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A Comprehensive Analysis of CMAS Characterization, Corrosion Scenarios, and Protective Measures

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Abstract:

Aero engines face significant corrosion risks from environmental sediments like volcanic ash, industrial smoke, automobile exhaust, and PM2.5 during high-altitude flights. These deposits, composed of CaO-MgO-Al_2O_3-SiO_2 (CMAS), have a melting point of 1230°C, substantially lower than the operating temperature of aero engines. However, advanced thermal barrier coatings (TBCs) have demonstrated effective resistance against CMAS-induced corrosion. This paper reviews the literature extensively, systematically reviews the composition of CMAS, its corrosion mechanism and protection strategies, focuses on the analysis of the corrosion mechanism of CMAS in different environments, and finds that the atmospheric corrosion mechanism is different from that of the ocean, which provides help for the improvement of TBCs, and provides suggestions and future research directions for the development of advanced aero engines.

Keywords: CMAS corrosion; thermal barrier coatings; Aerospace; aero engines; Protective technology

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1. Introduction

Volcanic ash poses significant safety risks to aviation operations. When volcanic ash enters an aero engine with a gas stream, its particles melt in a high-temperature combustion environment and subsequently form deposits on the surface of high-temperature areas of the turbine system, such as guide vanes and high-pressure turbine rotor blades. The main component of these deposits is CaO-Al_2O_3-MgO-SiO_2 (CMAS), which not only causes engine flow channel blockage, but also chemically attacks the thermal barrier coating that protects the surface of turbine components [1][2]. CMAS deposits exhibit a low melting point of 1230°C, substantially lower than the typical operational temperatures of aero engines [3]. Due to the difference in thermal expansion coefficient, CMAS deposits will cause TBCs to peel and fail when the engine is cooled, resulting in serious corrosion, thereby shortening the working life of the engine, increasing aviation hazards, and endangering the lives of passengers [4]. Through literature search, this paper summarizes the diversity of CMAS components, the different CMAS corrosion mechanisms in atmospheric and marine environments, and the latest progress in CMAS protection, so as to better improve TBCs and provide theoretical support for

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aviation safety and the service life of aero engines.

2. Physical properties of CMAS

It is found that there are different types of CMAS deposits in different environments, and these CMAS have different differences in physical composition and chemical properties, which will greatly increase the difficulty of the research problem. Therefore, the CMAS component studied by researchers has certain limitations, but there is some value in conducting research within a specific area.

2.1 Compositional complexity of CMAS

Industrialization and natural disasters increase sources of CMAS, including volcanic ash, sand dust, and automobile exhaust. Unpredicted volcanic eruptions or sandstorms could cause space shuttle damage. Variations in volcanic ash composition and physical properties pose challenges for experimental research. Table 1 lists the main components of CMAS in some authoritative reports, and it can be seen that the main components of synthetic CMAS are different from those of CMAS in nature: natural deposits exhibit higher SiO_2 content with lower CaO levels, contrasting with synthetic formulations [5][6]. Moreover, synthetic CMAS lacks trace elements, streamlining experimental configurations.

Table 1. Main components of CMAS[5-6]

Ash samples	SiO_2	Al_2O_3	FeO	CaO	K_2O	Na_2O	TiO_2	MgO	MnO	P_2O_5
Grímsvötn volcanic ash[5]	50.10	14.49	13.53	9.81	0.53	2.88	2.90	5.19	0.21	0.33
Santa María volcanic ash[5]	61.07	20.83	3.94	5.96	1.44	4.58	0.49	1.37	0.11	0.22
Dust1[5]	76.96	11.22	3.08	2.59	2.76	1.37	0.40	1.39	0.09	0.14
Dust2[5]	88.64	5.69	0.92	1.25	1.79	1.04	0.12	0.47	0	0.03
Synthesized CMAS1[6]	36.66	4.25	7.08	52.02						
Synthesized CMAS2[6]	32.70	6.37	11.50	47.77						
Synthesized CMAS3[6]	19.82	4.95	15.92	58.39						

2.2 Rheological properties of CMAS

In a completely molten CMAS system (Newtonian fluid character), the natural logarithm of viscosity is linearly correlated with the absolute temperature reciprocal, which can effectively predict the temperature dependence of molten CMAS viscosity. Song et al.used automated image analysis (Optical Dilatometry) to characterize the molten rheological characteristics of CMAS in nature, and summarized four characteristic temperatures: sintering temperature ST, deformation temperature DT, hemispherical temperature HT, and rheological temperature FT follow figure 1 [5]:

(1) Sintering Temperature (ST): The temperature at which particles sinter into a dense mass;

(2) Deformation Temperature (DT): The threshold for particle adhesion to surfaces due to partial melting;

(3) Hemispherical Temperature (HT): The point at which molten CMAS begins to wet and spread over surfaces;

(4) Rheological Temperature (FT): The temperature above which significant viscous flow occurs under gravity.

To compare the molten behavior of volcanic ash with that of other particulate matter inhaled by jet engines, previous studies using two types of CMAS to predict volcanic ash behavior were found to overestimate adhesion temperatures. This verifies that the thermodynamic behavior of volcanic ash could not be fully simulated using sand or dust. In order to accurately measure the characteristic temperature, the ash column sample of 3mm (ash sample size is 63~90μm) was used for the volcanic ash sample, and the heating rate was controlled at 10°C/min.

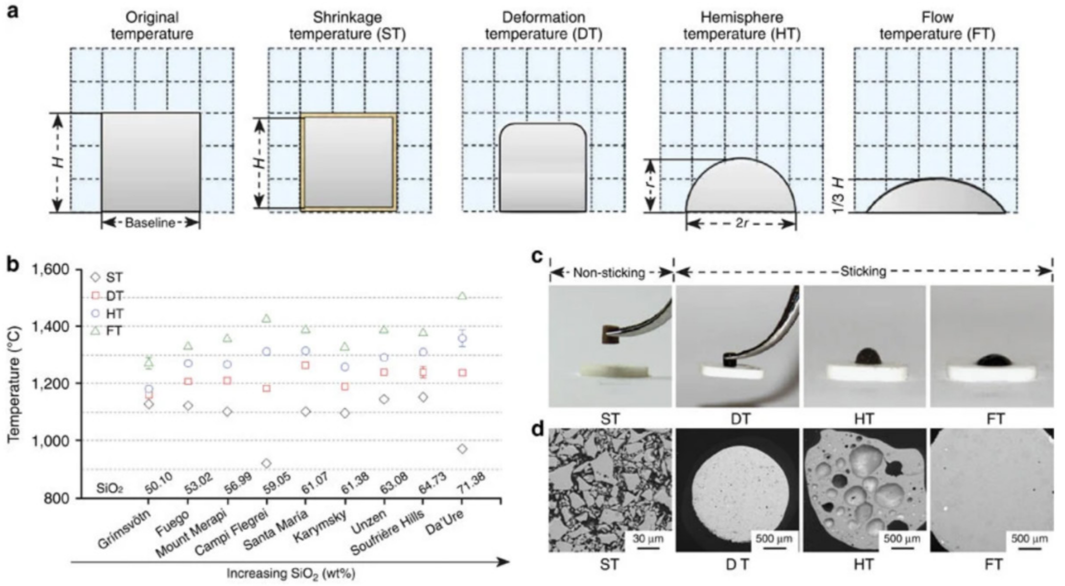

Fig.1 Geometric characterization of volcanic ash compacts at various characteristic temperatures[5]

3. Corrosion mechanism of thermal barrier coating CMAS

The molten CMAS adheres to the surface of TBCs and penetrates into the coating along the cracks and pores within the coating due to capillary force [7]. Some researchers have proposed that the failure mechanism of TBC is mainly manifested in two aspects: thermochemical failure and thermomechanical failure.

In the thermochemical failure mechanism, cation migration occurs at the interface between the YSZ protective layer and the CMAS melt, that is, Y^{3+} and Zr^{4+} diffuse from the YSZ lattice to the CMAS melt, and Zr^4will preferentially reach the saturation state due to low solubility, and then the ZrO_2 particles with low Y content will be precipitated in the interface region. Lacking sufficient Y^{3+} stabilizers, these Y-poor ZrO_2 phases undergo a thermally induced phase transformation during cooling—transitioning from the metastable tetragonal phase (t-ZrO_2) to the thermodynamically stable monoclinic phase (m-ZrO_2). This transition induces 3%–5% volume expansion, generating tensile stresses that drive microcrack formation and eventual spallation of thermal barrier coatings (TBCs) [8]. The thermomechanical failure mechanism reveals that CMAS melt invades the porous network structure and defect channel of thermal barrier coating through capillary action during high-temperature penetration. This destroys the coating's structural integrity and forms a dense amorphous substance. This results in thermal expansion mismatch, distortion of local stress field, and loss of porosity connectivity, weakening the coating's deformation adaptability [9].

4. CMAS protection strategy

In recent years, scholars at home and abroad have made significant achievements in CMAS protection technology. At present, the following three measures are mainly taken in the field of CMASA protection: (1) structural modification protective coating, that is, the microscopic scale effect or spraying process of the coating is used to reduce the damage of CMAS. (2) New ceramic materials, i.e., multi-component solid solutions formed by multiple atoms sharing one or more Wyckoff positions at the same time. (3) Chemical sacrifice layer, that is, another layer of coating is applied to the surface of TBCs.

4.1 Structural modification protective coatings

Fang and Cao systematically explored the doping effect of Yb elements and found that the modified YSZ coating based on the rare earth doping strategy exhibited significantly enhanced chemical inertness in the molten CMAS environments [10][11]. The introduction of Yb^3 in YSZ materials improves high-temperature phase stability by forming a high concentration of oxygen vacancy around the displaced cations. This reconfiguration of the O-O coordination mode creates a stable defect association, enhancing the coating's corrosion resistance. Additionally, Yb atom solid solutions reduce the diffusion mobility of active elements within the coating matrix, effectively

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suppressing interfacial reaction kinetics. Through this synergistic mechanism of defect engineering and diffusion control, a novel strategy emerges for optimizing thermal barrier coating material systems.

4.2 New ceramic materials

In view of the performance limitations of traditional YSZ thermal barrier coating materials, a series of breakthroughs have been made in the development of new ceramic systems in recent years. Among these, the $ScTaO_4$ system, a scandium-tantalum-based coating material, exhibits a unique anti-CMAS corrosion mechanism [12]. At 1300°C, it forms a barrier layer upon contact with CMAS, effectively impeding the diffusion of aggressive Ca, Mg, and Al ions due to its low solubility in molten silicates. Maintaining a stable monoclinic wolframite crystal structure, $ScTaO_4$ demonstrates exceptional interfacial stability. With the introduction of the concept of high-entropy ceramics, the paradigm of material design has undergone a revolutionary shift. Rostpioneered the construction of rock salt-type multi-principal element oxides (Mg, Ni, Co, Cu, Zn)O, which verified for the first time the feasibility of multi-component co-occupancy of the Wyckoff site to form a high-entropy solid solution [13]. With the unique configuration entropy stabilization effect, these materials show significant advantages in mechanical strength, high-temperature phase stability and thermal conductivity control. Building on this theoretical foundation, Sun and Chen developed high - entropy silicate systems that completely circumvent the blistering and cracking typical of traditional materials during CMAS corrosion [14]. This resilience stems from an entropy - stabilized barrier formed by the synergistic action of multiple rare earth elements, which significantly suppresses interfacial reactions. It is worth noting that lanthanides such as Ho^{3+} and Er^{3+} with large ionic radius can preferentially induce heterogeneous nucleation of apatite facies and construct a physical impermeability network due to their high matching degree with Ca^{2+} ionic radius.

4.3 Chemical sacrifice layer

Rare earth zirconates, such as $Gd_2Zr_2O_7$ or GZO, are promising materials for thermal barrier coatings (TBCs) [15]. The protection mechanism is that GZO dissolves and precipitates fluorite phases ($Zr(RE, Ca)O_x$) containing Zr, RE, and Ca, as well as the highly stable apatite-type silicate $Ca_2RE_8(SiO_4)_6O_2$. These newly formed phases effectively block the CMAS (calcium-magnesium-aluminosilicate) melt from further downward penetration. where RE can be any lanthanide in Y or La to Yb. At present, many scholars have studied the protection technology of chemical sacrifice layer (Table2).

Table 2. Main research contents [15]

Researchers	Research means	Findings:
Krämer	EB-PVD technology	The product is dense and inhibits the penetration of molten CMAS
Aygun	SPPS technology	Produces inert compounds with high melting points to prevent CMAS penetration
Tan	Solid-phase reaction and pressure-free sintering technology	A dense layer is generated to prevent CMAS from penetrating

5. Conclusion

TBCs are a key protection technology for aero engines. However, when the engine is working, a huge amount of heat will be generated, causing the working area to become hotter and higher, and the corrosion at high temperatures will lead to the premature failure of TBCs. This paper comprehensively reviews the physical and chemical properties, corrosion mechanisms, and protection strategies of $CaO-MgO-Al_2O_3-SiO_2$ (CMAS) deposits. The complex composition of CMAS poses significant challenges to experimental research. Given the variability in natural CMAS, it is nearly impossible to replicate all its characteristics using one or a few synthetic formulations; instead, only partial replication is achievable. This limitation restricts the scope of experimental investigations. Conversely, four newly defined characteristic temperatures have proven effective in elucidating CMAS rheological properties. Regarding CMAS corrosion mechanisms, the failure of TBCs induced by CMAS mainly involves two aspects, thermochemical failure and thermomechanical failure. For CMAS protection, common methods include structurally modified protective coatings, novel ceramic materials, and chemical sacrificial layers. Therefore, the following prospects are made for the high-temperature corrosion and protection of TBCs: In the case of atmospheric corrosion, it is still necessary to pay attention to marine corrosion. Establish connections from an interdisciplinary perspective, such as combining bionics, computer science, and materials science. Exploring the corrosion mechanism from a molecular perspective.

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