

Article

Interactions Between Sc_2O_3 Ceramics and Calcium–Magnesium–Alumina–Silicate (CMAS) at Elevated Temperature

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Abstract: The thermochemical interactions of Sc_2O_3 ceramics with CMAS at 1250 °C and 1300 °C were investigated in this paper. A continuously dense reaction layer (DRL) forms on the surface of the ceramic at the beginning of the reaction within 15 min, and temperature significantly affects the components of the DRL. The DRL is mainly composed of a diopside phase at 1250 °C, whose thickness decreases with reaction time, while it is composed of garnet and minor diopside phases at 1300 °C, and thickens in accordance with the parabolic law with exposure time. The DRL shows good effect on alleviating Mg^{2+} infiltration and some mitigating effect to Al^{3+} , and relatively inferior resistance to Ca^{2+} and Si^{4+} penetration. The concentration of Sc^{3+} in the residual CMAS increases with reaction temperature and time, and the average contents are about 0.7 at% and 3.7 at% after reactions at 1250 °C and 1300 °C, respectively. The mechanism is discussed systematically.

Keywords: Sc_2O_3 ; CMAS; thermochemical interaction; DRL; infiltration



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1. Introduction

Thermal barrier coatings (TBCs) are widely applied to gas turbine engines, resulting from the advantages of effectively insulating and protecting hot components during service [1,2]. The 7–8 wt.% yttria-stabilized zirconia (YSZ) is one of the current commercial TBC materials for excellent mechanical properties [3,4]. However, it is difficult for YSZ to meet the operating temperature requirement with the development of the advanced gas turbine engine. Particularly, the CMAS glass formed by environmental deposits such as sand and dust in the air will melt, penetrate and damage the YSZ coating through dissolution-precipitation within a very short period, leading to phase transition, stress cracking and eventual failure of the TBC [5–7]. This significantly damages the service performance and safety of the TBC. It is urgent to propose a new strategy or develop new TBCs to be used against molten CMAS attack.

Extensive research has been conducted to reduce CMAS infiltration and corrosion, including modification of the compositions and microstructures of the coatings [8,9], the application of overlaid protective coatings [10,11] and the development of novel ceramic coating materials [12,13]. It is reported that co-doping Sc_2O_3 – Y_2O_3 or co-doping Yb_2O_3 – Y_2O_3 in ZrO_2 exhibit superior phase stability and can significantly reduce CMAS corrosion

and infiltration compared to YSZ [14,15]. The former is attributed to the low solubility of Sc^{3+} as well as its weak affinity with Ca^{2+} , while the latter is a result of the low diffusion rate of Yb^{3+} in CMAS. The zirconates with a high concentration of RE_2O_3 (RE means the rare earth elements), such as $\text{La}_2\text{Zr}_2\text{O}_7$ [16,17], $\text{Gd}_2\text{Zr}_2\text{O}_7$ [18,19] and $\text{Y}_2\text{Zr}_2\text{O}_7$ [20], also show exceptional CMAS infiltration owing to forming a dense reaction layer (DRL) composed of an RE-apatite phase ($\text{Ca}_4\text{RE}_6(\text{SiO}_4)_6\text{O}$ or $\text{Ca}_2\text{RE}_8(\text{SiO}_6)_6\text{O}_2$) after the reaction of $\text{RE}_2\text{Zr}_2\text{O}_7$ and CMAS. The modification in microstructures of the coatings also show meaningful academic reference for the development of TBCs.

Overlayered protective coatings, such as Al_2O_3 [21,22], Y_2O_3 [23] and Pt [24,25], are also feasible methods to mitigate the attack of CMAS at high temperature. The overlayer can rapidly react with CMAS to form a continuous DRL composed of anorthite or an RE-apatite phase, which can greatly inhibit the CMAS infiltration and corrosion for weak wettability to the melt. Other materials such as RE-silicates [26,27], $\text{Ba}_2\text{REAlO}_5$ [28,29], $\text{BaLn}_2\text{Ti}_3\text{O}_{10}$ [30], $\text{LaMgAl}_{11}\text{O}_{19}$ [31,32], LnPO_4 (Ln refers to the rare earth lanthanides) [33], $\text{La}_2\text{Ce}_2\text{O}_7$ [34], YAlO_3 [35] and RE high-entropy ceramics [36,37] also can reduce the high-temperature penetration and corrosion of CMAS by forming an RE-apatite or anorthite DRL. In addition, the reaction of the coatings with CMAS leads to composition change and crystallization of the melts, which further inhibits CMAS infiltration [21,23]. The RE-apatite or anorthite DRL shows effective resistance to the molten CMAS attack, which is regarded as a promising method to protect against the penetration and corrosion of CMAS.

According to the present reports, zirconate doped with rich RE_2O_3 remains a valuable TBC material for its superior mechanical property and excellent resistance to infiltration and corrosion of CMAS [13,20]. Particularly, the addition of Sc_2O_3 can obviously enhance the phase stability and CMAS corrosion resistance of ZrO_2 -based materials. Wang [38,39] reported that the co-doping 2 mol.% Sc_2O_3 –16 mol.% CeO_2 in ZrO_2 shows better tetragonal phase (t-phase) stability and resistance to infiltration and corrosion of CMAS compared to YSZ, resulting from the low solubility of Sc^{3+} and chemical inertness of Ce^{2+} in CMAS. Fan [40] and Liao [41] revealed that co-doping Sc_2O_3 – Y_2O_3 in ZrO_2 exhibits good CMAS infiltration and corrosion resistance owing to the low solubility of Sc^{3+} , the difference in chemical potential and the poor affinity of Sc^{3+} with Ca^{2+} . Sc_2O_3 -based multi- R_2O_3 doping ZrO_2 still is an effective design for the new TBC ceramics for excellent comprehensive performance.

The addition of Sc_2O_3 is a feasible method for improving the resistance to melt corrosion of ZrO_2 -based TBCs due to the special properties of Sc^{3+} . However, research on the resistance of Sc_2O_3 to CMAS corrosion is relatively scarce, and its reaction products with CMAS, its effect against CMAS corrosion as well as its mechanism of corrosion resistance still need to be further investigated and improved. Therefore, it is of great significance to explore the thermochemical reaction of Sc_2O_3 with CMAS for the formation kinetics of the DRL and its inhibition on the infiltration of the melt. Aiming to reveal the thermochemical interactions of the Sc_2O_3 ceramic with the melt, the reaction products and penetration behavior of the CMAS at 1250 °C and 1300 °C are systematically investigated in this work. The growing of the DRL and its effect on inhibiting the melt infiltration also are analyzed. The interaction mechanism is discussed in detail.

2. Experimental Design

2.1. Ceramic Samples and CMAS Preparation

The Sc_2O_3 powders (99.9%, Aladdin reagents Co., Ltd., Shanghai, China) were cold-pressed at 250 MPa for 10 min to prepare a disc with dimensions of around $\varnothing 15 \text{ mm} \times 2 \text{ mm}$. Then, the Sc_2O_3 discs were sintered in a furnace at 1600 °C for 5 h to obtain a ceramic pellet. The chemical composition of glass CMAS in this work was

33CaO-9MgO-13AlO_{1.5}-45SiO₂ [42] (mol.%). The CaO, Si₂, Al₂O₃ and MgO powders (Aladdin Reagents Ltd.) were slurry-mixed with appropriate molar ratios thoroughly in full ethyl alcohol, through ball-milling for 6 h at 300 rph, followed by drying for 6 h, then annealed at 1300 °C for 4 h to form a transparent glass block. After crushing, grinding and 200 mesh sieve filtering, glass CMAS powder was obtained.

The Sc₂O₃ ceramics were uniformly coated by CMAS, and the content was 20 mg/cm². Then, the samples were heat-treated at various temperatures (1250 °C and 1300 °C) for 15 min, 4 h, 8 h and 24 h, respectively. To further understand the thermochemical behaviors and the reaction products between the Sc₂O₃ and CMAS, the mixture of the CMAS–Sc₂O₃ powders (1:1 wt.%) was heat-treated at 1250 °C and 1300 °C for different times (15 min and 4 h). Here, a furnace (KSL-1700X, MTI, Richmond, CA, USA) was used for the thermal reaction tests.

2.2. Characterizations

An X-ray diffractometer (XRD, Rigaku D/MAX2500V, Tokyo, Japan, Cu K α radiation) with a scan rate of 6°/min was used to identify the phase constitution of the sample after the high-temperature reaction. The cross-sectional morphology of Sc₂O₃ ceramics sheets after reaction with CMAS was examined by a PhenomProx type integrated scanning electron microscope (FESEM, SU8020, HITACHI, Tokyo, Japan), and energy dispersive spectroscopy (EDS, OXFORD X-MAX 80, Birmingham, UK) was used to observe the elements' distribution. Simultaneously, the reaction behavior of Sc₂O₃ with CMAS powder (1:1, wt.%) was carried out in air by differential scanning calorimetry (DSC, STA 449F3, NETZSCH, Selb, Germany) from room temperature to 1450 °C at a rate of 10 °C/min to further understand the thermochemical behaviors between Sc₂O₃ and CMAS.

3. Results and Discussion

3.1. Phase Analysis

The phase constituents of each set of the mixed powders of Sc₂O₃–CMAS (1:1 wt.%) under high temperatures for different times are shown in Figure 1. According to Figure 1a, the diopside (CaMgSi₂O₆, PDF#086-0932) and garnet (Ca₃Sc₂Si₃O₁₂, PDF#04-008-4631) phases and minor Sc₂Si₂O₇ (PDF#031-1225) phase are observed in the Sc₂O₃–CMAS mixed powder after reaction for 15 min, and Sc₂O₃ (PDF#023-1402) is still detected after reaction with CMAS at elevated temperature. The phases of the mixture after exposure for 4 h is similar to that after reaction for 15 min (Figure 1b), showing that the reaction of the Sc₂O₃–CMAS mixed powder is not drastic [43]. Note that the amount of the diopside phase is more than that of the garnet according to the higher diffraction peaks of diopside around 25–35°. It is indicated that the reaction of the mixed powder mainly causes CMAS crystallization when below 1300 °C. Furthermore, Sc-apatite could not be detected in Figure 1, resulting from the low reactivity of Sc₂O₃ in the CMAS and the poor affinity between the Ca²⁺ and Sc³⁺ [41,44]. The whole reactions are summarized as:

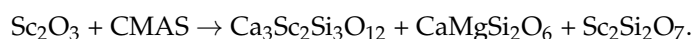


Figure 2 shows the reaction products of the reactions of the Sc₂O₃ ceramics with CMAS for different times at 1250 °C and 1300 °C. The samples are of single Sc₂O₃ phase before reaction (Figure 2a). According to Figure 2b, the products are the main diopside, minor garnet and anorthite (CaAl₂Si₂O₈, PDF#073-0264) phases on the surfaces of the ceramics after interactions at 1250 °C, while they are the diopside and garnet at 1300 °C (Figure 2c). Moreover, the reaction products of the ceramics with the melt are different to those of mixed powder, which is attributed to the different thermochemical reaction.

For the Sc_2O_3 ceramics, the anorthite phase is formed owing to the composition change to the melts [44]. Additionally, it has been reported that $\text{Sc}_2\text{Si}_2\text{O}_7$ will react with CMAS to form $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$ [45]. The formation of the DRL and the reduction in the grain boundary owing to the grain coarsening limit the diffusion of Sc^{3+} , leading to a decrease in the diffusion flux of Sc^{3+} . Combined with the low solubility of the Sc^{3+} in CMAS [40,41], the small amount of $\text{Sc}_2\text{Si}_2\text{O}_7$ formed in CMAS subsequently disappeared by continuing to react with CMAS to form garnet. It can be seen that the amount of diopside phase decreases, when the garnet phase increases with higher temperature. This is related to the gradual dissolution of the diopside phase [46]. Furthermore, Sc_2O_3 also exists after reaction with CMAS. It is a result of the low reactivity of Sc^{3+} in CMAS [40]. The reactions are summarized as:

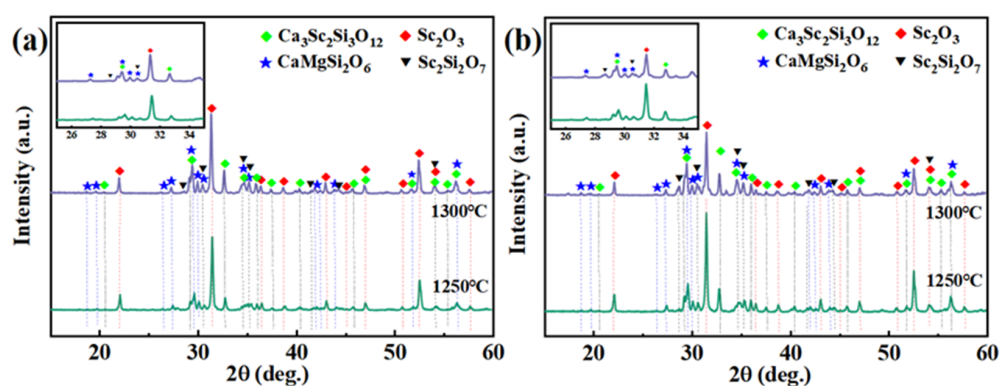


Figure 1. XRD patterns of mixed powders with Sc_2O_3 –CMAS (1:1 wt.%) after reaction at 1250 °C and 1300 °C for (a) 15 min and (b) 4 h.

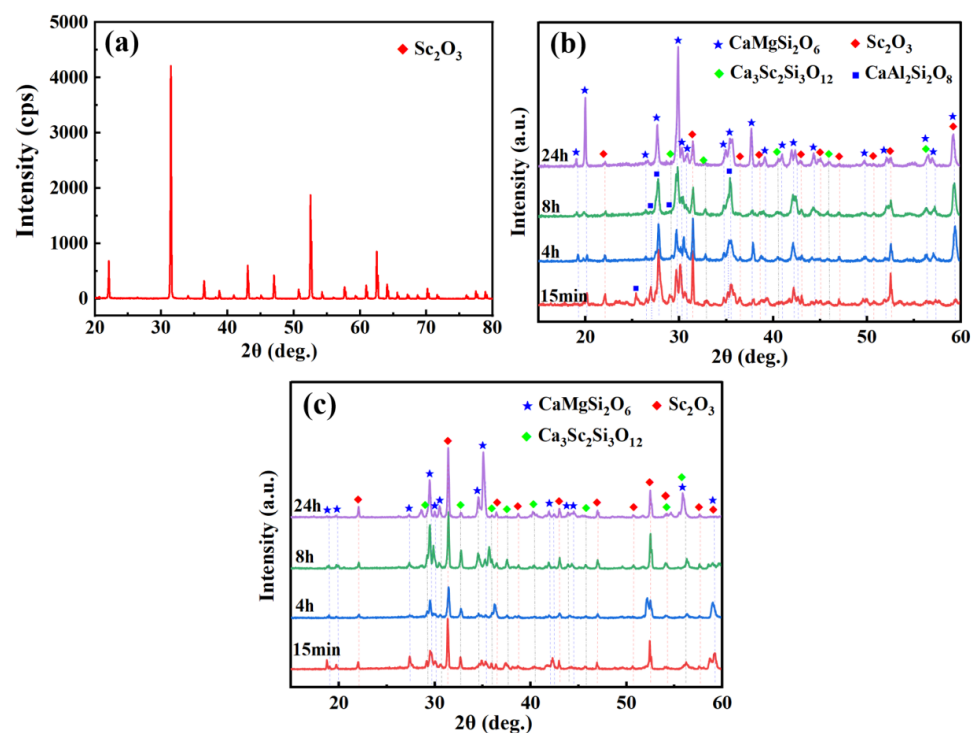


Figure 2. XRD patterns of the Sc_2O_3 ceramics after reaction with the melt for different times. (a) Sc_2O_3 ceramic, (b) 1250 °C and (c) 1300 °C.

3.2. Interactions of CMAS/ Sc_2O_3

The SEM graphs of the Sc_2O_3 ceramics after reaction with the melt at 1250 °C are presented in Figure 3 (the symbol “+” is used to highlight the zones, and the number is the name for the zones). It is clear that a distinct continuous DRL forms at the boundary of the Sc_2O_3 ceramic and CMAS. The DRL is mainly composed of the diopside phase (corresponding to regions #4, 8, 12 and 15 in Figure 3 and Table 1). The rod-like or block-like crystallization phases in CMAS mainly are diopside and a small amount of anorthite, which vertically grow into the CMAS. The diopside phase shows coarsening during the initial reaction stage, while it shows a short/small lumpy phase after long exposure. The diopside phase undergoes dissolution during reaction [46]. It is worth noting that no anorthite phase can be detected after reaction for 24 h, while it can be observed within 8 h (Figure 3a–c), indicating that the diopside and anorthite show poor thermostability in the molten CMAS.

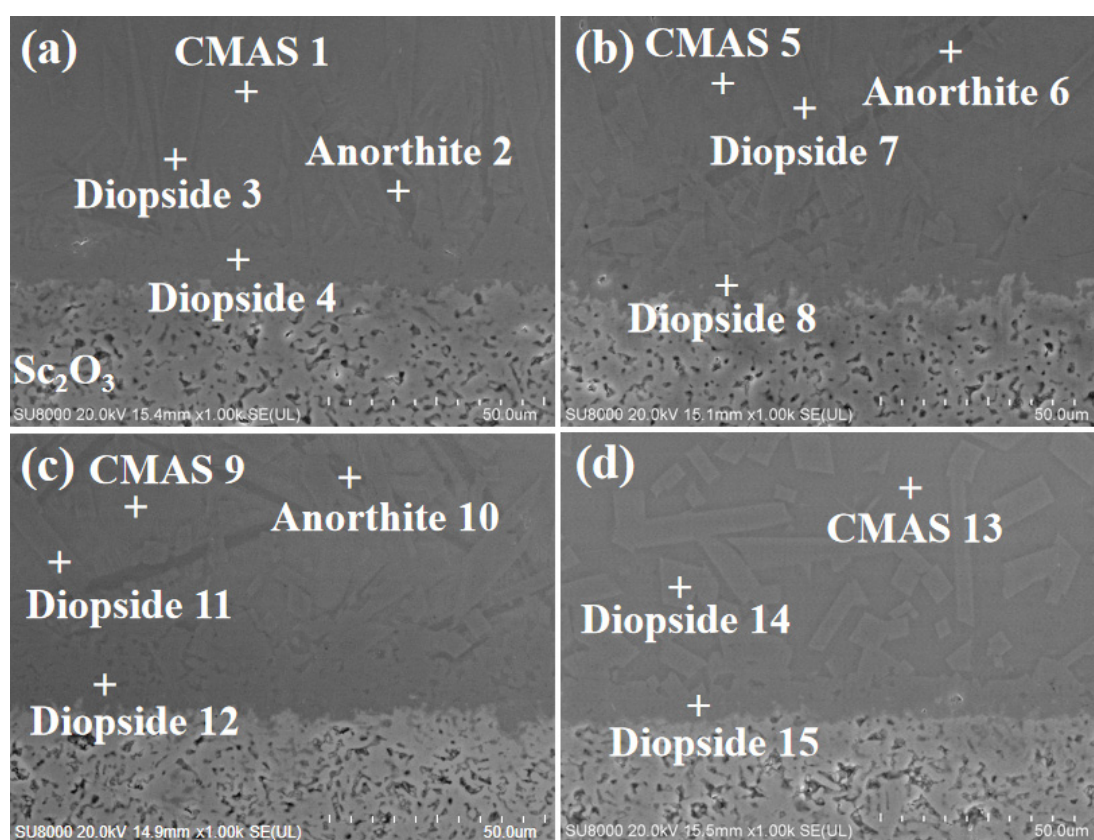


Figure 3. SEM graphs of the Sc_2O_3 ceramics after reaction with the melt at 1250 °C for (a) 15 min, (b) 4 h, (c) 8 h and (d) 24 h.

Table 1. Chemical compositions of the marked areas in Figure 3 (at%).

Zone #	Ca	Mg	Al	Si	Sc	Phase
1	33.4	3.1	16.5	46.7	0.3	CMAS
2	20.5	1.4	34.3	43.5	0.3	Anorthite
3	25.9	19.7	5.0	46.6	2.8	Diopside
4	25.8	19.6	6.4	43.9	4.3	Diopside
5	32.2	1.7	17.3	48.3	0.5	CMAS
6	19.6	1.4	33.5	45.2	0.3	Anorthite
7	25.2	18.3	6.0	45.4	5.1	Diopside
8	25.5	17.5	7.2	44.9	4.9	Diopside
9	32.0	1.7	18.2	47.5	0.6	CMAS

Table 1. Cont.

Zone #	Ca	Mg	Al	Si	Sc	Phase
10	19.1	1.5	32.1	47.0	0.3	Anorthite
11	25.3	17.3	7.4	44.4	5.6	Diopside
12	25.6	17.7	7.1	44.1	5.5	Diopside
13	25.7	2.3	19.2	51.8	1.0	CMAS
14	24.2	19.7	5.3	46.6	4.2	Diopside
15	24.1	20.8	4.3	47.7	3.1	Diopside

The reaction of the Sc_2O_3 ceramic with CMAS results in the crystallization of residual CMAS, resulting from the change in chemical composition [44]. According to Table 1, it can be seen that Ca^{2+} is one of the key ions from the CMAS. The concentration of Ca^{2+} in CMAS in region #1 (Figure 3a) is about 33.4 at% after reaction at 1250 °C for 15 min (Table 1), while it is 32.2, 32.0 and 25.7 (at%) for residual CMAS after reaction for 4 h, 8 h and 24 h (regions #5, 9 and 13 in Table 1), respectively. It decreases with reaction time, attributing to the formation of diopside and garnet phases. Furthermore, the content of Sc^{3+} in the remaining melt increases with time, resulting from the dissolution of the Sc_2O_3 ceramic when exposed to the molten CMAS, and the average content of Sc^{3+} is about 0.7 at% (except for that after 15 min). The contents of Si^{4+} , Mg^{2+} and Al^{3+} also vary with exposure time. The change in composition leads to the crystallization of CMAS, which increases the melt viscosity and mitigates the infiltration [23].

Figure 4 shows the elemental mappings of the Sc_2O_3 ceramics after reaction with the melt at 1250 °C (the dotted lines refer to the thickness of the reaction layer). The DRL exhibits an excellent effect on mitigating Mg^{2+} infiltration, and some blocking effect on Al^{3+} penetration within 8 h. However, the resistance to Ca^{2+} and Si^{4+} infiltration is relatively poor compared to Mg^{2+} and Al^{3+} . According to the Ca mapping, the infiltration depth of Ca^{2+} increases with reaction time, resulting in forming a Ca-rich zone beneath the DRL. The Ca^{2+} infiltration depths are 13.1 μm , 15.6 μm , 16.8 μm and 17.5 μm after reaction for 15 min, 4 h, 8 h and 24 h, respectively. As for the Al mapping, there is a localized enrichment of Al, showing the formation of the anorthite phase [21]. It is noted that the Sc content in CMAS is about 1.0 at% after 24 h (Table 1), suggesting that the amount of Sc^{3+} in the residual CMAS is very low at 1250 °C [40].

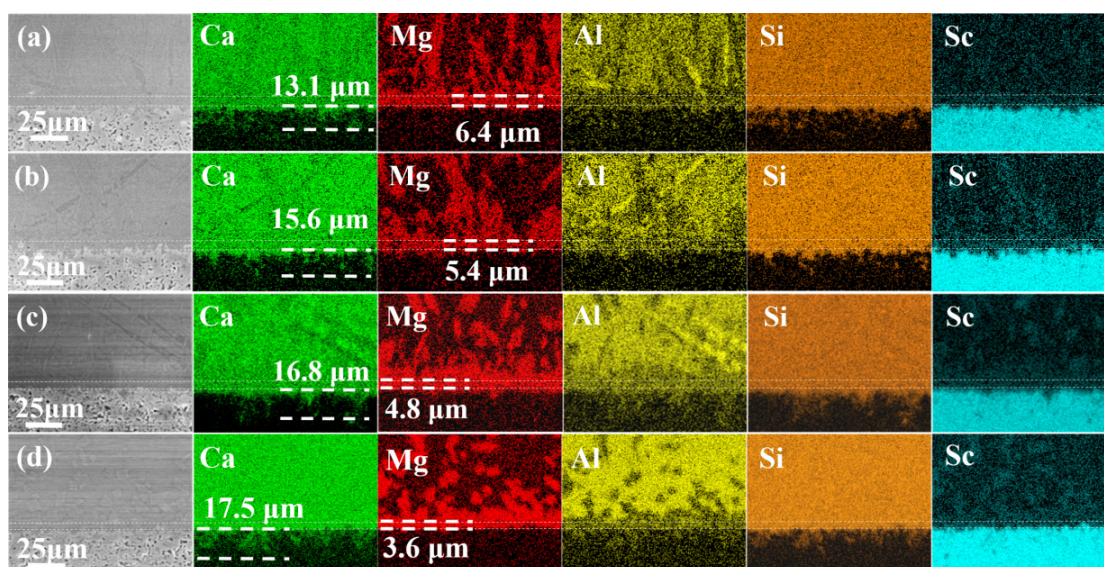


Figure 4. Elemental mappings of Sc_2O_3 ceramics after reaction with the melt at 1250 °C for (a) 15 min, (b) 4 h, (c) 8 h and (d) 24 h.

Figure 5 shows the SEM graphs of the Sc_2O_3 ceramics reacting with CMAS at 1300 °C. A DRL forms on the surface of the ceramic after 15 min reaction, which is mainly composed of the garnet ($\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$) and minor diopside phases according to the compositions of regions #3, 6, 9 and 13 in Figure 5 and Table 2. The garnet phase in the DRL and diopside phase in the residual CMAS increase and coarsen with prolonged exposure time [47]. No anorthite phase can be detected, consistent with the result in Figure 2c. According to Table 2, the concentration of Ca^{2+} in the melt as region #1 (Figure 5a) is about 30.2 at% after 15 min, and they are 30.1, 29.7 and 26.1 for the residual CMAS after reaction for 4 h, 8 h and 24 h (regions #4, 7 and 10), respectively. It decreases with time, resulting from the formation of more garnet and diopside phases. The content of Sc^{3+} in the remaining CMAS increases with time. The average content of Sc^{3+} is about 3.7 at% (except for that after 15 min), which is higher than that at 1250 °C. It is attributed to a more outward diffusion of Sc^{3+} from the substrate, as we know that the infiltration of the melt can greatly be improved due to the lower viscosity at higher temperature [23]. The penetrated melt reacts with the substrate Sc_2O_3 ceramic, resulting in generation and diffusion of Sc^{3+} . This then leads to a concentration increase in Sc^{3+} in the CMAS even despite the formation of the various crystallization phases.

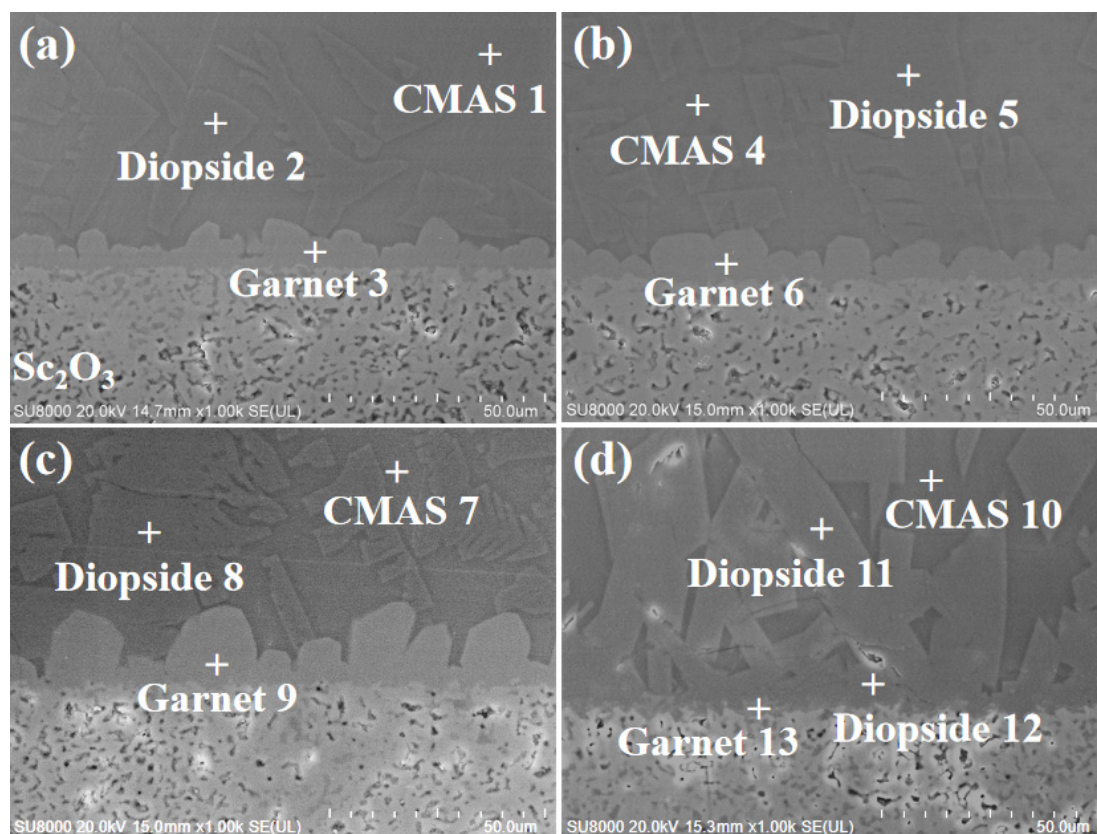


Figure 5. SEM graphs of the Sc_2O_3 ceramics after reaction with the melt at 1300 °C for (a) 15 min, (b) 4 h, (c) 8 h and (d) 24 h.

The elemental mappings of the Sc_2O_3 ceramics after reaction with the melt at 1300 °C are presented in Figure 6. The DRL shows a good effect on alleviating the Mg^{2+} infiltration and some mitigating effect on Al^{3+} . An infiltration zone with some Ca forms beneath the DRL according to the Ca mapping. The penetration depth increases with reaction time, whose depths are 13.6 μm , 15.0 μm , 28.9 μm and 68.5 μm after reaction for 15 min, 4 h, 8 h and 24 h, respectively. The infiltration of Si is similar to that of Ca. More melt crystallization for more diopside phases is detected in the CMAS from the elemental mapping of Mg. It

is a result of the composition change of the melt such as the decrease in Ca as well as the increase in Sc [21] (zones #1, 4, 7 and 10 in Table 2).

Table 2. Chemical compositions of the marked areas in Figure 5 (at%).

Zone #	Ca	Mg	Al	Si	Sc	Phase
1	30.2	3.3	15.7	48.2	2.6	CMAS
2	24.2	16.2	10.3	43.5	5.8	Diopside
3	34.4	1.5	2.2	38.1	23.8	Garnet
4	30.1	2.7	15.2	48.5	3.5	CMAS
5	24.3	16.2	10.6	42.8	6.1	Diopside
6	35.2	1.6	2.5	37.2	23.5	Garnet
7	29.7	3.6	15.0	48.1	3.6	CMAS
8	24.5	15.8	11.2	42.4	6.1	Diopside
9	34.7	1.8	2.6	37.4	23.5	Garnet
10	26.1	1.7	17.4	49.8	4.0	CMAS
11	23.8	10.2	13.2	38.9	13.9	Diopside
12	22.9	11.0	12.0	40.0	14.1	Diopside
13	31.0	4.0	4.9	38.1	22.0	Garnet

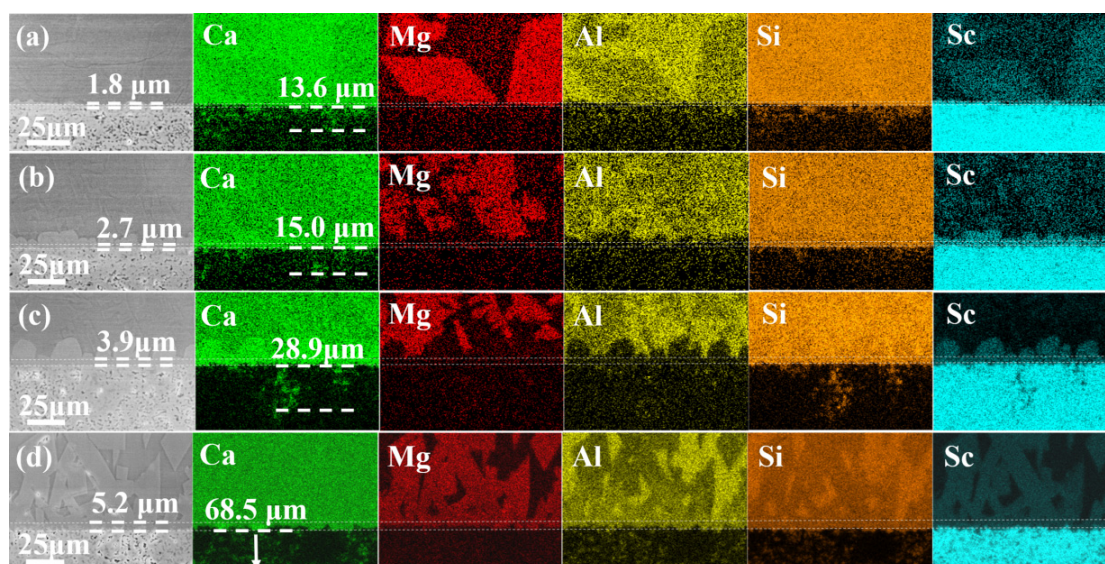


Figure 6. Elemental mappings of the Sc_2O_3 ceramics after reaction with the melt at 1300 °C for (a) 15 min, (b) 4 h, (c) 8 h and (d) 24 h.

A DRL forms at the Sc_2O_3 /CMAS interface after exposure to the molten CMAS for 15 min, and the changes of thickness of the DRL with reaction temperature and time are shown in Figure 7a. The growing of the thickness follows the parabolic law, and the corresponding equations are well fitted with $y = Ax^2 + Bx + C$. It is obvious that the DRL decreases with time at 1250 °C, resulting from the dissolution of the diopside phase, while the DRL thickens with time at 1300 °C. This is a result of the lower viscosity of CMAS [23] and the increasing concentration of the Sc^{3+} in the residual CMAS (Table 2) [48]. The growing DRL becomes steady after reaction for 24 h, indicating that there is a dynamic balancing state of thickening and dissolution for the DRL during exposure to the melt.

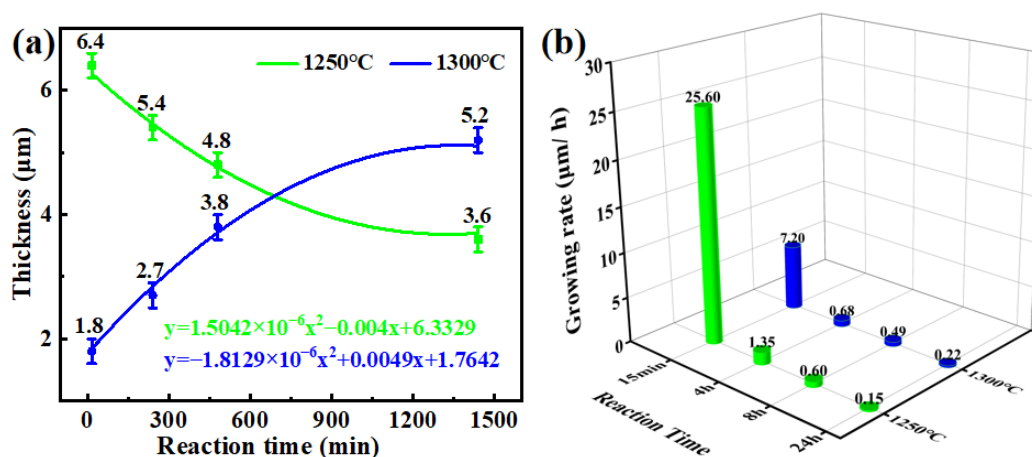


Figure 7. The thicknesses (a) and the growing rates (b) of the DRLs with temperature and time.

Figure 7b exhibits the growing speeds of the DRLs at 1250 °C and 1300 °C. The thickening rates of the DRL are about 25.6 and 7.20 μm/h for the Sc₂O₃ ceramics within the first 15 min of the reaction at two temperatures (1250 °C, 1300 °C), respectively, and the growing speeds are only around 0.15 and 0.22 μm/h after reaction for 24 h. It is obvious that the growing speed of the DRL decreases with time at high temperature. As for 1250 °C, it is attributed to the dissolution of the diopside phase [46]. At 1300 °C, it is related to the increase in DRL thickness and garnet grain coarsening, resulting in an increase in the diffusion path and fewer diffusion channels. Furthermore, the growing rate of the DRL at 1300 °C is slower compared to that at 1250 °C during the initial 8 h. It may be related to the growing behavior of the DRL and thermochemical stability of the diopside and garnet phases in the molten CMAS. While the growing speed of the DRL at 1300 °C is relatively higher after more than 8 h, it may be due to the decreasing viscosity and the severe infiltration of the melt.

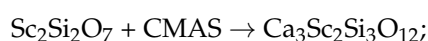
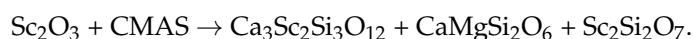
3.3. Mechanism Analysis

To further understand the reactions of the Sc₂O₃ ceramic with the CMAS at high temperature, the DSC tests were conducted on the CMAS and the mixed powders with Sc₂O₃–CMAS (1:1 wt.%) during heating from room temperature to 1450 °C, and the corresponding patterns are exhibited in Figure 8. A small peak exists at around 800 °C, representing the glass transition (GT) of CMAS [45]. Moreover, the CMAS begins to melt at about 1207.6 °C, and the endothermic peak P1 of the CMAS curve is around 1229.5 °C, close to that in Ref. [49]. The peak P1 of the mixed powder is around 1225.3 °C, indicating that Sc₂O₃ shows a small effect for the melting of CMAS. The reaction of Sc₂O₃ with CMAS causes peak P2, forming garnet, diopside and Sc₂Si₂O₇ phases. The Sc₂Si₂O₇ will react with CMAS to form Ca₃Sc₂Si₃O₁₂ [45], suggesting that Sc₂Si₂O₇ is a transition phase during thermochemical reactions. Peak P3 (1350.7 °C) indicates the melting of diopside [50]. Additionally, peak P4 may be related to the melting behavior of garnet. The whole thermochemical reaction processes are summarized as:

GT: CMAS undergoes glass transition;

P1: Sc₂O₃ and CMAS powders melt;

P2:



P3: The melting of CaMgSi₂O₆;

P4: The melting of Ca₃Sc₂Si₃O₁₂.

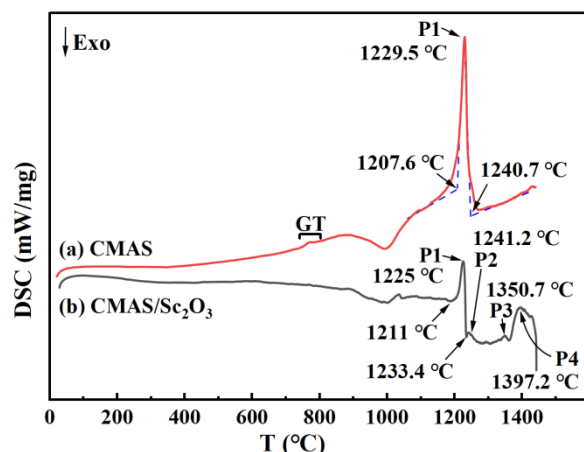


Figure 8. DSC curves of (a) CMAS and (b) mixture of CMAS–Sc₂O₃ (1:1 wt.%).

Figure 9 illustrates the thermochemical reaction mechanisms of the Sc₂O₃ ceramic and the CMAS at high temperature. At the beginning of the reaction at 1250 °C, the Sc₂O₃ ceramic reacts with the melt to form a DRL within the initial 15 min, and it is mainly the diopside phase. Then, the anorthite phase precipitates in the residual CMAS owing to the composition change in the CMAS (Figure 9b). The DRL becomes thin with reaction time, attributed to the dissolution of the diopside [46], and the anorthite phase disappears after 24 h. As for 1300 °C, the DRL is composed of the dominating garnet and minor diopside phases. The DRL thickens with reaction time, resulting from the good stability of the garnet phase and the increasing Sc³⁺ infiltration from the substrate [48]. The DRL shows good effect on inhibiting Mg²⁺ penetration and some blocking effect on Al³⁺, and relatively inferior resistance to Ca²⁺ and Si⁴⁺ penetration.

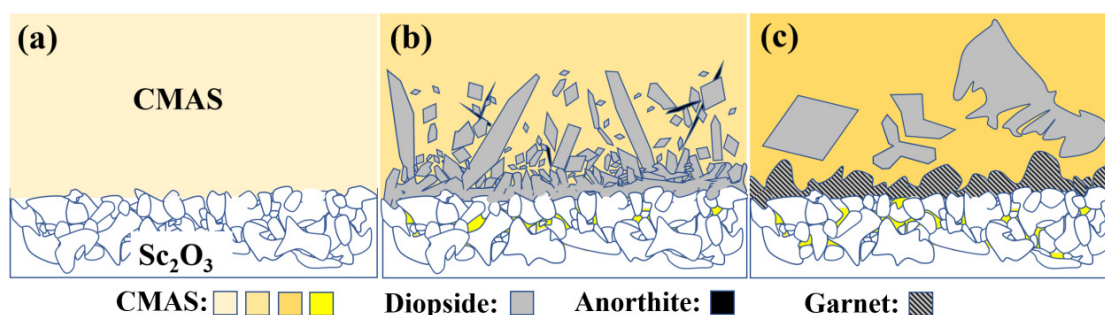


Figure 9. Schematics of the thermochemical interactions of the CMAS and Sc₂O₃ ceramic at high temperature (a) before interaction, (b) 1250 °C and (c) 1300 °C.

4. Conclusions

The thermochemical interactions of the Sc₂O₃ ceramic with CMAS at 1250 °C and 1300 °C were investigated in this work. Different reaction products and the CMAS crystallization phases form at various temperatures, resulting in distinct phase components for the dense reaction layer (DRL). The DRL is mainly composed of the diopside phase (CaMgSi₂O₆) at 1250 °C, decreasing with reaction time, while it is of the dominant garnet phase (Ca₃Sc₂Si₃O₁₂) at 1300 °C, increasing with exposure time. It is attributed to the difference in stability between the garnet and diopside phases in the molten CMAS. The thickening rate of the DRL decreases and following the parabolic law with duration time. They are about 25.6 and 7.20 (μm/h) after reaction for the initial 15 min, and only 0.15 and 0.22 (μm/h) after 24 h reaction at 1250 °C and 1300 °C, respectively. The DRL shows good effect on inhibiting Mg²⁺ and some blocking effect on Al³⁺ penetration, and relatively

inferior resistance to Ca^{2+} and Si^{4+} infiltration. It is indicated that a DRL composed of diopside and/or garnet phases is a potential strategy for protective coating against molten CMAS attack.

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