Rare Metal Materials and Engineering
Volume 46, Issue 8, August 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(8): 2097-2101.

ARTICLE

Ablation Resistance Property of TiC/ZrO₂ Coating Deposited by Plasma-spraying

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Abstract: In the high temperature ablation process, the TiC coating will be oxidized to TiO_2. The thickness of molten TiO_2 increases when the temperature is higher than 2000 °C, which decreases the bonding strength of the coating. In the present study, the TiC/ZrO_2 coatings with different contents of high melting phase ZrO_2 were deposited by plasma spraying, in order to improve the anti-scouring property of TiC coatings. The phase structure, microstructure and composition of the coatings, before and after ablation, were characterized by XRD, SEM and EDS, respectively. The ablation resistant mechanism of the coatings with high melting phase ZrO_2 was discussed. Results indicate that the TiC/ZrO_2 coating shows good ability of ablation resistance, and its mass loss is only 1.5×10^{-4} g cm^{-2} s^{-1} at 2000 °C. The ZrO_2 layer formed during the ablation can restrain the further oxidation of inner TiC and reduce the shearing force of oxyacetylene flame, which improves the anti-scouring property of the coatings.

Key words: plasma spraying; TiC/ZrO_2 coating; ablation resistance

Carbon fiber composites with SiC matrix (C_f/SiC composites) are attractive materials for structural applications due to their outstanding thermo-mechanical properties and low density[1,2]. However, when the temperature is much higher, the oxidation of C_f/SiC composites restricts their further applications in oxygenic environment[3,4]. To resolve this problem, ultra-high temperature ceramic coatings, such as refractory carbide coatings, are considered to be used at ultra-high temperature[5].

Among carbides, SiC and HfC coatings are widely investigated in recent years. However, at ultra-high temperature (>2000 °C), they are incompetent to meet the demand, because SiC coatings will be oxidized and evaporated rapidly[6], and the HfO_2 production of HfC oxidation is porous and pulverous[7]. Therefore, TiC, which has high melting point temperature (above 2000 °C), high thermal conductivity, and excellent thermal stability[8], becomes a promising thermal protection system material, because TiO_2, formed during the ablation of TiC, could fill the holes and cracks of coatings and in turn protect the C_f/SiC composite substrates from oxidation. However, at high temperature, the TiO_2 generation is easy to cause the coating peeling off during high speed gas flow erosion[9], so the protection effect of coating will be weakened. In order to resist this phenomenon, some kinds of materials with high melting point can be considered to be added in the TiC coating as second phase particle. During the ablation, the melting TiO_2 can be attached by these unmelted phases, and may not be easily corroded, which may improve the scouring resistance of the coating.

Up till now, several techniques have been developed to modify the C_f/SiC composites surface, such as chemical vapor deposition (CVD), embedding, painting, sol-gel and plasma spraying[4,10]. According to some studies[11,12], plasma spraying is an efficient way to prepare compact coatings.

In the present paper, TiC/ZrO_2 (TZ) coating was prepared on the C_f/SiC composites by plasma spraying. The anti-ablation property with different contents of ZrO_2 was evaluated under an oxyacetylene torch flame. The evolution of morphology and microstructure of TZ coating during ablation was also investigated.

Received date: August 25, 2016
Foundation item: National Natural Science Foundation of China (51302013)
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1 Experiment

C_f/SiC composites were used as substrates, and the specimens for ablation were in the size of 40 mm×30 mm×5 mm. The substrates were polished by 400 grit paper in order to improve the surface roughness and the binding ability between coatings and substrates can be improved. Polished substrates were cleaned using acetone.

The spraying particles were prepared by spray granulation using analytically pure raw materials: ZrO_2 (93wt% ZrO_2, 7wt% Y_2O_3, diameter of 10~45 μm), and TiC (99.9%, diameter of 20~80 μm). Due to the different thermal expansion coefficients of ZrO_2 and TiC, the content of ZrO_2 should not be too high. So the contents of ZrO_2 were chosen as 10wt% and 20wt%. The TZ coatings with different contents of ZrO_2 were deposited on treated substrates with the plasma spraying parameters shown in Table 1. The thickness of these coatings is all 0.2 mm.

Table 1 Parameters of plasma spraying

Materials	Current/A	Primary gas Ar/scfh*	Secondary gas He/scfh	Carrier gas Ar/scfh	Powder feed rate/r·min^{-1}
TiC+10wt%ZrO_2 (TZ1) TiC+20wt%ZrO_2 (TZ2)	950	90	60	10	3.0

*scfh = standard cubic feet per hour

The ablation behaviors of these two kinds of TZ coatings were tested using oxyacetylene ablation torch. The coated samples were placed vertically to the flame for 150 s. The fluxes of O_2 and C_2H_2 were 30 and 50 L/min, respectively. During ablation, the distance between the nozzle tip of the oxyacetylene gun and the surface of the coating was 155 mm, so the temperature of sample surface could be maintained between 1800~2000 ℃. After ablation, the mass and linear ablation rates of samples could be obtained according to the formula below:

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

where R_m is the mass ablation rate, g·cm^{-2}·s^{-1}; Δm is the sample mass difference before and after ablation, g; S is the area of ablation surface, cm^2; t is the ablation time, s.

The phase composition of coatings was characterized by X-ray diffraction (XRD, PANalytical Inc., X'Pert PRO MPD, Almelo, the Netherlands) with Cu Kα radiation. The surface morphologies and cross-sectional microstructure of coatings were examined using scanning electron microscope (SEM, HITACHI S4800, Tokyo, Japan) and the chemical analysis of coatings was carried out by energy dispersive spectrometer (EDS, TEAM, EDAXInc, USA, New Jersey). The porosities of coatings were calculated by Video Test-Master quantitative metallographic analysis system through the cross-sectional microstructure.

2 Results and Discussion

2.1 Analysis of pre-ablation coating

Fig.1 shows the XRD patterns of TZ coatings with different contents of ZrO_2. It is shown that the coatings are composed of TiC and ZrO_2, and only a little TiO_2 phase is detected because of the oxidation during the plasma spraying. There is no obvious phase composition difference between these two coatings.

Fig.2 is the surface morphologies of two TZ coatings. It

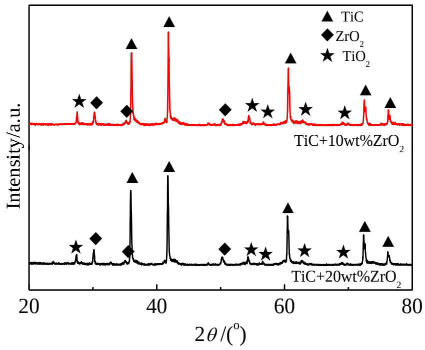

Fig.1 XRD patterns of TiC/ZrO_2 coatings

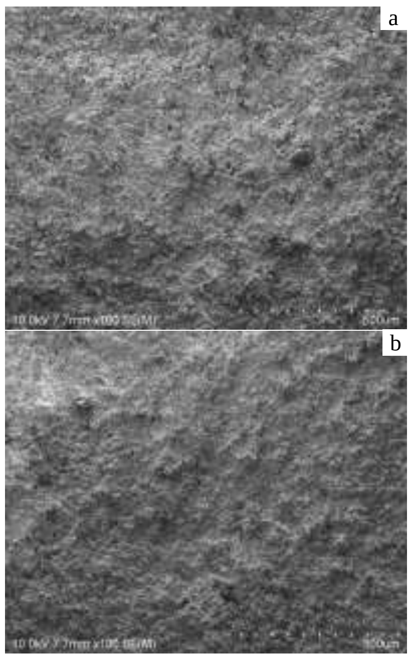

Fig.2 Surface morphologies of TZ coatings: (a) TZ1 and (b) TZ2

can be seen that the surfaces of coatings are compact without obvious cracks and holes. This is because during plasma spraying, ZrO_2 is much easier to flow and fill. But there is still some swell on the two coatings caused by the unmelted grains.

The cross-sectional microstructures of coatings are shown in Fig.3. It can be seen that the TZ coatings have a good adhesion to substrates, and no obvious cracks are observed. Meanwhile, the porosities of coatings were obtained by Video Test-Master quantitative metallographic analysis system, in which the black part was regarded as hole. The porosity of TZ1 and TZ2 coatings are 8.3% and 6.9%, respectively. The low porosity indicates that these two TZ coatings are dense and they may have good ablation resistance properties.

From the point of composition distribution, the compositions of TZ coatings prepared in the present study are uniformly distributed. In order to further clarify the distribution of ZrO_2, an image processing is taken on the cross section morphologies, and the black parts in Fig.4 represent ZrO_2 (the white phase in Fig.3). It's obvious that the ZrO_2 phases are uniformly distributed in the TZ coatings.

2.2 Analysis of ablated coating

2.2.1 Ablation morphology and microstructure

Ablation is an erosive phenomenon with a removal of material by a combination of thermo-mechanical, thermo-chemical, and thermo-physical factors from high temperature, pressure, and velocity of combustion flame[13,14].

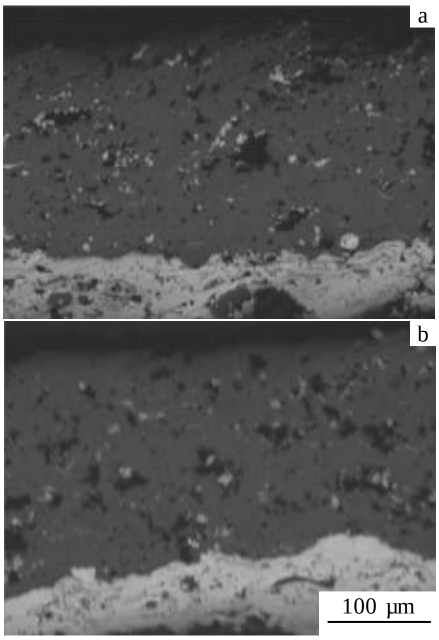

Fig.3 Cross section morphologies of composite coatings: (a) TZ1 and (b) TZ2

Fig.5 shows the surface macro morphologies of coatings after ablation for 150 s. As shown in Fig.5, four distinct regions (original coating region 1, border ablation region 2, transitional ablation region 3 and central ablation region 4) can be observed on the surface of the ablated samples, and an obvious compact coating forms in region 4. The morphologies of each region are apparently different. The area ratio of compact region 4 of TZ2 coating is approximately 61.8%, which is almost twice larger than that of TZ1 (34.4%). The larger compact area the coating has, the better ability to prevent the oxygen from diffusing inward the coating will have. This phenomenon suggests that TZ2 coating has a better ablation resistant property.

In the compact region 4 of coatings (Fig.6), it can be seen that there are no obvious cracks and holes, which suggests that the ablated oxide layer is sort of plastic to release the stress through deformation[15]. Compared with the coating TZ1, the surface of coating TZ2 is flatter and more compact.

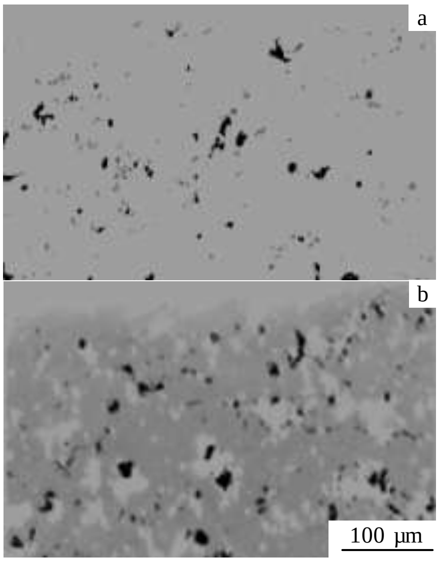

Fig.4 ZrO_2 distribution in TZ coatings: (a) TZ1 and (b) TZ2

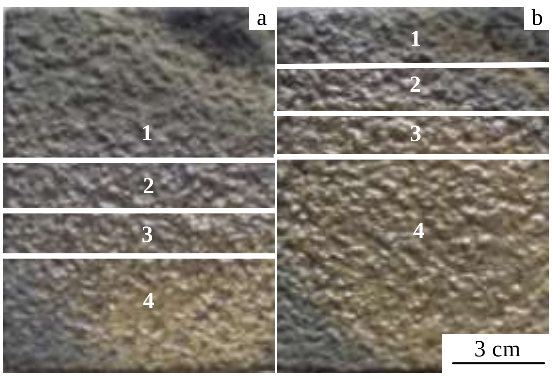

Fig.5 Macro morphologies of TZ coatings after ablation: (a) TZ1 and (b) TZ2

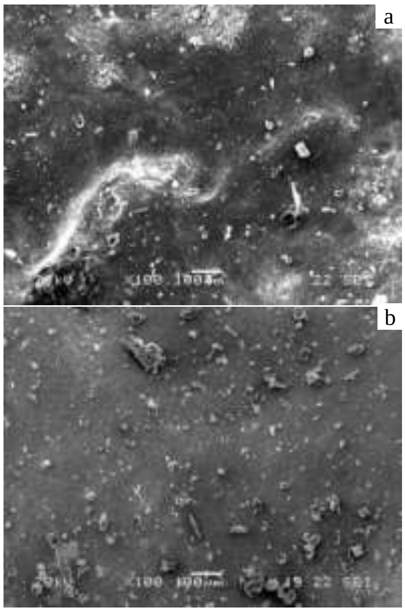

Fig.6 Surface morphologies of the compact region of the composite coatings: (a) TZ1 and (b) TZ2

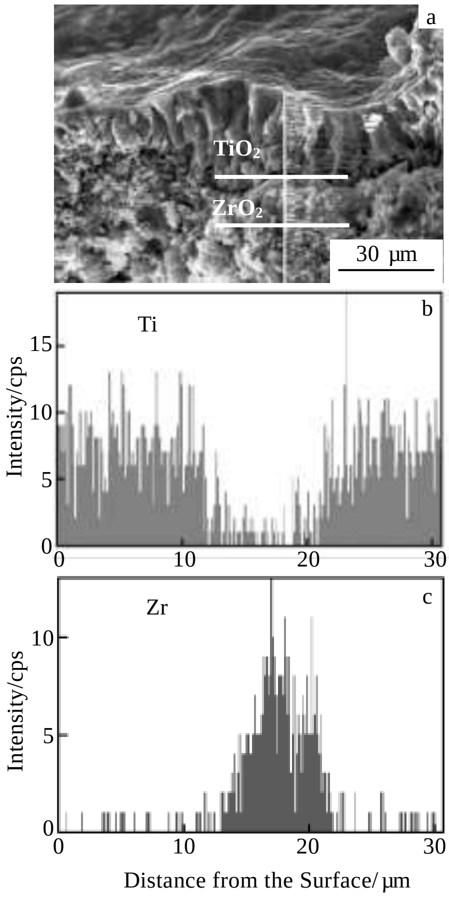

Fig.7 Cross-section microstructure (a) and EDS line scanning (b, c) of the dense region of the composite coating TZ2

This can be explained that ZrO_2 has a low thermal conductivity[16], so the heat cannot diffuse easily. More heat deposition causes the temperature of TZ2 surface much higher than that of TZ1, which promotes the oxidation of TiC and also the melting of TiO_2 on the surface. Therefore, TZ2 coating can form the dense structure rapidly and be flatter than TZ1.

2.2.2 Ablation properties and behavior

During the ablation for 150 s, the mass ablation rate of these two coatings (TZ1 and TZ2) are 1.8×10^{-4} and 1.5×10^{-4} $g\cdot cm^{-2}\, s^{-1}$, respectively. Compared to the TiC coating we have investigated previously (1.9×10^{-4} $g\cdot cm^{-2}\, s^{-1}$)[17], the coating with added ZrO_2 exhibits a better ablation resistant property. To a certain extent, the mass ablation rate decreases with the content of ZrO_2 increasing, because the high melting point phase ZrO_2 can resist the erosion of flame. Therefore, TZ2 coating prevents the substrate from ablation more efficiently.

In the oxyacetylene ablation, the following reactions can occur:

$$TiC+2O_2 \rightarrow TiO_2+CO_2 \quad (2)$$

$$2TiC+3O_2 \rightarrow 2TiO_2+2CO \quad (3)$$

Only the cross-section microstructure of TZ2 is exhibited for analyzing, since the cross-section structure of TZ1 and TZ2 coatings are similar. Fig.7 shows the cross-section microstructure and the EDS result of the compact region of TZ2 coating. During the ablation, the TiC in the coating is oxidized under oxyacetylene flame. It is apparent that after ablation there is an obvious boundary in the coating, and through the line scanning along the depth direction of the cross-section with EDS, it can be seen that around the boundary ZrO_2 is enrichment. Due to the existence of diffusion oxidation, TiC may diffuse to the surface and form the surface TiO_2 layer. However, in the present study, the ablation temperature cannot reach the melting point of ZrO_2 and the content of TiC in the surface is large enough to be oxidized and form the TiO_2 layer, so the enrichment of ZrO_2 around the boundary is mainly caused by the fact that TiO_2 has the lower melting point and lower density than ZrO_2. So during the ablation, TiO_2 melted and ZrO_2 sunk under the melting TiO_2. The formation of the melting TiO_2 attaching to ZrO_2 can form a stable compact layer, and this layer can not only restrain the further oxidation of inner TiC and delay the thickness increasing of TiO_2, but also reduce the shearing force of oxyacetylene flame. Besides, the ZrO_2 layer could be used as a thermal barrier layer to isolate the heat to transfer to inside, and thus reduce the temperature of the substrate. So TZ coating can provide a better ablation resistant property than TiC coating. The ZrO_2 addition in the TiC further improves the ablation resistant properties of the coating.

3 Conclusions

1) The TiC/ZrO_2 coatings show good ablation resistance properties, especially the coating with the mass ratio of 20wt% ZrO_2.

2) The minimum mass loss of the TiC/ZrO_2 coatings is only 1.5×10^{-4} g·cm^{-2} s^{-1} at 2000 ℃ during oxyacetylene ablation.

3) The ZrO_2 layer formed during the ablation can not only restrain the further oxidation of inner TiC, but also reduce the shearing force of oxyacetylene flame, which improves the anti-scouring property of coatings.

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等离子喷涂 TiC/ZrO_2 复相涂层的抗烧蚀性能研究

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摘　要：针对TiC涂层在高温烧蚀过程中氧化生成熔融TiO_2，当温度高于2000 ℃时，熔融TiO_2的厚度随之增加，这将进一步导致涂层结合强度降低，本文采用等离子喷涂方法制备了不同ZrO_2添加量的TiC/ZrO_2复相涂层，以提高涂层的抗冲刷性能。分别利用XRD、SEM和EDS对烧蚀前后材料的相结构、微观形貌和成分进行了分析，探讨了添加高熔点相ZrO_2的复合涂层的抗烧蚀机理。结果表明：TiC/ZrO_2复相涂层展现出更好的抗烧蚀性能，2000 ℃下的质量烧蚀率仅为1.5×10^{-4} g·cm^{-2} s^{-1}。烧蚀过程中产生的ZrO_2层可以阻止内部TiC的进一步氧化，并且可以在一定程度上降低氧乙炔焰对涂层产生的剪切力，以提高涂层的抗冲刷性能。

关键词：等离子喷涂；TiC/ZrO_2 涂层；抗烧蚀性

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