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Effects of Ti/Al addition on the microstructures and ablation properties of C_f/C–$MoSi_2$–SiC composites

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ABSTRACT

Porous carbon/carbon composites were infiltrated by Mo–Si–Ti/Al mixed powder to develop a C_f/$MoSi_2$–SiC–C based composites below 1600 °C in this research. Effects of Ti/Al addition on the microstructures and ablation properties of infiltrated samples were investigated and compared together with Si–Mo infiltrated samples. The infiltrated samples are composed of SiC, $MoSi_2$ and ceramic phases containing Ti or Al. Ceramic phases containing Al distribute close to carbon fiber bundles while ceramic phases containing Ti distribute far away from carbon fiber bundles. Samples infiltrated by Mo–Si–Ti showed excellent ablation properties. The linear ablation rate and mass ablation rate after ablated for 300 s under an oxyacetylene torch system are 0.002 mm/s and 0.01 mg/s, respectively. Addition of Al has not improved ablation resistance significantly in this research.

1. Introduction

Carbon fiber reinforced carbon matrix (C/C) composites have many excellent properties such as low density, high specific strength and modulus, retention of mechanical properties at high temperature, low coefficient of thermal expansion, good resistance to thermal expansion and ablation [1,2], which make them extremely attractive high temperature structure materials in aerospace propulsion system [3]. However, the thermal protection system of hypersonic space vehicles requires withstanding ultrahigh temperatures (>1800 °C) and high heat flux ablation [4]. Therefore, it is necessary to improve the ablation properties of C/C composites.

Many researches have been done to improve the ablation resistance of C/C composites as introducing refractory ceramics (such as SiC, ZrC, HfC and ZrB_2) into the matrix [5–7] or the coating [8–11]. Among these materials, SiC is a suitable choice due to its good thermodynamic compatibility with carbon and excellent oxidation resistance. Reactive melt infiltration is a successful methods to introduce SiC ceramics into C/C composites which have advantages such as short fabrication period, low cost, near net shape and low porosity [12]. Si–Mo alloy have been used as infiltration instead of pure Si to eliminate the residual Si during the RMI process as Mo can react with Si to form $MoSi_2$ [13,14].

The $MoSi_2$–SiC system have been proved to possess excellent oxidation protective ability for C/C composites below 1700 °C [15,16]. However, the protective ability may not be effective in an ablative environment above 1800 °C over a long period. Another issue is that the carbon fibers will react with the infiltrating melt at infiltration temperatures above 1600 °C [17]. Therefore, a third element (Ti or Al) is infiltrated together with Si–Mo alloy to lower the infiltration temperature, and the high-temperature mechanical properties of the infiltrated composites are investigated [18,19]. In fact, the oxides of Ti and Al have excellent oxidation resistance [5,20]. Therefore, the C/C composites infiltrated with Mo–Si–Ti/Al are expected to exhibit excellent ablation resistance. However, the ablation properties of such composites have not been reported so far.

Aim of this research is developing a kind of composites with excellent ablation resistance and mechanical properties by a simple and efficient method. In this work, porous C/C composites were infiltrated by mixed powder of different constituents to produce C_f/$MoSi_2$–SiC–C based composites. The microstructure and ablation properties (under an oxyacetylene flame) of the infiltrated samples are studied. The infiltration model and the ablation model will also be proposed in this work.

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Table 1
Compositions of the infiltration mixtures.

Samples	Infiltration constituent				
	Si (wt.%)	Mo (wt.%)	Ti (wt.%)	Al (wt.%)	$MoSi_2$ (wt.%)
S89M11	89	11	–	–	–
S63M23T14	63	23	14	–	–
S63M23A14	63	23	–	14	–
S63M23T7A7	63	23	7	7	–
S50MS36T14	50	–	14	–	36

2. Materials and methods

2.1. Material preparation

Pan-based carbon fibers (T700,12K) were employed as the preforms to produce porous C/C, and the pyrocarbon was used as the matrix. The preforms of the C/C composites were fabricated by stacked non-woven layers and carbon fiber webs by a needle-punching technique. Then the performs were densified by chemical vapor infiltration process with CH_4, H_2 and N_2. The final density of the porous C/C composites prepared was 1.5 g/cm^3, and the porous C/C composites were cut into several specimens with a dimension of Φ30 mm × 10 mm.Then the samples were placed in a graphite crucible together with mixed powder of different composition, respectively. Then the crucibles were heated in a high temperature furnace at 1550 °C for 6 h to finish the infiltration process. The compositions of the mixed powder were shown in Table 1, infiltrated samples are labeled according to the compositions of the infiltration mixtures. The powders were mixed by ball milling with alcohol then dried and filtered by sieves of 200 meshed before the infiltration process. During the infiltration process, the furnace was protected by argon.

2.2. Characterization

The phase composition of the samples was identified by a D/max 2550vb + 18 kW rotating target X-ray diffraction (XRD) analyzer (Rigaku ltd., Japan, Cu Ka radiation). The morphology of the samples were analyzed by a scanning electron microscopy (SEM, Fei CO., NOVA Nano230) equipped with energy dispersion spectroscopy (EDS). The phase distribution and content were investigated by electron probe microanalysis (EPMA, JEOL CO., Jxa8230).

2.3. Ablation test

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

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

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

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

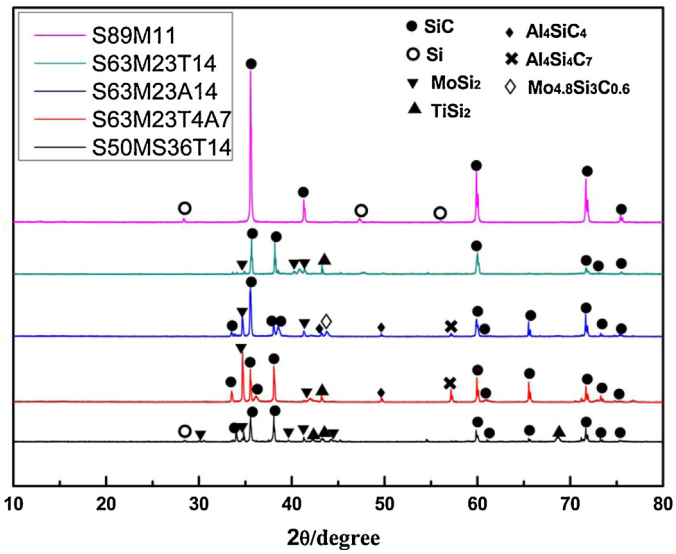

Fig. 1. XRD patterns of the infiltrated composites.

3. Results and discussion

3.1. Phase composition and Microstructure

Fig. 1 shows the XRD patterns of the infiltrated composites. Table 2 shows the phase composition and content calculated according to the XRD results. It can be seen that all the samples have diffraction peaks of SiC which comes from the reaction of Si and C during the infiltration process. Diffraction peaks of $MoSi_2$ can be observed in all of the XRD patterns except sample S89M11. It can be inferred that Mo can hardly react with Si without a third element (Ti or Al). Therefore, Mo can not form a stable ceramic phase in the composites and there are 2.7% residual Si in S89M11. When Ti is added into the infiltrants (sample S63M23T14, S63M23T7A7 and S50MS36T14), peaks of $TiSi_2$ can be found in corresponding XRD patterns. Addition of Al(sample S63M23A7 and S63M23T7A7) leads to the presence of diffraction peaks for Al_4SiC_4, $Al_4Si_4C_7$ and $Mo(SiAl)_2$ so the contents of SiC are lower. When $MoSi_2$ powder is used instead of Mo powder to be the origin of Mo element, a slight peak of Si can be observed in the patterns of the infiltrated composites, which indicates that Si can not completely react with C or Ti. Sample S63M23T7A7 has the lowest SiC content and highest $MoSi_2$ content which indicating that addition Ti and Al together can efficiently improve the reaction between Si and Mo to form $MoSi_2$.

Fig. 2 shows the surface morphology of the infiltrated composites. The observed region of sample S89M11 (Fig. 2(a)) is composed of two kinds of ceramic phases. According to the result of XRD and EDS, the gray phase (marked as 1) is SiC and the white phase (marked as 2) is Si. The dark phase of sample S63M23T14 is SiC and the white phase is the solid solutions of Mo–Si–Ti with different chemical compositions (see Fig. 2(b)). Fig. 2(c) shows the presence of three different phases in sample S63M23A14. The dark gray phase is SiC, white phase $Mo(SiAl)_2$ and light gray phase Al_4SiC_4. The phase composition of sample S63M23T7A7 (Fig. 2(d)) is the combination of sample S63M23T14's and sample S63M23A14's. The dark gray phase (marked as 1) is SiC, light gray phase(marked as 4) Al_4SiC_4, gray white phase(marked as 3) $Mo(SiAl)_2$ and pale white phase (marked as 2) solid solutions of Mo–Si–Ti. The phase composition of sample S50MS36T14 (Fig. 2(e)) is almost the same as that of sample S63M23T14 except the existence of Si. Furthermore, Si usually exists between SiC and Mo–Si–Ti solid solutions. It should be noted that when Al is added into the infiltrants the