. The results studied by Drexler *et al.* [16] show the reaction products of rare-earth zirconates and CMAS. However, little attention has been given to the element proportion and crystal structure of reaction products. Furthermore, evidence from previous research showed that rare-earth zirconates (such as $\text{Sm}_2\text{Zr}_2\text{O}_7$) also deteriorated slowly by CMAS with increasing penetration time [16–18]. This phenomenon may be related to subsequent changes in reaction products in excess CMAS. Therefore, the reaction products of CMAS and $\text{Sm}_2\text{Zr}_2\text{O}_7$ were accurately determined in this paper, and subsequent changes in the reaction products were also studied.

2 Experimental

Sm_2O_3 (99.9%; Forsman, Beijing, China) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99.5%; Forsman, Beijing, China) were employed as raw materials to produce $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders by chemical coprecipitation. Sm_2O_3 powders (80–120 μm) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved in nitric acid (mass fraction 65%–68%; Sinopharm Chemical Reagent Co., Shanghai, China) and deionized water, respectively [19]. 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 $^\circ\text{C}$ for 24 h and calcination at 1250 $^\circ\text{C}$ for 5 h for crystallization, the resultant powders were ground and sieved to remove the coarse agglomerates [20]. Then, the $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were obtained. The agglomerated $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were obtained from $\text{Sm}_2\text{Zr}_2\text{O}_7$ powder centrifugal spray granulation by centrifugal spray drying machine (LGZ-8, DongSheng, China). And agglomerated $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were spheroidized by the plasma spray gun (SG-100, USA) to obtain spherical $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders. The spheroidization parameters are shown in Table 1. Then, the spherical $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were sieved to obtain powders with uniform particle size (60–90 μm).

Table 1 Spheroidization parameters

Current (A)	Primary gas (SCFH)	Auxiliary gas (SCFH)	Carrier gas (SCFH)	Powder feeding rate (r/min)	Spraying distance (mm)
900	80	40	90	2.5	200

SCFH: standard cubic foot per hour.

CMAS with a composition of 38CaO–5MgO–8AlO_{1.5}–49SiO₂ in molar ratio was used in this study [21–23]. CaO ($\geq 99.7\%$; Aladdin, Shanghai, China), MgO ($\geq 99.7\%$; Aladdin, Shanghai, China), Al₂O₃ ($\geq 99.7\%$; Aladdin, Shanghai, China), and SiO₂ ($\geq 99.7\%$; 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 $^\circ\text{C}$ for 4 h and quenched in water [21,22]. By repeating the above steps once, CMAS glass for this study was obtained. As presented in Fig. 1, the $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders were uniformly placed on the top surface of the CMAS glass in a Pt-crucible. And the mass ratio of CMAS and $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders is 10:1. Then the samples were heat-treated at 1350 $^\circ\text{C}$ for 1, 4, and 24 h. Above 1200 $^\circ\text{C}$, CMAS gradually softens and melts [24]. $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders enter CMAS under the action of gravity, and are evenly wrapped by CMAS. This method is beneficial to the uniform distribution of $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders in CMAS.

The phase composition of $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders after reaction with CMAS was characterized by X-ray diffraction (XRD; X' Pert PRO MPD, PANalytical, the Netherlands) using Cu K α radiation. Data were digitally recorded in a continuous scan in the range of angles (2θ) from 10 $^\circ$ to 80 $^\circ$ with a scanning rate of 4 ($^\circ$)/min. The microstructure and composition of $\text{Sm}_2\text{Zr}_2\text{O}_7$ 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. The reaction product analysis and elemental mapping of $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders with CMAS after reaction were performed using transmission electron microscopy (TEM; TECNAI G²20, FEI, USA) with an energy dispersive spectrometer (EDS; TECNAI G²20, FEI, USA). The specimen used in TEM was prepared by a focused ion beam instrument (FIB; Crossbeam 540, Carl Zeiss, Germany).

Fig. 1 Schematic diagram of the experimental method.

3 Results and discussion

Figure 2 shows the XRD patterns of the powders after reacting with $\text{Sm}_2\text{Zr}_2\text{O}_7$ and CMAS. Compared with the standard peak PDF card, two kinds of peaks of reaction products can be found in Fig. 2. One is basically the same as the standard peak of $\text{Ca}_2\text{Sm}_8(\text{SiO}_4)_6\text{O}_2$ (PDF#29-0365). The peaks of $\text{Ca}_2\text{Sm}_8(\text{SiO}_4)_6\text{O}_2$ offset to high angles because the $\text{Ca}_2\text{Sm}_8(\text{SiO}_4)_6\text{O}_2$ 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 $\text{Ca}_2\text{Sm}_8(\text{SiO}_4)_6\text{O}_2$ and c-ZrO_2 in the reaction products. No $\text{Sm}_2\text{Zr}_2\text{O}_7$ remains in the powders.

The images and the EDS patterns of $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders corroded for 1 h at 1350 °C are shown in Fig. 3. As seen in Fig. 3(a), the powders after reacting from $\text{Sm}_2\text{Zr}_2\text{O}_7$ and CMAS have two morphological characteristics. One is the partly corroded-powder (P1), and the other is the completely corroded-powder (P2). P1 accounts for about 70% of corroded-powders, and P2 accounts for about 30%. Figure 3(b) is an enlarged view of P1. As seen in Fig. 3(b), P1 includes the light

Fig. 2 XRD patterns of the powders after reacting with $\text{Sm}_2\text{Zr}_2\text{O}_7$ and CMAS.

Fig. 3 Images and EDS patterns of $\text{Sm}_2\text{Zr}_2\text{O}_7$ powders corroded for 1 h at 1350 °C.

center area (Z1) and the dark shell area (Z2). There is a dividing line between Z1 and Z2, as shown by the blue dotted line. According to the EDS pattern, Z2 has Ca, Si, Zr, and Sm elements. Z1 has Zr and Sm but no Ca or Si elements. Ca and Si elements only exist in Z2.

To determine the composition of Z1, TEM was used to analyze the sample. The TEM bright field image of the light center area is shown in Fig. 4(a). Figure 4(b) shows the electron diffraction pattern of area S1. As shown in Fig. 4(b), the space group is $Fm-3m$. Combined with the elemental proportion of S1, it can be determined that S1 is $\text{Sm}_2\text{Zr}_2\text{O}_7$. Other areas in Fig. 4(a) are tested in the same way, and they are all $\text{Sm}_2\text{Zr}_2\text{O}_7$. This suggests that Z1 with Ca and Si free area is not corroded by CMAS. This dividing line is the boundary of the reaction zone and unreactive zone. This proves that the reaction product protects the $\text{Sm}_2\text{Zr}_2\text{O}_7$ ceramic from CMAS corrosion.

To study the effect of reaction products on corrosion, the boundary areas of the reaction zone and unreactive zone close to $\text{Sm}_2\text{Zr}_2\text{O}_7$ are analyzed by TEM, and the results are shown in Fig. 5. Figure 5(a) is a TEM bright field image of the reaction boundary areas close to $\text{Sm}_2\text{Zr}_2\text{O}_7$. As shown in Fig. 5(a), there is an obvious boundary between two different micromorphologies. As shown in the dotted line in Fig. 5, the energy spectrum of the S2 and S3 areas was analyzed, and the results are shown in Table 2. No element of CMAS is found in area S2. S2 is $\text{Sm}_2\text{Zr}_2\text{O}_7$. A small amount of Ca and Si elements of CMAS are found in area S3. S3 is SAED analyzed, and the results are shown in Fig. 5(b). The space group is $Fm-3m$. However, the lattice constant and the included angle are different from the standard value of $\text{Sm}_2\text{Zr}_2\text{O}_7$. This suggests that Ca and Si enter the lattice of $\text{Sm}_2\text{Zr}_2\text{O}_7$ and cause lattice distortion [25]. Therefore, S3 is the Si–Ca– $\text{Sm}_2\text{Zr}_2\text{O}_7$ solid solution.

Fig. 4 (a) TEM image and (b) electron diffraction pattern of the light center.

Fig. 5 (a) TEM image and (b) electron diffraction pattern of the boundary areas close to $\text{Sm}_2\text{Zr}_2\text{O}_7$.

Table 2 Energy spectra of S1–S8

	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

Figure 6 is a TEM bright field image of the reaction boundary areas close to CMAS. As shown in Fig. 6(a), 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 2. S4 and S5 are SAED analyzed, and the results are shown in Figs. 6(b) and 6(c). 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 S4 is $\text{Ca}_2\text{Sm}_8(\text{SiO}_4)_6\text{O}_2$ and S5 is a $c\text{-ZrO}_2$ solid solution.

The light color area of S6 is SAED analyzed, and the results are shown in Fig. 6(d). 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 2. Ca, Si, Mg, and Al elements of CMAS are found in area S6. Therefore, S6 is CMAS. As can be seen in Table 2, the content of Ca in S6 is 13.5 at%. Compared with the elemental proportions of $\text{C}_{38}\text{M}_5\text{A}_8\text{S}_{49}$, the content of Ca in S6 decreases significantly. S6 is surrounded by $\text{Ca}_2\text{Sm}_8(\text{SiO}_4)_6\text{O}_2$ and $c\text{-ZrO}_2$ solid solution, 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. 3(b). To study why protection against CMAS fails, the loose areas after reaction are analyzed by TEM, and the results are shown in Fig. 7. Figure 7(a) is a

Fig. 6 (a) TEM image of the boundary areas close to CMAS, (b) selected area electron diffraction pattern of S4, (c) selected area electron diffraction pattern of S5, and (d) selected area electron diffraction pattern of S6.

Fig. 7 (a) TEM image of the loose areas after reaction, (b) enlarged TEM view of the loose area after the reaction, (c) selected area electron diffraction pattern of S7, and (d) selected area electron diffraction pattern of S8.

TEM bright field image of the loose area after the reaction. As shown in Fig. 7(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. Figure 7(b) 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. 6. Area S8 is deformed aspherical crystal grains, and S9 is CMAS. The results of the energy spectra of S7 and S8 are shown in Table 2. Zr, Sm, and Ca are found in area S7. Sm, Ca, Si, and Zr elements are found in area S8. S7 and S8 are SAEDP (selected area electron diffraction pattern) analyzed, and the results are shown in Figs. 7(c) and 7(d). Combined with the elemental proportions of S7 and S8, it can be determined that S7 is a c-ZrO₂ solid solution (the space group is *Fm-3m*) and S8 is Ca₂Sm₈(SiO₄)₆O₂ (the space group is *P6₃/m*). S9 is residual CMAS. Compared with the elemental proportions of C₃₈M₅A₈S₄₉ and S6, the content of Ca in S9 decreases significantly. This is consistent with S6. In addition, the content of Si in S9 decreases from 49 to 40.67 at%. This is because Ca₂Sm₈(SiO₄)₆O₂ grain growth requires more Si from CMAS.

The common apatite crystal (space group is *P6₃/m*) formula is A₄A₆^{II}(SiO₄)₆O_x [26]. A^I and A^{II} are alkali metal ions (A^{I+}), alkali earth metal ions (A²⁺), or rare earth ions (A³⁺), and *x* is determined by the ionic valence of A. The coordination numbers of A^I and A^{II} are 9 and 7 [27], respectively. In Sm-apatite, A^I tends

to be occupied by Ca²⁺ with a larger ion radius. A^{II} tends to be occupied by Sm³⁺ with a smaller ion radius. Because the radii of Ca²⁺ (118 pm) [28] and Sm³⁺ (113 pm) [29] are similar, Sm³⁺ may account for up to half the seat of A^I. Therefore, it forms A₂A₈^{II}(SiO₄)₆O₂ Sm-apatite, and the formula is (Ca₂Sm₂)Sm₆(SiO₄)₆O₂. 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 Zr⁴⁺ may account for the seat of A^I or A^{II}. The radius of Zr⁴⁺ (72 pm) [30] is smaller than those of Ca²⁺ and Sm³⁺. Therefore, Zr⁴⁺ tends to occupy A^{II}. Due to the introduction of Zr⁴⁺, to achieve charge conservation, the low valence cation should increase and the high valence cation should decrease in A^I. Therefore, Ca²⁺ in A^I increases and Sm³⁺ in A^I decreases. And 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-x})(Sm_{1-x}Zr_x)₆(SiO₄)₆O₂, where E is the vacancy. In the following, it is called Sm-apatite for short.

The image of Sm₂Zr₂O₇ powders corroded for 4 h at 1350 °C is shown in Fig. 8(a). As shown in Fig. 8(a), all Sm₂Zr₂O₇ powders are corroded by CMAS. There are no P1 with core-shell structures. Figure 8(b) shows only rod crystal grains (Z5) and spherical crystal grains (Z6). The elements of Z5 and Z6 are shown in Table 3. According to the reaction results for 1 h, Z5 are Sm-apatite, and Z6 are c-ZrO₂ solid solution. This suggests that all Sm₂Zr₂O₇ powders are completely corroded by CMAS after a 4 h reaction. In addition,

Fig. 8 (a) Image of Sm₂Zr₂O₇ powders corroded for 4 h at 1350 °C, (b) partial enlarged view of (a), (c) image of Sm₂Zr₂O₇ powders corroded for 24 h at 1350 °C, and (d) partial enlarged view of (c).

Table 3 Elements of Z1–Z8

	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	—	—

compared with the results of reaction for 1 h, it can be found that the contents of Sm, Ca, and Si in c-ZrO₂ solid solution decrease.

The image of Sm₂Zr₂O₇ powders corroded for 24 h at 1350 °C is shown in Fig. 8(c). It can be found that there are only Z5 in CMAS. No S4 exist in this situation. The elements of Z7 (in Fig. 8(d)) are also shown in Table 3. Based on the previous results, the Z5 are still c-ZrO₂ solid solution. Compared with the results of the contents of elements in Z6, there is no Si in the c-ZrO₂ solid solution. The contents of Sm and Ca are reduced.

CMAS and Sm₂Zr₂O₇ react to form Sm-apatite and c-ZrO₂ solid solution, which can block the diffusion of the elements in CMAS at the beginning of the reaction. With increasing reaction time from 1 h to 4 h, the Sm₂Zr₂O₇ powders are completely corroded by CMAS. This is because of the excess CMAS in the reaction.

Excessive CMAS makes the barrier fail. Compared with 1 h sample, the grains of the Sm-apatite and c-ZrO₂ solid solution grew. However, from 4 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-ZrO₂ solid solution remains.

According to the above process, the corrosion model of excessive CMAS to Sm₂Zr₂O₇ material is established and shown in Fig. 9. First, CMAS melts at approximately 1200 °C [24]. Liquid CMAS spreads on the surface of Sm₂Zr₂O₇. Then, Ca and Si in CMAS mainly diffuse into Sm₂Zr₂O₇, which results in lattice distortion of Sm₂Zr₂O₇. Zr and Sm in Sm₂Zr₂O₇ 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-ZrO₂. A small amount of Sm and Ca dissolve in c-ZrO₂. A c-ZrO₂ solid solution is formed. Meanwhile, Sm, which diffuses from Sm₂Zr₂O₇, reacts with Ca and Si to form Sm-apatite. Because c-ZrO₂ solid solution grains are close to Sm-apatite grains, Sm-apatite and c-ZrO₂ solid solution 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 [31]. The c-ZrO₂ solid 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

Fig. 9 Corrosion model of excessive CMAS to Sm₂Zr₂O₇, (a) initial stage of corrosion, (b) middle stage of corrosion, (c) late stage of corrosion, and (d) initial stage of a new round corrosion.

than that of Zr in CMAS. Sm in Sm-apatite can diffuse into CMAS completely. However, Zr in c-ZrO₂ solid solution cannot. Therefore, only the c-ZrO₂ solid solution remains. The disappearance of Sm-apatite breaks the tight bond between the c-ZrO₂ solid solution and Sm-apatite. Therefore, the barrier layer will fail. CMAS will follow the above process and continue to corrode Sm₂Zr₂O₇. It can be inferred that Sm₂Zr₂O₇ will be completely corroded if the reaction time is long enough. In the end, only some c-ZrO₂ solid solution grains remain.

4 Conclusions

The Sm₂Zr₂O₇ powders were uniformly placed on the top surface of the CMAS glass and heat-treated at 1350 °C for 1, 4, and 24 h. After 1 h of reaction, Sm₂Zr₂O₇ powders were not completely corroded. P2 and P1 with core-shell structures were formed. The reaction products were Sm-apatite and c-ZrO₂ solid solution. Furthermore, because c-ZrO₂ solid solution grains were close to Sm-apatite grains, Sm-apatite and c-ZrO₂ solid solution constituted a dense barrier layer that can block the diffusion of the elements in CMAS. After 4 h of reaction, partly corroded powders disappeared, and all Sm₂Zr₂O₇ was corroded. The content of Sm-apatite in the reaction product decreased. The grains of Sm-apatite and c-ZrO₂ solid solution grew. After 24 h of reaction, Sm-apatite disappeared, and the c-ZrO₂ solid solution remained. The disappearance of Sm-apatite broke the tight bond between the c-ZrO₂ solid solution and Sm-apatite, which is the main reason for barrier layer failure.

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