Oxidation Behavior of SiCf/SiC Composites Modified by Layered-Y2Si2O7 in Wet Oxygen Environment

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Abstract: SiCf/SiC composites modified by layered Y2Si2O7 were presented in this research. Layered Y2Si2O7 was transformed from yttrium oxide by chemical vapor infiltration process in SiC fiber preform, in which yttrium oxide was generated by the solution impregnation and pyrolysis method. Oxidation behavior of the layered-Y2Si2O7-modified SiCf/SiC composites was studied in the wet oxygen environment at 1400 °C, showing that Y2Si2O7 can concentrate on the oxidation surface to form a protective layer during the oxidation process. The bending strengths of SiCf/SiC composites with one layer or three layers of Y2Si2O7 remain 60.38% and 71.93%, respectively, after the oxidation for 80 h. In contrast, it is only 50.11% for SiCf/SiC composites without Y2Si2O7. Therefore, layered distribution of Y2Si2O7 significantly improves the oxidation resistance of SiCf/SiC composites in wet oxygen environment.

Key words: ceramic composites; rare-earth silicate; oxidation

SiCf/SiC composites are considered as potential materials for hot-section components in advanced aircraft engine due to their outstanding properties, such as low density, superior toughness, high temperature resistance and non-brittle fracture failure[1-3]. However, because SiC reacts with water vapor and oxygen to form volatile silicon hydroxide (Si(OH)4)[4-5], the wet oxygen environment in aircraft engine leads to serious erosion or even failure for SiCf/SiC composites. Environmental barrier coatings (EBCs) were applied on SiCf/SiC composites to overcome the drawbacks as they could isolate the composites from the corrosion and avoid the reaction between SiC and wet oxygen environment[6-7].

The rare earth silicate (RE2Si2O7, RE=Y, Sc, Yb, Lu) were reported to show low volatilization rate in water vapor environment and the ability to endure temperature higher than 1482 °C for thousands of hours[8-9]. The multi-layer structure EBCs with rare earth silicate as the outermost layer has good corrosion resistance to water vapor and oxygen, which enabled them to be applied to the new generation of advanced aero-engine. Because of the coefficient of thermal expansion (CTE) mismatch[10], the peeling-off of EBCs may occur during the long-term service in aircraft engine and lead to the failure of the composites. Therefore, improving the oxidation resistance of SiC matrix to water vapor and oxygen is gradually becoming a research hotspot[11-14]. Y2Si2O7 has similar CTE with SiC (SiC: ~4.5×10^-6 K^-1, Y2Si2O7: ~4×10^-6 K^-1) and excellent chemical compatibility with SiC[15-16]. These properties motivate the investigation of Y2Si2O7 to modify the SiC matrix.

The aim of this research is to get a robust matrix with excellent corrosion resistance properties by introducing layered yttrium silicate (Y2Si2O7) in SiCf/SiC composites. In this study, yttrium oxide (Y2O3) was generated by the solution impregnation and pyrolysis method in SiC fiber preform firstly, and layered Y2Si2O7 was obtained from the transformation of Y2O3 during chemical vapor infiltration (CVI) process. It is expected that the service reliability of SiCf/SiC composites increases as long as the composites are modified by layered-Y2Si2O7.

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1 Experimental

1.1 Fabrication of the composites

2D stitched fabric of silicon carbide fibers (National University of Defense Technology, China) were used as the preforms. BN interphase was deposited by chemical vapor infiltration (CVI). Boron trichloride (BCl3) and Ammonia (NH3) (2:1, molar ratio) were carried by hydrogen (H2) to be deposited at 1073 K under a total pressure of 3.0 kPa. To prevent the erosion of BN interphase, a thin SiC layer was also prepared by isothermal CVI at 1000 ℃ under a total pressure of 5 kPa, in which methyltrichlorosilane (MTS) was used as the precursor of SiC. After the BN interphase and SiC layer were applied on the surface of the fibers, a solution made up of Y(NO3)3·6H2O (Aladdin, Shanghai, China, 99.99%) and ethanol was introduced into SiC preform by vacuum impregnation process. Then the preform was heated to 1000 ℃ for 0.5 h under argon atmosphere and the related preform was named P1. SiC matrix was then prepared under the same CVI condition as SiC layer. During the process, layered-Y2Si2O7 structure could be obtained in SiC/SiC composites. Solution impregnation pyrolysis process and isothermal CVI were repeated once or three times to obtain the dense composite C1 and C2, respectively, in which one layer or three layers of Y2Si2O7 in the matrix could be prepared. A reference sample named C0 was also prepared by the same method but without the solution impregnation pyrolysis.

1.2 Characterization

Phase composition of the samples was analyzed using a Micro-region X-ray diffraction (XRD) patterns of samples (a) C0, C1, C2 and P1 are shown in Fig. 1(a). It can be found that the matrix of sample C0 is mainly made of β-SiC, which is obtained from the pyrolysis of MTS by CVI. It is shown from sample P1 that Y2O3 can be formed in the preform after the pyrolysis of Y(NO3)3·6H2O. From the patterns of sample C1 and C2, β-SiC and Y2Si2O7 (z-Y2Si2O7: JCPDS Card 21-1459) are found. In order to understand the formation of Y2Si2O7, XRD of Y2O3 before and after CVI is carried out (Fig. 1(b)). It shows that Y2O3 can be transformed into Y2Si2O7 completely after CVI. In addition, Energy Disperse Spectroscopy (EDS) of the representative white region in sample P1 and C1 shows that the atomic ratio of Y to O changed from approximately 1:2 to 1:3.5 (Fig. 2(a-b)), and it can be inferred that Y exists in the form of Y2Si2O7 in sample C1. It demonstrates that the transformation of Y2Si2O7 from Y2O3 with CVI occurs.

2 Results and discussion

2.1 Chemical composition

Micro-region X-ray diffraction (XRD) patterns of C0, C1, C2 and P1 are shown in Fig. 1(a). It can be found that the matrix of sample C0 is mainly made of β-SiC, which is obtained from the pyrolysis of MTS by CVI. It is shown from sample P1 that Y2O3 can be formed in the preform after the pyrolysis of Y(NO3)3·6H2O. From the patterns of sample C1 and C2, β-SiC and Y2Si2O7 (z-Y2Si2O7: JCPDS Card 21-1459) are found. In order to understand the formation of Y2Si2O7, XRD of Y2O3 before and after CVI is carried out (Fig. 1(b)). It shows that Y2O3 can be transformed into Y2Si2O7 completely after CVI. In addition, Energy Disperse Spectroscopy (EDS) of the representative white region in sample P1 and C1 shows that the atomic ratio of Y to O changed from approximately 1:2 to 1:3.5 (Fig. 2(a-b)), and it can be inferred that Y exists in the form of Y2Si2O7 in sample C1. It demonstrates that the transformation of Y2Si2O7 from Y2O3 with CVI occurs.

![Fig. 1 Micro-region XRD patterns of samples (a) C0, C1, C2 and P1, and (b) Y2O3 before and after CVI](image-url)
2.2 Morphology of the samples surfaces before and after oxidation

Scanning electron microscope (SEM) images of the polished cutting surface of these composites are shown in Fig. 2. Y$_2$Si$_2$O$_7$ with layered distribution can be found around the fiber bundles before oxidation. Sample C$_1$ shows a single-layer distribution (Fig. 3(a)) while sample C$_2$ shows an obvious three-layer distribution (Fig. 3(b)). As it is not dense enough for Y$_2$O$_3$ after pyrolysis, SiC can be deposited in the enrichment area of Y$_2$Si$_2$O$_7$ due to the inner pores working as the deposition channels. Therefore, the white region is the mixing region of Y$_2$Si$_2$O$_7$ and SiC.

Fig. 4 illustrates the oxidation process. The oxidation of SiC matrix in wet oxygen consists of two parts: oxidation of SiC by O$_2$ to form silica which is a low viscosity melt in wet oxygen environment, and volatilization of the silica in the form of Si(OH)$_4$ (g) by reaction with H$_2$O. Both SiC and Y$_2$Si$_2$O$_7$ exist on the surface before oxidation, and Y$_2$Si$_2$O$_7$ remain stable in wet oxygen at high temperature. The volatilization of Si(OH)$_4$ will promote the redistribution of Y$_2$Si$_2$O$_7$ in the surface layer of silicate melt during the oxidation process. Therefore, a large amount of dispersed Y$_2$Si$_2$O$_7$ can be found on the surface of the composites after oxidation. In sample C$_2$, Y$_2$Si$_2$O$_7$ was more abundant and distributed more widely before the oxidation, so the degree of dispersion is more pronounced and the surface of Y$_2$Si$_2$O$_7$ is denser than that of sample C$_1$ after the oxidation (Fig. 3(c-f)). By contrast, for sample C$_0$, the silica glass phase precipitates into crystalline cristobalite in oxidation environment at 1400 °C. Due to the mismatch of the coefficients of thermal expansion (SiO$_2$ glass phase: $\sim 7\times 10^{-7}$ K$^{-1}$, crystalline cristobalite: $\sim 170\times 10^{-7}$ K$^{-1}$), a large number of cracks on the surface are formed during the cooling process (Fig. 3(d)), which provide a diffusion channel for oxidizing atmosphere.$^{[18]}$

2.3 Mechanical properties

The strength/oxidation time and strength retention rate/oxidation time of the composites are shown in Fig. 5. Before oxidation, the bending strength of C$_1$ and C$_2$ is (474.93±24.29) MPa and (383.61±30.29) MPa, respectively, while sample C$_0$ reaches (532.28±32.28) MPa. As the impregnation and pyrolysis times increases, the porosity of the composites increase gradually (Table 1) since Y$_2$O$_3$ can block some pores and hinder the permeation of reactive gases during the CVI process, which may lead to the difference of the mechanical properties. During the oxidation process, Y$_2$Si$_2$O$_7$ can disperse on the surface of sample C$_1$ and sample C$_2$ to prevent further diffusion of the oxidizing atmosphere. The mechanical properties of the materials after oxidation are better preserved. After 80 h of oxidation, the strength retention of sample C$_0$, C$_1$ and C$_2$ is about 50.11%, 60.38% and 71.93%, respectively.

3 Conclusion

Layered Y$_2$Si$_2$O$_7$ was prepared to modify SiC/SiC composites by solution impregnation and pyrolysis combining isothermal CVI process. The result shows that Y$_2$O$_3$ could be converted into Y$_2$Si$_2$O$_7$ by CVI. The oxidation behavior
of SiCf/SiC composites modified by layered-Y$_2$Si$_2$O$_7$ were tested in the wet oxygen environment at 1400 °C. It demonstrates that Y$_2$Si$_2$O$_7$ could form a protective layer over the sample surface and block the oxidizing atmosphere. After the oxidation for 80 h, the retention rate of bending strength of the composite with three layers of Y$_2$Si$_2$O$_7$ reaches 71.93%, which is 43.54% higher than SiCf/SiC without Y$_2$Si$_2$O$_7$. It indicates that the addition of rare earth silicate with layered structure could improve the oxidation resistance of SiCf/SiC composites in wet oxygen environment, which has beneficial effect on further application in engine components.

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层状硅酸钇改性 SiCf/SiC 复合材料湿氧化行为研究

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摘 要: 研究了层状硅酸钇的引入对 SiCf/SiC 复合材料湿氧化行为的影响。首先通过硝酸钇乙醇溶液浸渍热解法向碳化硅纤维引入 Y2O3，再采用化学气相渗透法沉积 SiC。层状 Y2Si2O7 主要通过 Y2O3 与沉积过程中的 SiC 反应转化而成。研究发现, Y2Si2O7 在 1400 ℃湿氧环境下发生富集, 在氧化层表面形成保护层, 氧化 80 h 后, 单层和多层 Y2Si2O7 改性的 SiCf/SiC 复合材料强度保留率分别达到 60.38% 和 71.93%, 而没有改性的 SiCf/SiC 复合材料强度保留率仅为 50.11%。结果表明: 层状 Y2Si2O7 的引入可显著提升 SiCf/SiC 复合材料在湿氧环境的抗氧化性能。

关 键 词: 陶瓷基复合材料; 稀土硅酸盐; 氧化

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