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A New Assistant Method for Characterizing Ablation Resistance of ZrC-SiC Dispersive Biphasic Coating on C/C Composites

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Abstract: To optimize the ablation resistance of ZrC coating, ZrC-SiC dispersive biphasic coating was prepared by chemical vapor co-deposition. The ablation resistances of the coatings were carried out by oxyacetylene flame tests. Compared with double-layered ZrC/SiC coating, the ablation resistance of ZrC-SiC coating was evaluated. On the basis of similar mass ablation rates of the two coatings, a new assistant method for characterizing the thermal protecting effect of coatings on carbon-carbon composites (C/C) composites was proposed. The thermal protecting ability of the coating was accurately reflected by the changes of hardness and elastic modulus of C/C substrate below the central region of ablated coatings before and after ablation. The ablation processes of two kinds of coatings were also discussed. The results showed that the hardness and elastic modulus of the C/C substrate protected by ZrC-SiC coating were higher than that of C/C coated with ZrC/SiC coating. The result convincingly illustrated the thermal protecting ability of ZrC-SiC coating was much better than that of ZrC/SiC coating, which attributed to the formation of Zr-SiO glass.

Keywords: ZrC-SiC coating; chemical vapor deposition; ablation resistance; ultrahigh temperature ceramic

1. Introduction

Carbon-carbon composites (C/C) have been widely applied in the aerospace industry, especially in ultrahigh-temperature thermal structural materials because of their excellent high-temperature mechanical properties [1–5]. However, in an ablation environment, rapid oxidation will occur, which reduces the mechanical property rapidly [5,6]. To guarantee the mechanical properties of C/C composites at high temperature, thermal protecting coatings are necessary. As a kind of ultrahigh- temperature ceramics (UHTC), zirconium carbide (ZrC) is regarded as a potential material for thermal protecting coating material to prevent C/C composites from ablation owing to its high melting point, good tribological behavior, thermal stability, high hardness, and low vapor pressure [7–11]. Besides, ZrO₂ (the oxidation product of ZrC) possesses a high melting point and low vapor pressure [12,13]. Up to now, in some reports, ZrC coating has been fabricated by chemical vapor deposition (CVD) [14,15], which is suitable for preparing UHTC coatings on thin-wall products with relatively low deposition temperature. Wang S. et al. [16] successfully prepared CVD-ZrC coating and studied its ablation resistance under different heat fluxes.

Although ZrC is a promising candidate for thermal protecting coating, the combination of single ZrC ($\alpha_{ZrC} \approx 7.6 \times 10^{-6} \,^{\circ}$ C) layer and C/C substrate ($\alpha_{C/C} \approx 1.1 \times 10^{-6} \,^{\circ}$ C) is disadvantageous because of the vast difference between the thermal expansion coefficients (CTE) of the two materials. To resolve



the problem, different efforts have been devoted to relieving the thermal stress between ZrC coating and C/C substrate [17–23]. After many attempts, it has been found that SiC ($\alpha_{SiC} \approx 4.4 \times 10^{-6}$ °C) is suitable as a transition layer and can relatively relieve the mismatch of CTE between the outer ZrC coating and inner C/C substrate. In addition, the oxide of SiC (SiO₂) has a self-healing capacity and good oxygen diffusion blocking effect below 1700 °C [20,24-26]. However, ZrC/SiC double-layered coating also has some problems, such as higher expense, the difficulty of fabrication, and the stress concentration at interfaces. Moreover, it has been reported that ZrC coating will be powdered and oxidized to produce ZrO₂ during the ablation process [14], which will reduce the cohesion of the coating. Therefore, serious mechanical denudation will take place under high speed oxyacetylene flame and particles, leading to high depletion of the coating. In view of the above problem, some researchers proposed using a thermal evaporation method and in situ reaction to prepare ZrC-SiC biphasic coating [27], inhibiting the mechanical denudation efficaciously. Nevertheless, this method has high cost, higher preparation temperature, and complex steps. Especially, the biphasic ceramic particles (SiC and ZrC) present mosaic distribution leading to large reaction-diffusion free path. To reduce the preparation temperature and make the biphasic ceramic particles (ZrC and SiC) disperse uniform distribution, one-step chemical vapor deposition is a good choice.

Up to now, many works about ablation behavior of single coating (ZrC coating, SiC coating) or multilayers coating (ZrC/SiC coating) has been reported [28,29]. Little work is reported about the ablation behavior of ZrC-SiC double-phase coating fabricated by a one-step CVD method [30]. Linear and mass ablation rates are common methods for characterizing ablation resistance of thermal protective coatings. Nevertheless, the ablation process is often accompanied with the generating of oxidation products [24] resulting in mass increase of the coating materials. Thus, the oxidation of coating materials leads to mass gain; but the mechanical erosion of the coating and oxidation of C/C substrate results in mass loss. Therefore, it is difficult to analyze the reasons for mass changes of specimens after ablation. It is also confused to judge the ablation resistances of protective coatings for C/C composites just from mass ablation rates. In addition, the coating may influence the linear and mass ablation rates of the coatings. So, the ablation rates could not present the thermal protecting effect accurately. Based on this problem, a new method characterizing thermal protective effect for C/C composites has been proposed in this paper.

In the present study, ZrC-SiC double-phase coating was fabricated by one-step chemical vapor deposition at a relatively low temperature. The phase composition and microstructure were characterized. The ablation test was carried out on oxyacetylene ablator. The thermal protective ability of the coating was accurately reflected by the change of hardness and elastic modulus of C/C substrate before and after ablation.

2. Material and Methods

2.1. Materials and Preparation

C/C composite (1.7 g·cm⁻³), which would be used as substrate of coatings, prepared by chemical vapor infiltration (CVI) were machined into a dimension of Φ 30 × 6 mm³. After 340 and 500 mesh sandpaper grinding, all specimens were cleaned with ethanol. Then, the specimens were dried for 8 h to stand by.

The ZrC-SiC biphasic coating was deposited by one-step chemical vapor deposition on the surface of C/C substrates with $ZrCl_4$ -CH₄-Si-H₂-Ar system. Among them, $ZrCl_4$ (purity: 98.7%) acts as Zr source precursor of ZrC; Si powder acts as Si source of SiC; CH₄ gas provides C source of the two ceramics; H₂ and Ar are reductive and protective gases, respectively. The schematic diagram of the deposition equipment is shown in Figure 1a. The powder feeder can precisely control the feeding rate of ZrCl₄ precursor.



Figure 1. The schematic sketches of ZrC-SiC biphasic coating deposition equipment (**a**) and introducing method of methyltrichlorosilane (MTS) (**b**).

The specimens prepared above were positioned in the constant temperature area of the furnace. The deposition temperature was 1350~1550 °C; and the pressure inside the furnace cavity ranged from 10~40 kPa. The feeding rate of ZrCl₄ was 0.7 ± 0.1 g/min. The flow speeds of CH₄, H₂, and Ar were 100 ± 50 mL/min, 1500 ± 400 mL/min, and 200 ± 50 mL/min, respectively. The deposition process lasted for 8 h; the heating and cooling rates were both 7.0 °C/min.

For comparison, the double-layered ZrC/SiC coating was also deposited by two-step CVD. Firstly, the specimens were positioned in the constant temperature region to prepare SiC coating with methyltrichlorosilane (MTS)-H₂-Ar deposition system. The methyltrichlorosilane (MTS) was introduced by volatilization at low pressure and constant temperature (30 °C) shown in Figure 1b. The deposition temperature was 1250 °C; the feeding rate of MTS was 0.3 \pm 0.05 g/min; the flowing rates of H₂ and Ar were 1000 \pm 300 mL/min and 200 \pm 40 mL/min, respectively; the deposition process lasted for 8 h. After that, the specimens coated with SiC coating were put into the furnace again for ZrC layer deposition. During the deposition process, the temperature was 1350~1550 °C; the flow rates of gases including CH₄, H₂, and Ar were 80 \pm 20 mL/min, 800 \pm 200 mL/min and 100 \pm 20 mL/min, respectively. The heating and cooling rates of two deposition processes were all 7.0 °C/min.

2.2. Performance Tests

The ablation resistances of ZrC/SiC coating and ZrC-SiC coating were characterized through oxyacetylene flame test according to the GJB323A-96 ablation standard of China [20]. The standard mainly unified and testified the ablation properties of high-temperature composites and coatings to obtain linear ablation rate and mass ablation rate. The specific test parameters were as follows: The oxyacetylene flame was perpendicular to the center of specimens coated with coatings. The distance between the gun tip and the surface of the specimen was 10 mm. The diameter of oxyacetylene flame core was 2 mm. The pressures of O_2 and C_2H_2 were 0.4 MPa and 0.095 MPa, respectively. The flow rates of O_2 and C_2H_2 were 0.244 L/s and 0.167 L/s, respectively.

The ablation resistances of the coatings were reflected by linear and mass ablation rates. And the equations were displayed as the following:

$$R_l = \frac{\Delta d}{t} \tag{1}$$

where R_l means linear ablation rate, R_m means mass ablation rate, Δd and Δm are the changes of thickness and mass, respectively, and *t* is the ablation time.

Because the volume change and warping of the coatings may influence the linear and mass ablation rates of the coatings, the ablation rates could not present the thermal protecting effect accurately. To confirm the protective effect of the two coatings, the hardness and elastic modulus of the C/C substrates coated by two ablated coatings were measured and compared. Micro indentation tests were carried out with MHT-M system produced by NANOVEA. The maximum load was 4 N, and the loading increasing rate was set as 8 N/min.

2.3. Morphology and Phase Characterization Method

The phase composition and microstructure were investigated by X-ray diffraction (XRD, X'Pert Pro MPD), scan electron microscope (SEM, Tescan Vega 3) with energy dispersive spectroscopy (EDS, INCA).

3. Results and Discussion

Composition and Microstructure of the Coatings

After deposition processes, the phase compositions of the coatings were characterized. The results are shown in Figure 2. From the XRD pattern of ZrC/SiC coating (curve a), it is revealed that there are only several ZrC characteristic peaks, indicating that there is no other phase on the surface of the specimens coated with the double-layered coating. Judging from the narrow peaks of ZrC (pdf: 65-4932) peaks of two patterns in Figure 2, the ZrC phases in two coatings presented high crystalline. Meanwhile, it can be observed that curve b contains both SiC and ZrC peaks implying ZrC-SiC coating is a dispersive double-phase coating consisting of ZrC and SiC phases.



Figure 2. The XRD results of ZrC/SiC and ZrC-SiC coatings.

The SEM pictures of double-layered ZrC/SiC coating and ZrC-SiC coating are exhibited in Figure 3. From Figure 3a, the surface of ZrC/SiC coating is relatively smooth; no hole can be found on the surface of the coating. It can be seen that the cracking of the double-layered ZrC/SiC coating is obvious. The surface morphology of ZrC-SiC coating is rougher than that of double-layered ZrC/SiC coating; but the cracks cannot be found on the coating surface. The thickness of ZrC/SiC coating is about 50~70 μ m. Combining with Figure 3b,e,f, there is an obvious gap in the double-layered ZrC/SiC coating implying the poor bonding strength between different layers, which may be caused by the thermal stress concentration at interface generated during deposition process. That of ZrC-SiC coating

(about 40~60 µm) is much different: Two ceramic phases (SiC and ZrC) disperse uniformly with each other from Figure 3d. Comparing with the cross-section of the two coatings mentioned above, it can be deduced that stress concentration could be relieved in ZrC-SiC coating significantly. Because the CTE of SiC phase ($\alpha_{SiC} \approx 4.4 \times 10^{-6} \circ C^{-1}$) is much lower than that of ZrC ($\alpha_{ZrC} \approx 7.6 \times 10^{-6} \circ C^{-1}$), the CTE of diphasic ZrC-SiC can be calculated by Equation (3).

$$\alpha_{ZS} = \alpha_S \cdot v_s + \alpha_Z \cdot v_z \tag{3}$$

where α_{ZS} , α_S , and α_Z are the CTE of diphasic ZrC-SiC, SiC and ZrC phases, respectively; v_s and v_z are the volume ratios of SiC and ZrC phases.



Figure 3. The surface morphology of ZrC/SiC coating (**a**) and ZrC-SiC coating (**c**); the cross-section of ZrC/SiC coating (**b**) and ZrC-SiC coating (**d**); the electron spectroscopy (EDS) results of Area A (**e**), Area B (**f**) and Area C (**g**).

Therefore, the mismatch between the ZrC-SiC double-phase coating and C/C substrate is lower than that of C/C coated with ZrC coating. Besides, there is no phase interface of different layers where stress concentration always occurs.

After ablation tests for 60 s, the linear and mass ablation rates of two prepared coatings were obtained as displayed in Figure 4. The linear and mass ablation rates of ZrC/SiC coating were $0.402 \pm 0.03 \mu m/s$ and $0.18 \pm 0.03 mg/s$; and those of ZrC-SiC coating were $0.153 \pm 0.02 \mu m/s$ and $0.19 \pm 0.05 mg/s$. Compared with ZrC/SiC coating, the linear ablation rate of ZrC-SiC coating decreased by 75%; the mass ablation rate of ZrC/SiC and ZrC-SiC coating were nearly similar.



Figure 4. The results of ablation tests.

To analyze the reason for lower linear ablation rate of ZrC-SiC coating, the phase compositions of two ablated coatings were characterized by XRD. Figure 5 exhibits the XRD patterns of ablated ZrC/SiC and ZrC-SiC coatings. It can be observed that the ablated double-layered ZrC/SiC coating consists of ZrO₂ and SiC phases. Obviously, the phases in ablated ZrC-SiC are different than those of ZrC/SiC coating including not only ZrO₂ and SiO₂, but also ZrSiO₄, which may attribute to the dispersion distribution of ZrC and SiC phases. Based on the above results, it could be inferred that peeling and denudation of the double-layered ZrC/SiC coating occurred during the ablation process.



Figure 5. The XRD patterns of ZrC/SiC and ZrC-SiC coatings after ablation.

Figure 6 shows the macroscopic pictures of two ablated specimens. From the macroscopic morphology of ZrC/SiC coating (Figure 6a,c), there are plenty of cracks on its surface. Meanwhile, the damage traces at the central ablation area is obvious, resulting in the serious mechanical denudation. On the contrary, the surface of ablated ZrC-SiC coating was intact with no obvious cracks, indicating that the mechanical denudation was inhibited effectively. Meanwhile, no damage trace can be seen from Figure 6b,d. Comparing the macroscopic morphologies, it can be concluded that the mechanical denudation resistance of ZrC-SiC coating is higher than that of double-layered ZrC/SiC coating.



Figure 6. The macroscopic and SEM pictures of ablated ZrC/SiC coating (a,c) and ZrC-SiC coating (b,d).

Figure 7 reflects the morphology of ZrC/SiC and ZrC-SiC coatings at the central ablation region. Figure 7a,c corresponds to the central ablation region of ZrC/SiC coating. Serious warpage and mechanical denudation occurred in the central ablation zone, so that the outer ZrO_2 layer was exfoliated and inner SiC layer was exposed and oxidized, which is consistent with the XRD result of ablated ZrC/SiC coating. Observed from Figure 7c, grain boundary and crack are obvious among ZrO₂ grains. Besides, the sizes of ZrO₂ grains are about 2~4 µm. From Figure 7b, it is exciting that the surface of the ablated ZrC-SiC coating kept intact with no exfoliation. The surface is similar to a bubbly-like structure. From Figure 7d, no obvious grain boundary and crack could be seen. The ZrO₂ grain sizes of ablated ZrC-SiC coating are smaller than that of ablated ZrC/SiC coating. The holes (shown in Figure 7c,d) are generated due to the oxidation of ZrC accompanied with CO gas. CO gas is hardly insoluble in ZrO₂, resulting in the connected holes formed by the escaping of CO.



Figure 7. The surface morphology of ablated ZrC/SiC coating (**a**,**c**) and ZrC-SiC coating (**b**,**d**) at central ablation region.

The morphology of ablated ZrC/SiC and ZrC-SiC coatings at the transition ablation region present as shown in Figure 8. On the surface of the ablated ZrC/SiC coating, obvious cracks and exposed inner SiC layer can be found, implying that cracking and denudation occurred during the ablation process. Moreover, it can be clearly observed from Figure 8a that the mechanical denudation of the ZrO₂ layer along the direction of the crack propagation is especially serious. The cracking phenomenon may be caused by the CTE mismatch between SiC and ZrC. On the contrary, there is neither cracking nor damage at the transition region of ablated ZrC-SiC coating. Combining the XRD (shown in Figure 5) and EDS (shown in Figure 9 Area C) results, it can be implied that the gray phase is Zr-Si-O glass phase (ZrO₂-ZrSiO₄-SiO₂). From Figure 8b, the gray glass phase and white phase present mosaic distribution indicating the adhesion effect of the glass phase. Because of the adhesion effect, ZrO₂ grains were trapped by the sticky glass phase during ablation, resulting in that the mechanical denudation of ZrC-SiC coating was inhibited.



Figure 8. The SEM pictures of ablated ZrC/SiC coating (**a**) and ZrC-SiC coating (**b**) at transition ablation region.

The morphology of cross-section is an impactful way to confirm the consumption of the coating during the ablation process. Figure 9 displays the cross-section morphology of ablated ZrC/SiC coating and ZrC-SiC coating. Meanwhile, it also gives the element compositions of two ablated coatings. Observing Figure 9a, there is an obvious gap between the outer layer and inner layer, which may influence the judgment from the ablation rates. Correspondingly, no gap can be seen from Figure 9b, illustrating that the stress concentration phenomenon did not occur in ZrC-SiC coating during ablation. Ignoring the gap, the thickness of the ablated ZrC/SiC double-layer coating decreased a lot compared with Figure 3b. Meanwhile, the thickness decreasing of ZrC-SiC coating was less than that of the ZrC/SiC double-layer coating, illustrating that the mechanical erosion of ZrC-SiC coating was slighter than that of ZrC/SiC coating during the ablation process. Combining the XRD result, it can be confirmed the phase composition of ablated ZrC-SiC coating was Zr-Si-O glass phase. Observed from Figure 9b, the gray phase can be seen in C/C substrate. And the EDS result of the gray phase illustrated the phase is SiC, which means Si element diffused into C/C substrate during the ablation process.

From the linear ablation rate results, the ablation resistance of ZrC-SiC coating might be better than that of double-layered ZrC-SiC coating. But the mass ablation rates of the two coatings are similar, which is miserable to judge the ablation resistance. During the ablation test, the oxidation of coating materials is the main reason for mass gain. Meanwhile, the mechanical erosion of coating and oxidation of C/C substrate are the reasons for mass loss. Therefore, oxidation degrees, densities, and mechanical denudation of coatings can influence the mass ablation rates. The reactions of the coated specimens are as follows:

$$ZrC(s) + 2O_2(g) \rightarrow ZrO_2(s) + CO_2(g)$$
(4)

$$\operatorname{SiC}(s) + 2O_2(g) \to \operatorname{SiO}_2(s) + CO_2(g)$$
(5)

$$SiO_2(s) + ZrO_2(s) \rightarrow ZrSiO_4(s)$$
(6)

$$C(s) + O_2(g) \rightarrow CO_2(g) \tag{7}$$

$$2C(s) + O_2(g) \rightarrow 2CO(g) \tag{8}$$

According to the above-mentioned reactions, the reactions (Equations (4) and (5)) lead to mass gain, and the reactions (Equations (7) and (8)) lead to mass loss. Moreover, the coating materials might be consumed to result in mass loss by the mechanical denudation from airflow scouring. Therefore, mass ablation rates cannot reflect directly and accurately the ablation resistances of coatings.



Figure 9. The cross-section morphology and corresponding EDS results of ablated ZrC/SiC and ZrC-SiC coatings. (**a**) ablated ZrC/SiC coating; (**b**) ablated ZrC-SiC coating.

As the warping and weight gain due to oxidation of the coating may affect the accuracy of the judgment from the ablation rates, the thermal protection effect of the two coatings needs to be judged by the mechanical properties of C/C substrates below ablated coatings as assistant method. Figure 10 shows the results of micro-indentation tests to C/C substrates covered by ZrC/SiC and ZrC-SiC coatings before and after ablation for 60 s. From Figure 10a,c, the hardness and elastic modulus of C/C substrate covered by ZrC/SiC coating decreased by 17% and 20%, respectively, after ablation, which was caused by the oxidation of C/C composite. On the contrary, it is interesting that the hardness of C/C substrate covered by ZrC-SiC coating increased rather than decreased after ablation for 60 s, which was caused by diffusion of Si element during high-temperature (>2000 °C) ablation. The elastic modulus of C/C substrate below ZrC-SiC coating increased slightly after ablation. Comparing the hardness and modulus of elasticity changes of ZrC/SiC and ZrC-SiC coatings before and after ablation for 60 s, it can be inferred that the latter has better thermal protection property.

In addition, before ablation, the hardness and modulus of C/C substrate covered by ZrC-SiC coating were higher than that of substrate covered by ZrC/SiC coating, which was caused by the damage from twice thermal cycle shock during the deposition process of ZrC/SiC coating. Meanwhile, the damage on hardness and elastic modulus of the substrate below ZrC-SiC coating prepared by one-step CVD were relatively little.



Figure 10. The micro-indentation test results of C/C substrates covered by ZrC/SiC and ZrC-SiC coatings before and after ablation for 60 s. The load-depth curves (**a**) and mechanical properties (**c**) of C/C substrate coated with ZrC/SiC double-layer coating before and after ablation; (**b**) and mechanical properties (**d**) of C/C substrate coated with ZrC-SiC coating before and after ablation.

We studied the phase transition of C/C substrates during high-temperature ablation. The raman spectrum results of C/C substrates covered by ZrC/SiC coating and ZrC-SiC coating before and after ablation exhibited are displayed Figure 11. It can be seen that the intensity ratio of the D and G peaks decrease after ablation for 60 s, meaning that the graphitization transition occurred during the ablation process. After a certain degree of graphitization transition, the elastic modulus increased slightly.



Figure 11. The raman spectrum results of C/C substrates covered by ZrC/SiC coating and ZrC-SiC coating before and after ablation. (**a**) C/C coated with ZrC/SiC coating; (**b**) C/C coated with ablated ZrC/SiC coating; (**c**) C/C coated with ZrC-SiC coating; (**d**) C/C coated with ablated ZrC-SiC coating.

Based on all the above results, the ablation mechanism of the two coatings can be concluded (shown in Figure 12). Because of the CTE mismatch between the SiC and ZrC phases, the peeling phenomenon occurred during ZrC/SiC coating deposition process (shown in Figure 3b). Moreover, the oxidation of ZrC is accompanied with CO gas escaping and the generation of porous ZrO_2 structure during the ablation process. Then the cohesion of outer ZrO_2 became weak, resulting in serious mechanical denudation under high speed airflow and particles scouring. These explanations can be confirmed from Figures 6c and 7a. After that, the damages were generated. The damages could be new paths for oxygenated gas diffusing into inner C/C substrate, which led to the reduction of its hardness and elastic modulus. The CO and CO₂ gases generated from the oxidation of C/C substrate would accelerate the damages of ablated ZrC/SiC coating.



Figure 12. The diagram of ZrC/SiC and ZrC-SiC coatings during ablation process.

On the contrary, the ZrC-SiC coating fabricated by one-step chemical vapor deposition is different. Firstly, ZrC-SiC coating has no interface between different ceramic layers, indicating that the stress concentration phenomenon could not occur at the interface of different layers. Secondly, the oxygen diffusion blocking effect of Zr-Si-O glass would protect the inner coating from further oxidation; and the adhesion effects could inhibit the powdering oxidation of ZrC, trap ZrO₂ grains, and reduce depletion of coating materials. So, the decrease of the cohesion of the coating would be inhibited effectively. Therefore, the surface of the coating could remain intact after ablation for 60 s; and the inner C/C substrate was prevented from oxidation. Without oxidation and damages, the hardness and elastic modulus of C/C substrate would maintain well. These explanations can be supported by Figure 3c,d, Figures 4, 7, 9 and 10.

4. Expectation

C/C composites are potential thermal structure materials in the aerospace field. Various kinds of coatings for protecting C/C composites under oxidation and ablation environment have been reported in recent years. However, traditional judging standard (linear and mass ablation rates) could not accurately characterize the protective effects of the coatings gradually. Based on this problem, the new assistance method introduced in this paper can effectively and accurately judge the ablation resistance

of coatings under the condition of low cost. It also might be a new standard to judge the ablation resistances of coatings for protecting C/C composites in the future.

5. Conclusions

To protect C/C composites from ablation, a ZrC-SiC double-phase coating was fabricated by one-step chemical vapor deposition. A new assistant method for characterizing ablation resistance of ZrC-SiC dispersive biphasic coating on C/C composites was firstly proposed. The change of hardness and elastic modulus of C/C substrate before and after ablation were measured, which can reflect the thermal protective ability of the coating accurately. The ablation resistance of the coating was characterized by both this new assistant method and traditional ablation rates. The linear ablation rate of ZrC-SiC coating is about 1/4 of that of ZrC/SiC coating. The surface of ablated ZrC-SiC coating can still keep intact, compared with that of ZrC-SiC coating. The hardness and elastic modulus of C/C substrate below ZrC/SiC coating. Combining the results obtained from micro-indentation and the ablation rates, it is more convincing that the thermal protective ability of ZrC-SiC coating is better than that of ZrC/SiC coating. In general, the good ablation resistance can be attributed to the oxygen diffusion blocking and the adhesion effects of Zr-Si-O glass phase. Moreover, the new assistant method for characterizing ablation resistance could be also applied to other coatings for protecting C/C composites in the future.

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References

- 1. Chang, P.P.; Wang, C.Y.; Kinumoto, T.; Tsumura, T.; Chen, M.M.; Toyoda, M. Frame-filling C/C composite for high-performance EDLCs with high withstanding voltage. *Carbon* **2018**, *131*, 184–192. [CrossRef]
- 2. Mikociak, D.; Rudawski, A.; Blazewicz, S. Mechanical and thermal properties of C/C composites modified with SiC nanofiller. *Mater. Sci. Eng. A* 2018, *716*, 220–227. [CrossRef]
- 3. Deng, H.; Li, K.; Cui, H.; Li, H.; He, Y.; Zheng, J.; Song, G. Floating catalyst chemical vapor infiltration of nanofilamentous carbon reinforced carbon/carbon composites–Tribological behavior and wear mechanism. *Tribol. Int.* **2018**, *121*, 231–240. [CrossRef]
- 4. Jia, Y.; Li, K.; Zhang, S.; Ren, J. Microstructure and Mechanical Properties of Multilayer-textured 2D Carbon/Carbon Composites. *J. Mater. Sci. Technol.* **2014**, *30*, 1202–1207. [CrossRef]
- 5. Yao, X.; Li, H.; Zhang, Y.; Wang, Y. Oxidation and Mechanical Properties of SiC/SiC-MoSi₂-ZrB₂ Coating for Carbon/Carbon Composites. *J. Mater. Sci. Technol.* **2014**, *30*, 123–127. [CrossRef]
- 6. Huo, C.; Guo, L.; Cao, A.; Wang, Z.; Wang, C.; Kou, G.; Zhang, Y. The degradation behavior of C/C composites in high-energy atomic oxygen. *Vacuum* **2017**, *146*, 120–129. [CrossRef]
- 7. Wen, G.; Sui, S.; Song, L.; Wang, X.Y.; Xia, L. Formation of ZrC ablation protective coatings on carbon material by tungsten inert gas cladding technique. *Corros. Sci.* **2010**, *52*, 3018–3022. [CrossRef]
- 8. Zhang, Q.; He, J.; Liu, W.; Zhong, M. Microstructure characteristics of ZrC-reinforced composite coating produced by laser cladding. *Surf. Coat. Technol.* **2003**, *162*, 140–146. [CrossRef]
- 9. Jong, H.P.; Choong, H.J.; Do, J.K.; Ji, Y.P. Temperature dependency of the LPCVD growth of ZrC with the ZrCl₄-CH₄-H₂ system. *Surf. Coat. Technol.* **2008**, 203, 324–328.

- Clavería, I.; Lostalé, A.; Fernández, Á.; Castell, P.; Elduque, D.; Mendoza, G.; Zubizarreta, C. Enhancement of Tribological Behavior of Rolling Bearings by Applying a Multilayer ZrN/ZrCN Coating. *Coatings* 2019, 9, 434. [CrossRef]
- 11. Zhang, Y.; Hu, H.; Zhang, P.; Hu, Z.; Li, H.; Zhang, L. SiC/ZrB₂-SiC-ZrC multilayer coating for Carbon/Carbon composites against ablation. *Surf. Coat. Technol.* **2016**, *300*, 1–9. [CrossRef]
- 12. Li, B.; Deng, J.; Li, Y. Oxidation behavior and mechanical properties degradation of hot-pressed Al₂O₃/ZrB₂/ZrO₂ ceramic composites. *Int. J. Refract. Met. Hard Mater.* **2009**, *27*, 747–753. [CrossRef]
- 13. Li, K.Z.; Wang, S.L.; Li, H.J.; Zhang, Y.L.; Wang, Y.J.; Chen, Z.S. Microstructure and growth mechanism of ZrO₂ nanorod network via oxyacetylene torch ablation. *Mater. Lett.* **2014**, *123*, 217–220. [CrossRef]
- 14. Wang, S.L.; Li, K.Z.; Li, H.J.; Zhang, Y.L.; Wang, Y.J. Effects of microstructures on the ablation behaviors of ZrC deposited by CVD. *Surf. Coat. Technol.* **2014**, 240, 450–455. [CrossRef]
- 15. Zhu, Y.; Cheng, L.; Ma, B.; Gao, S.; Feng, W.; Liu, Y.; Zhang, L. Calculation and synthesis of ZrC by CVD from ZrCl₄-C₃H₆-H₂-Ar system with high H₂ percentage. *Appl. Surf. Sci.* **2015**, *332*, 591–598. [CrossRef]
- Wang, S.L.; Li, K.Z.; Li, H.J.; Zhang, Y.L.; Zhang, W.Y. Ablation behavior of CVD-ZrC coating under oxyacetylene torch environment with different heat fluxes. *Int. J. Refract. Met. Hard Mater.* 2015, 48, 108–114. [CrossRef]
- Xu, Y.; Sun, W.; Xiong, X.; Peng, Z.; Chen, Y.; Hao, Z. Microstructure and properties of ZrC-SiC multi-phase coatings prepared by thermal evaporation deposition and an in-situ reaction method. *Surf. Coat. Technol.* 2018, 349, 797–806. [CrossRef]
- 18. Jia, Y.; Li, H.; Fu, Q.; Zhao, Z.; Sun, J. Ablation resistance of supersonic atmosphere plasma spraying ZrC coating doped with ZrO₂ for SiC-coated carbon/carbon composites. *Corros. Sci.* **2017**, *123*, 40–54. [CrossRef]
- 19. Xu, J.; Yang, T.; Yang, Y.; Qian, Y.; Li, M.; Yin, X. Ultra-high temperature oxidation behavior of micro-laminated ZrC/MoSi₂ coating on C/C composite. *Corros. Sci.* **2018**, *132*, 161–169. [CrossRef]
- 20. Zhou, Z.; Sun, Z.; Ge, Y.; Peng, K.; Ran, L.; Yi, M. Microstructure and ablation performance of SiC-ZrC coated C/C composites prepared by reactive melt infiltration. *Ceram. Int.* **2018**, *44*, 8314–8321. [CrossRef]
- 21. Zhuang, L.; Fu, Q.G.; Zhang, J.P.; Guo, Y.A.; Li, H.J.; Shan, Y.C. Effect of pre-oxidation treatment on the bonding strength and thermal shock resistance of SiC coating for C/C–ZrC–SiC composites. *Ceram. Int.* **2015**, *41*, 6956–6964. [CrossRef]
- Jia, Y.; Li, H.; Li, L.; Fu, Q.; Li, K. Effect of Monolithic LaB6 on the Ablation Resistance of ZrC/SiC Coating Prepared by Supersonic Plasma Spraying for C/C Composites. J. Mater. Sci. Technol. 2016, 32, 996–1002. [CrossRef]
- Shi, X.H.; Huo, J.H.; Zhu, J.L.; Liu, L.; Li, H.J.; Hu, X.J.; Li, M.Y.; Guo, L.J.; Fu, Q.G. Ablation resistance of SiC-ZrC coating prepared by a simple two-step method on carbon fiber reinforced composites. *Corros. Sci.* 2014, *88*, 49–55. [CrossRef]
- 24. Xu, Y.; Sun, W.; Xiong, X.; Zhan, Z.; Tian, T.; Chen, Y.; Peng, Z. Microstructure and ablation resistance of ZrC_xN_y -modified ZrC-SiC composite coating for carbon/carbon composites. *J. Eur. Ceram. Soc.* **2018**, *38*, 4363–4372. [CrossRef]
- 25. Bu, A.; Zhang, Y.; Zhang, Y.; Chen, W.; Cheng, H.; Wang, L.; Wang, Y. A Novel Electrolytic Plasma Spraying Preparation SiO₂/SiC Coating on Carbon Fiber Fabric. *Coatings* **2018**, *8*, 344. [CrossRef]
- 26. Mallik, M.; Ray, K.; Mitra, R. Effect of Si₃N₄ Addition on Oxidation Resistance of ZrB₂-SiC Composites. *Coatings* **2017**, *7*, 92. [CrossRef]
- 27. Zhang, Z.; Nan, C.; Xu, J.; Gao, Z.; Li, M.; Wang, J. Oxidation Behaviors of C-ZrB₂-SiC Composite at 2100 degrees C in Air and O₂. *J. Mater. Sci. Technol.* **2014**, *30*, 266–268.
- 28. He, Q.; Li, H.; Wang, C.; Li, T.; Lu, J. Microstructure and ablation property of gradient ZrC SiC modified C/C composites prepared by chemical liquid vapor deposition. *Ceram. Int.* **2019**, *45*, 20414–20426. [CrossRef]
- 29. Liu, T.; Niu, Y.; Pan, X.; Shi, M.; Zheng, X.; Yu, J.; Ding, C. Laser ablation behaviors of vacuum plasma sprayed ZrC-based coatings. *J. Am. Ceram. Soc.* **2019**, *102*, 4247–4258. [CrossRef]
- 30. Liu, Q.; Liu, J.; Luan, X. Preparation of ZrC-SiC composite coatings by chemical vapor deposition and study of co-deposition mechanism. *J. Mater. Sci. Technol.* **2019**. [CrossRef]



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