Laser Cladding and Anti-Laser Ablative Behaviour of Si-SiC-MoSi₂-ZrB₂ Composite Coatings on Carbon Surface

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Abstract

A Si-SiC-MoSi₂-ZrB₂ antioxidation composite coating was fabricated by laser cladding technology on the graphite matrix surface, and laser ablation was carried out on the coating surface to evaluate the anti-ablation capability of the coating surface. The phase transformation, microstructure reconstruction and the change of binding strength between the coating and the matrix during the laser cladding and ablation were investigated. The coating of Si-SiC-MoSi₂ series modified by 40wt% ZrB₂ had the lowest weight loss rate and the highest coating bonding strength. The oxide mostly existed in amorphous form after laser cladding, and the semi-melting particles in laser path lap zone on the coating surface disappeared. The oxide layer peeled off and Mo-Zr-Si-O composite glass phase was formed on the coating surface. The internal microstructure of the coating co-existed with non-oriented fine needle-like dendrites and irregular particles, which improved the coating strength. After laser ablation, the coating modified by 40wt% ZrB₂ had lower weight loss rate and higher scratch bonding strength compared with the unmodified coating of Si-SiC-MoSi₂ series, which indicated that the ablation resistance of the coating was improved by the formation of continuous oxide layer on the surface.

1. Introduction

Carbon materials are ideal high temperature materials in aerospace and other industrial fields because of their excellent material properties such as high melting point, low density, with high strength and high modulus, high heat stability, low thermal expansion coefficient, stable friction coefficient, high thermal conductivity, heat resistant corrosion resistance and other excellent performances. Even at high temperature (2200°C) under inert atmosphere, it still remain good mechanical properties comparable to room temperature^[1-3], thus in the aerospace, nuclear, chemical, and other fields it has a broad application prospect^[4-6]. However, in the air atmosphere, the untreated carbon materials oxidized at 450°C, and the rate increased rapidly with the increase of temperature^[7-8].

In general, matrix modification technology and coating technology are mainly used to improve the high-temperature antioxidant performance of C materials, so that it can continue to work effectively under high temperature oxygen atmosphere. Among them, coating technology is more practical because it doesn't need to sacrifice the excellent performance of the material, and the produced material has high usage temperature, long service life, and can be designed for a variety of composite coatings according to the actual needs^[9-10]. The coating of silica-based materials has excellent antioxidant performance under high temperature environment. Among them, Si^[11-12], MoSi₂^[13-14], SiC^[15], as common raw material of silica-based antioxidant coating, can be used for the antioxidant coating on the surface of C materials. In addition, as an ultra-high temperature ceramic, ZrB₂ has excellent high-temperature strength stability, antioxidant performance and chemical erosion resistance, and shows excellent ablative performance in C materials^[16-18]. However, the traditional preparation method of antioxidant coating has some disadvantages such as long production cycle, insufficient binding force and easy formation of pores. As a new coating preparation technology, laser cladding has many advantages, such as compact structure,

good metallurgical combination between cladding material and substrate material, controllable morphology of cladding material and small dilution degree of substrate coating.

In this work, the anti-oxidation coating of Si-SiC-MoSi₂-ZrB₂ was prepared by laser cladding technology, and the anti-laser ablation performance was characterized by laser ablation method. The phase and microstructure of the coating after laser cladding were analyzed by means of quality change, XRD, SEM and EDS.

2. Material And Methods

The graphite samples with dimensions of 10×10×1mm were used as substrate in this work. It should be sanded until the surface is bright. Then cleaned it with deionized water and placed in an oven at 60°C for 30 minutes. After that, roughened it with sandblasting machine. After sandblasting, the surface residual particles were washed with anhydrous ethanol and deionized water by ultrasonic cleaning, and then dried in a 60°C oven for 30min.

The prefabricated powder used in this work were prepared from Si, SiC, MoSi₂ and ZrB₂ powders. The raw materials were weighted according to a certain mass ratio and then mixed by TJGN high-energy planetary ball mill with 600RPM for 2h. After the end, rinsed and poured into the beaker with alcohol, and then putted in a 60°C oven to dry for 10-12h.

Weighed 3.28g of deionized water and 0.72g of raw powder placed in a 10mL beaker, added 300μL of alcohol and stirred with a magnetic stirrer for 20min. Then the beaker was placed in an ultrasonic cleaner for ultrasonic oscillation for 10min to disperse agglomerated powder particles. Then, placed the graphite samples in a rotator, used a pipette to draw 100μL solution from the 10mL beaker onto the surface of the samples and rotate the coating. The samples were then removed and placed in a petri dish to dry naturally. Finally, the anti-oxidation coating of Si-SiC-MoSi₂-ZrB₂ was obtained through laser cladding using a CO₂ laser (JQ1390), which was also used for laser ablation.

The weight loss of samples was measured by an analytical balance (Shanghai Youke Instrument Co., LTD., FB224). The coating adhesion was characterized by the scratch tester (Lanzhou Zhongke Kaihua Technology Development Co., LTD., WS-2005). The composition of the powders was measured by X-ray diffraction(XRD, BrukerD8-ADVANCE, German). The morphology of the powders was examined by tungsten filament scanning electron microscope(SEM, Hitachi High-tech SU3500, Japan).

3. Results And Discussion

3.1 Quality change of the coating and contrast of scratch adhesion via laser cladding

As shown in Fig.1, after ZrB₂ coating is modified, the weight loss rate slightly increases after laser cladding. When the content of ZrB₂ is 40wt%, the coating has a small weight loss rate, which is still a little higher than that of Si-SiC-MoSi₂ coating. The mass loss is partially due to the self-volatilization of Si and

oxidation products, such as MoO_3 and B_2O_3 when the temperature exceeds 1155°C . In addition, the air in the hole of the coatings expanded when being heated by laser and eventually burst, which caused some powders taken away from the coating's surface during laser cladding process. The scratch adhesion of coating after coating modified by 40 wt% ZrB_2 was increased about 10.87% compared with that before, because ZrB_2 particles changed the structure of ternary coating to form disordered dendrites and particle mixture structures, which improved the adhesion of coating. However, the ZrB_2 on the surface would react with oxygen to form volatile B_2O_3 phase, which makes it unable to fill the holes and cracks in the coating. Also, the high temperature during the laser cladding process would increase the oxidation and volatilization of Si and MoSi_2 phases, which introduced some defects on the coating, such as holes and cracks. This resulted in the decrease of coating adhesion, which is also the reason why the scratch adhesion of the coating coated with 20wt% ZrB_2 is low.

3.2 Microstructure and phase composition of laser cladding coating

As shown in fig.2, with the increase of ZrB_2 phase content, the intensity of diffraction peak increases continuously, while the intensity of other phases decreases. After laser cladding, the coating of Si-SiC- MoSi_2 series modified by 40wt% ZrB_2 has obvious amorphous diffraction peak, because the surface oxidized Si-O compound exists in the form of amorphous glass layer due to rapid cooling. The oxide layer will prevent oxygen from diffusing into the coating and improve the coating's antioxidant performance.

As one can clearly see in Fig.3(a), the holes on the surface of the coating are the defects left by mass transfer during the solidification process of the molten pool, but there are no obvious cracks. The semi-melting particles disappear in the lap zone of laser path, and the number of holes decreases, and the surface flatness of the coating is better. Fig.3(b) shows the surface of the uncoated oxide layer, which can be seen that the layered oxide layer is the surface layer exfoliated during the process of gas escape. As shown in Fig.3(c), there are signs of the overall peeling of the loose surface oxide layer. After measurement, the thickness of the peeling layer is about $7\mu\text{m}$. The thickness of the oxide layer is limited due to the decrease of oxygen diffusion rate by itself. The whole stripping is mainly caused by the obstruction of gas escaping during laser cladding in this area. Fig.3(d) shows the dense structure after the surface oxide layer is exfoliated. The improvement of surface density and flatness and the reduction of the number of holes can improve the adhesion of coating scratches. Combined with EDS results, it can be seen that the stripping layer is mainly loose Si-O compounds, and the content of Mo and Zr elements is extremely low. This is due to the rapid rise and fall of temperature in the laser cladding process, the oxidation reaction between Si and SiC forms Si-O compound, and MoO_3 phase has a low boiling point and is easy to volatilize.

As shown in Fig.4, the coating after laser cladding includes surface Si-O glass layer, laser cladding coating and carbon substrate, the average thickness of laser cladding coating is about $31.5\mu\text{m}$. After laser cladding, the coating showed obvious mixed state of unoriented dendrites and irregular particles, and three different regions could be seen in Fig.4(b). Region I was the mixing region of unoriented

dendrites and irregular particles, while region II was mainly the mixing region of irregular particles, and region III was mainly the mixing region of dendrites and a few particles. The characteristics of the region III can be seen more clearly in Fig.4(c), the dendrites are cross distributed and have no obvious orientation. The results of EDS showed that the distribution of Mo and Si was almost overlapped, while the distribution of Zr was characterized by local enrichment and granular dispersion. O was mainly enriched on the surface of the coating, which was caused by the rapid oxidation of the cladding material during laser cladding. The surface glass layer hindered the further diffusion of O element into the coating, thus the antioxidant capacity of the coating could be improved.

Combined with the grain distribution and element distribution, it could be determined that MoSi_2 phase was needle like dendrite after laser cladding, while ZrB_2 phase was granular dispersed in the coating. This was because a large number of ZrB_2 phase existed as particles in the molten pool, leading to heterogeneous nucleation of MoSi_2 phase attached to ZrB_2 particles in the solidification process, which greatly improved nucleation rate and refine grains. At the same time, due to the influence of temperature gradient and composition of coating, MoSi_2 phase grewed in a dendrite manner. However, due to the difference of laser heat flow, surface tension and viscous force in the molten pool, the ZrB_2 particles moved irregularly and destroyed the dendrite oriented growth state. Moreover, the existence of particles would also restrict the growth of dendrites. Finally, most of MoSi_2 grewed into fine non-oriented dendrites. The toughness of the coating could be improved by the non-oriented growth of fine dendrites and the dispersion of ZrB_2 as the second phase.

3.3 Quality change of the coating and contrast of scratch adhesion via laser ablation

It can be seen from Fig.5 that the weight loss rate of the coating modified by 20wt% ZrB_2 increased after laser ablation, but the coating modified by 40wt% ZrB_2 has the lowest weight loss rate. The main reason is that ZrB_2 is oxidized during laser ablation, and the continuous formation and volatilization of B_2O_3 phase would aggravate the peeling off of the surface glass layer. Therefore, the mass loss of low content ZrB_2 coating would increase. However, the ZrO_2 phase produced at the same time has a high melting point, which can weaken the disturbance of laser heat flow on the coating surface and slow down the coating weight loss. Moreover, the oxygen partial pressure of ZrO_2 phase is low, and the ZrO_2 phase produced by oxidation will disperse on the coating surface to protect the coating. In addition, the surface of 40wt% ZrB_2 modified coating after laser cladding was relatively flat and the number of holes was less, which would also have a positive effect on the laser ablation performance.

In the other hand, the scratch adhesion force of 20wt% ZrB_2 phase modified coating decreased compared with that of unmodified coating, while scratch adhesion force of 40wt% ZrB_2 phase modified coating was increased. This indicated that the addition of 40wt% ZrB_2 significantly improved the laser ablation resistance of the coating, while the 20wt% ZrB_2 addition did not improve the laser ablation resistance of the coating, mainly because there are a lot of cracks and oxide layer peeling off from the coating surface in the process of continuous laser ablation. The cracks weakened the coating strength and reduced the

coating adhesion, while the continuous peeling of the oxide layer aggravated the continuous oxidation of the coating and had a negative impact on the adhesion of the coating. When the content of ZrB_2 phase was increased to 40wt%, ZrB_2 phase was oxidized in the process of continuous laser ablation to form continuous ZrO_2 phase with high melting point and low oxygen pressure, which protected the coating from continuous oxidation. With the laser ablation time increasing, coating on the surface effectively inhibited the peeling off of the oxide layer and the internal microstructure reconstructs to form a "Semi-melting ice structure" of Zr-Mo-Si-O from the oxidation products of the coating, which further improved the laser ablation resistance of the coating.

3.4 Microstructure and phase composition of coating after laser ablation

As shown in fig.6, the crystal phase of the coating changed and a small amount of MoB phase formed after laser ablation. The diffraction peak intensity of Si, SiC, MoSi_2 and ZrB_2 phases in the cladding layer is significantly reduced, while the intensity of monoclinic ZrO_2 phase is significantly enhanced. It could be seen that obvious oxidation reaction, as shown in (1) - (5) ^[19-21], would occur after laser ablation. ZrB_2 reacted with O_2 to generate ZrO_2 and B_2O_3 , and oxidation of SiC and Si occurred as well with O_2 to form corresponding oxides.

In addition, in the early stage of laser ablation, when the temperature was between 400-800 °C, a "pestring" reaction of MoSi_2 began to take place and oxidation products of MoO_3 and SiO_2 were formed ^[22]. The MoO_3 phase produced by this reaction has poor mechanical properties, and was easy to volatilize and form holes, which affected the coating performance. However, as shown in formula (4), B_2O_3 generated by ZrB_2 and O_2 would react with MoSi_2 to form MoB and SiO_2 . Therefore, the increase of ZrB_2 phase could effectively reduce the occurrence of "pestring" reaction and improve the performance of the coating. In addition, during the laser cladding and ablation, the temperature of the coating fastly increased to above 1500°C, which would inhibit the "pestring" reaction of MoSi_2 and form a continuous layer of dense SiO_2 , ZrO_2 and etc. This continuous oxide layer would protect the coating from further oxidation. Under the influence of high energy laser beam, Si, B_2O_3 , MoO_3 , SiO_2 and other oxides will undergo phase transformation as shown in formula (6) - (8). Therefore, there are no diffraction peaks of MoO_3 , SiO_2 and B_2O_3 in XRD patterns.

Because of the oxide volatilization and continuous peeling of the surface coating during laser ablation, the oxide tends to form amorphous coating in the process of rapid temperature rise and fall. Therefore, in the low angle range, the peak intensity of amorphous steamed bread before laser ablation is greater than that after laser ablation. In addition, the original powder can still be detected in the XRD of the coating after laser ablation, which indicates that the coating has a certain anti laser ablation ability.

$2\text{ZrB}_2(\text{s})+5\text{O}_2(\text{g})=2\text{ZrO}_2(\text{s})+2\text{B}_2\text{O}_3(\text{s})$	(1)
$\text{Si}(\text{s})+\text{O}_2(\text{g})=\text{SiO}_2(\text{s})$	(2)
$2\text{SiC}(\text{s})+3\text{O}_2(\text{g})=2\text{SiO}_2(\text{s})+2\text{CO}(\text{g})$	(3)
$4\text{MoSi}_2(\text{s})+5\text{O}_2(\text{g})+2\text{B}_2\text{O}_3(\text{s})=4\text{MoB}(\text{s})+8\text{SiO}_2(\text{s})$	(4)
$2\text{MoSi}_2(\text{s})+7\text{O}_2(\text{g})=2\text{MoO}_3(\text{s})+4\text{SiO}_2(\text{s})$	(5)
$\text{B}_2\text{O}_3(\text{s})=\text{B}_2\text{O}_3(\text{l})=\text{B}_2\text{O}_3(\text{g})$	(6)
$\text{Si}(\text{s})+\text{SiO}_2(\text{s})=2\text{SiO}(\text{g})$	(7)
$\text{MoO}_3(\text{s})=\text{MoO}_3(\text{g})$	(8)

It can be seen from Fig. 7 (a) that the surface of the coating is smooth and dense even after 10 times laser ablation, which is the result of surface remelting in the process of continuous laser ablation and continuous reconstruction of the internal structure of the coating. This remelting and reconstruction process of the coating also healed the existing holes and cracks, which indicated the good resistance to laser ablation and oxidation. In Fig.7(b), there are two forms of light gray phase covering the surface layer and the phase partially covering the surface layer. In Fig.7(c), there are obvious cracks, but the crack opening presents zigzag structure. The change of crack shape requires greater crack growth formation energy. In addition, there is bifurcation and refinement phenomenon in the front of the crack. In addition, the cracks in Fig.7(d) are surrounded by "ice melting" Zr-Mo-Si-O compound, which indicates that the microstructure can hinder the crack growth.

Combined with the EDS results, it is known that the content of Mo on the surface of the material is very low. This is due to the continuous volatilization of volatile oxides such as MoO_3 during laser ablation. The results show that the whole gray coverage area of the material surface is Zr-O compound, which helps to improve the laser ablation resistance of the coating.

4. Conclusion

In this work, the coating of Si-SiC-MoSi₂ series modified by ZrB₂ were prepared on the graphite matrix surface by laser cladding technology, and laser ablation was carried out on the coating surface. The coating modified by 40 wt% ZrB₂ had the lowest weight loss rate and the highest coating binding strength after laser cladding, which is better than that of unmodified Si:SiC:MoSi₂ coating. The oxide layer peeled off and Mo-Zr-Si-O composite glass phase was formed on the coating surface, and the internal microstructure of the coating co-existed with non-oriented fine needle-like dendrites and irregular particles, which improved the coating strength. After laser ablation, the weight loss rate of 20 wt% ZrB₂ modified Si-SiC-MoSi₂ coating increased, and the scratch adhesion decreased. After laser ablation, the coating

modified by 40 wt% ZrB₂ had lower weight loss rate and higher scratch bonding strength compared with the unmodified coating of Si-SiC-MoSi₂ series, which indicated that the ablation resistance of the coating was improved by the formation of continuous oxide layer on the surface.

Declarations

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References

1. Ren XR, Wang WH, Shang TQ et al (2019) Dynamic oxidation protective ultrahigh temperature ceramic TaB₂-20%wt SiC composite coating for carbon material. *Compos B Eng* 161:220–227
2. Wang L, Fu QG, Zhao FL, Zhao ZG (2018) Constructing self-healing ZrSi₂-MoSi₂ coating for C/C composites with enhanced oxidation protective ability. *Surf Coat Technol* 347:257–269
3. Zhen Q, Li Z, Hu PF et al (2018) A glass-ceramic coating with self-healing capability and high infrared emissivity for carbon/carbon composites. *Corros Sci* 141:81–87
4. Ansar SA, Bhattachary A, Dutta S, Ghosh SS, Mukhopadhyay S (2010) Development of mullite and spinel coatings on graphite for improved water-wettability and oxidation resistance. *Ceram Int* 36:1837–1844
5. Zhou LM, You QB, Xiong J et al (2018) Dry wear behaviors of graphite/cermet self-lubricating composite under different sliding conditions and simulation of temperature field. *Int J Refract Met Hard Mater* 73:85–90
6. Li CY, Li FA (2006) Research progress of Carbon/carbon composites. *New Chem Mater* 34(3):18–20
7. Huang JF, Li HJ, Xiong XB (2005) Research progress of high temperature anti-oxidation coatings for carbon/carbon composites. *New Carbon Mater* 20(4):373–379
8. Li L. Study on oxidation mechanism of Carbon/carbon composites under multiple environments. Ph.D. Thesis. Xian (China): Northwestern polytechnical university, 2005
9. Zou X, Fu QG, Liu L et al (2013) ZrB₂-SiC coating to protect carbon/carbon composites against ablation. *Surf Coat Technol* 226:17–21
10. Yan ZQ, Xiong X, Xiao P et al (2009) Oxidation behavior of oxidation protective coatings for C/C-SiC composites at 1500°C. *Trans Nonferrous Met Soc China* 19:61–64
11. Zhu Q, Qiu X, Ma C et al (1999) Oxidation resistant SiC coating for graphite materials. *Carbon* 37(9):1475–1484
12. Fu Q, Li H, Wang Y et al (2009) B₂O₃ modified SiC-MoSi₂ oxidation resistant coating for carbon/carbon composites by a two-step pack cementation. *Corros Sci* 51(10):2450–2454

13. Chu Y, Fu QG, Cao C et al (2011) Microstructure and oxidation resistant property of C/C composites modified by $\text{SiC-MoSi}_2\text{-CrSi}_2$ coating. *Surf Eng* 27(5):355–361
14. Huang M, Li K, Li H et al (2007) A Cr–Al–Si oxidation resistant coating for carbon/carbon composites by slurry dipping. *Carbon* 45(5):1124–1126
15. Xiang ZD, Rose SR, Datta PK et al (2003) Codeposition of Al and Si to form oxidation-resistant coatings on $\gamma\text{-TiAl}$ by the pack cementation process. *Mater Chem Phys* 80(2):482–489
16. Neuman EW, Hilmas GE. Mechanical Properties of Zirconium-Diboride Based UHTCs// Ultra-High Temperature Ceramics. John Wiley & Sons. Inc. 2014
17. Liu XZ, Deng CM, Deng CG et al (2018) Mullite-modified $\text{ZrB}_2\text{-MoSi}_2$ coating for carbon/carbon composites to withstand long term ablation. *Ceram Int* 44:4330–4337
18. Wang DN, Zeng Y, Xiong X et al (2014) Preparation and ablation properties of $\text{ZrB}_2\text{-SiC}$ protective laminae for carbon/carbon composites. *Ceram Int* 40:14215–14222
19. YANG X, Li W, Wang S et al (2012) Oxidation behavior of oxidation protective coatings for PIP–C/SiC composites at 1500 °C. *Ceram Int* 38:9–13
20. Fu QG, Li HJ, Li KZ et al (2006) Study on the thermal fatigue behavior of SiC coated carbon/carbon composites. *Mater Sci Eng A* 434:335–338
21. Astapov AN, Pogozhev YS, Prokofiev MV et al (2019) Kinetics and mechanism of high-temperature oxidation of the heterophase $\text{ZrSi}_2\text{-MoSi}_2\text{-ZrB}_2$ ceramics. *Ceram Int* 45(5):6392–6404
22. McKamey CG, Tortorelli PF, DeVan JH, Carmichael JH (1992) A study of pest oxidation in polycrystalline MoSi_2 . *J Mater Res* 7(10):2747–2755

Figures

Figure 1

The weight change ratio and scratching failure load of the Si-SiC-MoSi₂-ZrB₂ coating modified by different contents of ZrB₂ after laser cladding

Figure 2

The XRD patterns of the Si-SiC-MoSi₂-ZrB₂ coatings after laser cladding

Figure 3

The SEM morphology (a), (b), (c), (d) and EDS of the Si:SiC:MoSi₂=20:16:64wt% coating modified by 40wt% ZrB₂ after laser cladding (e) Map scanning region (f) Ratio of the element (g)-(l) The element distribution of the map scanning

Figure 4

The cross section SEM (a),(b),(c) and EDS of the Si:SiC:MoSi₂=20:16:64wt% coating modified by 40wt% ZrB₂ after laser cladding (a) Map scanning region (d)-(h) The element distribution of the map scanning

Figure 5

The weight change ratio and scratching failure load of the Si:SiC:MoSi₂=20:16:64wt% coating modified by ZrB₂ with different content after laser ablation

Figure 6

The XRD of the Si:SiC:MoSi₂=20:16:64wt% coating modified by 40wt% ZrB₂ after laser ablation

Figure 7

The SEM (a),(b),(c),(d) and EDS of the Si:SiC:MoSi₂=20:16:64wt% coating modified by 40wt% ZrB₂ after 10 times laser ablation (e) Map scanning region (f) Ratio of the element (g)-(l) The element distribution of the map scanning