Fabrication and microstructure of ZrB$_2$–ZrC–SiC coatings on C/C composites by reactive melt infiltration using ZrSi$_2$ alloy

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Abstract: ZrB₂–ZrC–SiC ternary coatings on C/C composites are investigated by reactive melt infiltration of ZrSi₂ alloy into pre-coatings. Two different pre-coating structures, including porous B₄C–C and dense C/B, are designed by slurry dip and chemical vapor deposition (CVD) process respectively. The coating prepared by reactive melt infiltration (RMI) into B₄C–C presents a flat and smooth surface with a three-layer cross-sectional structure, namely interior SiC transition layer, gradient ZrB₂–ZrC–SiC layer, and ZrB₂–ZrC exterior layer. In comparison, the coating prepared by RMI into C/B shows a more granular surface with a different three-layer cross-sectional structure, interior unreacted B–C pre-coating layer, middle SiC layer, and exterior ZrB₂–ZrC–ZrSi₂ layer. The forming mechanisms of the specific microstructures in two coatings are also investigated and discussed in detail.

Keywords: ultra-high temperature ceramics (UHTCs); coating; reactive melt infiltration (RMI); alloy

1 Introduction

Carbon fiber reinforced carbon matrix (C/C) composites with many merits, like low density, high retention rate of high temperature strength under inert environment, low coefficient of thermal expansion, and so on, are well regarded as one of the most promising thermal structure materials applied in aerospace fields such as nose cones and leading edges of the aircrafts \cite{1}, whereas the poor oxidation resistance of the C/C composites at temperature above 773 K seriously inhibits the further application in high temperature oxidizing atmosphere \cite{2}. Surface coating and matrix modification are two main solutions to reduce oxygen attack level of C/C composites \cite{3,4}. Since surface coating is already a matured technology, it is widely used in nowadays to improve the oxidation resistance properties of C/C composites.

Ultra-high temperature ceramics (UHTCs) have been increasingly developed in the past several decades in various components of reentry vehicles. It is reported that the SiC-based UHTCs, such as binary systems ZrB₂–SiC and ZrC–SiC ceramics can produce ZrO₂ and SiO₂, and form ZrSiO₄ by the reaction of
ZrO₂ and SiO₂ in the high temperature oxidizing atmosphere, which is considered as oxygen diffusion inhibition layer. Moreover, ZrSiO₄ not only has low permeability for oxygen and high thermal stability at high temperature, but also can reduce the consumption of SiO₂ and to a large extent improve the oxidation resistance ability of ceramics [5–7]. Owing to these advantages, introducing UHTCs into coating is considered to be a promising solution to the poor oxidation resistance of C/C composites. Up to now, a large number of efforts have been made to fabricate UHTCs–SiC coatings, and some key methods have been adopted like reactive melt infiltration (RMI), pack cementation, and supersonic plasma spraying (SPS), etc. [8–14]. Zhang et al. [15] selected supersonic atmosphere plasma spraying (SAPS) with ZrB₂–SiC–ZrC as raw materials to form ZrB₂–SiC–ZrC coating by the high temperature of a plasma arc and the high velocity of particles. Qi et al. [16] prepared ZrB₂–SiC/SiC coating on C/SiC composites at 1900 ℃ by pack cementation. Compared to SPS and pack cementation, RMI can avoid the oxidation during the fabrication, needs lower temperature with alloy, and can form a dense structure. It is well known that preparation of porous structure is critical to the RMI for a dense structure and better oxidation/ablation resistance properties [17–22]. As we know, slurry dip with resin phenolic as material is usually used to introduce carbon to the composites, and it can produce porous structure after pyrolysis.

In this work, a ZrB₂–ZrC–SiC ternary system coating is prepared on C/C composites by RMI using ZrSi₂ alloy based on slurry dip prepared B₄C/C pre-coating. A porous B₄C/C pre-coating is prepared by slurry dip and pyrolysis with resin phenolic as raw material and then the molten ZrSi₂ alloy is infiltrated into the porous pre-coating and finally ZrB₂–ZrC–SiC coating is obtained after in-situ reaction between B₄C/C and ZrSi₂. For a comparison, a boron and carbon containing pre-coating prepared by chemical vapor deposition (CVD) is applied as well. The microstructure and formation mechanisms of the ZrB₂–ZrC–SiC coatings are studied and discussed in detail.

2 Experimental procedures

2.1 Pre-coating preparation

B₄C/C pre-coating and boron and carbon containing pre-coating were prepared by slurry dip and CVD respectively in this paper. For B₄C/C pre-coating, B₄C powder (98.5% purity, Mudanjiang Abrasive and Grinding Tools, China) and phenolic resin (Shanghai Qinan Adhesive Material Factory, China) were mixed in alcohol through ball milling to obtain a slurry. Substrates (40 mm × 6 mm × 3.5 mm) were machined from 2D C/C composites which were fabricated through polymer infiltration and pyrolysis (PIP). Its density and open porosity are 1.6 g/cm³ and 9% respectively measured by Archimedes method with deionized water as medium. Then, substrates were dipped in the above-mentioned slurry and dried in air. After that, the slurry dip coating was cured at 120–150 ℃ for 1 h. The above processes were repeated for several times to obtain an expected thickness for pre-coating. Ultimately, the pre-coating was heated at 1500 ℃ before RMI for sake of transferring B₄C/resin into B₄C/C pre-coating. For boron and carbon containing pre-coating, BCl₃ and C₂H₄ gases were selected as the sources of B and C respectively, H₂ as the catalyst, and Ar as the carrier gas. Procedures like putting the C/C substrates in CVD device, controlling calculated flux of those mixed gases by flow controller, heating the device with the rate of 5 ℃/min to 1000 ℃ and maintaining 14 h were carried out to obtain boron and carbon containing pre-coating.

2.2 Coating preparation

C/C composites coated with B₄C/C or boron and carbon containing pre-coating were placed in a graphite crucible containing some ZrSi₂ alloy at the bottom. Then the furnace was heated to 1800 ℃ and dwelled for 2 h in vacuum. During the process, the molten ZrSi₂ penetrated into the pre-coating and reacted with carbon, B₄C, or boron and carbon containing phase to form ZrB₂–ZrC–SiC coating.

2.3 Microstructure analysis

The composition variation of the coating was analyzed by X-ray diffraction (Model D/max 2550 V, Rigaku, Japan) with Cu Kα source. The microstructure was observed by a S4800 field emission scanning electron microscope (Hitachi, Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS, Inca Energy) for elemental analysis. The densities and open porosities of substrates were measured by Archimedes method with deionized water.
3 Results and discussion

3.1 Pre-coating

Figure 1 shows the SEM images of cross-sections and surfaces of slurry dip prepared B₄C/C pre-coating after heat treatment at 1500 °C and CVD prepared boron and carbon containing pre-coating. It can be observed that both pre-coatings are continuous and integral. As shown in Fig. 1(a), the slurry dip pre-coating is well connected with substrate without obvious cracks and the thickness of the pre-coating is about 130 μm. Due to the volume shrinkage and emission of gas products during the resin organic compound pyrolysis at high temperature, this pre-coating structure is loose and quite a few pores could be observed. In addition, it is clear that B₄C particles are surrounded by pyrolysis carbon and many pores can be discovered in Fig. 1(b). It is well known that the porous structure has a positive effect on the densification during RMI process, which is helpful to obtain a dense structure.

In Figs. 1(c) and 1(d), the CVD prepared pre-coating is also well connected with the substrate without any cracks. But unlike the slurry dip pre-coating, the CVD prepared pre-coating structure is exceedingly compact. In addition, the CVD prepared pre-coating surface morphology shows a micro-scale nodular structure, which is in accordance with results presented in literatures [23–25].

Figure 2 represents the XRD patterns of both pre-coatings. Clearly, B₄C and carbon diffraction peaks could be found in slurry dip pre-coating in Fig. 2(a). Although only low crystalline pyrolytic carbon (PyC) diffraction peak is detected on the XRD pattern of

3.2 ZrB₂–ZrC–SiC coating

During RMI process, the molten ZrSi₂ would infiltrate into the pre-coating by capillary force and react with pre-coating. Figure 3 shows morphology of the RMI prepared coating based on slurry dip pre-coating. As shown in Fig. 3(a), the coating surface is flat and smooth without any apparent defects like large cracks or bumps, which would reduce the passage for oxygen going through the substrate and decrease the heat flow scouring. The XRD results of the surface in Fig. 4(a) indicate that the diffraction peaks of ZrB₂ and ZrC phases are detected, while SiC phase cannot be observed. From Figs. 3(b) and 3(c), it could be observed that the molten ZrSi₂ alloy reacts with B₄C/C pre-coating completely and the thickness of the coating increases from 130 to ~180 μm. The increment of its thickness is attributed to the volume expansion by reactions. The molar volumes of B₄C, ZrC, and ZrB₂ are 21.93, 15.34, and 18.54 cm³/mol, respectively. Therefore, when B₄C reacts with Zr to form ZrC and ZrB₂, the volume expands by 139%. Besides, it is generally believed that the similar volume expansion occurs during the reaction between carbon and Zr–Si eutectic.

In addition, there are only white and gray phases in cross-section backscattered images of the coating in Fig. 3(b). From EDS analysis (Spot1, Spot2, Spot3) in Fig. 3 and XRD pattern result of coating surface in Fig. 4(a), it could be revealed that the white phase is mixed phase of ZrC and ZrB₂ and the gray phase is SiC.
Interestingly, it can also be observed that the coating is comprised of three layers with different constituent distribution. The exterior layer is a white phase with a thickness of about 18 μm, which could explain the absence of SiC phase in the XRD pattern result. The middle layer is composed of white phase and gray phase, which are both distributed in a slight gradient trend. The interior layer is SiC, which is known as reaction bonding layer. It can finely enhance the boning strength between substrate and the coating and has a positive effect on declining the mismatch of coefficient of thermal expansion (CTE) between them.

Figure 5 shows the microstructure of ZrB₂–ZrC–SiC coating obtained from CVD pre-coating. In Fig. 5(a), it can be found that the surface of coating is also smooth but more granular compared to the coating based on slurry dip pre-coating, and the salient tetragonal grain morphology belongs to ZrB₂. Besides ZrB₂, ZrC, and SiC, ZrSi₂ phases are also detected by the XRD pattern of coating surface in Fig. 4(b). Similar to the coating based on slurry dip pre-coating, this coating is also divided into three layers namely exterior white layer, middle gray layer, and interior unreacted dark layer.

As marked in Fig. 5(b), the exterior and middle layers are only about 33 μm in total and the interior unreacted layer is amounted to 77 μm, which suggests only a small part of CVD pre-coating reacts with ZrSi₂. From the high magnification backscattered cross-section image of the coating in Fig. 5(c), it could be discovered that the exterior white layer is composed of two phases, distinguished by their slightly different contrasts. Through the EDS (Spot2, Spot3) in Fig. 5, and the XRD pattern result in Fig. 4(b), it could be inferred that in the exterior white layer, the darker part is ZrSi₂ and the whiter part is composed of ZrB₂ and ZrC. There is also a little SiC observed in the exterior layer, which results in the existence of SiC phase in the XRD pattern of the coating surface. As for the middle gray layer, it should be SiC phase, as detected by EDS (Spot1) in Fig. 5.

### 3.3 Coating formation mechanism

From the Zr–Si phase diagram [26], it can be known that the melting point of ZrSi₂ alloy is 1620 °C and at this temperature the alloy is consisted of solid β-ZrSi phase and liquid Zr–Si eutectic. As temperature increases, more β-ZrSi will transfer to Zr–Si eutectic according to lever principle. Therefore, when the...
temperature is raised up to 1800 °C, Zr–Si eutectic will account for a large proportion and react with pre-coating. All the reactions involved in the whole process are given as below:

1. \( \text{Si} + \text{C} = \text{SiC} \)
2. \( \text{Zr} + \text{C} = \text{ZrC} \)
3. \( 4\text{B}_4\text{C} + \text{Zr} = \text{ZrC} + 2\text{ZrB}_2 \)
4. \( \text{SiC} + \text{Zr} = \text{ZrC} + \text{Si} \)

Changes in Gibbs free energy of reactions as a function of temperature are shown in Fig. 6. The Gibbs free energies of reactions from reactions (1) to (4) at 1800 °C are \(-10.36\), \(-41.93\), \(-162.21\), and \(-31.57\) kJ·mol\(^{-1}\), respectively. The negative Gibbs free energy demonstrates that all the reactions are favorable thermodynamically. Besides, the more negative Gibbs free energy of reactions (2), (3), and (4) than that of reaction (1) indicates that Zr element is more active than Si element during the reactions.

The schematic diagram of ZrB\(_2\)–ZrC–SiC coating based on slurry dip pre-coating during the RMI process is presented in Fig. 7. In step (a), owing to the porous and loose structure of slurry dip pre-coating, molten Zr–Si eutectic will infiltrate into the pores by the capillary force. In step (b), the constantly proceeding Zr–Si eutectic through the pores would simultaneously react with B\(_4\)C/C to form ZrB\(_2\)/ZrC and SiC by above reactions, which also makes the pores smaller due to the volume expansion. In step (c), as the infiltration and reaction continue, Zr–Si eutectic goes deeper and more B\(_4\)C/C is transformed into ZrB\(_2\)/ZrC and SiC. As mentioned above, Zr is more active than Si, which means that the consumption rate of Zr is faster than Si during the infiltration. Moreover, the amount of Si is more than Zr in the eutectic originally. Therefore, it is unavoidable that the proportion of Zr becomes less compared to Si in Zr–Si eutectic as the infiltration continues. Finally, it leads to the slightly gradient distribution of SiC and ZrB\(_2\)/ZrC along coating direction. It is worth noting that the replacement reaction between Zr and SiC according to reaction (4) is favorable when the quantity of Zr is adequate at the beginning of infiltration but impractical as the infiltration goes deep, leading to fewer SiC in the exterior layer. In step (d), near the end of the infiltration, the most outer pores are fully filled by ZrB\(_2\)/ZrC and SiC, leaving a small inner part still containing some Zr–Si eutectic which is dominated by
Si with few Zr. In step (e), the remained Zr–Si eutectic would finally contact with surface of C/C composites to form a reaction bonding SiC layer between the C/C composites and exterior coating.

The formation mechanism of ZrB₂–ZrC–SiC coating from CVD pre-coating is shown in Fig. 8. In step (a), unlike slurry dip pre-coating, CVD pre-coating has a compact and dense structure, where the molten Zr–Si eutectic could not directly infiltrate into the pre-coating by capillary force. It has been reported that the formation of ceramic–metal composites was proposed by following: heating the reactive metal particulates to be molten, then molten metal wetting the ceramic and reacting with boron carbide [27]. Thus, in CVD–RMI process, it can be deduced that when the ZrSi₂ alloy melts and contacts with the pre-coating, it would wet the pre-coating by the surface tension (γ_{SV}, γ_{LV}, γ_{SL}). Zr–Si eutectic will gradually spread and finally cover
Among Zr–Si eutectic, B 4C, and C. The as-prepared ZrB 2–ZrC–SiC coating possesses a flat and smooth surface morphology and three-layer cross structure. The thickness of the coating expanded from 130 to ~110 μm. While CVD prepared pre-coating has an extremely compact and dense structure which severely inhibits the infiltration of Zr–Si eutectic. Consequently, the formation mechanism of ZrB 2–ZrC–SiC coating based on CVD prepared C/B pre-coating is mainly via the spread of Zr–Si eutectic by surface extension effect on the coating surface and reactions between dissolved pre-coating and Zr–Si eutectic. CVD combined RMI prepared coating presents a smooth but more granular surface morphology than the former and has three-layer cross structure namely interior unreacted C/B pre-coating layer, SiC middle layer, and ZrB 2–ZrC–ZrSi 2 exterior layer. The thickness of the coating expanded from 100 to ~110 μm.

4 Conclusions

In this work, ZrB 2–ZrC–SiC coatings were successfully prepared by RMI of ZrSi 2 alloy into porous B 4C–C or C/B pre-coatings, where the pre-coatings were fabricated by slurry dip and CVD. Slurry dip prepared pre-coating has a porous and loose structure which is beneficial for deep infiltration of Zr–Si eutectic. The formation of ZrB 2–ZrC–SiC coating based on porous B 4C–C pre-coating is mainly by capillary force and reactions among Zr–Si eutectic, B 4C, and C. The as-prepared ZrB 2–ZrC–SiC coating possesses a flat and smooth surface morphology and three-layer cross structure namely SiC interior transition layer, gradient ZrB 2–ZrC–SiC middle layer, and ZrB 2–ZrC exterior layer. The thickness of the coating expanded from 130 to 180 μm. While CVD prepared pre-coating has an extremely compact and dense structure which severely inhibits the infiltration of Zr–Si eutectic. Consequently, the authors are grateful to the financial support from the National Key Research and Development Program of China (No. 2017YFB0703200), and the research grant from Science and Technology Commission of Shanghai Municipality (No. 16DZ2260600).

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