Influence of MoSi₂ on oxidation protective ability of TaB₂-SiC coating in oxygen-containing environments within a broad temperature range

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Research Article

Keywords: MoSi₂, TaB₂-SiC coating, Liquid phase sintering, Ta-Si-O-B compound glass layer, Relative oxygen permeability

Posted Date: March 24th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-18927/v1>

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Version of Record: A version of this preprint was published at Journal of Advanced Ceramics on August 13th, 2020. See the published version at <https://doi.org/10.1007/s40145-020-0406-5>.

Abstract

TaB₂-SiC coating modified by different content of MoSi₂ was fabricated on graphite substrate with SiC inner coating by liquid phase sintering to elevate the anti-oxidation capability of the TaB₂-SiC coatings. As compared to the sample with the TaB₂-40wt.%SiC coating, the coating sample modified with MoSi₂ exhibited a weight gain trend at lower temperatures, the fastest weight loss rate went down by 76%, and the relative oxygen permeability value reduced from about 1% to near 0. More importantly, the large amount of SiO₂ glass phase produced over the coating during oxidation was in contact with the modification of MoSi₂, which was proved to be beneficial to the dispersion of Ta-oxides. A concomitantly formed continuous Ta-Si-O-B compound glass layer showed excellent capacity to prevent oxygen penetration. However, when the TaB₂ content was sacrificed to increase the MoSi₂ content, the relative oxygen permeability of the coating increased instead of decreased. Thus, on the basis of ample TaB₂ content, increasing the MoSi₂ content of the coating is conducive to reducing the relative oxygen permeability of the coatings in a broad temperature region.

1. Introduction

Carbon materials, especially carbon/carbon composites are deemed to be the most potential materials in the field of aerospace and aeronautical owing to their superior high-temperature mechanical properties, for instance, low coefficient of thermal expansion, outstanding thermal shock resistance, high strength at extreme temperature and so on [1–4]. Unfortunately, the defect that carbon materials easily fail above 500 °C due to the oxidation of carbon is unable to be ignored [5], which causes the applications of carbon materials are severely hampered in an oxygen-containing environment. At present, in order to cope with this imperative problem, ceramic coating technology is widely applied to avoid the oxidation of carbon materials in a wide temperature range as much as possible.

It has been commonly accepted that ultra-high temperature ceramics (UHTC_s) with high hardness, high melting point and outstanding thermal conductivity are extensively utilized as structure materials in rocket nozzles and other components that work in extreme high temperature environments [6–9]. Moreover, UHTC_s have attracted the attention of many scholars in the field of anti-oxidation coatings, because the refractory oxide formed during the oxidation process will effectively enhance the stability of the compound oxide layer [10, 11].

As one of UHTC_s, TaB₂ possesses a great deal of outstanding properties including extremely high melting point (3200 °C), high hardness (24.5 GPa), and excellent chemical stability [12, 13]. Up till now, numerous TaB₂-added coatings have been fabricated to protect carbon substrates from oxidation. For example, Jiang et al. [14] fabricated a single-layer TaB₂-SiC-Si coating on graphite surface by in-situ reaction and impregnation method to defend graphite materials against oxidation. The results of the oxidation test at 1550 °C for 168 h showed that the SiO₂ and Ta₂O₅ layers formed on the outer layer caused 2% mass gain. In view of this, oxidation products played a key role in excellent protection of the coating. Qu et al. [15] prepared a dense TaB₂-SiC coating by pack cementation method to protect C/C composites from oxidation, and the ablation behavior of the samples was investigated. The results that the linear ablation rate for 30 s was 4.2 μm/s illustrated the unique oxidation-inhibition capability of the coating, which was associated with the generation of a Ta-Si-O compound glass layer. Therefore, TaB₂ is an ideal candidate for protecting carbon materials in high-temperature aerobic atmosphere. This is not only because the B₂O₃ layer formed provided fine protection below

1100 °C, but also because the Ta-Si-O compound glass layer with strong stability in higher temperatures was generated when TaB₂ was introduced into the Si-based coatings [16–18]. But frankly speaking, the oxidation protective capacity of the fabricated TaB₂-SiC coating still needs to be improved.

It's common knowledge that Si-based coatings are broadly exploited to the oxidation protection for carbon materials because of the generation of abundant SiO₂ glass phase on the coating surface at high temperatures. The SiO₂ glass phase created an impactful barrier to oxygen and filled the gap between refractory oxide skeletons [19–21]. Thus, adding sorts of silicide into ultra-high temperature ceramics to construct compound coatings is considered as an effective route. SiC has a similar thermal expansion coefficient as carbon materials, so it is commonly used in the construction of anti-oxidation coatings [22]. However, since a large amount of gas products, such as CO₂ and CO, are released during the oxidation of SiC, large bubbles formed will expose a fresh surface after bursting, and channels for oxygen diffusion will also be formed, which will reduce the protective effect of the glass film [23]. As one of multitudinous silicides, MoSi₂ is a kind of material with dual characteristics of metal and ceramic, and it is able to produce a continuous SiO₂ glass layer to protect its substrate from oxidation at temperatures as high as 1700 °C [24]. As a result, it has already been used in the preparation of electric heating elements. Conceivably, MoSi₂ is regarded as a high temperature anti-oxidation coating material [25]. At present, a number of coatings based on MoSi₂ have been prepared to protect carbon materials from oxidation. Huang et al. [26] prepared an outer MoSi₂ layer on SiC inner layer by hydrothermal electrophoretic deposition to protect C/C composites. After undergoing isothermal oxidation tests at 1500 °C for 346 h, the sample possessed a weight loss of 2.49 mg·cm⁻². Wu et al. [27] fabricated a MoSi₂-based coating composed of MoSi₂, Mo₅Si₃ and SiO₂ on the surface of SiC inner coating by supersonic plasma spraying to defend C/C composites against oxidation. After oxidation tests for more than 400 h at 1500 °C, the result showed that the weight loss of the specimen was only 1.14%. Briefly, the excellent oxidation protective performance shown by these coatings is ascribed to the generation of a continuous SiO₂ glass layer on the coating surface. In addition, MoSi₂ as a sintering aid can effectively increase the density of the coatings [28, 29], which can decelerate further corrosion of the coating by oxygen.

At the moment, because of the fact that MoSi₂ possesses superior anti-oxidation performance, MoSi₂-added UHTC coatings, such as the ZrB₂-MoSi₂-SiC coating [30–32] and the HfB₂-MoSi₂-SiC coating [33], have attracted lots of attention. Yet, until now, few studies have been able to elaborate the unique role of MoSi₂ in multiphase coating. Consequently, in this paper, MoSi₂ was used as the second silicon source, and a TaB₂-MoSi₂-SiC coating was fabricated. In detail, the influence of MoSi₂ modification on the oxidation protective capacity of the coatings in an oxygen-containing atmosphere within a wide temperature region and the generation mechanisms of the compound glass layer were studied.

In addition, in order to synthesis the coatings that can provide long-term protection for carbon materials, the liquid phase sintering method has been widely applied in our previous work [34], which is an ideal method because the content of various components in the coatings can be adjusted so that a coating with better oxidation resistance is available. Likewise, in this paper, the coatings were synthesized by the combination of liquid phase sintering and in-situ reaction, and partial SiC was obtained by in-situ reaction between Si and C.

2. Materials And Method

The TaB₂-MoSi₂-SiC coatings were fabricated by liquid phase sintering on the SiC buffer layer that was prepared by pack cementation to protect graphite substrates (3mm × 3mm × 3 mm). The raw materials consisted of TaB₂ powders, MoSi₂ powders and SiC powders (Licheng Innovation Metal Materials Technology Co., Ltd, Beijing, China), graphite powders (Hongtu Burden Co., Ltd, Liaoyang, China), silicon powders (Yuancheng New Material Industry Group Co., Ltd, Yinchuan, China) and silica sol (SiO₂·nH₂O) (the M_{other raw materials} : V_{silica sol} = 0.6–1.7 g/ml) (City Fire Crystal Glass Co., Ltd, Dezhou, China). It also should be noted that the composite coating consists of an outer layer and an inner SiC buffer layer. Therefore, as schematically represented in Fig. 1, the preparation process of the coatings consists of three steps. First, in order to alleviate the mismatch of the thermal expansion coefficients of the substrate and the outer layer, the inner SiC layer was fabricated by pack cementation which is in widespread use [35]. Second, the raw materials were weighed in different proportions, and then they were mixed as slurries for the preparation of the coatings. Next, brush the prefabricated slurry onto the surface of SiC covered graphite substrate, and dry the specimens at 100 °C for half an hour later, repeating the above operation three times. Ultimately, the coatings were sintered at 2100 °C for 2 h in argon atmosphere. In addition, partial SiC was formed by in-situ reaction between Si and C.

The phase composition of the coatings before and after oxidation were studied by X-ray diffractometer (Bruker D8 ADVANCE XRD, BRUKER AXS, Germany). Field Emission Scanning Electron Microscopy (JSM-6700F FE-SEM, JEOL, Japan) was used to observe the micro-morphology of the prepared coatings before and after oxidation, and the energy dispersive spectroscopy was applied to analyze the elemental composition of the compound glass layer. To research the dynamic oxidation behavior of the coatings in oxygenated atmosphere from 25 °C to 1500 °C, Thermogravimetric Analyzer (STA 449 F3, TGA, Netzsch, Germany) with a heating rate of 5 °C/min was employed.

3. Results And Discussion

The XRD pattern of the TaB₂-MoSi₂-SiC coating synthesized by liquid phase sintering is displayed in Fig. 2. As shown in Fig. 2, the composite coating contains MoSi₂, SiC and TaB₂ phases, illustrating successful preparation of the multiphase coating. In addition, note that there is no other impurity phase in the coating because Si powders and carbon powders both participated in the generation of SiC through in-situ reaction between Si and C.

The BSE image for observing the surface microstructure of the fabricated coating is presented in Fig. 3. According to the results of EDS analysis, the white and grey particles are TaB₂, MoSi₂ phases, respectively. What's more, it is evident that these fine particles were distributed evenly over the black SiC layer and embedded in loose SiC inner layer, which is favorable to elevate the oxidation resistance of the fabricated coating. This is because it is desirable that the refractory oxidation products will be uniformly distributed in the amorphous SiO₂ after the oxidation process.

The cross-sectional backscatter image of the fabricated coating is demonstrated in Fig. 4. Obviously, the fabricated coating consists of two layers and bonds tightly with the graphite substrate, which is attribute to the exceptional preparation method. The first layer is a multiphase coating including TaB₂, MoSi₂ and SiC phases

prepared by liquid phase sintering. The second layer is inner SiC fabricated by pack cementation. In addition, there is no distinct gap or void in the interface, which is a prerequisite for the coating providing protection against oxidation to the graphite matrix. Consequently, liquid phase sintering is considered to be an extraordinary method to fabricate the coating with outstanding oxidation protective performance.

The TGA tests of pure graphite substrate and the samples coated by two different coatings were performed in air within a wide temperature range to demonstrate the superior behavior of MoSi₂ compared with SiC in the application of anti-oxidation coatings. As shown in Fig. 5 (a), the pure graphite suffered fearful destruction from 700 °C, but the weight loss of the other samples both presented a marked decrease under the protection of fabricated coatings. With the aim of visually observing the initial oxidation characteristic of the samples, Fig. 5(b) displays the TGA curves from 500 °C to 900 °C. Clearly, the pure graphite began to be oxidized when the temperature reached about 570 °C, whereas the initial weight loss temperatures of the specimen with the SiC/SiC coating and the specimen with the SiC-MoSi₂/SiC coating were around 700 °C, 900 °C, respectively. Significantly, the weight loss of the sample with the SiC-MoSi₂/SiC coating was lower than that of the sample with the SiC/SiC coating in a wide temperature range, indicating that MoSi₂ performed better than SiC when it was applied to the anti-oxidation coating. In addition, the weight change rate curve over a wide temperature range are analyzed to elucidate the anti-oxidation process in detail. As displayed in Fig. 5(c), the fastest weight loss range was from 1000 °C to 1300 °C. The modification of MoSi₂ reduced the fastest weight loss rate although it failed to narrow the fastest weight loss region, which decreased the damage of carbon material during oxidation.

Since the oxidation of carbon is the main cause of sample weight loss, the weight loss of the sample to some extent reflects the degree of oxygen penetration into the carbon matrix. Thus, a concept called relative oxygen permeability was proposed to describe the ability of the coating to prevent oxygen penetration in our previous work [36]. Relative oxygen permeability was defined by the following formula.

$$RP_{O_2} = \frac{\Delta m_1 * S_2}{\Delta m_2 * S_1} * 100\%$$

Δm_1 : Weight change of the sample covered by fabricated coating

Δm_2 : Weight change of the pure carbon sample

S_1 : Superficial area of the sample covered by fabricated coating

S_2 : Superficial area of the pure carbon sample

The weight loss of the substrate was primarily concentrated in the fastest weight loss region. For purpose of clarifying the capability of MoSi₂ to prevent the oxygen delivery from outside to substrate, Fig. 6 shows the relative oxygen permeability of the SiC/SiC coating and the SiC-MoSi₂/SiC coating. Owing to the modification of MoSi₂, the relative oxygen permeability value of the SiC/SiC coating reduced from about 5–3% in the fastest

weight loss region, which further demonstrates that MoSi_2 plays a noteworthy role in enhancing the oxidation protective ability of the coatings.

Previously, the protective capability of the TaB_2 -SiC coating has been investigated [36]. To verify the improvement in the oxidation resistance of the coating modified with MoSi_2 , TGA tests were performed in an air atmosphere from indoor temperature to 1500 °C. The samples with different coatings both presented mild weight loss in the initial stage from room temperature to about 650 °C, as shown in Fig. 7(a). Additionally, the two dynamic oxidation curves didn't display an increasing trend until the temperature reached about 700 °C. It should be noted, however, that the sample with the TaB_2 -20wt.% MoSi_2 -20wt.%SiC/SiC coating manifested an earlier trend of weight gain due to the addition of MoSi_2 . And in general, sample weight gain means the formation of passive oxidation products with protective capabilities. Therefore, the formation of an oxide layer at lower temperatures contributes to extend the protective temperature range of the coating. Moreover, the curve representing the sample with the TaB_2 -40wt.%SiC/SiC coating showed two different declining tendencies, comprising a relatively rapid decline from 850 °C to 1200 °C and a gentle decrease from 1200 °C to 1500 °C. In the other hand, evidently, the weight of the sample with the MoSi_2 modified coating only decreased slightly after a rapid increase, suggesting that the coating modified with MoSi_2 presented better oxidation resistance.

As presented in Fig. 7(b), the fastest weight loss zone of the sample with the TaB_2 -40wt.%SiC/SiC coating is wider than that of the MoSi_2 modified sample. At the same time, the fastest weight loss rate of the MoSi_2 modified sample was descending, compared with that of the sample with the TaB_2 -40wt.%SiC/SiC coating. In light of this, coatings with wider protection temperature range and stronger protection capability can be available through MoSi_2 modification.

The relative oxygen permeability curve reflects the ability of the coatings to prevent oxygen diffusion. As shown in Fig. 8, it should be emphasized the negative portion of the curve means that the specimen increased in weight relative to the initial state. In the fastest weight loss region, the relative oxygen permeability of the MoSi_2 modified coating was lower than that of the TaB_2 -40wt.%SiC/SiC coating. Besides, the value of the MoSi_2 modified coating approached zero earlier, which means that the coating modified with MoSi_2 established a defense against oxygen at a lower temperature. Accordingly, MoSi_2 presents superior performance in fending off the oxygen penetration when it is applied to the anti-oxidation coatings.

The XRD pattern of the TaB_2 - MoSi_2 -SiC coating after oxidation is displayed in Fig. 9. The diffraction peaks of several refractory Ta-oxides comprising TaO, TaO_2 and Ta_2O_5 were detected. These Ta-oxides remained stable even at elevated environments. Moreover, the formation of SiO_2 filling cracks and voids was due not only to the oxidation of SiC but also to the oxidation of MoSi_2 . The SiC peaks remained visible, indicating that the oxide layer was thin, which further illustrated the good protective ability of the coating. Mo_5SiB_2 that is a promising high temperature structure material with superb oxidation and creep resistance was detected after oxidation [37], hence it aids in enhancing the stability of the oxide layer in ultra-high temperature environments. In addition, the existence of B_2SiO_5 is attributed to the reaction between SiO_2 and B_2O_3 . Nevertheless, MoO_3 and B_2O_3 phases were not detected because of their evaporation at low temperatures.

In the interest of clarifying the mechanism of improving the oxidation resistance of the coating by MoSi_2 modification, the surface microstructure of the TaB_2 -40wt.%SiC/SiC coating and the TaB_2 -20wt.% MoSi_2 -20wt.%SiC/SiC coating after TGA tests are displayed in Fig. 10. As presented in Fig. 10(a), it is evident that the Ta-oxides, the grey particles, were uniformly distributed on the coating surface at a low magnification. However, Fig. 10(b), the magnification of Fig. 10(a), shows the existence of the Ta-oxides aggregate structure which is incapable of greatly improving the stability of the glass layer [38]. In contrast, a novel phenomenon that more SiO_2 glass phase was generated on the coating with MoSi_2 modified can be observed from Fig. 10(c). Moreover, it should be noted that the traces of liquid flow and Ta-oxides dispersion can be found distinctly from Fig. 10(d). Numerous tiny Ta-oxides were able to be dispersed in the glass layer on account of the excellent fluidity provided by a large quantity of SiO_2 glass phase. In this case, the outermost glass layer became viscous and stable, providing a more efficient barrier against oxygen than the pure SiO_2 glass layer. Thus, the addition of MoSi_2 significantly elevated the oxidation protective property of the coatings. What's more, what the SEM micrographs shows are coincident with the results of the TGA tests.

To study the influence of the MoSi_2 content of the coatings on the anti-oxidation performance in a dynamic aerobic environment, the TGA tests of the coatings with different component ratios were carried out. As can be seen in Fig. 11(a), for curve 2,3,4, the weight loss manifested a distinct decrease as a whole in a broad temperature range with the increasing of MoSi_2 content in the coatings, indicating that the partial substitution of MoSi_2 for SiC significantly improved the oxidation protective performance of the coatings in aerobic environments. On the contrary, the weight loss of the sample with the TaB_2 -60wt.% MoSi_2 -20wt.%SiC/SiC coating is higher than that of the sample with the TaB_2 -40wt.% MoSi_2 -20wt.%SiC/SiC coating, indicating that increasing the amount of MoSi_2 excessively at the expense of the TaB_2 content in the construction of anti-oxidation coating cannot lead to a better result. The critical role of TaB_2 in Si-based coatings was illustrated from the other hand.

The weight change rate curves of the coatings are displayed in Fig. 11(b). As shown in curves 2, 3, 4, the effect of MoSi_2 modification on narrowing the fastest weight loss region was negligible, but the reduction of the fastest weight loss rate was obvious. Also, the more MoSi_2 was added, the more obvious the reducing effect was. In consequence, the damage of the carbon matrix in the fastest weight loss zone was decreasing due to the addition of MoSi_2 , illustrating that MoSi_2 improved the oxidation resistance of the coatings especially in the fastest weight loss zone. In line with Fig. 11(a), the coating with the highest MoSi_2 content failed to exhibit the best protection performance. This could be caused by the lack of refractory oxide during the oxidation process. The stability of the glass layer was decreased, although the amount of SiO_2 formed was increased.

In order to describe the effect of MoSi_2 content on the capacity of the coating to block oxygen infiltration, Fig. 12 shows the relative oxygen permeability curves of the TaB_2 - MoSi_2 -SiC/SiC coatings with dissimilar MoSi_2 or TaB_2 contents. As can be seen in Fig. 12, for curve 2, 3, 4, the relative oxygen permeability of the samples gradually declined with the increasing of MoSi_2 content, indicating that the adding of MoSi_2 improved the ability of the coating to prevent oxygen infiltration in the fastest weight loss region. In addition, due to the generation of the oxide layer, all the curves tended to gentle in the end, which is consistent with that shown in Fig. 11(a). Nevertheless, as seen in Fig. 12, the relative oxygen permeability of the coatings with high MoSi_2

content tended to 0.5% at about 1050 °C, while other coatings with low MoSi₂ content did not reach the same level until 1400 °C, suggesting that the modification of MoSi₂ effectively boosted the formation of the ability to prevent oxygen penetration during the initial stage of oxidation.

After isothermal oxidation tests at 1500 °C in an aerobic environment, the SEM micrographs of the coating surface are displayed in Fig. 13. Clearly, there are a large quantity of bulk Ta-oxides on the coating without the addition of MoSi₂, which is shown in Fig. 13(a). On the other hand, surprisingly, due to the modification of MoSi₂, the aggregation phenomenon of Ta-oxides is negligible as shown in the other figures. Since MoSi₂ provided abundant SiO₂ glass phase with wonder quality and high fluidity after its oxidation at high temperature, the bulk aggregated Ta-oxides were separated into nanocrystals under the action of liquid flow. Hereafter, the tiny particles were evenly dispersed in the SiO₂ glass phase. In the end, a compound glass layer, the gray area shown in Fig. 13, was formed. It is the dominant coating protection mechanism that the compound glass layer is responsible for preventing oxygen penetration. As shown in Fig. 13(a), obviously, the compound glass layer failed to completely cover the black glass layer, because the lack of liquid flow during oxidation resulted in the local aggregation of the Ta-oxides. In this case, although the bulk Ta-oxides which were defined as a pinning phase enabled to oblige the cracks to deflect or terminate, numerous cracks were distributed in the black glass region. Clearly, as the MoSi₂ content in the coating increased, the area covered by the compound glass layer enlarged. This proves that the modification of MoSi₂ significantly improved the oxidation resistance of the coatings. In addition, as can be seen in Fig. 13(c), there are a number of micron scale Ta-oxide particles distributed at the growth interface. These particles provided nuclei for dendrite growth so that the part area of the coating surface was covered by the dendrites. It is beyond disputed that the dendrite structure contributes to the deflection of the cracks and the relaxation of the stress [39]. Furthermore, as show in Fig. 13(d), the compound glass layer covered most of the coating surface because of the addition of 60wt.% MoSi₂. But at the same time, lots of gas products such as MoO₃ were released, resulting in the formation of holes as the paths for oxygen transport. Also, the drop in TaB₂ content caused the increasing instability of the compound glass layer. Therefore, excessively increasing the amount of MoSi₂ while decreasing the amount of TaB₂ reduced the protective effect of the coating. Thus, on the premise that the amount of TaB₂ is sufficient, the TaB₂-MoSi₂-SiC/SiC coating possesses more outstanding oxidation protective property than the TaB₂-SiC/SiC coating.

Based on the discussion above, the compound glass layer consists of the SiO₂ glass phase and particulate refractory oxides dispersed therein. To further illustrate this conclusion, the specific elemental composition of the oxidized coating surface was disclosed by the surface EDS analysis spectrum, which is presented in Fig. 14. As can be seen, the area of the orange circle, the black region, is rich in Si and O elements, illustrating that this area is SiO₂ glass layer that was not covered by the compound glass layer. Even more important, most areas were covered by the continuous compound glass layer that is constituted by Ta, Si, O and B elements. Besides, the presence of B element was not unexpected because B₃SiO₅ phase was detected in the XRD pattern displayed in Fig. 9. Thus, the results of EDS analysis further demonstrated the generation of the Ta-Si-B-O compound glass layer.

4. Conclusions

In conclusion, the liquid phase sintering was used for fabricating the TaB₂-MoSi₂-SiC outer coating with no crack or void to enhance protective ability of the TaB₂-SiC coating. The sample with the coating modified by MoSi₂ exhibited a weight gain trend at lower temperatures and the fastest weight loss rate of this sample in the fastest weight loss zone goes down by 76%. After the modification of MoSi₂, it was found that more SiO₂ glass phase was generated during the oxidation process. For this reason, bulk Ta-oxides were stripped into tiny nanocrystals more easily, and then the Ta-oxides nanocrystals were diffusely distributed in the SiO₂ glass layer. The Ta-Si-B-O compound glass layer was formed in this way, and it is the key to blocking oxygen infiltration. The addition of MoSi₂ availably improved the anti-oxidation performance of the TaB₂-SiC coating when the content of TaB₂ is fixed. Nevertheless, the coating with the highest MoSi₂ content but low TaB₂ content failed to present the best anti-oxidation performance because the instability of the compound glass layer increased.

Declarations

Acknowledgements

This work has been supported by the Fundamental Research Funds for the Central Universities (No. 2018GF14).

References

- [1] Parshant Kumar, V. K. Srivastava. Tribological behaviour of C/C-SiC composites—A review. *J Adv Ceram* 2016, **5**: 1-12.
- [2] Jacobson NS, Curry DM. Oxidation microstructure studies of reinforced carbon/carbon. *Carbon* 2006, **44**: 1142-1150.
- [3] Chu YH, Fu QG, Li HJ, *et al.* SiC coating toughened by SiC nanowires to protect C/C composites against oxidation. *Ceram Int* 2012, **38**: 189-194.
- [4] Ren JC, Zhang YL, Zhang J, *et al.* Improving the flexural property and long-lasting anti-ablation performance of the CVD-HfC coating by in-situ growing HfC nanowires. *Ceram Int* 2019, **45**: 24294-24302.
- [5] Fu QG, Zhang JP, Zhang ZZ, *et al.* SiC-MoSi₂/ZrO₂-MoSi₂ coating to protect C/C composites against oxidation. *T Nonferr Metal Soc* 2013, **23**: 2113-2117.
- [6] Xue CQ, Zhou HJ, Hu JB, *et al.* Fabrication and microstructure of ZrB₂-ZrC-SiC coatings on C/C composites by reactive melt infiltration using ZrSi₂ alloy. *J Adv Ceram* 2018, **7**: 64-71.
- [7] Liu D, Liu HH, Ning SS, *et al.* Synthesis of high-purity high-entropy metal diboride powders by boro/carbothermal reduction. *J Am Ceram Soc* 2019, **102**: 7071-7076.
- [8] Liu D, Wen TQ, Ye BL, *et al.* Synthesis of superfine high-entropy metal diboride powders. *Scripta Mater* 2019, **167**: 110-114.
- [9] Liu D, Wen T, Ye B, *et al.* Molten salt synthesis, characterization, and formation mechanism of superfine (Hf_xZr_{1-x})B₂ solid-solution powders. *J Am Ceram Soc* 2019, **102**: 3763-3770.

- [10] Jiang Y, Liu T, Ru H, *et al.* Oxidation and ablation protection of double layer $\text{HfB}_2\text{-SiC-Si/SiC-Si}$ coating for graphite materials. *J Alloys Compd* 2019, **782**: 761-771.
- [11] Wang L, Fu QG, Liu NK, *et al.* Supersonic plasma sprayed $\text{MoSi}_2\text{-ZrB}_2$ antioxidation coating for SiC-C/C composites. *Surf Eng* 2016, **32**: 508-513.
- [12] Licheri R, Orrù R, Musa C, *et al.* Efficient Technologies for the Fabrication of Dense TaB_2 -Based Ultra-High-Temperature Ceramics. *ACS Appl Mater Inter* 2010, **2**: 2206-2212.
- [13] Zhang X, Hilmas GE, Fahrenholtz WG. Synthesis, densification, and mechanical properties of TaB_2 . *Mater Lett* 2008, **62**: 4251-4253.
- [14] Jiang Y, Liu T, Ru H, *et al.* Ultra-high-temperature ceramic $\text{TaB}_2\text{-SiC-Si}$ coating by impregnation and in-situ reaction method to prevent graphite materials from oxidation and ablation. *Ceram Int* 2019, **45**: 6541-6551.
- [15] Qu JL, Fu QG, Zhang JP, *et al.* Ablation behavior of $\text{TaB}_2\text{-SiC}$ coating for carbon/carbon composites under oxyacetylene torch. *Vacuum* 2016, **131**: 223-230.
- [16] Li L, Li H, Yin X, *et al.* Oxidation protection and behavior of in-situ zirconium diboride-silicon carbide coating for carbon/carbon composites. *J Alloys Compd* 2015, **645**: 164-170.
- [17] Feng T, Li HJ, Shi XH, *et al.* Sealing role of B_2O_3 in $\text{MoSi}_2\text{-CrSi}_2\text{-Si/B}$ -modified SiC coating for C/C composites. *Corros Sci* 2012, **60**: 4-9.
- [18] Fu QG, Li HJ, Wang YJ, *et al.* B_2O_3 modified SiC-MoSi_2 oxidation resistant coating for carbon/carbon composites by a two-step pack cementation. *Corros Sci* 2009, **51**: 2450-2454.
- [19] Chen P, Zhu L, Ren XR, *et al.* Preparation of oxidation protective $\text{MoSi}_2\text{-SiC}$ coating on graphite using recycled waste MoSi_2 by one-step spark plasma sintering method. *Ceram Int* 2019, **45**: 22040-22046.
- [20] Li SP, Zhang MY, Huang D, *et al.* Preparation and antioxidation property of a $\text{SiC-MoSi}_2\text{-Si}$ multilayer coating on a C/C composite. *New Carbon Mater* 2018, **33**: 82-87.
- [21] Li CY, Li GB, Ouyang H, *et al.* ZrB_2 particles reinforced glass coating for oxidation protection of carbon/carbon composites. *J Adv Ceram* 2019, **8**: 102-111.
- [22] Huang JF, Zeng XR, Li HJ, *et al.* Influence of the preparation temperature on the phase, microstructure and anti-oxidation property of a SiC coating for C/C composites. *Carbon* 2004, **42**: 1517-1521.
- [23] Fu QG, Li HJ, Shi XH, *et al.* Silicon carbide coating to protect carbon/carbon composites against oxidation. *Carbon* 2005, **52**: 923-927.
- [24] Ma QS, Cai LH. Fabrication and oxidation resistance of mullite/yttrium silicate multilayer coatings on C/SiC composites. *J Adv Ceram* 2017, **6**: 360-367.

- [25] Zhu L, Zhu YS, Ren XR, *et al.* Microstructure, properties and oxidation behavior of MoSi₂-MoB-ZrO₂ coating for Mo substrate using spark plasma sintering. *Surf Coat Technol* 2019, **375**: 773-781.
- [26] Huang JF, Wang B, Li HJ, *et al.* A MoSi₂/SiC oxidation protective coating for carbon/carbon composites. *Corros Sci* 2011, **53**: 834-839.
- [27] Wu H, Li HJ, Ma C, *et al.* MoSi₂-based oxidation protective coatings for SiC-coated carbon/carbon composites prepared by supersonic plasma spraying. *J Eur Ceram Soc* 2010, **30**: 3267-3270.
- [28] D Sciti, L Silvestroni, M Nygren. Spark plasma sintering of Zr- and Hf-borides with decreasing amounts of MoSi₂ as sintering aid. *J Eur Ceram Soc* 2008, **28**: 1287-1296.
- [29] Ghaffari SA, Faghihi-Sani MA, Golestani-Fard F, *et al.* Spark plasma sintering of TaC-HfC UHTC via disilicides sintering aids. *J Eur Ceram Soc* 2013, **33**: 1479-1484.
- [30] Fu QG, Jing JY, Tan BY, *et al.* Nanowire-toughened transition layer to improve the oxidation resistance of SiC-MoSi₂-ZrB₂ coating for C/C composites. *Corros Sci* 2016, **111**: 259-266.
- [31] Wang L, Fu QG, Zhao FL, *et al.* A novel gradient SiC-ZrB₂-MoSi₂ coating for SiC coated C/C composites by supersonic plasma spraying. *Surf Coat Technol* 2017, **313**: 63-72.
- [32] Yao XY, Li HJ, Zhang YL, *et al.* Oxidation and Mechanical Properties of SiC/SiC-MoSi₂-ZrB₂ Coating for Carbon/Carbon Composites. *J Mater Sci Technol* 2014, **30**: 123-127.
- [33] Wang PP, Li HJ, Ren XR, *et al.* HfB₂-SiC-MoSi₂ oxidation resistance coating fabricated through in-situ synthesis for SiC coated C/C composites. *J Alloys Compd* 2017, **722**: 69-76.
- [34] Ren XR, Wang LF, Feng PZ, *et al.* Preparation of TaB₂-SiC oxidation protective coating for carbon materials by liquid phase sintering. *Ceram Int* 2018, **44**: 10708-10715.
- [35] Ren XR, Li HJ, Chu YH, *et al.* Preparation of oxidation protective ZrB₂-SiC coating by in-situ reaction method on SiC-coated carbon/carbon composites. *Surf Coat Technol* 2014, **247**: 61-67.
- [36] Ren XR, Wang WH, Chen P, *et al.* Investigations of TaB₂ on oxidation-inhibition property and mechanism of Si-based coatings in aerobic environment with broad temperature region for carbon materials. *J Eur Ceram Soc* 2019, **39**: 4554-4564.
- [37] Lemberg JA, Ritchie RO. Mo-Si-B Alloys for Ultrahigh-Temperature Structural Applications. *Adv Mater* 2012, **24**: 3445-3480.
- [38] Ren XR, Wang LF, Feng PZ, *et al.* Low temperature synthesis of pure phase TaB₂ powders and its oxidation protection modification behaviors for Si-based ceramic coating in dynamic oxidation environments. *Ceram Int* 2018, **44**: 15517-15525.
- [39] Ren XR, Wang WH, Shang TQ, *et al.* Dynamic oxidation protective ultrahigh temperature ceramic TaB₂-20%wtSiC composite coating for carbon material. *Composites Part B* 2019, **161**: 220-227.

Figures

Figure 1

The fabricating process of the TaB₂-SiC-MoSi₂ coatings.

Figure 2

XRD pattern of the TaB₂-MoSi₂-SiC coating fabricated by liquid phase sintering.

Figure 3

Surface backscatter SEM micrographs of the TaB₂-MoSi₂-SiC coating.

Figure 4

Cross-section morphology of the fabricated TaB₂-MoSi₂-SiC coating.

Figure 5

(a) TGA curves of the samples from room temperature to 1500 °C; (b) TGA curves of the samples from 500 °C to 900 °C; (c) weight loss rate curves of the samples from room temperature to 1500 °C.

Figure 6

Relative oxygen permeability curves of the SiC/SiC coating and the MoSi₂-SiC/SiC coating.

Figure 7

(a) TGA curves of the samples from room temperature to 1500 $^{\circ}\text{C}$; (b) weight loss rate curves of the samples from 25 $^{\circ}\text{C}$ to 1500 $^{\circ}\text{C}$.

Figure 8

Relative oxygen permeability curves of the coatings from 800 °C to 1200 °C.

Figure 9

XRD pattern of the TaB₂-MoSi₂-SiC coating after oxidation.

Figure 10

(a) the SEM micrographs of the TaB2-40wt.%SiC/SiC coating after TGA tests; (c) the SEM micrographs of the TaB2-20wt.%MoSi2-20wt.%SiC/SiC coating after TGA tests; (b), (d) the magnification of (a), (c).

Figure 11

(a) TGA curves of the samples with different MoSi₂ contents or TaB₂ contents; (b) weight change rate curves of the samples with different MoSi₂ contents or TaB₂ contents.

Figure 12

Relative oxygen permeability curves of the fabricated different coatings.

Figure 13

SEM micrographs of the 40wt.%TaB₂-MoSi₂-SiC/SiC coatings with different MoSi₂ contents after oxidation at 1500 °C, (a) 0 wt.%, (b) 20 wt.%, (c) 40 wt.%; (d) SEM micrograph of the 20wt.%TaB₂-60wt.%MoSi₂-SiC/SiC coating after oxidation at 1500 °C.

Figure 14

Surface EDS spectrum of the TaB₂-MoSi₂-SiC/SiC coating surface after isothermal oxidation test at 1500 °C.

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