Microstructure and ablation properties of a gradient C_f/C-XSi₂-SiC (X=Mo,Ti) composite fabricated by reactive melt infiltration

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ABSTRACT

Porous carbon/carbon composites were infiltrated by mixed Si-Mo-Ti powder with different Ti content below 1600°C to produce an ablative C_f/C-(Mo,Ti)Si₂-SiC composite. Microstructure, mechanical properties and ablation properties of the infiltrated composites were investigated. Results show that composites infiltrated by mixed powders with 14%wt Ti content have dense gradient structure and good mechanical properties. Three different kinds of typical morphologies can be distinguished on the surface of infiltrated composites according to the distribution of MoSiTi solid solutions. Formation mechanisms of the three kinds of typical morphologies are also analyzed. Ablation resistance improvement is attributed to the dense and continuity ceramic phases which distribute from inside to surface of the composites. Composites infiltrated with 14%wt Ti have the best ablation resistance due to the protective oxide layer formed by type I and type III morphologies during the ablation process. Linear and mass ablation rates of such composites are 0.002mm/s and 0.01mg/s, respectively.

Keywords: Carbon fibre; SiC; MoSi₂; Composites; Infiltration.

1. Introduction

Carbon fibre reinforced carbon matrix(C/C) composites have many excellent properties such as low density, good resistance to thermal shock and ablation [1], which make them attractive structure materials in advanced propulsion system [2]. However, the thermal protection system of hypersonic space vehicles requires withstanding ultra high temperatures (>1800°C) and high heat flux ablation in oxidizing atmospheres [3]. Therefore, it is necessary to improve the ablation resistance of C/C composites in oxidizing atmosphere.

Much attention has recently been focused on the ablation resistance improvement by introducing ceramics (such as SiC, ZrC, HfC, ZrB₂ and HfB₂) into matrix [4-10] or coating [11-15] of the C/C composites. SiC-MoSi₂ based coatings has been proved to have good bonding strength with C/C matrix when prepared by pack cementation[16] and excellent oxidation protective ability for C/C composites below 1700°C[17,18]. Esfehanian et.al [19,20] reported that the bending strength of C_f/XSi₂-SiC

(X=Mo,Ti) composite at 1600°C is better than that at room temperature. However, for complete protection of C/C composites, the introduced ceramics should exist in the matrix as well as on the outer faces of the C/C composites. And the ceramics phase should be adherence, continuity and mechanical compatibility to resist spallation due to thermal expansion mismatch during the extreme thermal excursions [21]. Combination of matrix modification and coating technology can provide better ablation resistance, but the process is complex and time consuming[22,23]. Previous research [24] indicated that C/C composites infiltrated by Si-Mo-Ti mixed powder possess good ablation resistance at 2500°C. Moreover, it was found that a dense ceramic coating can be obtained after the infiltration process. It is indicated that preparation of an ablation resistance coating can be combined in this one step infiltration process with mixed powder.

In this research, gradient Cf/C-XSi₂-SiC composites with ablative ceramic surface were prepared by an easy and fast one step reactive melt infiltration process with Si-Mo-Ti mixed powder. Effects of Ti content on surface morphologies of infiltrated composites were investigated. Three kinds of typical morphologies and their formation mechanism were analyzed. Ablation properties of the infiltrated composites are investigated under an oxy-acetylene torch flame. Relationship between microstructure and ablation properties was studied. This approach has the potential to develop an easy, fast and economic method to provide complete protection for C/C composites without mechanical properties decrease.

2. Experimental

2.1 Material preparation

Table1 Compositions of the infiltration mixtures.

Sample	Infiltration constituent		
	Si (wt. %)	Mo (wt. %)	Ti (wt. %)
T14	63	23	14
T47	23	30	47
T23	63	14	23

Porous C/C composites were infiltrated by mixed Si-Mo-Ti powder to produce the Cf/C-XSi₂-SiC (X=Mo, Ti) composites. Details of the porous C/C composites have been presented elsewhere [24]. The porous C/C composites were cut into specimens with a dimension of Φ30mm×10mm. Then the samples were placed in graphite crucibles together with mixed powder of different compositions, respectively. The powders were mixed by ball milling in alcohol then dried and filtered by sieves of 200 meshed before the infiltration process. Then the crucibles were heated in a high temperature furnace at 1550°C for 6h to finish the infiltration process. The furnace was protected by argon during the infiltration process. The mixed powder will melt then infiltrate into the porous C/C composites and reacted with the pyrolytic carbon during this process. Samples were numbered according to the compositions of infiltration mixtures as shown in table 1.

2.2 Characterization

Phase composition of the samples was identified by a D/max 2550vb+18kW rotating target X-ray

diffraction (XRD) analyzer (Rigaku Ltd., Japan, Cu K α radiation). Morphologies of the samples were analyzed by a scanning electron microscopy (SEM, Fei CO., NOVA Nano230) equipped with energy dispersion spectroscopy (EDS).

2.3 Mechanical tests

Mechanical properties of the samples were measured by material mechanical testing machine (Instron 3369, American). The cross speed of three-point bending test was 1mm/min at room temperature. Vertical and horizontal mechanical properties present mechanical properties when loading direction is perpendicular and horizontal to the no-woven layers, respectively.

2.4 Ablation tests

Ablation properties of the infiltrated composites were tested by an oxyacetylene torch system. The pressure and flow rates of oxygen were 0.4Mpa and 1.960L/s, and 0.095Mpa and 0.696L/s for acetylene. The distance between the surface of the composites and gun tip was 20mm and inner diameter of the gun tip was 2mm. During the test, highest temperature of the oxy-acetylene flame was measured 2500°C by an optical pyrometer. Ablation time was 300s for all of the samples in this research. Ablation rates of the samples were calculated according to the following formulas:

$$R_m = \frac{\Delta m}{t} \quad (1)$$

$$R_l = \frac{\Delta l}{t} \quad (2)$$

where R_m is the mass ablation rate, Δm the mass change of the sample, R_l the linear ablation rate, Δl the thickness change and t the ablation time.

3. Results and discussion

3.1 Microstructure characterization on the cross-section and mechanical properties

Fig.1. SEM image and XRD patterns of sample T14 (a) Back-scattered electron images for cross-section of T14; (b) XRD patterns for cross-section of sample T14 at different depth.

Table.2 Density and mechanical properties of T14 and C/C-SiC-ZrC composites.

Materials	Density(g/cm ³)	Bending strength(MPa)		Compressive strength(MPa)	
		Vertical	Horizontal	Vertical	Horizontal
T14	3.03±0.04	165±9	190±15	195±13	286±25
C/C-SiC-ZrC[25]	2.04	55.09		—	

Fig.1 (a) shows the back-scattered electron images on cross section of T14 and fig1 (b) shows the XRD patterns for cross-section of sample T14 at different depth. Table.2 shows the density and mechanical properties of T14 and C/C-SiC-ZrC composites. It is seen that ceramic phases distribute from surface to inside of the infiltrated sample and a dense ceramic coating can be observed on the surface. The inner structure of T14 is dense without pores and the density of T14 reaches 3.03g/cm³ which is shown in table.2. From fig.2 (b) we can deduced that the ceramic coating is composed of SiC, TiSi₂ MoSi₂ and (Ti_{0.8}Mo_{0.2}) Si₂ without carbon. The infiltrated sample shows a gradient structure that the content of carbon increases with depth and (Ti_{0.8}Mo_{0.2}) Si₂ disappears on the 4mm inside cross section. It is obvious that this gradient structure could provide complete protections for carbon fibre. Furthermore, no residual Si can be detected in whole of the sample. Since there is no residual Si in the matrix, the carbon (mainly carbon fibers) in the matrix can preserve high mechanical properties after infiltration at a relative lower temperature(1550°C). The bending strength of T14 is much higher than C/C-SiC-ZrC composites produced by reactive melt infiltration. Moreover, the horizontal mechanical properties of T14 are better than the vertical properties which indicates that the ceramic phases in the composite have a good bonding with carbon fibers. The good bonding between carbon fibers and ceramic phases should provide strong resistance to mechanical denudation during the ablation process.

3.2 Microstructure characterization on the surface

Fig.2.XRD patterns on the surface of samples infiltrated by Si-Mo-Ti mixed powder with different compositions.

The microstructure on the surfaces of infiltrated samples is focused because most of significant changes would occur on the surface during ablation process. Fig.2 shows XRD patterns on the surface of samples infiltrated by Si-Mo-Ti mixed powder with different compositions. XRD patterns of all the infiltrated samples show the presence of SiC and MoSi₂. Sample T14 contains TiSi₂ and (Ti_{0.8}Mo_{0.2})Si₂ besides SiC and MoSi₂. To sample T47, a considerable TiSi₂ peak could not be detected and a slight peak of MoC can be observed. TiSi₂ is the only phase which contains Ti element in the XRD patterns of sample T23. It can be concluded that higher Ti content and lower Si content goes against the generation of TiSi₂, higher content of Mo and lower content of Ti will lead to the generation of (Ti_{0.8}Mo_{0.2})Si₂.

Fig.3.Low magnification SEM images of samples infiltrated by Si-Mo-Ti mixed powder with different compositions (a)Sample T14; (b)samle T47 and (c)samle T23.

Table.3 Chemical composition of MoSiTi solid solutions on the surface of infiltrated samples.

MoSiTi solid solutions	Si(at.%)	Mo (at. %)	Ti (at. %)
Point 1	63.5	18.49	18.01
Point 2	33.78	11.53	54.69
Point 3	53.24	19.35	27.41

Fig.3 shows the SEM images of samples infiltrated by Si-Mo-Ti mixed powder with different composition. All of the infiltrated samples are composed of SiC (black phase) and solid solutions of MoSiTi (pale grey phase). The MoSiTi solid solutions of different samples have different chemical composition which is shown in table.3. All SiC particles are polyhedral while just a few of MoSiTi solid solutions are polyhedral. It is known that SiC follows the faceted growth. So we can deduced that when the solid solutions have lower content of Ti the solid solutions of MoSiTi are polyhedral particles and follows faceted growth, and when the solid solutions have higher content of Ti growth of MoSiTi solid solutions changes to unfaceted growth. And major of the surface region on sample T47 is covered by solid solutions of MoSiTi when the solid solutions have highest content of Ti.

3.3 Typical surface morphologies

Fig.4.High magnification SEM images for typical morphologies of samples infiltrated by Si-Mo-Ti mixed powder with different compositions (a) Type I; (b) type II and (c) (d) type III.

Fig.5. Formation mechanism of three kinds of typical morphologies.

Fig.4 shows the three kinds of typical morphologies that may affect the ablation properties. Fig.5 shows the formation mechanism of them. Fig.4a shows the morphology type I which can only be founded on sample T14. In some regions of sample T14 where liquid melt has a higher content of Mo and Si, the solid solution of MoSiTi and SiC will solidify at the same time as shown in fig5. Then the residual Si will solidify between SiC and solid solution of MoSiTi. Fig.4b shows the morphology type II which can only be founded on sample T47 which was infiltrated by mixed powders with highest Ti content. During the infiltration process, a SiC layer will be generated on the interface of porous C/C and melt. Then the major phase, solid solutions of MoSiTi solidified on the SiC layer which was shown in fig5. Finally, major of the surface region are covered by a layer of MoSiTi solid solutions and only a few SiC particles can be observed. Fig.4c shows the morphology type III which can be founded on sample T14 and T23. In these regions, SiC solidified first and then the solid solution of MoSiTi solidified between SiC particles. Type I and III morphologies may improve the ablation resistance of the composites cause the ceramic phases are combined to a stable structure.

3.4Ablation properties

Table.4 Linear and mass ablation rates of the infiltrated samples.

Sample	Linear ablation rate(mm/s)	Mass ablation rate(mg/s)
T14	0.002±0.001	0.01±0.01
T47	0.011±0.003	1.47±0.22
T23	0.006±0.002	0.91±0.17

Fig.6.XRD patterns of infiltrated samples after ablation.

Table.4 shows linear and mass ablation rate of the infiltrated samples. It can be seen that sample T14 has lowest linear and mass ablation rate. The lowest ablation rate of sample T14 is attributed to the dense gradient structure and the type I and III morphology. It is obvious that excess content of Ti leads to worse ablation properties because higher Ti content leads to the generation of type II morphology.

From the XRD patterns of samples after ablation(fig.6) we can figure out that sample T14 is mainly composed of SiC and oxides of Ti after ablation while sample T47 and T23 are mainly composed of TiO₂ and trace amount of SiC after ablation. The presence of Ti₃O and strong diffraction peaks of SiC indicate that oxidation degree is lower on the surface of sample T14. A slight peak of SiO₂ can be observed besides SiC and TiO₂ for sample T23. The presense of SiC and SiO₂ indicates that oxides of Ti can efficiently prevent SiC and SiO₂ from blowing away as anylysed above. In addition, the following reaction would occur during the ablation process according to the comparision of the XRD results:

Fig.7. Macroscopic photograph of the ablated surface of infiltrated samples (a) Sample T14; (b) sample T47 and (c) sample T23.

Three regions can be distinguished on the surface of the samples after ablation from centre to edge: central region (1), transitional region (2) and edge region (3) which was shown in fig.7. Some non-oxide ceramic phase with silver colour can be found in the central region of sample T14. It can be induced that the oxidation degree is lower on sample T14 which is consistent with the XRD results before. The edge region of sample T14 is smooth which proved that no severe chemical or physical reactions occurs here. Several pits can be observed in the central region of sample T47 which indicates that the sample suffers severe damage during the ablation process. Several recrystallized grains can be found in the edge region of sample T47 which indicates that the temperature is higher on the surface of sample T47 during the ablation process. The surface of sample T23 is similar to that of sample T14 except it doesn't have visible non-oxide ceramic regions.

Fig.8. Morphologies and EDS results of the edge region on ablated face (a)(d)(g) Sample T14; (b)(e)(h) sample T47 and (c)(f)(i) sample T23.

Fig.8 shows morphologies of the edge region on the ablated face. Many polyhedral particles can be observed in the edge region of sample T14(fig.8a). Some fibrous oxide and small recrystallized grains can be observed in the high magnification image(fig.8d). EDS result(fig.8g) indicates that some SiC haven't been oxidized. The edge region of sample T47 is completely oxidized as the EDS results shows and flocculent oxide can be found. The edge region of sample T23 is composed of polyhedral SiC particles and recrystallized SiC grains.

Fig.9. Morphologies of the transitional region of the ablated samples (a)(d) Sample T14; (b)(e) sample T47 and (c)(f) sample T23.

Fig.9 shows the morphologies of the transitional region of the ablated samples. The transitional regions of all samples are covered by an oxide layer. Large polyhedral particles can be found in the transition region of sample T14 which are not existed in the transition regions of sample T47 and T23. EDS results shows that it is SiC and it haven't been oxidized after the ablation process. Some recrystallized grains can be observed in the transition region of sample T47, and the oxide layer of sample T47 has many pores. The oxide layer of sample T23 is dense and continuous. It can be deduced that the T47 may have the worst ablation properties.

Fig.10. Morphologies of the central region of the ablated samples (a) Sample T14; (b) sample T47; (c) sample T23 and (d) EDS results of point 1.

Fig.10 shows the morphologies of the central region of the ablated samples. The central region suffers most serious damage during the ablation process. Many pores caused by heavy evaporation can be observed in the central region of all samples. The pores of sample T14 are smaller and well distributed. Oxide of Ti are also well distributed among the oxide layers so that this oxide layer can resist high speed flux during the ablation process. Such distribution for oxide of Ti may benefit from type I and III morphologies. The ceramic phases in type I and III morphologies were oxidized and enhanced each other during the ablation process. The central region of sample T47 has fewest pores because most oxides of sample T47 are oxides of Ti which have a higher boiling point. However, cracks would be generated because that the volume change of a single phase layer is significant. And no self sealed pores can be observed on sample T47. Furthermore, the oxide layer may be spalled from the surface of the sample easily due to the. The pores of sample T23 have a larger size because it has less Ti than sample T47 and the oxide of Ti is not well distributed. It should be noticed that carbon fibres haven't been exposed for all samples after ablation.

It can be concluded that the carbon fibres are well protected by the designed gradient structure. The ceramic surface has good ablation resistance and good bonding with matrix. Therefore, the differences in ablation properties for composites infiltrated with different composition mainly comes from the surface structure. Type I and III morphologies could form a stable structure that the oxides of Ti can protect the SiC from blowing away by high speed flux during the ablation process as they are combined with each other, in the same time SiO_2 generate by oxidation of SiC or Si in the ablation

process could seal the pores in the surface. Therefore, T14, whose surface is composed of Type I and III morphologies, have the best ablation properties. However, for type II morphology, the ceramic phases could be spalled from the surface of the sample easily as the oxide of Ti and SiO₂ may separated with each other. Therefore, T47 has the worst ablation properties due to its type II morphology.

4 . Conclusions

C/C composites were infiltrated by Si-Mo-Ti powder with different compositions. The major phases of infiltrated samples is SiC and XSi₂(X=Mo,Ti). The infiltrated composites have a dense gradient structure which can provide complete protection for carbon fibres. Three kinds of typical morphology were formed during the infiltration process according to the compositions of the mixed powder. Type I and III morphologies can provide better ablation resistance. Sample T14 has best ablation resistance after ablation for 300s under an oxyacetylene torch. The linear and mass ablation rates of the Si₆₃Mo₂₃Ti₁₄ sample are 0.002mm/s and 0.01mg/s, respectively. Excellent ablation resistance of sample T14 benefits from its type I and III morphologies.

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