A novel design of Al-Cr alloy surface sealing for ablation resistant C/C-ZrC-SiC composite

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ABSTRACT

To improve anti-ablation property of C/C-ZrC-SiC composite, a novel design of Al-Cr alloy surface sealing was performed by liquid melt impregnation. Results show that Al_8Cr_5 formed on the surface which could effectively seal the holes and cracks. The cooperation of metal and ceramics contribute a better anti-ablation performance to the obtained composite, and its mass and linear ablation rates decrease by 98.3% and 81.2% respectively. This special surface structure evolves into a highly dense oxide scale comprising various solid solutions(including Al-Cr-O, Al-Si-O, Cr-Si-O) and ZrO_2 , which could significantly improve the anti-ablation performance of C/C-ZrC-SiC composite.

Key words: C/C composite; ultra-high temperature ceramics; surface sealing; Al-Cr alloy; ablation

1. Introduction

High strength-to-weight-ratio and excellent high temperature mechanical behaviors make C/C composite an attractive candidate for reentry hyper-sonic vehicles with sharp aerosurfaces[1]. However, the rapid oxidation and ablation in oxidizing atmosphere restrict its applications[2]. These contradictory properties of C/C composite motivate the development of external coatings and internal modification for protection[3-8]. ZrC/SiC ceramics modified C/C composite(C/C-ZrC-SiC) has been proved to be an effective solution due to its good anti-oxidation and anti-ablation between 1800 and 2500°C[9-13], but it has been still facing two big issues in service when temperatures are higher than 2000°C. Firstly, regardless of preparation methods, the open porosity of C/C-ZrC-SiC composite is around 10Vol% [3, 12]. In addition, cracks will be also generated during the preparation process. The residual holes and cracks would provide diffusion paths of oxygen and thus accelerate the oxidation of the composite. The other is active oxidation of SiC above 1800°C[14], which would cause severe depletion of SiC and leave a porous ZrO₂ oxide scale on the ablated surface[3,10,12,15]. However, the porous ZrO₂ can hardly inhibit the diffusion of heat and oxygen into the composites and will be easily peeled off in thermal shocks. Therefore, in consideration of designing a better ablation-resistant C/C-ZrC-SiC composite, two requirements should be met: 1) surface sealing: to reduce the diffusion paths of oxidizing atmosphere; 2) a continuous dense oxide scale: to inhibit heat and oxygen diffusion, as well as provide good thermal shock resistance.

The conventional surface sealing method is to prepare ultra-high temperature ceramic(UHTC) coatings on the surface of C/C-ZrC-SiC composite. But the intrinsic brittleness of ceramics and the thermal expansion coefficient(CTE) mismatch between coatings and matrix have limited their use in structural components. Even toughening and gradient treatments cannot prevent crack initiation and

propagation, which would lead to the failure of external coatings.

Introducing oxidation-resistant alloys should be an effective surface sealing solution to C/C-ZrC-SiC composite. Firstly, the high ductility of alloys can solve the CTE mismatch with the matrix. In particular, some low-melting point alloys can form dense and self-healing oxide scales at high temperatures, which would seal the porous ZrO_2 layer. Recent researches show that Al enables carbon-based composites endure severe ablation owing to its dissipative thermal protection and the formation of Al-Si-O solid solution[16-18]. However, there are a large number of metastable phases in Al_2O_3 , which would decrease the thermal stability of the coatings[19]. Researches show that the addition of Cr_2O_3 makes Al_2O_3 more stable at elevated temperatures[20]. Besides, Al-Cr alloy shows superior oxidation resistance at 850°C for a long time owing to the formation of highly densified oxide films. Moreover, $(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solutions show excellent mechanical properties and thermal shock resistance which are very suitable for the protection of reentry vehicles[21]. On the other hand, the Al_2O_3 - ZrO_2 system possesses good oxidation resistance and mechanical properties at high temperatures, especially for the eutectic phase owing to dispersion strengthening, stress-induced transformation toughening and crack deflection[22].

Despite of these advantages of Al-Cr alloy in oxidation protection, it has not been reported to protect C/C-ZrC-SiC composite unfortunately till now. Given that carbides(SiC/ZrC) can be well wetted by molten Al-based alloy at elevated temperatures above 1200°C [23], Al-Cr alloy is used to seal the pores and cracks of C/C-ZrC-SiC composite by liquid metal impregnation for the first time in this paper. It is also expected the introduction of Al-Cr alloy could contribute to the formation of a dense oxide scale containing Al-Cr-Zr-O solid solution and reduce the consumption of SiO_2 by forming Al/Cr-Si-O solid solutions during ablation.

2. Experiment

2.1 Materials

The preparation processes comprise the following steps: 1) 2.5D needled integral C/C preform (T700, PAN-based carbon fibers, Japan) was prepared by a needle-punching technique, then densified to 1.25g/cm^3 by isothermal CVD with CH_4 , H_2 and N_2 at 1050°C ; 2) Zr, Si mixed powders (Zr and Si powder: $d\sim 50\mu\text{m}$, 99.99% purity, Beijing Xing Rong Yuan Technology Co., Ltd. China) with Zr/Si atomic ratio of 1/4 were ball milled in absolute ethanol with a speed of 180rpm for 24h. The milling media were zirconia balls and the ball-to-powder weight ratio was 15:1. And then the mixed powders were dried in vacuum. Al, Cr mixed powders (Al and Cr powder: $d\sim 50\mu\text{m}$, 99.99% purity, Beijing Xing Rong Yuan Technology Co., Ltd. China) with Al/Cr atomic ratio of 2:1 were also prepared using the same method; 3) then C/C preform was placed in the graphic crucible together with Zr, Si mixed powders to obtain a C/C-ZrC-SiC composite. The crucible was heated at an average rate of 10°C to 2000°C in flowing argon and kept for 2 hours, finally cooled at 5°C/min to room temperature; 4) After that, Al, Cr mixed powders were firstly melted in a graphite crucible at 1500°C in vacuum, and then the obtained C/C-ZrC-SiC composite was immersed into Al, Cr melt via a mechanical device for 30min. Meanwhile, the furnace was fastly filled with inert argon gas to reach atmospheric pressure. Then the furnace was cooled at 5°C/min to room temperature. Finally, Al/Cr-C/C-ZrC-SiC composite was obtained. Fig.1 shows the schematic of liquid Al-Cr impregnation.

2.2 Characterization

The microstructures of obtained composites were characterized by scanning electron microscopy (FEI Electron Optics B.V, Nova NanoSEM 230) equipped with an energy disperse

spectroscopy(EDS). The phase compositions of the surface before and after ablation were identified by D/max 2550vb+18kW rotating target X-ray diffraction analyzer(XRD, Rigaku Co.). The elements distribution was analyzed by electron probe microanalysis(EPMA, JEOL CO., Jxa8230).

2.3 Ablation tests

The ablation tests of C/C-ZrC-SiC and Al/Cr-C/C-ZrC-SiC composites($\Phi 30 \times 10$ mm) were performed using an oxyacetylene torch (according to the GJB323A-96 Standard) for 200s, the pressures and fluxes of oxygen and acetylene were 0.4Mpa and 1.960L/s, 0.095MPa and 0.696L/s, respectively. The distance between gun tip and ablated surface was 30mm and the inner diameter of the gun tip was 2mm. The maximum temperature on the ablated surface of the sample was about 2500°C measured by an optic pyrometer. The mass and linear ablation rates of ablated composites were calculated according to the following formulates (1) and (2), respectively. Final ablation rates were the average of three ablated samples:

$$R_m = \frac{\Delta m}{t}$$

$$R_l = \frac{\Delta l}{t}$$

Where R_m is the mass ablation rate; Δm is the mass change before and after ablation; R_l is the linear ablation rate; Δl is the thickness change in the ablation center; t is the ablation time.

3 Results and discussion

As shown in Table 1, after infiltrated by Al-Cr molten, the open porosity of C/C-ZrC-SiC composite significantly decreases from 8.3% to 3.5%, and the density correspondingly increases from $2.42\text{g}\cdot\text{cm}^{-3}$ to $2.63\text{g}\cdot\text{cm}^{-3}$. It indicates that Al-Cr alloy can effectively seal the open pores of C/C-ZrC-SiC composite. The mass and linear ablation rates of C/C-ZrC-SiC composite(Table 1) are

$1.19 \times 10^{-3} \text{g/s}$ and $1.33 \times 10^{-3} \text{mm/s}$, respectively. It is interesting that Al/Cr-C/C-ZrC-SiC composite exhibits superior anti-ablation performance with mass and linear rates of $0.02 \times 10^{-3} \text{g/s}$ and $0.25 \times 10^{-3} \text{mm/s}$, respectively, nearly one/two magnitude lower than that of C/C-ZrC-SiC composite. Apparently, the considerably improved ablation resistance is attributed to the surface sealing by Al-Cr alloy.

Microstructure comparison of C/C-ZrC-SiC and Al/Cr-C/C-ZrC-SiC composites was conducted by SEM(Fig.2). As shown in Fig.2a, micro-cracks and holes are observed on the surface. The cross-sectional image(Fig.2b) also confirms that there are some holes existing on the cross section. The ceramics consist of two phases: white phase and gray phase, which are ZrC and SiC identified by EDS and XRD patterns. On the contrary, after surface sealing treatment(Fig.2c), the pores appeared in Fig.2a are sealed by a gray phase, which is composed of Al, Cr determined by EDS(before characterized by SEM, the residual solidified melt was removed by diamond grinding). In addition, the cross-section image(Fig.2d) shows that the gray phase can wet the ceramics and infiltrate the holes well.

XRD patterns of the Al/Cr-C/C-ZrC-SiC composite before(areas comprising solidified melt) and after ablation(ablation center) are shown in Fig.3. It reveals that the gray phase is Al_8Cr_5 , which is close to the atomic ratio of Al/Cr, and no other Al-Cr compounds are found[24]. After being ablated for 200s, the surface of Al/Cr-C/C-ZrC-SiC is composed of $(\text{Al}_{0.96}\text{Cr}_{0.04})_2\text{O}_3$, $(\text{Al}_{0.9}\text{Cr}_{0.1})_2\text{O}_3$, little Cr_2SiO_4 , $\text{Al}_{1.95}\text{Si}_{0.05}\text{O}_{2.95}$ and ZrO_2 . But in the case of C/C-ZrC-SiC, no silicon-containing phase can be found on the ablation center. Therefore, the existence of Cr_2SiO_4 and $\text{Al}_{1.95}\text{Si}_{0.05}\text{O}_{2.95}$ on the surface of ablated Al/Cr-C/C-ZrC-SiC composite indicates that the introduction of Al_8Cr_5 can avoid over-consumption of SiO_2 by forming Si-containing solid solution, and it has obtained the expected results of surface sealing using Al-Cr alloy previously.

To better understand the microstructure evolution and ablation mechanism, SEM images and element distribution of the ablated Al/Cr-C/C-ZrC-SiC composite are shown in Fig.4. As seen in Fig.4a, a highly dense oxide scale comprising two distinct areas(black and white) formed on the ablation center. The magnification image(Fig.4b) of black area shows that the large grains(around 5 μ m) are surrounded by white continuous phase, which are $(Al_{1-x}Cr_x)_2O_3$ (where, $x=0.04, 0.1$) solid solution and ZrO_2 respectively confirmed by EDS and XRD patterns. It can be seen clearly in Fig.4c that dispersing submicron ZrO_2 (less than 1 μ m) particles are embedded in $(Al_{1-x}Cr_x)_2O_3$ matrix. Noted that it is a typical microstructure of eutectic Al_2O_3/ZrO_2 with excellent mechanical and oxidation resistance properties[25].

The element distribution of black area in Fig.4d-i shows that the distribution of Cr within $(Al_{1-x}Cr_x)_2O_3$ grains is nonuniform compared to Al and O, which probably due to the higher volatilization rate of Cr_2O_3 than that of Al_2O_3 [9]. On the other hand, the completely miscible solid solution($(Al_{1-x}Cr_x)_2O_3$) would decomposed by spinodal mechanism under 950 $^{\circ}$ C, which would induce the segregation of Cr and the formation of two different phases: $(Al_{0.96}Cr_{0.04})_2O_3$ and $(Al_{0.9}Cr_{0.1})_2O_3$ [26]. It should be noted that the spinodal decomposition is a slow process, but the cooling stage is so fast(500~1000 $^{\circ}$ C/s) that the atomic diffusion is hindered, so the compositions of these two solid solutions show no big changes. In addition, Si is also observed in $(Al_{1-x}Cr_x)_2O_3$ grains. Distribution of Zr indicates that continuous ZrO_2 phase is developed around $(Al_{1-x}Cr_x)_2O_3$ grains. The element distribution of the white grains(which is not shown here) also confirmed that the white Zr-containing phase uniformly distributes in Al/Cr-containing matrix and the segregation of Cr also occurred.

It should be pointed out that the concentration variation of ZrO_2 leads to the formation of two distinct microstructures. During the ablation, when the ablated area contains much more Al_8Cr_3 , such as

holes and cracks that sealed by alloy, the oxidation products would contain much more $(Al_{1-x}Cr_x)_2O_3$ melt. According to the Al_2O_3 - ZrO_2 phase diagram[27], $(Al_{1-x}Cr_x)_2O_3$ would precipitate and grow first from the melt, then ZrO_2 would be enriched at the grain boundaries. So the ZrO_2 particles distribute around the $(Al_{1-x}Cr_x)_2O_3$ grains. Meanwhile, the oxidation products in areas comprising slight alloy would contain much more ZrO_2 . Then eutectic Al_2O_3/ZrO_2 phase can precipitate from the melt when the concentration of ZrO_2 reaches about $40\pm 1\%$. Finally, an eutectic phase $(Al_{1-x}Cr_x)_2O_3/ZrO_2$ is developed.

Unlike the porous surface of the ablated C/C-ZrC-SiC composite, the cross-section images(Fig.5) show that a continuous and dense oxide scale was developed. As shown in Fig.5a, the thickness of the oxide scale was about $150\mu m$. Besides, it also indicates that the oxide scale combines the matrix well and no visible crack can be found. The magnification image of the oxide scale(circled area in Fig.5a) reveals that two distinct microstructures were also developed inside the scale, which is consistent with the previous analysis .

4.Conclusion

In this paper, to design a better ablation-resistant material, holes and cracks of C/C-ZrC-SiC composite are successfully sealed by Al_8Cr_5 via liquid metal impregnation at $1500^\circ C$. The mass and linear ablation rates of C/C-ZrC-SiC composite are $1.19\times 10^{-3} g/s$ and $1.33\times 10^{-3} mm/s$ respectively. The mass and linear ablation rates, by contrast, decrease by 98.3% and 81.2% with $0.02\times 10^{-3} g/s$ and $0.25\times 10^{-3} mm/s$ respectively. Moreover, compared with the porous oxide scale of C/C-ZrC-SiC composite, the oxide scale of Al/Cr-C/C-ZrC-SiC composite was highly dense, and no obvious holes and cracks can be observed even in the sub-micro scale(about $5\mu m$). Besides, two different

microstructures of the oxide scale are found in the ablation center which is owing to the concentration variation of ZrO_2 .

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Fig.1 - Schematic of liquid Al-Cr impregnation

Fig.2 - Surface and cross-section images of (a), (b): C/C-ZrC-SiC composite;
(c), (d) : Al/Cr-C/C-ZrC-SiC composite

Fig.3 - XRD patterns of the Al/Cr-C/C-ZrC-SiC composite before and after ablation

Fig.4 - SEM images of ablation center of the Al/Cr-C/C-ZrC-SiC composite(a), (b) and (c); Elements distribution of the magnification image of Fig.4(d); (e) Al distribution; (f) O distribution ; (g) Cr distribution ; (h) Si distribution (i) Zr distribution

Fig.5 - SEM images of cross-section of the ablated Al/Cr-C/C-ZrC-SiC composite (a);
(b) magnification image of the oxide scale(circled using a red square)

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Table 1 - density, porosity and ablation results of C/C composites before and after modification

Sample	Density (g.cm ⁻³)	Open porosity (%)	Mass ablation rate (10 ⁻³ g/s)	Linear ablation rate (10 ⁻³ mm/s)
C/C preform	1.24±0.06	32±0.5	-	-
C/C-ZrC-SiC	2.42±0.10	8.3±0.2	1.19±0.02	1.33±0.03
Al/Cr-C/C-ZrC-SiC	2.63±0.10	3.5±0.4	0.02±0.01	0.25±0.01