Optimization of 3D Inlay Mode of “Z-Pins Like” V_{0.9}-Si_{0.1} Rods and Their Improvement Effect on the Anti-Ablative Performance of C/C-ZrC-SiC

Tian Tian

Central South University

Wei Sun (✉ sunweimse@csu.edu.cn)

Central South University

Xin Qing

Central South University

Yuhao Chu

Central South University

Haikun Chen

Central South University

Yufeng Liu

Science and Technology on Advanced Functional Composites Laboratory, Aerospace Research Institute of Material and Processing Technology

Xiang Xiong

Central South University

Hongbo Zhang

Central South University

Research Article

Keywords: “Z-pins like” vanadium_{0.9}-silicon_{0.1} rods, Polybasic multiphase oxide compensator, Anti-ablative performance, liquid/gaseous multicomponent oxide compensation mechanism.

Posted Date: February 17th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-199354/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Optimization of 3D inlay mode of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods and their improvement effect on the anti-ablative performance of C/C-ZrC-SiC

Tian Tian¹, Wei Sun^{1,2,*}, Xin Qing¹, Yuhao Chu¹, Haikun Chen³, Yufeng Liu³, Xiang Xiong¹,
Hongbo Zhang¹

¹State Key laboratory of Powder Metallurgy, Central South University, Changsha, 410083, China;

²National Key Laboratory of Science and Technology for National Defence on High-strength Structural Materials, Central South University, Changsha, 410083, China;

³Science and Technology on Advanced Functional Composites Laboratory, Aerospace Research Institute of Material and Processing Technology, Beijing, 100076, China.

Abstract: Neoteric “Z-pins like” vanadium_{0.9}-silicon_{0.1} rods ($V_{0.9}\text{-Si}_{0.1}$ rods) as polybasic multiphase oxide compensators were prepared to improve the anti-ablation of C/C-ZrC-SiC over 2500 °C. The microstructure and improvement effect on the anti-ablation of different C/C-ZrC-SiC surface were investigated. Results show that the density of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod was effectively improved after adding Si. When ablation time was less than 180 s, “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods perpendicular to non-woven cloth layer presented the best improvement of the anti-ablation performance by liquid/gaseous multicomponent oxide compensation. However, when ablation time was greater than 180 s, “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods perpendicular to non-woven cloth layer increased another harm that weaken the anti-ablative performance of C/C-ZrC-SiC, namely, the corrosion damage of oxide layer on the matrix surface caused by excessive oxide melt. Therefore, there is a best improvement of the anti-ablation performance of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods parallel to non-woven cloth layer.

Keywords: “Z-pins like” vanadium_{0.9}-silicon_{0.1} rods, Polybasic multiphase oxide compensator, Anti-ablative performance, liquid/gaseous multicomponent oxide compensation mechanism.

1. Introduction

Ultra-high temperature ceramic and SiC modified C/C composites (C/C-UHTCs) have become one of the most significant thermal protection materials, especially ZrC-SiC modified C/C-ZrC-SiC composites by reactive melt infiltration (C/C-ZrC-SiC) [1-6]. Because C/C-ZrC-SiC can generate a layer of dense $\text{ZrO}_2\text{-SiO}_2$ composite oxide layer to avoid further ablation at 2000 °C or a short-time service condition of 2500 °C [7,8]. However, when its service temperature above 2500 °C, the protective oxide layer is porous, which loses its properties of oxidation resistance and anti-ablation ultimately. Because the self-healing SiO_2 melt is washed away by high-speed airflow or even evaporated [9, 10], original micro-cracks, pores, and porous ZrO_2 generated during the ablation will not be filled [11, 12]. In addition, some carbon fibers are exposed on the composites surface prepared by reactive melt infiltration, which are preferentially oxidized to generate micro grooves. These micro grooves will decrease the continuity of oxide layer. Under the strong shear force of the high-speed airflow, the defective oxide layer is eroded mechanically [13]. Therefore, in order to improve the integrity of oxide layer on the ablated surface of C/C-ZrC-SiC and broaden service temperature, it is necessary to avoid the dissipation of oxides, especially the self-sealing SiO_2 liquid.

At present, modifying the surface microstructure of materials will become one of the important methods to enhance the stability of SiO_2 melt. B. Woolford et al found that the flow resistance of the liquid increased, when the groove was perpendicular to the flow direction [14]. Jung et al. found that grooves effectively reduced erosion caused by the impact of particle-laden flow [15]. Feng et al. improved the oxidation resistance of SiC matrix composites by designing specified bio-inspired microstructure of micro grooves [16-18]. The unique structure design can prevent the liquid SiO_2 from being flushed away at high temperature (1700-1800 °C). When temperature exceeds 2500 °C, however, this method to improving ablation resistance of C/C-ZrC-SiC is disabled due to the large amount of SiO_2 evaporation. Therefore, there are two issues must be solved to improve ablation resistance of C/C-ZrC-SiC when ablation temperature above 2500 °C. The first one is how to prevent the SiO_2 from dissipating, and another is compensating oxides with high boiling point to replace SiO_2 to play the self-healing role in real time. Based on above requirements, we designed “Z-pins like” V rods as oxide compensator and “Z-pins like” Si rod as

dissipative agent [19, 20]. When ablation temperature above 2500 °C, the ablation temperature field of the composite surface changes gradient in the plane [21]. Results showed that “Z-pins like” V rods mainly promoted the densification of the oxide layer on the ablative central and transitional surface by compensating V_2O_3 melt with a high melting point. “Z-pins like” Si rods improved the densification of oxide layer by dissipative thermal protection. Meanwhile, they also provided low melting point SiO_2 phase and SiO_2 vapor in the low temperature zone (such as transition zone and marginal zone) to ensure the densification of oxide layer on different area with different temperature. However, this structure was only suitable for the service condition of relatively short ablation time (2600 °C for 300 s).

Therefore, in order to satisfy the requirement of “Z-pins like” rods to play their oxide compensation role in different temperature domains, and broaden their service life, vanadium (V) and silicon (Si) were selected as the components of the structure in this study. Because the stable oxidative product at high temperature (over the 1957 °C) of vanadium or vanadium-based compound is V_2O_3 with high boiling point 3000 °C [22-25]. Meanwhile, V is easy to react with Si to form V_5Si_3 [26], so Si is also selected. In addition, the addition of Si also reveals other three effects: 1) Increasing the density of “Z-pins like” rods by forming liquid phase at low sintering temperature (about 1500 °C); 2) Providing liquid SiO_2 compensating oxide for ablation transition area; 3) Providing abundant gaseous SiO_2 and SiO compensating oxide for ablative edge region by vapor-liquid-solid (VLS) mechanism and oxide-assisted growth (OAG) model [27]. However, Feng et al. found that the content of SiO_2 melt on the C/C-ZrC-SiC surface directly affected its ablation resistance[3]. According the phase diagram of ZrO_2 - SiO_2 system, with the increased of SiO_2 melt content, the melting point temperature of solid solution decreased gradually, the viscosity of oxide melt also decreased gradually, and the oxide melt was easier to be washed by high-speed airflow [28]. In addition, Zeng et al. [29] showed that different fiber structures had great influence on the ablative properties of composites. Anisotropic 2.5D fabric C/C-UHTCs with a property of layer alternating presented different ablation performance on alternative layers [30]. Therefore, in order to avoid the formation of erosion damage caused by excessive oxide melt, the surface states (phase composition and distribution) of the matrix materials also be included into the research scope for the “Z-pins like” structure, which can form sufficient multiphase oxides.

In this work, in order to research the improvement difference in ablating resistance of different C/C-ZrC-SiC surface by three-dimensional embedded “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods, two samples strengthened by “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods in the direction of perpendicular to (ZCC-1) and parallel to non-woven cloth layer (ZCC-2) were prepared by liquid sintering. Their ablation performance and ablation behavior on different ablation surface were discussed. The distinct law of microstructure evolution and novel liquid/gaseous multicomponent oxide compensation mechanism of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods were summarized.

2. Experimental

2.1 Preparation of $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites

The “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites were fabricated in a four-step process. At first, the preparation of C/C-ZrC-SiC: 1) A pyrolytic carbon densified C/C composite with a density of $1.4 \pm 0.01 \text{ g/cm}^3$ and porosity of $3.4 \pm 0.1\%$ was used as the matrix of reactive melt infiltration. The C/C prefabricated body was formed by continuous needling between layers of long fiber non-woven cloth layer and short-cut web layer. 2) The C/C composites were placed in a graphite crucible filled with a Zr and Si mixed powder (Zr:Si mole ratio of 1:4) to generate the C/C-ZrC-SiC (density of $3.0 - 3.2 \text{ g/cm}^3$) by reactive melt infiltration at 2050°C for 3 h.

Then, the process of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods: 1) At first, pre-prepared C/C-ZrC-SiC matrix was cut into round block with a diameter of 30 mm and a thickness of 10 mm using a Computerized Numerical Control (CNC, JASU V-850). Uniformly distributed blind vias (diameter of 1.8 mm and depth of 6 mm) were machined on the surface (blind vias were perpendicular (Fig. 1(a₁)) and parallel (Fig. 1(a₂)) to non-woven cloth layer, respectively. Blind vias were distributed in a ring shape around the round block. The centers of the two holes are 4 mm apart, and the angle between three blind vias was 60 degrees (Fig. 1(a)). 2) Meanwhile, the mixed powder composed of pure vanadium, silicon ($d \sim 50 \mu\text{m}$, 99.99% purity, Beijing Xing Rong Yuan Technology Co. Ltd. China) and liquid paraffin (density: $0.830\text{-}0.860 \text{ g/mL}$, Sinopharm Chemical Reagent Co. Ltd. China) with the mass rate of $(0.9/0.1)/0.02$ were prepared (Fig. 1(b)). 3) After that, the prepared mixed powder was filled into blind vias of the substrate (Fig. 1(c)), and sintered at 1450°C for 3 h to

form two “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites. Fig. 1(d₁) is the sample that the “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod is perpendicular to non-woven cloth layer, namely ZCC-1. Fig. 1(d₂) is the sample that the “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod is parallel to non woven cloth layer, namely ZCC-2.

Fig. 1 Process flow chart of "Z-pins like" $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites.

2.2 Ablation experiment

The ablation resistance of two “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites were tested by oxy-acetylene ablation test for 180 s and 240 s (according to the GJB323A-96 standard [31, 32]). The pressures and fluxes of acetylene and oxygen were 0.095 MPa and 0.696 L/s and 0.4 MPa and 1.960 L/s respectively. During the test, an infrared thermometer (error of $\pm 0.75\%$, Raytek MR1SCSF) was indicated that the highest temperature of C/C-ZrC-SiC and “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites were 2650 ± 10 °C and 2455 ± 10 °C at the distance of 22 mm between the torch nozzle and the sample surfaces, respectively. The mass ablation rates and linear ablation rate of two samples were calculated by Eq. (1), Eq. (2) and Eq. (3).

$$R_m = \Delta m / t \quad (1)$$

$$R_{L1} = \Delta L1 / t \quad (2)$$

$$R_{L2} = \Delta L2 / t \quad (3)$$

Where R_m is the mass ablation rate, Δm is the mass change of the sample. R_{L1} and R_{L2} are the linear ablation rate of C/C-ZrC-SiC and “Z-pins like” rods in the sample, which are measured separately. $\Delta L1$ and $\Delta L2$ are the thickness change of “Z-pins like” rods and matrix respectively, and t is the ablation time.

2.3 Characterization

The phase compositions of ZCC-1 and ZCC-2 before and after ablation were measured by D/mas 2550vb+18KW rotating target X-ray diffraction analyzer (XRD, Rigaku Co.). Their interface between the “Z-pins like” rod and C/C-ZrC-SiC substrate, surface microstructures of ZCC-1 and ZCC-2 before and after ablation were characterized by scanning electron microscopy (SEM, Fei Na Pro X) with energy dispersion spectroscopy (EDS). And the elements distribution of the “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod after sintering were analyzed by electron probe microanalysis (EPMA, JEOL CO., Jxa8230).

3 Results and discussion

3.1 Different surface ablating microstructure of C/C-ZrC-SiC inspired optimization for the 3D inlay mode of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods

Due to the porosity of non-woven cloth layers are much lower than that of short-cut web layers, the content of ceramic of the former is lower than that of the latter. Therefore, when ablation direction is perpendicular or parallel to non-woven cloth layer, the phase distribution on the ablative surface is greatly different.

As Fig. 2(a) shown, when ablation direction is perpendicular to non-woven cloth layer (Sample CC-1), ceramic distribution of ablative surface is relatively continuous (Fig. 2(a)A), but bare carbon fiber tows still expose on there (Fig. 2(a)B). However, when ablation direction is parallel to non-woven cloth layer (Sample CC-2), the bare carbon fiber-rich non-woven cloth layer and ceramic-rich short-cut web layer on the ablative surface are arranged with each other, and the continuity of ceramic distribution is relatively low (Fig. 2(d)). After ablating at 2654 °C for 180 s, although ZrO_2 layer formed in the ablative center of sample CC-1 is relatively continuous, which is full of holes and cracks with different sizes (Fig. 2(b)). And the ablative edge

area of the exposed carbon fiber tows are ablated seriously (Fig. 2(c)). However, due to a large number of regularly exposed non-woven cloth layer on the ablative surface of sample 2, many regularly arranged grooves are formed in the ablative central area and the edge area. Finally, the oxide layer on the entire sample CC-2 surface is porous and discontinuous.

Fig. 2 (a) Macro/micro-structures of C/C-ZrC-SiC in different ablation layer. (a) Macro picture of the sample with ablation surface parallel to non-woven cloth layer. (b) and (c) Central and marginal microstructures of the sample after ablation. (d) Macro picture of the sample with ablation surface perpendicular to non-woven cloth layer. (e) and (f) Central and marginal microstructures of the sample after ablation.

In order to increase the density of oxide layer at all areas and enhance the ablation resistance of C/C-ZrC-SiC, a novel binary “Z-pins like” $V_{0.9}Si_{0.1}$ rods with liquid/gaseous multicomponent oxide compensation effect were designed and fabricated on C/C-ZrC-SiC surface. For these rods of a particular component, the morphology and phase composition of the oxide layer on the matrix surface will directly affect the spreading rate of the compensating melt, and then effect the ablation resistance improvement of the composites. The affecting mechanism of the oxide density of matrix on the spreading behavior of compensating oxide melt is

explained using the models illustrated in Fig. 3. The spreading of compensating oxide melt is divided into two stages: the first one is the spreading of the matrix surface around the structure (Stage I in Fig. 3), and the second is the spreading away from the structure (Stage II in Fig. 3).

When “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods are perpendicular to non-woven cloth layer (Fig. 1(d₁)), the density and continuity of ZrO_2 -rich layer on the substrate surface (Fig. 2(b)) are higher than that in the parallel direction (Fig. 1(d₂) and Fig. 2(e)). The flow resistance of the compensating oxide melt of the first is lower than that of the latter. Therefore, when “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods are perpendicular to non-woven cloth layer (Stage I in Fig. 3(a)), the compensating oxide melt spreading, compensating oxide melt flows faster than the parallel direction (Stage I in Fig. 3(b)) in the first stage.

In the second stage, when “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods are perpendicular to non-woven cloth layer, the compensating oxide melt still flows on the continuous matrix oxide layer (Stage II in Fig. 3(a)). And the continuous ablation pits formed by the oxidation of exposed carbon fibers in the short-cut web layer are conducive to the flow and aggregation of oxide melt. However, when “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods are parallel to non-woven cloth layer, the regular grooves formed by the oxidation of the short-cut web layer act as an obstacle to the oxide melt flow in the second stage (Stage II in Fig. 3(b)).

Therefore, when “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods are perpendicular to the non-woven cloth layer (Fig. 1(d₁)) of the the ablation surface or parallel (Fig. 1(d₂)), the spreading effect of compensating oxide melt and the improvement effect of the structure on the ablation resistance of the composite all need test and contrastively analyse, and then optimize the three-dimensional embedding mode of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods.

Fig. 3 The spreading model of compensating oxide melt.

3.2 Phase composition and microstructure of $V_{0.9}-Si_{0.1}$ rods reinforced C/C-ZrC-SiC composites

The sintered “Z-pins like” $V_{0.9}-Si_{0.1}$ rods were taken out from C/C-ZrC-SiC and detected by XRD. Results show that “Z-pins like” $V_{0.9}-Si_{0.1}$ rod is chiefly composed of V_5Si_3 , VC and V_2C (Fig. 4)). The reason for the generation of ZrO_2 is that original V particles are oxidized during the filling process of vanadium powder and the crushing process of “Z-pins like” rod (Eq. (4)). And then, abundant C is provided by decomposition of forming agent or matrix, which reduces VO to form V and O_2 during sintering (Eq. (5)). V particles have high affinity to the C and Si, and form VC under 800-1000 °C and V_5Si_3 under 1160-1260 °C respectively [33-35]. Finally, V particles are carbonized (Eqs. (6) and (7)) and siliconized (Eqs. (8) and (9)) , and O_2 reacts with ZrC to form ZrO_2 (Eq. (10)).

Fig. 4 XRD analysis results of “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rods after sintering.

As Fig. 5(a) shown, the density of “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod is significantly improved comparing with “Z-pins like” V rod [17]. The holes and gaps between each V particle are filled with Si melt generated during sintering. Wherein, the white phase is VC, the gray phase is V_2C , and the gray phase is V_5Si_3 (Fig. 5(b)). “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod is closely bonded with the ceramic region and the carbon fiber tow region of the matrix (Fig. 5(c)).

Fig. 5 (a) and (b) The microstructure of “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod and its enlarged picture of (a).

(c) The interface between “Z-pins like” $V_{0.9}Si_{0.1}$ rod and ZrC-SiC ceramics and carbon fibers.

Fig. 6 is the distribution of C, Si and V on the surface of "Z-pins like" $V_{0.9}Si_{0.1}$ rod. Among them, V element (Fig. 6(b)) is mainly distributed in the white phase area of Fig. 6(a). C element (Fig. 6(c)) is only distributed at the center of V-rich region (the white phase region in Fig. 6(a)). Si element (Fig. 6(d)) is abundantly enriched in the dark gray region and decreases toward the V-rich area. Combining with XRD pattern, it is known that the dark gray phase and its periphery are mainly composed of intermediate compounds V_5Si_3 and V_3Si . Silicon is not found in the center of V-rich region. It is attributed to that V particles preferentially react with C to form VC and V_2C , and then to react with the liquid phase Si to form V_5Si_3 and V_3Si .

Fig. 6 Elemental distributions of electron probe microanalysis of “Z-pins like” $V_{0.9}Si_{0.1}$ rod after sintering. (b) V. (c) C. (d) Si.

3.3 Ablation property and macro-profiles of “Z-pins like” $V_{0.9}Si_{0.1}$ rods reinforced C/C-ZrC-SiC composites.

As Fig. 6 shown, When “Z-pins like” $V_{0.9}Si_{0.1}$ is perpendicular to the non-woven cloth layers (Fig. 7(a) and (b)), the spreading area of the oxide formed by “Z-pins like” $V_{0.9}Si_{0.1}$ rods towards the matrix is much larger than that of the

horizontal action on non-woven cloth layers (Fig. 7(c) and (d)). Moreover, when the ablation time is extended to 240 s, ZCC-1 begins to be eroded by excess oxide melt (Fig. 7(b)). According to the spread area of oxidation products of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod and the color depth of surface oxide layer, the surface ablative morphology of each sample is divided into three areas, namely, the ablation center, the transition and the edge.

Fig. 7 The macroscopic features of ZCC-1 and ZCC-2. (a) and (b) ZCC-1 after ablating for 180 s and 240 s, respectively. (c) and (d) ZCC-2 after ablating for 180 s and 240 s, respectively.

Table 1 is the mass and linear ablation rates of ZCC-1 and ZCC-2 after ablating for different time. Results show that the mass ablation rate increases with the ablation time extension. The linear ablation rate of C/C-ZrC-SiC matrix of ZCC-1 changes from minus to positive with the ablation time extension, which indicates that the thickness in this region first increases and then decreases. However, the linear ablative rate of the C/C-ZrC-SiC matrix of ZCC-2 is minus, and its value increases with the time prolonging. The linear ablation rate of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod of ZCC-1 and ZCC-2 all increase with the time lengthening.

Table 1 The linear ablation rate and mass ablation rate of ZCC-1 and ZCC-2 under different ablation processes

sample	ZCC-1	ZCC-2
--------	-------	-------

Ablation temperature		2600 °C			
Ablation time (s)		180	240	180	240
Mass ablation rate (mg/s)		0.12	0.38	0.05	0.25
Linear ablation rate	L ₁	-0.51	2.08	-0.38	-0.43
($\mu\text{m/s}$)	L ₂	1.32	3.32	0.82	1.33

As XRD patterns of two samples after ablation for 180 s and 240 s shown (Fig. 8(a) and (b)), oxide layers on the two samples surface are all composed of m-ZrO₂, SiO₂, quartz SiO₂ and V₂O₅. With the ablation time extending, the diffraction peaks intensity of V₂O₅, SiO₂ and quartz SiO₂ on ZCC-1 surface are slightly enhanced. However, when “Z-pins like” V_{0.9}-Si_{0.1} rods parallel to non-woven cloth layer, the diffraction peaks intensity of quartz SiO₂ is stronger than that on the ZCC-1 surface, and other phases all basically remain the same.

Fig. 8 The XRD results of ZCC after ablating for 180 s and 240 s respectively. (a) ZCC-1. (b) ZCC-2.

3.4 Ablative microstructure of ZCC-1

In order to explore the evolution of the surface ablation microstructure of ZCC-1 after ablating for 180 s in accordance with the ablating center, transition, inner edge and outer edge shown in Fig. 7(a) is detected. The yellow arrow in Fig. 7(a) represents the representation sequence. Microstructure of all regions marked with capital letters in Fig. 7(a) are selected to detect surface and interface of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod (Areas A, C, E and G in Fig. 7(a)), as well as C/C-ZrC-SiC matrix surface far away from “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod (Area B, D, F and H in Fig. 7(a)). In addition, the ablative center and transition of ZCC-1 ablated for 240 s (Fig. 7(b)) are characterized and analyzed.

Fig. 9 is the ablative central microstructure of ZCC-1 after ablating for 180 s. “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod surface in the ablation center is composed of a large amount of radial and acicular V_2O_5 and bits of SiO_2 (Fig. 9(a)). No ZrO_2 skeleton is found on the surface of C/C-ZrC-SiC near “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod, only a few of agglomerated ZrO_2 spheres. But their surfaces are all covered with a $V_2O_5\text{-SiO}_2$ composite layer (Fig. 9(c)). This is because $V_5\text{Si}_3$ from “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod preferentially oxidizes, and generates a large amount of SiO_2 to reduce the central ablation temperature by its evaporation. Meanwhile, the consumption of SiO_2 is much lower than its production. Finally, C/C-ZrC-SiC surface still retain a handful of SiO_2 . However, due to a large number of oxide melts producing, ZrO_2 skeleton on the matrix surface will be washed. By amplifying the agglomerated ZrO_2 sphere, it can be clarified that the compensating vanadium oxide generated during the high temperature ablation process shows radial flow after bypassing the agglomerated ZrO_2 sphere (Fig. 9(b)). Meanwhile, the interface between “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod and C/C-ZrC-SiC generates thermal stress Crack.

Fig. 9 Microstructures of the “Z-pins like” $V_{0.9}Si_{0.1}$ rod-reinforced C/C-ZrC-SiC composites in the ablation center after ablating for 180 s. (a) and (b) The border between “Z-pins like” $V_{0.9}Si_{0.1}$ rod and C/C-ZrC-SiC and the enlarged picture of the area A. (c) The microstructure of the matrix.

As the transitional ablating SEM picture shown in Fig. 10(a), SiO_2 is also residual on the surface of “Z-pins like” $V_{0.9}Si_{0.1}$ rod, and its content is higher than that in the center. In addition, some tetragonal ZrO_2 particles are found as the impact of V element (Fig. 10(a)) [36]. However, no Zr element is found in “Z-pins like” $V_{0.9}Si_{0.1}$ rod by EPMA (Fig. (5)). Therefore, the main reason for the appearance of ZrO_2 on “Z-pins like” $V_{0.9}Si_{0.1}$ rod surface is that the compensating oxide melt carries ZrO_2 particles in the flow process. It is worth mentioning that extensive SiO_2 film appear on the substrate surface that closes to or far from “Z-pins like” $V_{0.9}Si_{0.1}$ rod. There are three typical topographical features appearing on the substrate surface near “Z-pins like” $V_{0.9}Si_{0.1}$ rod (Fig. 10(b)). The first one is agglomerated ZrO_2 spheres (Fig. 10(c)) which are surrounded by V_2O_5 . The second is a mixed region of SiO_2 and ZrO_2 (Fig. 10(d)B), where SiO_2 is uniformly filled between ZrO_2 particles. And the last one is a thicker SiO_2 layer completely covering on ZrO_2 skeleton (Fig. 10(d)C).

On the matrix surface far from “Z-pins like” $V_{0.9}Si_{0.1}$ rod, there is a homogeneous dense SiO_2 - V_2O_5 composite film attaching some agglomerated ZrO_2 spheres (Fig. 10(e)) and remaining unfilled holes. All reunited ZrO_2 spheres are tightly bonded to a SiO_2 - V_2O_5 - ZrO_2 oxides layer. And the ZrO_2 skeleton is always looming at the bottom of SiO_2 film (Fig. 10(f)). These fully demonstrate that the oxides act compensating oxide in this region are both SiO_2 and V_2O_3 during ablation. After the compensating of two glassy oxide melts, the protective oxide layer on substrate surface is more dense.

In conclusion, abundant SiO_2 remains in the transition region, which sufficiently prove that the temperature in this region is lower than ablation center. Moreover, SiO_2 melt from “Z-pins like” $V_{0.9}Si_{0.1}$ rods can adequately play the oxide compensation effect, so as to ensure the densification of the oxide layer at the mid-temperature.

Fig. 10 Microstructures of the “Z-pins like” $V_{0.9}Si_{0.1}$ rod-reinforced C/C-ZrC-SiC composites in the ablation transition after ablation for 180 s. (a) The microstructure of the “Z-pins like” $V_{0.9}Si_{0.1}$ rod. (b) and (c) The border between “Z-pins like” $V_{0.9}Si_{0.1}$ rod and C/C-ZrC-SiC and the enlarged picture of the area A. (d) The enlarged picture of the area B and C in (b). (e) and (f) The microstructure of the matrix and the enlarged picture of the area D.

In the ablation edge, due to the completely different morphology of oxide film, it can be divided into two distinct areas to analyze. They are the inner edge region nearing the ablation transition (Fig. 11(a-c)) and the outer edge away from (Fig. 11(d-f)), respectively. The main reason for the two topographical features is the different effect of gaseous SiO_2 compensation.

In the inner edge area, the oxide layer on “Z-pins like” $V_{0.9}Si_{0.1}$ rod surface is composed of gray V_2O_5 and dark gray SiO_2 (Fig. 11(a)). SiO_2 is largely enriched in the marginal area of “Z-pins like” $V_{0.9}Si_{0.1}$ rod, and only a small amount of SiO_2 spreading to C/C-ZrC-SiC matrix surface. This fully indicates that SiO_2 preferentially melts and acts the oxide compensating effect. C/C-ZrC-SiC far away from “Z-pins like” $V_{0.9}Si_{0.1}$ rod is covered with a dense cauliflower-shape SiO_2 molten layer decorated with V_2O_5 (Fig. 11(b)).

In the outer edge area, C/C-ZrC-SiC surface near or away from “Z-pins like”

$V_{0.9}\text{-Si}_{0.1}$ rod are all covered with a dense SiO_2 layer (Fig. 11(c) and (e)). No oxide melt from “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod spreads to substrate (Fig. 11(c)), which certifies that the protective SiO_2 layer generates from gaseous SiO_2 and SiO by VLS mechanism and OAG model [27]. The exposed carbon fiber bundles are substantially free of damage, and their surface are all covered with a protective SiO_2 layer which distributes many SiO_2 nanoparticles (Fig. 11(d)). The holes between carbon fibers are also sealed (Fig. 11(d)). Simultaneously, there is a pyknotic oxide layer deposited by SiO_2 and SiO vapor on the substrate surface away from “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod. Plentiful SiO_2 nanoparticles distributed on the SiO_2 film and some are almost integrated with SiO_2 layer (Fig. 11(e)). These phenomenons fully clarify the formation process of SiO_2 film in the ablated edge, which undergoes three processes of nucleation of SiO_2 nanoparticles, growth of SiO_2 nanoparticles, and aggregation of spherical SiO_2 into a dense film [37-39]. These can also effectively prove that when Si elements are added to “Z-pins like” rods, sufficient SiO_2 and SiO vapor can be provided to the ablative edge area of during the ablation process, so as to effectively avoid oxidative damage of exposed carbon fibers.

Fig. 11 The microstructure of the “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites edge after ablating for 180 s. The inner edge: (a) The border between “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod and matrix. (b) The matrix surface. The outer edge: (c) and (d) The border between “Z-pins like”

$V_{0.9}Si_{0.1}$ rod and matrix and the enlarged picture of the area A. (e) The matrix surface.

After ablating for 240 s, the ablative central spacing between two “Z-pins like” $V_{0.9}Si_{0.1}$ rods reduced from the original 4 mm to 0.847 mm (Fig. 12(a)). This is mainly due to the surface matrix of ZCC-1 begins to suffer from melting erosion by excess oxide melt generated from “Z-pins like” $V_{0.9}Si_{0.1}$ rods. As Fig. 12(b) shown, there is no residual SiO_2 , only a dense V_2O_5 layer with square ZrO_2 particles.

Fig. 12 The central microstructure of the “Z-pins like” $V_{0.9}Si_{0.1}$ rod-reinforced C/C-ZrC-SiC composites after ablating for 240 s. (a) The boundary between the “Z-pins like” $V_{0.9}Si_{0.1}$ rods and C/C-ZrC-SiC. (b) The “Z-pins like” $V_{0.9}Si_{0.1}$ rods.

In summary, after adding Silicon, the “Z-pins like” rod can compensate different oxides in different areas of C/C-ZrC-SiC surface, and promote the formation of a dense gradient oxide protective layer in all regions of matrix. However, when the ablation time increases to 240 s, excessive compensating oxide melt will damage the matrix by melting corrosion, which is unfavourable for the improvement of the anti-ablation performance.

3.5 Ablative microstructure of ZCC-2

The microstructure of the ablative central and marginal regions of ZCC-2 is characterized by yellow arrows in Fig. 7(c). The surface and interface microstructures of “Z-pins like” $V_{0.9}Si_{0.1}$ rod (Areas A and C in Fig. 7(c)), and C/C-ZrC-SiC surface far away from “Z-pins like” $V_{0.9}Si_{0.1}$ rod (Area B and D in Fig. 6(c)) are characterized and analyzed.

After ablating for 180 s, there is a small amount of consumption of “Z-pins like” $V_{0.9}Si_{0.1}$ rod in ablation center. Some micro grooves are formed after extensive

oxidative damage of bare non-woven cloth layers, and the ZrO_2 skeleton layer on C/C-ZrC-SiC surface is very loose and discontinuous (Fig. 13(a)). In addition, there is no radial V_2O_5 , only a uniformly dense mixed fusion $\text{V}_2\text{O}_5\text{-SiO}_2$ layer formed on the surface of “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod (Fig. 13(b)). As the enlarging picture of area B in Fig. 13(a) shown, despite the exposed non-woven cloth layers encounter oxidative damage, a dense SiO_2 layer from “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod is covered on its surface (Fig. 13(c)). Meanwhile, the holes in the ZrO_2 skeleton nearing the interface are partly filled with compensating oxides from “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod (Fig. 13(d)). However, the oxide melt compensation of “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod is poor on the matrix surface far away from it, and a loose and heterogeneous $\text{ZrO}_2\text{-SiO}_2$ layer is still formed on the matrix surface. The main reason why the integrity and compactness of the oxide layer on ZCC-2 are lower than that of ZCC-1 is that the oxide layer formed by the initial oxidation of C/C-ZrC-SiC matrix in ZCC-2 is looser than that of ZCC-1. Therefore, the oxidation products of “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod are difficult to spread to the substrate surface.

Fig. 13 The central microstructure of ZCC-2 after ablating for 180 s. (a) and (b) The microstructure of the “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod and the enlarged picture of the area A. (c) The boundary between “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod and carbon fiber tows. (d) The boundary between “Z-pins like” $\text{V}_{0.9}\text{-Si}_{0.1}$ rod and ceramic. (e) The microstructure of the matrix.

After ablating for 240 s, ZCC-2 has better ablative performance than ZCC-1

(Table 1). In the ablating center, C/C-ZrC-SiC around “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod is not damaged by melting corrosion (Fig. 14(a)). The content of SiO_2 on “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod surface is reduced, and the radial and needle V_2O_5 phases have been highlight (Fig. 14(b)). In addition, the density of ZrO_2 layer on C/C-ZrC-SiC surface away from “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod is denser than the sample after ablated for 180 s (Fig. 14(c)). The gaps between two ZrO_2 particles are sealed with radiating V_2O_5 from “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod (Fig. 14(d)). No exposed carbon fibers are found in the microscopic grooves (Fig. 14(e)), which are all covered with a dense SiO_2 -rich layer (Fig. 14(f)). This fully proves that “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod can effectively play its role in oxide melt compensation at this stage.

Fig. 14 The central microstructure of the “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod-reinforced C/C-ZrC-SiC composites after ablating for 240 s. (a) and (b) The microstructure of the “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod and the enlarged picture of the area A. (c) and (d) The microstructure of the matrix and the enlarged picture of the area B. (e) and (f) The microstructure of groove from the oxidation of carbon fiber tows and the enlarged picture of the area C.

As the marginal microstructure of C/C-ZrC-SiC of ZCC-2 shown in Fig. 15, Whether ZCC-2 ablating for 180 s or 240 s, there is no deposited SiO_2 layer on fringe ZCC-2 surface as shown in Fig. 13, only a loose $\text{ZrO}_2\text{-SiO}_2$ layer ((Fig. 15(a)). And the bare carbon fibers are damaged serious (Fig. 15(b)). Clearly, when “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods are parallel to non-woven cloth layer, the spreading rate of glass SiO_2

melt from themselves towards C/C-ZrC-SiC is relatively slow, resulting in relatively small spreading area of exposed SiO₂ melt, and ultimately leading to a decrease in the content of vapor phase SiO₂ used for depositing SiO₂ layer in the marginal area.

Fig. 15 The marginal microstructure of C/C-ZrC-SiC of ZCC-2 after ablating for 180 s and 240 s.

(a) 180 s. (b) 240 s.

To sum up, when the ablation time is no longer than 180 s, the improvement of anti-ablation performance from “Z-pins like” V_{0.9}-Si_{0.1} rod perpendicular to the direction of non-woven cloth layer is the best. Since the C/C-ZrC-SiC surface can form a continuous ZrO₂-rich layer, the flow resistance of compensation oxide melt formed by “Z-pins like” V_{0.9}-Si_{0.1} rod is relatively small, which can effectively promote the formation of a dense one-dimensional gradient composite oxide layer in all regions of the matrix. In contrast, when the ablation time is longer than 180 s, the improvement of anti-ablation performance from “Z-pins like” V_{0.9}-Si_{0.1} rod parallel to the direction of non-woven cloth layer is the best. Because some micro grooves formed after oxidation of exposed non-woven cloth layer in C/C-ZrC-SiC effectively can evacuate the compensating oxide melt formed by “Z-pins like” V_{0.9}-Si_{0.1} rods, finally avoid the melting corrosion on the matrix surface.

3.6 Liquid/gas multicomponent oxide compensation mechanism

According to special ablative morphology of ZCC-1 and ZCC-2, the ablative model of “Z-pins like” V_{0.9}-Si_{0.1} rods acting on different ablation surface of C/C-ZrC-SiC is finally concluded (Fig. 16).

When the ablation temperature (T_{abl}) is lower than the melting point of SiO₂, ZCC-1 and ZCC-2 all begin to oxidize. However, “Z-pins like” V_{0.9}-Si_{0.1} rods can not provide liquid compensating oxide, only generate solid V₂O₃ and SiO₂ (Eq. 11, 12).

Due to C/C-ZrC-SiC surfaces of ZCC-2 exposes a lots of non-woven cloth layers, which rapidly oxidize to generate micro grooves (Eq. 13). Therefore, only a discontinuous porous ZrO₂-rich layer is generated here (Eq. 14, 15). However, the porous ZrO₂-rich layer on C/C-ZrC-SiC surface of ZCC-1 is relatively denser and more continuous.

With the ablation time prolonging, T_{abl} is higher than the melting temperature of SiO₂ but lower than that of V₂O₃, SiO₂ from the oxidation product of “Z-pins like” V_{0.9}-Si_{0.1} rods and SiC performs self-sealing effect. Therefore, C/C-ZrC-SiC surface of ZCC-1 is covered with a dense ZrO₂-SiO₂ layer. However, under the hindrances of the micro-pores and grooves of ZrO₂ layer, the flow rate of SiO₂ melt generated on the ZCC-2 surface slows down, and the surface oxide layer density is lower than that of ZCC-1.

When T_{abl} continues to rise to about 2200 °C, SiO₂ on ZCC-1 and ZCC-2 surface evaporates largely. However, at this time, “Z-pins like” V_{0.9}-Si_{0.1} rods can form moderate V₂O₃ (with high melting boiling point) melt and SiO₂ (with low melting point) melt that is close to the demand. Under the scouring action of high-speed airflow, these melts quickly spread to C/C-ZrC-SiC surface, so as to effectively conduct oxide melt compensation to ensure oxide layer density on ZCC-1 surface, and avoid mechanical denudation of oxide layer. Meanwhile, micro grooves of ZCC-2 surface start to be filled, and the further oxidation of the non-woven cloth layer will be completely prevented.

However, When the temperature continues to rise, the content of compensating oxide melt generated by “Z-pins like” V_{0.9}-Si_{0.1} rods is higher than the filling content of defects such as holes and cracks on the ZCC-1 surface, then the surface of ZCC-1 will suffer from superfluous melt erosion and form ablation pit. But because ZCC-2 surface forms many micro grooves in the initial oxidation, which can consume excess

oxide melt. Therefore, no high temperature oxide melt concentration area in the ablation center of ZCC-2, and the melting corrosion will be avoided.

During the cooling process, all of the gaseous SiO and SiO₂ are deposited to generate a dense SiO₂ film on the ablating edge via VLS and OAG mechanisms. Finally, V₂O₃ will continue to oxidize, and ZCC-1 (ZCC-2) surface are all covered a dense gradient oxide in plane, which is combined with V₂O₅-rich layer of ablation center, V₂O₅-SiO₂ composite layer of ablation transition and SiO₂ layer of ablation edge (V₂O₅-ZrO₂ layer of ablation center, V₂O₅-SiO₂-ZrO₂ layer of ablation transition and SiO₂ layer of ablation edge).

Ablation unit
Temperature	$T_{abl} < T_{mel-SiO_2}$	
Initial oxidation
Temperature	$T_{mel-SiO_2} < T_{abl} < T_{mel-V_2O_5}$	
Compensating oxide generation (Early Stage of Ablation)
Temperature	$T_{mel-V_2O_5} < T_{abl} < 2200\text{ }^{\circ}\text{C}$	
Velocity	$V_{eva} < V_{sea} < V_{gen}$	$V_{eva} < V_{gen} < V_{sea}$
Oxide melt spreading (Mid-Stage of Ablation)
Temperature	$T_{abl} > 2200\text{ }^{\circ}\text{C}$	
Velocity	$V_{eva} < V_{sea} < V_{gen}$	$V_{eva} < V_{gen} < V_{sea}$
Later stage of ablation (After ablating for 240s)
Cooling Stage

Fig. 16 Schematic of liquid/gaseous multicomponent oxide compensation mechanism.

4 Conclusions

In this paper, the microstructure of C/C-ZrC-SiC composite reinforced by “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods was studied. The difference of ablation performance of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods acting on the different C/C-ZrC-SiC surface, the evolution of ablated surface micro-morphology, and the difference of oxide compensation behavior of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod were studied. On this basis, a new anti-ablative mechanism, namely liquid/gaseous multicomponent oxide compensation mechanism, is proposed. The main conclusions are as follows:

(1) After adding silicon, liquid silicon was produced to assist the forming of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods during the sintering, and the density of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod was improved.

(2) When the ablation time was less than 180 s, there is a best improvement of the anti-ablation performance of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods perpendicular to non-woven cloth layer, and “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rod gave full play to the oxide compensation effects. However, when the ablation time was greater than 180 s, there is a best improvement of the anti-ablation performance of “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods parallel to non-woven cloth layer. However, when “Z-pins like” $V_{0.9}\text{-Si}_{0.1}$ rods is perpendicular to non-woven cloth layer, they increased another harm that weaken the anti-ablative performance of C/C-ZrC-SiC composite, namely, the corrosion damage of oxide layer on the matrix surface caused by excessive oxide melt.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No: U19A2099), and the CAS Key Laboratory of Carbon Materials (No: KLCMKFJJ2005).

Reference

[1] Y. B. Chang, W. Sun, X. Xiong, Z. K. Chen, Y. L. Wang, Z. H. Hao, Y. L. Xu, Microstructure and ablation behaviors of a novel gradient C/C-ZrC-SiC composite fabricated by an improved reactive melt infiltration, *Ceram. Int.*,

42(2016)16906-16915.

- [2] S. L. Wang, H. Li, M. S. Ren, Y. Z. Zuo, M. Yang, J. B. Zhang, J. L. Sun, Microstructure and ablation mechanism of C/C-ZrC-SiC composites in a plasma flame, *Ceram. Int.*, 43(2017)10661-10667.
- [3] B. Feng, H. J. Li, Y. L. Zhang, L. L. Liu, M. Yan, Effect of SiC/ZrC ratio on the mechanical and ablation properties of C/C-SiC-ZrC composites, *Corros. Sci.*, 82(2014)27-35.
- [4] X. W. Chen, Q. Feng, H. J. Zhou, S. M. Dong, J. X. Wang, Y. P. Cao, Y. M. Kan, D. W. Ni, Ablation behavior of three-dimensional Cf/SiC-ZrC-ZrB₂ composites prepared by a joint process of solgel and reactive melt infiltration, *Corros. Sci.*, 134(2018)49-56.
- [5] Z. Zhao, K. Li, W. Li, Q. Liu, G. Kou, Y. Zhang, Preparation, ablation behavior and mechanism of C/C-ZrC-SiC and C/C-SiC composites, *Ceram. Int.*, 44 (2018)7481-7490.
- [6] S. L. Wang, K. Z. Li, Y. L. Zhang, Y. J. Wang, Effect of microstructures on the ablation behaviors of ZrC deposited by CVD, *Surf. Coat. Technol.* 240(2014)450-455.
- [7] X. H. Shi, J. H. Huo, J. L. Zhu, L. Liu, H. J. Li, X. J. Hu, M. Y. Li, L. J. Guo, Q. G. Fu, Ablation resistance of SiC-ZrC coating prepared by a simple two-step method on carbon fiber reinforced composites, *Corros. Sci.*, 88(2014)49-55.
- [8] S. L. Wang, H. L. M. S. Ren, Y. H. Zuo, M. Yang, J. B. Zhang, J. L. Sun, Microstructure and ablation mechanism of C/C-ZrC-SiC composites in a plasma flame, *Ceram. Int.*, 43(2017)10661-10667.
- [9] C. L. Yan, R. J. Liu, Y. B. Cao, C. R. Zhang, D. K. Zhang, Ablation behavior and mechanism of C/ZrC, C/ZrC-SiC and C/SiC composites fabricated by polymer infiltration and pyrolysis process, *Corros. Sci.*, 86(2014)131-141.
- [10] C. X. Liu, J. X. Chen, Z. A. Su, X. Yang, L. X. Cao, Q. Z. Huang, Pyrolysis mechanism of ZrC precursor and fabrication of C/C-ZrC composites by precursor infiltration and pyrolysis, *T. Nonferr. Metal. Soc.*, 24(2014) 1779-1784.
- [11] L. Liu, H. J. Li, W. Feng, X. H. Shi, K. Z. Li, L. J. Guo, Ablation indifferent heat fluxes of C/C composites modified by ZrB₂-ZrC and ZrB₂-ZrC-SiC particles,

Corros.Sci., 74(2013)159-167.

[12] L. Zhuang, Q. G. Fu, B. Y. Tan, Y. A. Guo, Q. W. Ren, H. J. Li, B. Li, J. P. Zhang, Ablation behaviour of C/C and C/C-ZrC-SiC composites with cone shaped holes under an oxyacetylene flame, Corros. Sci., 102(2016)84-92.

[13] M. Balat-Pichelin, L. Charpentier, F. Panerai, O. Chazot, B. Helber, K. Nickel, Passive/active oxidation transition for CMC structural materials designed for the IXV vehicle re-entry phase, J. Eur. Ceram. Soc., 35(2015)487-502.

[14] B. Woolford, D. Maynes, W. Webb, Liquid flow through microchannels with grooved walls under wetting and superhydrophobic conditions, Micro. Nano., 1(2008)121-135.

[15] S. Jung, E. Yang, W. Jung, H. Y. Kim, Anti-erosive mechanism of a grooved surface against impact of particle-laden flow, Wear, 406-407(2018)166-172.

[16] F. Song, S. H. Meng, X. H. Xu, Y. F. Shao, Enhanced thermal shock resistance of ceramics through biomimetically inspired nanofins, Phys. Rev. Lett., 12502(2010)1-4.

[17] X. F. Fang, F. S. Liu, B. W. Lu, X. Feng, Bio-Inspired microstructure design to improve thermal ablation and oxidation resistance: Experiment on SiC, J. Am. Ceram. Soc., 98(2015)4010-4015.

[18] X. F. Fang, F. S. Liu, B. Xia, D. P. Ou, X. Feng, Formation mechanisms of characteristic structures on the surface of C/SiC composites subjected to thermal ablation, J. Eur. Ceram. Soc., 36(2016)451-456.

[19] T. Tian, W. Sun, X. Xiong, Y. L. Xu, Y. T. Chen, Y. Zeng, F. Q. Liu, Novel “Z-pins like” Vanadium rods prepared by solid phase sintering to improve ablation resistance of the C/C-ZrC-SiC composites, J. Eur. Ceram. Soc., 39 (2019) 1696-1702.

[20] T. Tian, W. Sun, X. Qing, X. Xiong, H. B. Zhang, Y. H. Chu, Z. K. Chen, Y. Zeng, Intelligent cooling structure design of “Z-pins like” silicon rods to enhance the ablation resistance of C/C-ZrC-SiC composites above 2500 °C, J. Eur. Ceram. Soc., 40(2020)3875-3886.

[21] G. Feng, H. Li, L. Yang, B. Li, J. Xu, X. Yao, Investigation on the ablation performance and mechanism of HfC coating modified with TaC, Corros. Sci., 170(2020)108649.

- [22] C. Z. Zhang, Q. Q. Yang, C Koughia, F. Ye, M. Sanayei, S. J. Wen, S. Kasap, Characterization of vanadium oxide thin films with different stoichiometry using Raman spectroscopy. *Thin Solid Films*, 620 (2016) 64-69.
- [23] D. S. Su, R. Schlögl, Thermal decomposition of divanadium pentoxide V_2O_5 : towards a nanocrystalline V_2O_3 Phase, *Catal. Lett.*, 83(2002)115-119.
- [24] J. Y. Chen, *Hydrometallurgical Manual: Hydrometallurgy of Vanadium and chromium*, Metal. Indus. Press, Beijing, 2005, pp. 938.
- [25] H. A. Wriedt, The O-V (Oxygen-Vanadium) system, *Bull. of Alloy Phase Diag.*, 10 (1989) 271-277.
- [26] X. M. Tao, H. M. Chen, X. F. Tong, Y. F. Ouyang, P. Jund, J. Tedenac, Structural, electronic and elastic properties of V_5Si_3 phases from first-principles calculations, *Comput. Mater. Sci.*, 53 (2012) 169-174.
- [27] Z. Q. Li, H. J. Li, K. Z. Li, S. Y. Zhang, Growth mechanism of silica nanowires without a metal catalyst via oxyacetylene torch ablation, *Mater. Lett.*, 74(2012)118-120.
- [28] R. G. J. Ball, M. A. Mignanelli, T. I. Barry, J. A. Gisby, The calculation of phase equilibria of oxide core-concrete systems, *J. Nucl. Mater.* 201(1993)238-249.
- [29] Y. Zeng, X. Xiong, G. Li, Z. Chen, W. Sun, D. Wang, Y. Wang, Effect of fiber architecture and density on the ablation behavior of carbon/carbon composites modified by Zr-Ti-C, *Carbon*, 63(2013)92-100.
- [30] J. Xie, K. Li, G. Sun, H. Li, X. Su, Y. Han, T. Li, Effects of surface structure unit of 2D needled carbon fiber preform on the microstructure and ablation properties of C/C-ZrC-SiC composites, *Ceram. Inter.*, 45(2019)11912-11919.
- [31] Y. L. Xu, W. Sun, X. Xiong, F. Q. Liu, X. G. Luan, Ablation characteristics of mosaic structure ZrC-SiC coatings on low-density, porous C/C composites, *J. Mater. Sci. Tech.*, 35(2019)2785-2798.
- [32] National Standard Committee of China, GBJ323A-96: Measurement Standard of Ablation Properties of Materials, Beijing, 1996.
- [33] S. Z. Yang. *The metallurgy of Vanadium*, first ed., Metal. Indus. Press, Bei Jing, 2010, pp.24.

- [34] C. Zhang, Y. Du, W. Xiong, H. H. Xu, P. Nash, Y. F. Ouyang, R. X. Hu, Thermodynamic modeling of the V-Si system supported by key experiments, CALPHAD, 32(2008)320-325.
- [35] J. Qi, Preparation of Vanadium Oxides As Well As Application, Chem. Indus. Press, Bei Jing, 2017, pp. 94-95.
- [36] L. Fabiángos, L. Cedeño-Caero, V Loading Effect on V₂O₅/ZrO₂ Catalysts for Oxidative Desulfurization, Ind. Eng. Chem. Res., 50(2011)2659-2664.
- [37] R. Q. Zhang, Y. Lifschitz, S. T. Lee. Oxide-assisted growth of semiconducting nanowires. Adv. Mater., 15(2003)635-640.
- [38] J. J. Niu, J. N. Wang. A study in the growth mechanism of silicon nanowires with or without metal catalyst. Mater. Lett., 62(2008)767-771.
- [39] W. S. Shi, H. Y. Peng, Y. F. Zheng, N. Wang, N. G. Shang, Z. W. Pan. ChemInform Abstract: Synthesis of large areas of highly oriented, very long silicon nanowires. Adv. Mater., 12(2000)1343-1345.

Figures

Figure 1

Process flow chart of "Z-pins like" $V_{0.9}Si_{0.1}$ rod-reinforced C/C-ZrC-SiC composites.

Figure 2

(a) Macro/micro-structures of C/C-ZrC-SiC in different ablation layer. (a) Macro picture of the sample with ablation surface parallel to non-woven cloth layer. (b) and (c) Central and marginal microstructures of the sample after ablation. (d) Macro picture of the sample with ablation surface perpendicular to non-woven cloth layer. (e) and (f) Central and marginal microstructures of the sample after ablation.

(a) Perpendicular to non-woven cloth layers

(b) Parallel to non-woven cloth layers

■ Non-woven cloth layer • $V_2O_5-SiO_2$ melt ■ Porous ZrO_2 layer
 ■ Carbide ■ Dense ZrO_2 layer ■ "Z-pins like" $V_{0.9}-Si_{0.1}$ rod

Figure 3

The spreading model of compensating oxide melt.

Figure 4

XRD analysis results of “Z-pins like” V_{0.9}-Si_{0.1} rods after sintering.

Figure 5

(a) and (b) The microstructure of “Z-pins like” V0.9-Si0.1 rod and its enlarged picture of (a). (c) The interface between “Z-pins like” V0.9-Si0.1 rod and ZrC-SiC ceramics and carbon fibers.

Figure 6

Elemental distributions of electron probe microanalysis of “Z-pins like” V0.9-Si0.1 rod after sintering. (b) V. (c) C. (d) Si.

Figure 7

The macroscopic features of ZCC-1 and ZCC-2. (a) and (b) ZCC-1 after ablating for 180 s and 240 s, respectively. (c) and (d) ZCC-2 after ablating for 180 s and 240 s, respectively.

Figure 8

The XRD results of ZCC after ablating for 180 s and 240 s respectively. (a) ZCC-1. (b) ZCC-2.

Figure 9

Microstructures of the "Z-pins like" $V_{0.9}Si_{0.1}$ rod-reinforced C/C-ZrC-SiC composites in the ablation center after ablating for 180 s. (a) and (b) The border between "Z-pins like" $V_{0.9}Si_{0.1}$ rod and C/C-ZrC-SiC and the enlarged picture of the area A. (c) The microstructure of the matrix.

Figure 10

Microstructures of the “Z-pins like” V0.9-Si0.1 rod-reinforced C/C-ZrC-SiC composites in the ablation transition after ablation for 180 s. (a) The microstructure of the “Z-pins like” V0.9-Si0.1 rod. (b) and (c) The border between “Z-pins like” V0.9-Si0.1 rod and C/C-ZrC-SiC and the enlarged picture of the area A. (d) The enlarged picture of the area B and C in (b). (e) and (f) The microstructure of the matrix and the enlarged picture of the area D.

Figure 11

The microstructure of the “Z-pins like” V0.9-Si0.1 rod-reinforced C/C-ZrC-SiC composites edge after ablating for 180 s. The inner edge: (a) The border between “Z-pins like” V0.9-Si0.1 rod and matrix. (b) The matrix surface. The outer edge: (c) and (d) The border between “Z-pins like” V0.9-Si0.1 rod and matrix and the enlarged picture of the area A. (e) The matrix surface.

Figure 12

The central microstructure of the “Z-pins like” V_{0.9}-Si_{0.1} rod-reinforced C/C-ZrC-SiC composites after ablating for 240 s. (a) The boundary between the “Z-pins like” V_{0.9}-Si_{0.1} rods and C/C-ZrC-SiC. (b) The “Z-pins like” V_{0.9}-Si_{0.1} rods.

Figure 13

The central microstructure of ZCC-2 after ablating for 180 s. (a) and (b) The microstructure of the “Z-pins like” V0.9-Si0.1 rod and the enlarged picture of the area A. (c) The boundary between “Z-pins like” V0.9-Si0.1 rod and carbon fiber tows. (d) The boundary between “Z-pins like” V0.9-Si0.1 rod and ceramic. (e) The microstructure of the matrix.

Figure 14

The central microstructure of the “Z-pins like” V0.9-Si0.1 rod-reinforced C/C-ZrC-SiC composites after ablating for 240 s. (a) and (b) The microstructure of the “Z-pins like” V0.9-Si0.1 rod and the enlarged picture of the area A. (c) and (d) The microstructure of the matrix and the enlarged picture of the area B. (e) and (f) The microstructure of groove from the oxidation of carbon fiber tows and the enlarged picture of the area C.

Figure 15

The marginal microstructure of C/C-ZrC-SiC of ZCC-2 after ablating for 180 s and 240 s. (a) 180 s. (b) 240 s.

Figure 16

Schematic of liquid/gaseous multicomponent oxide compensation mechanism.