Effects of pellet surface roughness and pre-oxidation temperature on CMAS corrosion behavior of Ti$_2$AlC

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Abstract: Calcium–magnesium–alumina–silicate (CMAS) corrosion is a serious threat to thermal barrier coatings (TBCs). Ti$_2$AlC has been proven to be a potential protection layer material for TBCs to resist CMAS corrosion. In this study, the effects of the pellet surface roughness and temperature on the microstructure of the pre-oxidation layer and CMAS corrosion behavior of Ti$_2$AlC were investigated. The results revealed that pre-oxidation produced inner Al$_2$O$_3$ layer and outer TiO$_2$ clusters on the pellet surfaces. The content of TiO$_2$ decreased with decreasing pellet surface roughness and increased along with the pre-oxidation temperature. The thickness of Al$_2$O$_3$ layer is also positively related to the pre-oxidation temperature. The Ti$_2$AlC pellets pre-oxidized at 1050°C could effectively resist CMAS corrosion by promoting the crystallization of anorthite (CaAl$_2$Si$_2$O$_8$) from the CMAS melt rapidly, and the resistance effectiveness increased with the pellet surface roughness. Additionally, the CMAS layer mainly spalled off at the interface of CaAl$_2$Si$_2$O$_8$/Al$_2$O$_3$ layer after thermal cycling tests coupled with CMAS corrosion. The Al$_2$O$_3$ layer grown on the rough interface could combine with the pellets tightly during thermal cycling tests, which was attributed to obstruction of the rough interface to crack propagation.

Keywords: thermal barrier coatings (TBCs); Ti$_2$AlC; surface roughness; pre-oxidation temperature; calcium–magnesium–alumina–silicate (CMAS) corrosion; thermal cycling

1 Introduction

Thermal barrier coatings (TBCs) are widely used in gas turbines, aeroengines, and other high-temperature components. They can reduce the operation temperature and prolong service life of high-temperature components [1,2]. A typical TBC system is usually composed of a ceramic top coating, a bond coating, and a superalloy substrate [1,3]. Yttria partially stabilized zirconia (YSZ) is the most widely used ceramic coating material because of its low thermal conductivity and high melting point [4,5]. However, YSZ coating would get
corroded easily when exposed to the molten CMAS (CaO–MgO–Al2O3–SiO2), which mostly happens under extreme engine working situations in desert or volcanic regions, posing risks to the failure of TBCs [6–8].

A lot of research has been carried out on the damage mechanism of CMAS to YSZ coating, which could be explained from two aspects. Firstly, the damage is relevant to the thermal–mechanical interaction. The molten CMAS penetrates into YSZ coating at high temperature and blocks the gaps in the coating, which would cause a decrease in strain tolerance of the coating. Upon cooling, the coating would be densified by the penetrated CMAS, producing large stresses ascribed to the mismatch of the coefficient of thermal expansion (CTE) between CMAS glass and TBCs. The stress accumulates during thermal cycling tests, and then promotes the formation and propagation of cracks, which eventually leads to the premature failure of TBCs [8–10]. Another relevant factor is the thermal–chemical interaction, which is a kind of chemical reaction between CMAS and coating composition. That is, the Y element in the coating would dissolve into the molten CMAS, resulting in the transformation from t’-ZrO2 to m-ZrO2. As a result, the morphology, microstructure, and composition of the coating are changed. Ultimately, premature failure of TBCs occurs [8,11].

As one of the most important factors threatening aviation safety, CMAS attack has attracted a lot of attention. In view of the damage that CMAS poses to YSZ coating, researchers have put forward a few solutions: (1) spraying an extra outer layer on YSZ coating. It has been reported that an extra Al2O3 coating has been sprayed on the top of YSZ coating to be used as a barrier layer against CMAS attack. The reaction of Al2O3 and CMAS could form a dense layer to hinder the penetration of CMAS [12,13]; (2) modifying YSZ coating. Ayjun et al. [14] modified YSZ coating by doping Al and Ti to resist CMAS corrosion, where Al and Ti are considered to facilitate the crystallization of anorthite (CaAl2Si2O8) from CMAS to hinder melt penetration; (3) developing new TBC materials. Recently, some new TBC materials, such as Sm2Zr2O7, LaPO4, and GdZr2O7, have also been developed to resist CMAS attack. These new TBC materials can react with CMAS to form a dense reaction layer, which can prevent the penetration of CMAS [15–17]. According to the above reports, it could be found that one strategy to resist CMAS corrosion is to prevent CMAS penetration. Ti2AlC, a compound containing Al and Ti, has been proven to be a promising CMAS-resistant material by reacting with CMAS to form a dense CaAl2Si2O8 layer to resist melt penetration [18,19]. Thus, Ti2AlC has been proposed to be a CMAS-resistant top layer of TBCs. It has been reported that after pre-oxidation in the temperature range of 1000–1300 °C, a continuous inner Al2O3 layer and discontinuous outer TiO2 clusters would appear on the Ti2AlC surface [20], and compared with non-oxidized Ti2AlC, the pre-oxidized Ti2AlC pellet could resist CMAS better, attributing to that the formed pre-oxidation layers promote the crystallization of CaAl2Si2O8 from CMAS [21]. However, the effect of pre-oxidation layer microstructure on CMAS corrosion resistance is not clear, and the influencing factors and accurate control methods of the pre-oxidation layer microstructure need to be mastered.

According to Badie et al. [22] and Yang et al. [23], the variation of Ti2AlC surface roughness would affect the microstructure of Al2O3 layer and the distribution of TiO2. It has also been reported that with the increase of the oxidation temperature in a certain range, the contents of oxidation products will increase [24]. Therefore, it is hoped to obtain pre-oxidation layers with different microstructures by changing the surface roughness and pre-oxidation temperature, and then explore the influence on CMAS resistance behavior of Ti2AlC.

Furthermore, in service, TBCs face an extreme thermal shock environment, and the residual CMAS would be heated and melted again among engine serving cycles, which would cause secondary damage to TBCs [3,9]. Steinke et al. [25] proposed a test approach to combine thermal gradient cycling testing and CMAS deposition and to explore the thermal cycling behavior of YSZ coating prepared by atmospheric plasma spraying (APS). It was found that the thermal cycling lifetime of the coating decreased by nearly two orders of magnitude under the CMAS condition. Rezanka et al. [26] manufactured YSZ coating through plasma spray-physical vapor deposition (PS-PVD) and explored the thermal cycling behavior with or without CMAS deposition. The results revealed that the thermal cycling lifetime also decreased significantly under the CMAS condition. Zhou et al. [27] used APS and suspension plasma spraying (SPS) to manufacture...
double-layered YSZ/GZO (Gd$_2$Zr$_2$O$_7$) TBCs and triple-layered YSZ/GZO TBCs. The triple-layered YSZ/GZO TBCs had the longest thermal cycling lifetime under CMAS conditions. These results show that CMAS would have an adverse effect on the thermal cycling response of TBCs. Therefore, for the practical application of Ti$_2$AlC, it is also necessary to investigate the thermal cycling behavior of pre-oxidized Ti$_2$AlC coupled with CMAS corrosion.

In this paper, Ti$_2$AlC pellets were prepared with different surface roughness followed by the pre-oxidation at temperatures of 1050, 1150, and 1250 °C. Then the CMAS powders were deposited on Ti$_2$AlC pellets with different surface microstructures and heated to 1250 °C for 2 h. The focus was placed on the effects of pellet surface roughness and pre-oxidation temperature on CMAS resistance behavior of Ti$_2$AlC. Additionally, the thermal cycling behavior of the pre-oxidized Ti$_2$AlC coupled with CMAS corrosion was also explored. The work could provide experimental support for the practical application of Ti$_2$AlC layer on TBCs for protecting against CMAS attack.

2 Experimental procedures

The dense Ti$_2$AlC bulk used in this work was prepared by solid–liquid reaction synthesis and simultaneous densification process, and more details of the preparation process can be checked in Ref. [28]. The prepared bulk was cut into a lot of pellets with the standard sizes of 12 mm × 11 mm × 2 mm by machining process. To facilitate the description and analysis of each experimental process, these Ti$_2$AlC pellets were divided into three groups, each containing four standard size pellets. The surface of each Ti$_2$AlC pellet was sanded by silicon carbide sandpapers of 100#, 1000#, 3000#, and 5000#, successively. Then, these pellets were cleaned in acetone by ultrasonication and dried in an oven. The groups and experimental conditions of the Ti$_2$AlC pellets in this research are listed in Table 1.

The chemical composition of CMAS used in this work was 33CaO–9MgO–13Al$_2$O$_3$–45SiO$_2$ (in mol%). This CMAS composition is the most widely used composition in related studies, reflecting the average composition of environmental sediments deposited on the hot components. The CMAS preparation process can be described as follows: Firstly, the CaO, MgO, Al$_2$O$_3$, and SiO$_2$ powders were preheated in an electric furnace (SX-1600 °C, 150 mm × 190 mm × 160 mm, Zhong-Huan Experimental Electric Furnace Co., Ltd., China) at 200 °C for 8 h. Before they were mixed with deionized water, the powders were carefully weighed at an appropriate molar ratio. Then, the mixed powders were milled in planetary ball milling (QM-3SP4) for 8 h at a speed of 400 r/min. After that, the suspension was dried at 130 °C for 10 h to evaporate the water vapor, followed by heat treatment at 800 °C for 6 h to convert the Ca(OH)$_2$ to CaO completely. Next, the mixed powders were melted in the box electric furnace (SX-1600 °C) at 1400 °C for 1 h, followed by rapid cooling to ambient temperature in deionized water. Ultimately, the obtained glass was ground into fine powders.

The overall experimental processes included the pre-oxidation of pellets, CMAS corrosion, and thermal cycling tests. Firstly, the Ti$_2$AlC pellets with different roughness were pre-oxidized at 1050, 1150, and 1250 °C for 20 h in the box electric furnace (SX-1600 °C), and the heating rate was 10 °C/min. To evenly cover the surface of each pellet with the CMAS powders, a 400# sieve was used. By referring to the work of Yan et al. [19], the coverage concentration of the CMAS powders in this work was determined to be 15 mg/cm$^2$. This value can provide sufficient CMAS glass in the experiment, and the thickness of CMAS layer formed at high temperature would not interfere with the experimental results. Afterwards, the samples covered with the CMAS powders were put into the box electric furnace.
furnace and heated at 1250 °C for 2 h, and then immediately removed from the electric furnace and cooled down to room temperature. The thermal cycling test was on manual, using an openable air-furnace (SX-G05165, Zhong-Huan Experimental Electric Furnace Co., Ltd., China). To start this test, the electric furnace was firstly heated up to 1250 °C, and then the CMAS-corroded sample was put into the furnace immediately and heated for 10 min. After that, the sample was taken out and put in the deionized water for 1 min. In this way, one thermal cycling test was completed. Then, using the same procedure, 50 thermal cycling tests were repeated.

The polished cross-section workpieces were prepared as follows: The samples were put into a mold after being fixed with triangular fixtures. Then the prepared curing liquid (the mass ratio of resin to curing agent is 2:1) was slowly poured into the mold. The samples were embedded in the workpieces for condensation for 3 h. After that, the pellet was successively ground with 400#, 800#, 1500#, and 3000# silicon carbide sandpaper (Eagle Brand) on manual. Finally, the workpiece was mechanically polished on a rotary polishing machine (MP-2B) with a velvet polishing cloth.

An atomic force microscope (AFM; Afm5500, Agilent, USA), equipped with a silicon AFM probe (Tap 190-G budget sensor), was used to measure the surface roughness. The AFM probe works at horizontal scanning length with the scanning rate of 0.7 lines/s, constant force of 48 NGM, and resonance frequency of 190 kHz. Repeated measurements from multiple sites on each Ti2AlC pellet surface were undertaken to establish statistical analysis. The data for roughness values were calculated by 5 repeated measurements. An X-ray diffractometer (D8 Advanced, Bruker, Germany) with Cu Kα radiation was used to characterize the phase composition of the materials and reaction products. The scanning rate is 0.2 (°)/s, and the scanning range is 10°–80°. The X-ray diffraction (XRD) diagrams were refined with the Rietveld method using the MDI Jade 9 software package, and the phase contents were calculated [29]. For the Al2O3, TiO2, and Ti2AlC phases, the space groups used for Rietveld refinement were R-3c (167), P42/mnm (136), and P63/mmc (194), respectively. The surface morphologies and cross-section microstructures were observed by the scanning electron microscope (SEM; Tdcls4800, Hitachi, Japan), equipped with an energy dispersive spectrometer (IE350).

3 Results and discussion

3.1 Effects of pellet surface roughness and the pre-oxidation temperature on the microstructure of the pre-oxidation layer

Figure 1 is the XRD pattern of the Ti2AlC pellet. It is clear that the prepared Ti2AlC pellet is pure and contains no impurity phase. Figure 2 shows the AFM images of Ti2AlC pellets with different sanding conditions. The surface of Ti2AlC pellet sanded with 100# sandpaper is the roughest, with the arithmetic mean deviation (Ra), maximum peak to valley (Rp–v), and maximum roughness depth (Rmax) values of 1.63, 2.72, and 2.58 μm, respectively. The surface conditions of Ti2AlC pellets sanded with 1000#, 3000#, 5000# sandpaper are similar, among which the pellet sanded with 5000# sandpaper is the smoothest. The other Ti2AlC pellet roughness values are shown in Table 2. Ra, Rp–v, and Rmax all can be used to characterize surface roughness, and Ra is the most widely used. Therefore, in this work, Ra is used to represent the surface roughness of Ti2AlC pellets.

The XRD patterns of Ti2AlC pellets pre-oxidized at different temperatures for 20 h are shown in Fig. 3.

![Fig. 1 XRD pattern of the Ti2AlC pellet and the standard PDF card of Ti2AlC.](image)

![Table 2 Roughness values of Ti2AlC pellets with different sanding conditions](table)

| Sanding condition | Ra (μm) | Rp–v (μm) | Rmax (μm) |
|------------------|---------|-----------|-----------|
| 100# sanding     | 1.63±0.20 | 2.72±0.25 | 2.58±0.27 |
| 1000# sanding    | 0.32±0.10 | 0.73±0.16 | 0.61±0.18 |
| 3000# sanding    | 0.20±0.09 | 0.41±0.13 | 0.36±0.12 |
| 5000# sanding    | 0.10±0.05 | 0.29±0.08 | 0.24±0.08 |
Fig. 2 AFM images of Ti$_2$AlC pellets sanded by (a) 100# sandpaper, (b) 1000# sandpaper, (c) 3000# sandpaper, and (d) 5000# sandpaper.

Fig. 3 XRD patterns of Ti$_2$AlC pellets pre-oxidized at different temperatures for 20 h: (a) sample III-1, (b) sample III-4, (c) sample II-4, and (d) sample I-4. Standard PDF cards of Al$_2$O$_3$, TiO$_2$, and Ti$_2$AlC are also presented.

these patterns, in addition to the detected signals revealing the presence of the Ti$_2$AlC substrate, diffraction peaks corresponding to Al$_2$O$_3$ and TiO$_2$ phases are also identified, indicating the formation of Al$_2$O$_3$ and TiO$_2$ after pre-oxidation. Comparing Fig. 3(a) with Fig. 3(b), it is clear that at the same pre-oxidation temperature, the highest intensity peak of TiO$_2$ on the smooth surface ($R_a = 0.10$ μm) is lower than that of TiO$_2$ on the rough surface ($R_a = 1.63$ μm). The software package calculation shows that the contents of TiO$_2$ grown on samples III-1 and III-4 are 3.4 and 13.5 wt%, respectively (Table 3), which indicates that a rough surface is more conducive to the production of TiO$_2$. Furthermore, the change trend from Figs. 3(b) to 3(d) shows that with the increasing pre-oxidation temperature, the highest intensity peak of Al$_2$O$_3$ increases. The results of the software package calculation reveal that the content of Al$_2$O$_3$ increases from 40.5 to 72.1 wt%, suggesting that increasing the pre-oxidation temperature could increase the content of Al$_2$O$_3$.

Figure 4 shows the surface morphologies of the samples from Group I to Group III. Clusters composed of rod-shaped crystals could be observed after pre-oxidation. The energy dispersive spectroscopy (EDS) result (table in Fig. 4(a)) indicates that the contents of Ti and O in the rod-shaped crystal are 35.39 and 64.61 at%, respectively, which could be confirmed to be TiO$_2$. The layer, which is composed of Al and O (table in Fig. 4(b)), could be confirmed as Al$_2$O$_3$. As shown in Figs. 4(a)–4(d), at the same pre-oxidation temperature (1050 °C), with increasing surface roughness, the TiO$_2$ cluster size increases from ~5 to ~35 μm. Comparing Figs. 4(a), 4(e), and 4(i) with each other, the TiO$_2$ cluster size increases from ~35 to ~60 μm as the pre-oxidation temperature increases from 1050 to 1250 °C, when the surface roughness is identical ($R_a = 1.63$ μm). It is clear that whether around the larger

Table 3 Phase contents of the pre-oxidized samples (Rietveld analysis)

| Sample | Ti$_2$AlC (wt%) | Al$_2$O$_3$ (wt%) | TiO$_2$ (wt%) |
|--------|----------------|------------------|---------------|
| I-4    | 58.3±1.1       | 40.5±1.0         | 1.2±0.3       |
| II-4   | 43.2±0.8       | 54.2±0.7         | 2.6±0.2       |
| III-4  | 24.5±0.9       | 72.1±1.7         | 3.4±0.8       |
| III-1  | 21.8±1.4       | 64.7±1.2         | 13.5±0.4      |

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TiO₂ clusters (such as Fig. 4(a)) or around the smaller TiO₂ clusters (such as Fig. 4(d)), many TiO₂ particles are dispersed around the clusters. The increase in TiO₂ cluster size is obviously due to the aggregation of TiO₂ particles, which means that the larger TiO₂ clusters contain more TiO₂ particles. In summary, the content of TiO₂ increases with increasing pre-oxidation temperature and surface roughness.

The oxidation process of Ti₂AlC includes the inward diffusion of O₂ and the outward diffusion of Al³⁺ and Ti⁴⁺ [24,30]. In the initial oxidation stage of Ti₂AlC, the oxygen partial pressure at the air–Ti₂AlC interface is high enough for the oxidation of Al³⁺ and Ti⁴⁺, so that Al₂O₃ and TiO₂ can nucleate and grow on the surface of Ti₂AlC [30]. With increasing oxidation time, the Al₂O₃ scale is gradually formed, and the inward diffusion of O₂ becomes difficult, which means that the oxygen partial pressure in the Al₂O₃ scale is low. On the one hand, the oxygen partial pressure for the formation of Al₂O₃ is lower than that for the formation of TiO₂ [24,31]. On the other hand, compared with Ti, Al is weakly bound in the layered structure of Ti₂AlC, which means that Al³⁺ more easily disengages from Ti₂AlC than Ti⁴⁺ [32,33]. Therefore, at this stage, more Al₂O₃ grains would nucleate and grow. Finally, a continuous inside Al₂O₃ scale and a discontinuous outer TiO₂ layer would form on the Ti₂AlC pellet.

Compared with smooth surface, the specific surface area of the rough surface is much larger, and the formation speed of continuous Al₂O₃ layer is lower, which provides time for the growth of TiO₂. Therefore, the content of TiO₂ growing on the rough surface is greater [30]. Furthermore, during the oxidation process, a higher oxidation temperature could provide higher power for atomic diffusion. When the pre-oxidation temperature increases from 1050 to 1250 °C, the diffusion rate of Ti increases [24,34]. In addition, the increase in temperature would also make more Ti break away from the Ti₂AlC layered structure. This means that more Ti diffuses outward and combines with O⁻² to form TiO₂.

Figure 5 shows the cross-section microstructures...
corresponding to Fig. 4. As represented in Fig. 5(a), a dark gray contrast inner layer and white contrast particles are produced after pre-oxidation. The EDS mapping results in Fig. 5(a) suggest that the layer and clusters are composed of $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$, respectively. The $\text{Al}_2\text{O}_3$ layer in Fig. 5(a) shows a certain fluctuation, and some pores could be observed in the layer. Nevertheless, as shown in Fig. 5(d), the $\text{Al}_2\text{O}_3$ layer is flat with a dense microstructure, and few $\text{TiO}_2$ clusters can be observed. Interestingly, under a constant pre-oxidation temperature ($1050\,^\circ\text{C}$), the thickness of $\text{Al}_2\text{O}_3$ layer has no obvious difference (Figs. 5(a)–5(d)), which is approximately 2 $\mu\text{m}$. However, the amount of $\text{TiO}_2$ decreases significantly with decreasing surface roughness. Figures 5(e)–5(h) and 5(i)–5(l) also show similar characteristics. In addition, as represented in Figs. 5(a), 5(e), and 5(i), at the same surface roughness ($R_a = 1.63\,\mu\text{m}$), the thickness of $\text{Al}_2\text{O}_3$ layer gradually increases from ~2 to ~6 $\mu\text{m}$ as the pre-oxidation temperature increases from 1050 to 1250 $^\circ\text{C}$.

According to Badie et al. [22], He et al. [35], and Balint and Hutchinson [36], the fluctuation and pores in $\text{Al}_2\text{O}_3$ layer on the rough surface might be related to the plane stress in $\text{Al}_2\text{O}_3$ layer, which is generated during the isothermal oxidation of $\text{Ti}_2\text{AlC}$ and would be released by the stretching of $\text{Al}_2\text{O}_3$ layer. In addition, according to Refs. [22,24,37], the diffusivity of Al plays a leading role in the formation of $\text{Al}_2\text{O}_3$. Actually, increasing the pre-oxidation temperature would increase the power of atomic diffusion, leading to the improved diffusivity of atoms. This means that the thickness of $\text{Al}_2\text{O}_3$ layer would inevitably increase when the pre-oxidation temperature increases from 1050 to 1250 $^\circ\text{C}$.

In summary, the influence of pellet surface roughness and pre-oxidation temperature on the microstructure of the pre-oxidation layer could be described as follows: Increasing the pellet surface roughness could increase the content of $\text{TiO}_2$. In the range of 1050–1250 $^\circ\text{C}$, the $\text{Al}_2\text{O}_3$ layer thickness and $\text{TiO}_2$ amounts would increase with the pre-oxidation temperature. When
samples with different surface microstructures were obtained, the effect of surface microstructure on the CMAS resistance behavior of Ti₂AlC was subsequently investigated.

3. 2  CMAS resistance behavior of pre-oxidized Ti₂AlC

3.2.1  CMAS resistance of Ti₂AlC with pre-oxidation layer formed at 1050 ℃

The XRD patterns of the samples of Group I reacting with CMAS at 1250 ℃ for 2 h are shown in Fig. 6. Observing the XRD pattern of CMAS-corroded sample I-1 (Fig. 6(a)), in addition to the diffraction peaks of CaAl₂Si₂O₈, the diffraction peaks of melilite can also be detected. However, only the diffraction peaks of CaAl₂Si₂O₈ could be observed in the XRD patterns of CMAS-corroded samples I-2 and I-4. The XRD pattern of CMAS-corroded sample I-3 is similar to that of I-4, so it is not provided. The difference indicates that a rough surface is beneficial to the precipitation of crystalline phase. The surface morphologies of the samples of Group I reacting with CMAS at 1250 ℃ for 2 h are shown in Fig. 7. After CMAS corrosion, the rod-shaped products crystallize from CMAS, and the number of crystallization products decreases as the surface roughness decreases from 1.63 to 0.10 μm.

The cross-section microstructures and EDS mapping results of the samples of Group I reacting with CMAS at 1250 ℃ for 2 h are shown in Fig. 8. The Al₂O₃ layers in all the samples are basically intact with no trace of CMAS penetration, indicating that these samples could form strong protection against CMAS corrosion. Some dark gray contrast phases and light white contrast phases can be observed in Fig. 8(a), which are marked as A and B, respectively. The EDS analysis shows that A has Ca, Al, Si, and O, with an atomic ratio close to 1:2:2:8, and B has Ca, Mg, Al, Si, and O. Combined with the XRD patterns in Fig. 6, it could be further determined that A is CaAl₂Si₂O₈, and B is melilite. Observing the difference from Figs. 8(a) to 8(d), as the roughness decreases from 1.63 to 0.10 μm, the amount of CaAl₂Si₂O₈ decreases, which is consistent with the results in Fig. 7. Interestingly, only CaAl₂Si₂O₈ could be observed in Figs. 8(b), 8(c), and 8(d) (corresponding to the CMAS-corroded samples I-2, I-3, and I-4, respectively), suggesting that the rough surface is conducive to the crystallization of melilite from CMAS.

Figure 9 is a pseudo-quaternary CaO–Al₂O₃–SiO₂ with constant 9 mol% MgO phase diagram at 1300 ℃ [38]. The diagram could be used to explain the effect of Al₂O₃ on CMAS corrosion. When the molten CMAS is in contact with the pre-oxidized Ti₂AlC pellet, TiO₂ particles and part of Al₂O₃ would dissolve into the CMAS melt. The dissolution of Al₂O₃ would result in an increase in the Al content in the molten CMAS, causing the CMAS to move from the liquid region to the CaAl₂Si₂O₈ region to precipitate the CaAl₂Si₂O₈. The formation and growth of CaAl₂Si₂O₈ need to consume the Ca, Al, and Si in CMAS, leading
Fig. 8 Cross-section microstructures of the samples (a) I-1, (b) I-2, (c) I-3, and (d) I-4 reacting with CMAS at 1250 °C for 2 h, and the EDS results of (a).

Fig. 9 Pseudo-quaternary CaO–Al2O3–SiO2 with constant 9 mol% MgO phase diagram at 1300 °C (upper, reproduced with permission from Ref. [38], © Acta Materialia Inc. 2016) and interaction mechanism between Ti2AlC and CMAS (bottom).

to the local concentration of Mg near the CaAl2Si2O8. Finally, when the CMAS near the CaAl2Si2O8 meets the specific composition ratio of melilite, the melilite grains form near the CaAl2Si2O8 grains. When the CaAl2Si2O8 layer is formed, the CMAS would be prevented from penetrating, meaning that the remaining pre-oxidized scale will not continue to dissolve. In this work, no CMAS penetration trace can be observed in the CMAS-corroded Group I samples, which means that the pre-oxidized scale with Al2O3 content approximately 40–67 wt% is sufficient to resist the CMAS corrosion.

The amount of CaAl2Si2O8 decreases as the roughness decreases from 1.63 to 0.10 μm, which can be explained
as follows: When the molten CMAS contacts the pre-oxidized scale, TiO$_2$ particles dissolve in the molten CMAS. By referring to the SiO$_2$–TiO$_2$ and CaO–SiO$_2$–TiO$_2$ phase diagrams [39,40], the lowest melting eutectics correspond to TiO$_2$ contents of approximately 10 and 17.5 wt%. This means that more than 10 wt% TiO$_2$ additions might be better for the CaAl$_2$Si$_2$O$_8$ crystallization from CMAS. According to Yan et al. [19] and Webster and Opila [41], TiO$_2$ additions of approximately 5–10 wt% (3.6–7.2 mol%) will likely not aid CaAl$_2$Si$_2$O$_8$ crystallization from CMAS. Significant CaAl$_2$Si$_2$O$_8$ crystallization could be detected until the TiO$_2$ additions were approximately 12.5–15 wt%.

In this work, the contents of TiO$_2$ grown on the rough surface ($R_a = 1.63 \mu$m) and smooth surface ($R_a = 0.10 \mu$m) were approximately 13.5 and 3 wt%, respectively. This means that Ti$_2$AlC with a rougher surface can promote the crystallization of CaAl$_2$Si$_2$O$_8$ from CMAS. In contrast, because fewer TiO$_2$ particles were produced on a smoother surface (e.g., $R_a = 0.10 \mu$m), the crystallization of CaAl$_2$Si$_2$O$_8$ depends on the CMAS self-crystallization, which means that CaAl$_2$Si$_2$O$_8$ would be present in small quantities. Meanwhile, because the crystallized CaAl$_2$Si$_2$O$_8$ in the CMAS-corroded samples of I-2, I-3, and I-4 are in small quantities, the remaining elements in residual CMAS do not meet the crystallization point of melilite, giving rise to no precipitation of melilite in these samples.

The role of CaAl$_2$Si$_2$O$_8$ in resisting CMAS corrosion has been confirmed by scholars; that is, the formation of a CaAl$_2$Si$_2$O$_8$ layer could effectively block the penetration of CMAS [12–14]. In this work, the crystallized CaAl$_2$Si$_2$O$_8$ in CMAS-corroded sample I-1 is in large quantities, which would undoubtedly provide better CMAS corrosion resistance. In summary, the mechanism that surface roughness affects the CMAS resistance behavior of Ti$_2$AlC by influencing microstructure of the pre-oxidation layer could be explained as follows: The surface with larger roughness could produce more TiO$_2$ during the pre-oxidation of Ti$_2$AlC, which could dissolve into the CMAS melt to make more CaAl$_2$Si$_2$O$_8$ crystallize and have a better blocking effect. This means that larger surface roughness is expected in this work.

### 3.2.2 CMAS resistance of Ti$_2$AlC with pre-oxidation layer formed at 1150 and 1250 °C

Figure 10 shows the surface morphologies of the samples of Group II (Figs. 10(a)–10(d)) and Group III (Figs. 10(e)–10(h)) reacting with CMAS at 1250 °C for 2 h. As represented in Fig. 10, it is obvious that after CMAS corrosion, a large number of rod-shaped crystals appear in both group samples, suggesting that all the samples could promote the crystallization in CMAS at 1250 °C.

The cross-section microstructures corresponding to Fig. 10 are shown in Fig. 11. In all the samples, the dark gray contrast phases can be observed, and in previous discussion, this phase has been proven to be CaAl$_2$Si$_2$O$_8$. More importantly, from the EDS mapping results in Figs. 11(a) and 11(e), it could be clearly found that CMAS does not penetrate into the substrate, and no trace of CMAS penetration can be found in the other samples (Figs. 11(b)–11(h)), which suggests that these samples possess excellent CMAS resistance. Figure 11(i) is an enlarged image of the marked area in

![Fig. 10](https://example.com/fig10.png) Surface morphologies of the samples of (a–d) Group II and (e–h) Group III reacting with CMAS at 1250 °C for 2 h.
Fig. 11 Cross-section microstructures and EDS mapping results of the samples of (a–d) Group II and (e–h) Group III reacting with CMAS at 1250 °C for 2 h; (i) enlarged image and corresponded EDS mapping results of the marked area in (e).

Fig. 11(e). Interestingly, some bright white contrast phases could be observed in the sample III-1. The EDS results show that these phases are rich in Ti and contain Ca, Al, and Si, marked as Ti-rich phase. According to Cui et al. [20], when the dissolved Ti exceeds a certain content in CMAS, it would combine with CMAS constituents to precipitate a Ti-rich phase. In this work, compared with the other samples, the sample III-1 has the highest roughness ($R_a = 1.63 \, \mu m$), and is pre-oxidized at the highest temperature (1250 °C), leading to the production of the most TiO$_2$ particles. Therefore, the Ti-rich phase could be observed in this sample.

Briefly, in the studied temperature range, the influence of the pre-oxidation temperature on the CMAS resistance behavior of Ti$_2$AlC is as follows: Increasing the pre-oxidation temperature could increase the oxide content of Ti$_2$AlC, which promotes CaAl$_2$Si$_2$O$_8$ crystallization when the pre-oxidized Ti$_2$AlC reacts with CMAS. Although all the three groups of the samples could resist the CMAS corrosion effectively, the thickness of Al$_2$O$_3$ layer is thicker after pre-oxidation at 1250 °C, which would lead to an increase in the coating mass in practical applications. The Al$_2$O$_3$ layer thickness is close after the pre-oxidation at 1050 or 1150 °C, and the CMAS resistance is similar. Moreover, in the practical application of Ti$_2$AlC as a protective layer against CMAS corrosion, if the pre-oxidation temperature is too high, it would lead to the phase transformation and sintering of YSZ coating. This means that the Ti$_2$AlC pellet pre-oxidized at 1050 °C is sufficient to resist CMAS corrosion. Therefore, in this work, the pre-oxidation temperature of the Ti$_2$AlC pellet is determined to be 1050 °C.

3.3 Thermal cycling behavior of Ti$_2$AlC with pre-oxidized layer coupled with CMAS corrosion

As discussed above, the pre-oxidation temperature of the Ti$_2$AlC pellet is determined to be 1050 °C. For the practical application of Ti$_2$AlC, it is also necessary to investigate the thermal cycling behavior of Ti$_2$AlC with pre-oxidized layer coupled with CMAS corrosion. Thus, the thermal cycling tests were carried out on the CMAS-corroded samples of Groups I and II. Figure 12 shows the variation of the macroscopic morphologies...
of the samples of Groups I and II during thermal cycling tests coupled with CMAS corrosion. After 20 thermal cycling tests, CMAS on the two group samples has begun to spall off at the marked areas. Additionally, due to the low toughness of Ti2AlC bulk [42], all the samples have cracked, which would have no effect on the experimental results. Obviously, the CMAS spallation areas on the two groups of samples have increased after 50 thermal cycling tests.

Figure 12 shows the cross-section microstructures of the spallation area of the samples of Groups I (Figs. 13(a)–13(d)) and II (Figs. 13(e)–13(h)) after 50 thermal cycling tests coupled with CMAS corrosion. As shown in Fig. 13, whether in Group I or Group II samples, cracks could be observed at the interface of CaAl2Si2O8/Al2O3, which implies that CMAS would spall off at this position during thermal cycling tests. Interestingly, for the sample with a rough surface, as illustrated in Fig. 13(a), there is no crack at the interface of Al2O3/Ti2AlC substrate, suggesting the adhesion between the Al2O3 layer and the substrate is strong. However, when the surface roughness decreases, microcrack and loophole can be observed at the interface of Al2O3/Ti2AlC (Figs. 13(b)–13(d)). Especially,
observing Fig. 13(d) (sample I-4), it is clear that the Al2O3 layer has been detached from the smooth Ti2AlC substrate with a linked crack at the interface of Al2O3/Ti2AlC, showing a low interfacial bonding strength. Combining Fig. 13(a) with Fig. 13(d), it could be summarized that compared with the rough surface, the Al2O3 layer grown on the smooth surface is easier to spall off during the thermal cycling tests.

For the samples of Group II after 50 thermal cycling tests coupled with CMAS corrosion, the CMAS spallation positions in all the samples are at the CaAl2Si2O8/Al2O3 interface, showing similar spalling characteristics to those of Group I. Besides, with the decrease of interface roughness, the interface of Al2O3/Ti2AlC also gradually changes from tight connection to debonding (Figs. 13(e)–13(h)), implying that reducing the surface roughness would weaken the interfacial bonding strength.

In this work, the CMAS/Ti2AlC system contains CaAl2Si2O8/Al2O3 interface and Al2O3/Ti2AlC interface, which is schematized in Fig. 14(a). As mentioned above, cracks appear at the interface of CaAl2Si2O8/Al2O3 after 50 thermal cycling tests. According to the previous researches [42–45], the CTEs of CaAl2Si2O8, Al2O3, and Ti2AlC are (4–5)×10−6 K−1, (7–9)×10−6 K−1, and (8–9)×10−6 K−1, respectively. The CTE mismatch between CaAl2Si2O8 and Al2O3 could result in the initiation of crack at the interface of Al2O3/CaAl2Si2O8, and lead to the spallation of CMAS during thermal cycling tests. In addition, as shown in Fig. 13(a), when cracks appear at the interface of Al2O3/CaAl2Si2O8, the interface of Al2O3/Ti2AlC still remains tight connection. This could be attributed to the fact that the CTE mismatch between Al2O3 and CaAl2Si2O8 is greater than that between Al2O3 and Ti2AlC, which means under the same thermal cycling conditions, the interfacial bonding strength of CaAl2Si2O8/Al2O3 is weaker than that of Al2O3/Ti2AlC.

Fig. 13 Cross-section microstructures of the spallation area of the samples of (a–d) Group I and (e–h) Group II after 50 thermal cycling tests coupled with CMAS corrosion.

Fig. 14 Schematic drawing showing (a) cross-section of CMAS/Ti2AlC system and (b) failure mechanism for the interface of Al2O3/Ti2AlC with the studied surface roughness.
Based on the cross-sections of the samples I-1 and I-4 (II-1 and II-4) after 50 thermal cycling tests coupled with CMAS corrosion, a schematic drawing (Fig. 14(b)) is derived to illustrate the effect of surface roughness on the thermal cycling performance of the CMAS/Ti2AlC system. According to the above discussion, the CMAS/Ti2AlC system contains an Al2O3/Ti2AlC interface, and the CTE mismatch between Al2O3 and Ti2AlC would lead to the initiation of crack during thermal cycling tests. For the sample with a smooth surface, due to the little resistance to crack propagation, it is easy to propagate and link rapidly along the interface after crack nucleation [46], resulting in the debonding of Al2O3 layer and Ti2AlC substrate. For the sample with a rough surface, according to Quadakkers et al. [47], the preferred sites for crack nucleation are the convex connection regions. Additionally, when the crack propagates through the concave connection regions, where compressive stress generally exists, they would be hindered, making the cracks hard to link [48–50]. To sum up, the crack is easier to propagate and link at the smooth surface than at the rough surface, resulting in Al2O3 layer being more easily deboned from the smooth Ti2AlC substrate.

As mentioned above, residual CMAS would cause secondary damage to the coating in the practical applications. The pre-oxidation layer debonding with the Ti2AlC substrate would seriously affect the CMAS resistance of Ti2AlC, which needs to be avoided. A rough surface has better bonding strength at the interface of Al2O3/Ti2AlC. Besides, it was also found that a rough surface could resist CMAS corrosion more efficiently through the previous discussion. Hence, Ti2AlC pellets sanded by 100# sandpaper are desirable for practical application according to this study. For the samples of Groups I and II, the thermal cycling response of CMAS/Ti2AlC system is similar. On the one hand, CMAS would spall off at the CaAl2Si2O8/Al2O3 interface; on the other hand, the interface of Al2O3/Ti2AlC also gradually changes from tight connection to debonding with the decrease of interface roughness. Considering a low pre-oxidation temperature could not only save energy, but also avoid adverse effects on YSZ coating in practical applications. Therefore, the pre-oxidation temperature of 1050 °C is desirable.

4 Conclusions

In this study, the effects of pellet surface roughness and pre-oxidation temperature on the pre-oxidation layer microstructure of Ti2AlC are investigated, followed by studying the CMAS corrosion behavior of the pre-oxidized Ti2AlC. The conclusions are as follows:

1. An inner continuous Al2O3 layer and outer TiO2 clusters were produced on the Ti2AlC pellet surface after pre-oxidation. The content of TiO2 was reduced as the pellet surface roughness decreased. In the range of 1050–1250 °C, both the Al2O3 layer thickness and the TiO2 content increased with the pre-oxidation temperature.

2. The pellets pre-oxidated at a low temperature (1050 °C) exhibited efficient CMAS resistance. Increasing the pellet surface roughness was conducive to the crystallization of CaAl2Si2O8, which could block the penetration of CMAS effectively.

3. The CMAS layer mainly spalled off at the interface of CaAl2Si2O8 crystals and Al2O3 layer after thermal cycling tests coupled with CMAS corrosion. The interfacial bonding strength of CaAl2Si2O8/Al2O3 layer was weaker than that of Al2O3 layer/Ti2AlC pellet. Compared with the smooth interface, the Al2O3 layer grown on the rough interface combined with the pellet more tightly, which attributes to the obstruction of rough interface to crack propagation.

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