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Thermal fatigue behavior of C/C composites modified by SiC–$MoSi_2$–$CrSi_2$ coating

Yanhui Chu, Qiangang Fu*, Hejun Li, Kezhi Li

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

Carbon/carbon (C/C) composites were modified by SiC–$MoSi_2$–$CrSi_2$ multiphase coating by pack cementation, and their thermal fatigue behavior under thermal cycling in Ar and air environments was investigated. The modified C/C composites were characterized by scanning electron microscopy and X-ray diffraction. Results of tests show that, after 20-time thermal cycles between 1773 K and room temperature in Ar environment, the flexural strength of modified C/C samples decreased lightly and the percentage of remaining strength was 94.92%. While, after thermal cycling between 1773 K and room temperature in air for 20 times, the weight loss of modified C/C samples was 5.1%, and the flexural strength of the modified C/C samples reduced obviously and the percentage of remaining strength was only 75.22%. The fracture mode of modified C/C samples changed from a brittle behavior to a pseudo-plastic one as the service environment transformed from Ar to air. The decrease of the flexural strength during thermal cycle in air was primarily attributed to the partial oxidation of modified C/C samples.

1. Introduction

Anti-oxidation is a key requirement for carbon/carbon (C/C) composites to be used as high-temperature structural materials in an oxygen-containing environment [1–3]. To prevent C/C composites from oxidation, Si–Mo–Cr alloy has been extensively used as the coating material because a compound glass layer involving SiO_2 and Cr_2O_3 would be formed, thus effectively prevent C/C composites from oxidation due to its high resistance to both volatilization and oxygen diffusion [4,5]. In addition, provided that the coating materials could infiltrate into C/C composites deeply through the cracks or holes, the favorable inlaid structure and intensive interfacial bonding would be formed at the C/C-coating, which could further improve the oxidation resistance and mechanical properties of coated C/C composites. Low-density C/C composites have been considered as potential candidates into which could be readily infiltrated by the coating materials through the simple and low-cost techniques [6–8].

The oxidation protection ability of the coating was commonly tested at an invariable temperature [9–11]. However, the static oxidation test cannot entirely reflect the anti-oxidation ability of the coating because the ultimate application environment of C/C composites usually relates to a thermal cycle between low and high temperatures. So study on the thermal fatigue behavior of the coated C/C composites under thermal cycling is of vital importance to the application of C/C composites. Up to now, there has been considerable work focusing on the thermal fatigue behavior of the coated C/C composites under thermal cycling [12–14], whose failure mechanism is considered in the following two aspects: first one is that the partial oxidation of C/C composites resulted in the decrease of properties; second one is that the interface between carbon fiber and pyrolytic carbon was partially destroyed during quick thermal shock due to their different thermal expansion coefficients. However, in the open literatures little work has been reported on the various-degree effect of substrate oxidation and interface damage on the mechanical behavior of the coated C/C composites under thermal cycling.

In the work reported here, C/C composites were modified by SiC–$MoSi_2$–$CrSi_2$ multiphase coating by a two-step pack cementation, and the thermal cycling tests were conducted in air and Ar environments, respectively. The microstructure and the thermal fatigue behavior of the modified C/C composites were investigated.

2. Experimental

Rectangular specimens (55 mm × 10 mm × 4 mm) used as substrates were cut from bulk 2-D C/C composites with a density of 1.58×10^3 kg/m^3. These C/C composites were hand-polished using 300-grit SiC paper, cleaned ultrasonically with ethanol and dried at 373 K for 2 h. C/C samples modified by SiC–$MoSi_2$–$CrSi_2$ multiphase coating were prepared by a two-step pack cementation. The temperature for preparing modified C/C samples was 1973–2173 K. Details of preparing modified C/C samples were reported in Ref. [7].

To investigate the thermal fatigue behavior of modified C/C samples in the different environment, firstly, thermal shock experiments between 1773 K and room temperature were performed in air and Ar environment in a corundum tube furnace, respectively. At the designated time, the samples were pulled directly out of the furnace and quickly cooled to room temperature. Weights of the samples were measured by a precision balance with sensitivity of ±0.1 mg, and then the samples were put directly into the furnace again for the next oxidation period.

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* Corresponding author. Tel.: +86 29 88494197; fax: +86 29 88495764.
E-mail address: fuqiangang@nwpu.edu.cn (Q. Fu).

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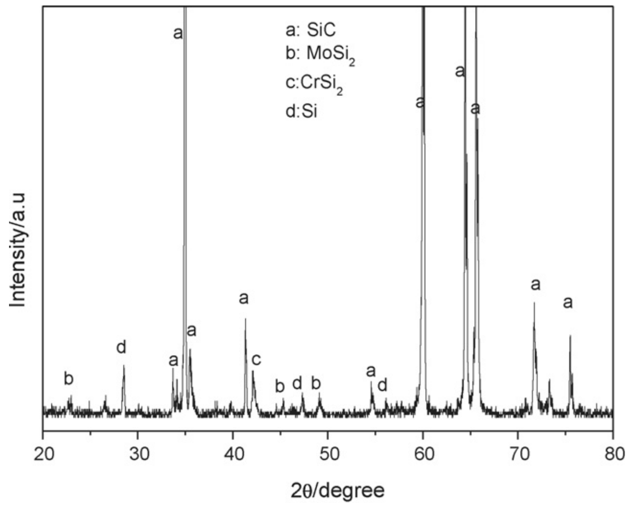

Fig. 1. XRD pattern of the surface of modified C/C samples obtained by pack cementation.

Cumulative weight changes (weight loss percentage, %) of the samples were calculated and reported as a function of thermal cycling time. Then, three-point bending tests were carried out in a servohydraulic machine of 8871 (INSTRON CO., Ltd., USA) to evaluate the mechanical properties of the samples. The span was 40 mm and the crosshead speed was 0.5 mm/min. Five samples for each kind of sample were tested and the final flexural properties were obtained by computing the average values of five samples.

The morphologies and crystalline structures of modified C/C samples were analyzed by a scanning electron microscopy (SEM, JSM-6460, JEOL Ltd., Mitaka, Japan) with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD, X′Pert PRO, PANalytical, Almelo, the Netherlands).

3. Results and discussion

XRD pattern of the surface of modified C/C samples is shown in Fig. 1, which shows that the coating is composed of SiC, Si, $MoSi_2$ and $CrSi_2$. As seen in Fig. 1, the peaks of SiC are rather strong, illustrating that the coating is primarily composed of SiC. In addition, the peaks of Si are also rather strong compared with the one of $MoSi_2$ and $CrSi_2$, inferring that a large number of Si phases are existent in the coating, which is advantageous to the compactness of the multiphase coating [15].

Fig. 2(a) displays the surface SEM image of modified C/C samples prepared by pack cementation. A dense and crack-free structure can be observed from the surface of modified C/C samples. Some small particles adhere to the surface of big particles, which is conducive to reduce the defects in the coating. Cross-section SEM image of modified C/C samples also shows the formation of a dense and defect-free structure (Fig. 2(b)). Three kinds of crystalline particles

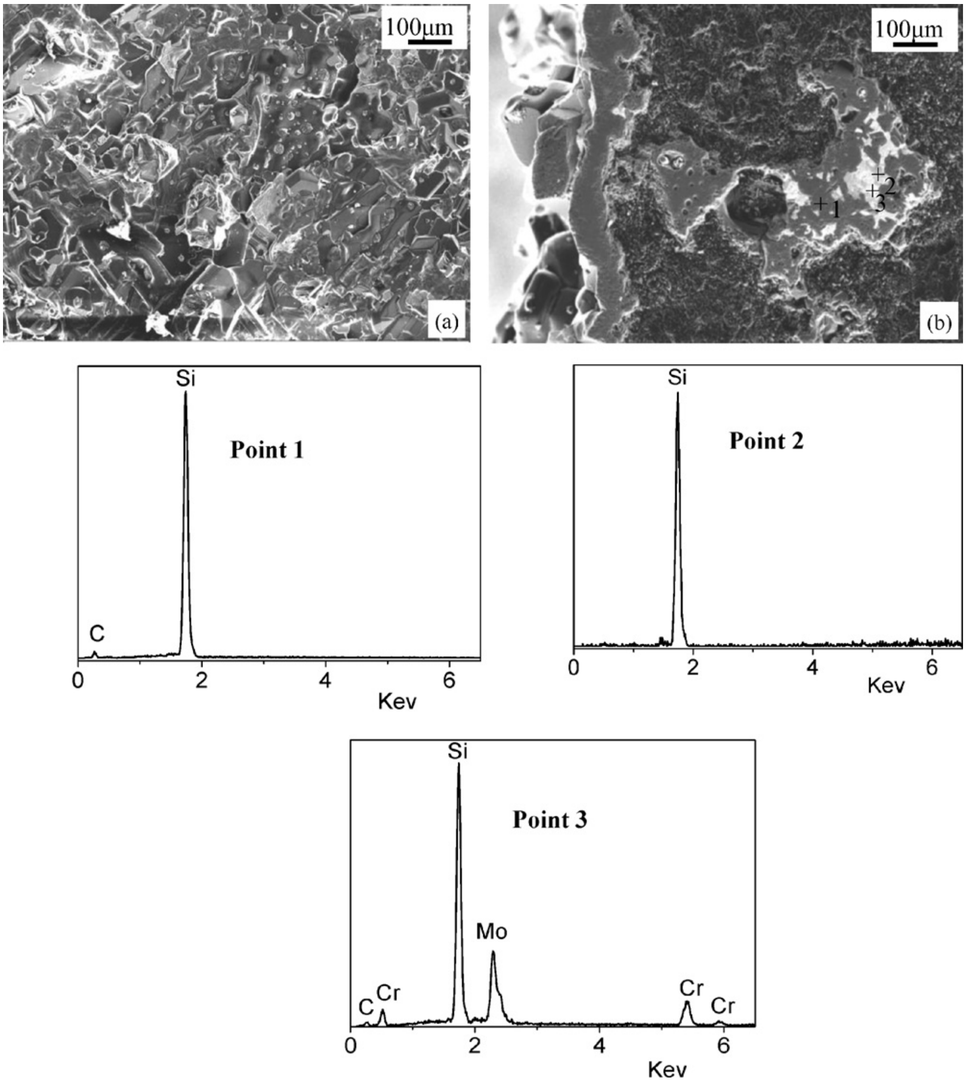

Fig. 2. SEM images of the (a) surface and (b) cross-section of modified C/C samples prepared by pack cementation, and the corresponding EDS patterns.

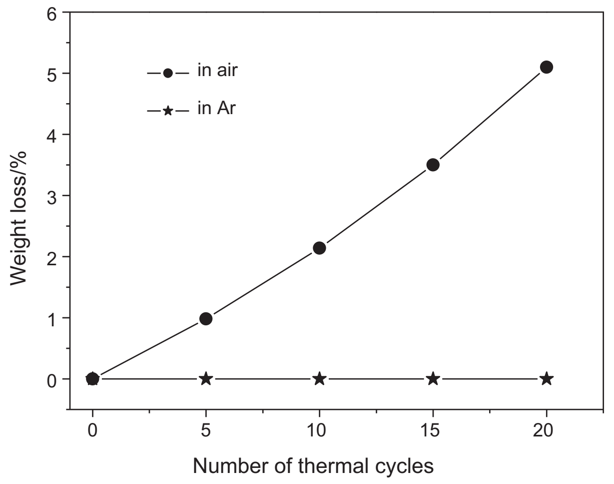

Fig. 3. Weight loss curves of modified C/C samples during thermal shock between 1773 K and room temperature.

characterized as black, grey and white are existent in the coating (Fig. 2(b)). By EDS and XRD analysis, the black, grey and white phases can be distinguished as SiC (1), Si (2), $MoSi_2$ and $CrSi_2$ (3), respectively. On one hand, during the preparation of modified C/C composites, Si in the original pack powders melted and infiltrated readily to the inside of C/C composites through holes and cracks in these composites during the heat treatment of pack cementation. Then molten Si congregated to the surface of C/C composites would react with C/C to form SiC coating, which tends to reduce the defects in C/C composites and relax the stress at the tip of cracks and heal up cracks in the coating [6]. On the other hand, holes in the porous structure of the coating were filled with some $CrSi_2$ and $MoSi_2$ grains in company with the flow of liquid Si, forming a dense and multiphase inlaid coating [15]. This inlaid structure is advantageous in avoiding the formation of through-coating cracks and improving the oxidation protective ability of the coating. Consequently, it can be obviously observed that the dense and multiphase coating deeply infiltrated into the C/C substrate through the cracks or holes, forming intensive interfacial bonding with C/C substrate and decreasing the defects in C/C composites (Fig. 2(b)).

Fig. 3 shows the weight loss curves of modified C/C samples during thermal cycling between 1773 K and room temperature. The weight loss curve of modified C/C samples after thermal cycling between 1773 K and room temperature in Ar for 20 times was almost a horizontal and straight line with values approaching zero, indicating that the modified C/C samples were not oxidized. While that of modified C/C samples after thermal cycling between 1773 K and room temperature in air for 20 times can be characterized by a sloping and straight line, by reason that the oxidation process of C/C matrix is mainly controlled by the rate of O^{2-} reaction with C/C matrix [15]. Although modification by SiC–$MoSi_2$–$CrSi_2$ multiphase coating could improve the thermal shock resistance of C/C samples, the existence of edges and corners on the surface of C/C samples would cause the stress concentration at the tip of these edges and corners due to the mismatch of thermal expansion coefficients between the coating ($\alpha_{MoSi2} = 8.1 \times 10^{-6}\,K^{-1}$, $\alpha_{CrSi2} = 10.5 \times 10^{-6}\,K^{-1}$, $\alpha_{Si} = 2.6 \times 10^{-6}\,K^{-1}$, $\alpha_{SiC} = 4.5 \times 10^{-6}\,K^{-1}$,) and C/C composites ($\alpha_{C/C} = 1.0 \times 10^{-6}\,K^{-1}$) during thermal cycling [16–18]. Finally, large numbers of defects were formed in the coating, which led to the linear increasing of the weight loss. Thus, the weight loss of modified C/C samples is up to o 5.1% after 20-time thermal cycles between 1773 K and room temperature in air.

Fig. 4(a) and (b) shows the surface SEM micrographs of modified C/C samples after thermal cycling between 1773 K and room temperature for 20 times. Some microcracks can be observed on the surface of modified C/C samples. The formation of these microcracks was caused by thermal stress during thermal cycling between 1773 K and room temperature due to the mismatch of thermal expansion coefficients between the coating and C/C composites [15]. Though some coating materials deeply infiltrated into the C/C substrate through cracks or holes eliminated the defects in C/C composites (Figs. 2(b) and 4(c)), cross-section SEM image (Fig. 4(c)) displays that, after thermal cycling in Ar for 20 times, some penetration microcracks can be formed in the coating. Moreover, some defects can also be observed at the C/C-coating interface. However,

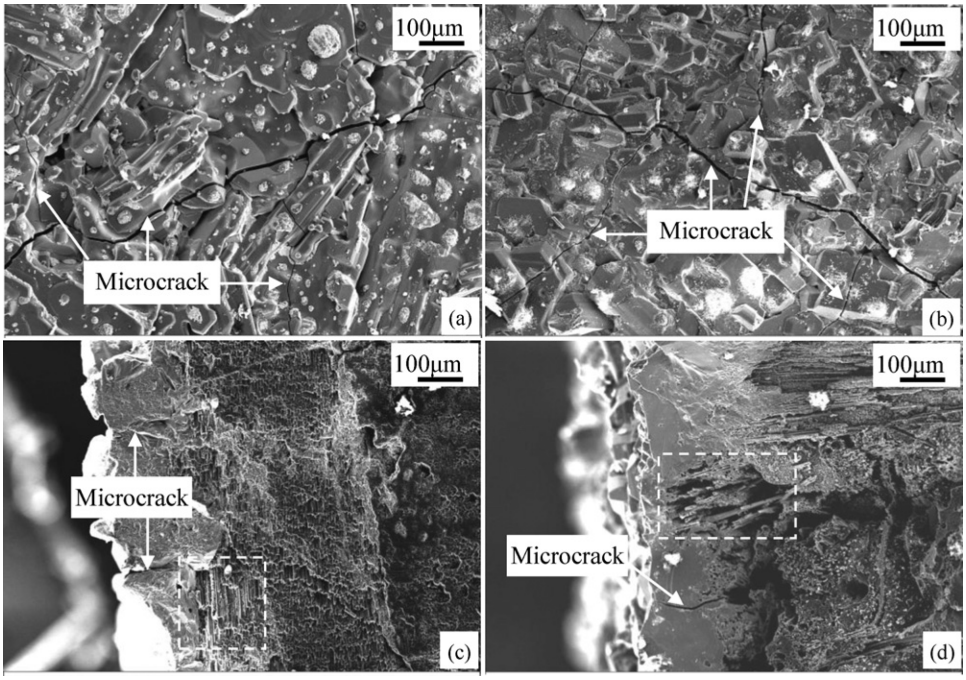

Fig. 4. SEM micrographs of modified C/C samples. (a) Surface of the samples after thermal cycling in Ar for 20 times, (b) surface of the samples after thermal cycling in air for 20 times, (c) cross-section of the samples after thermal cycling in Ar for 20 times, (d) cross-section of the samples after thermal cycling in air for 20 times.

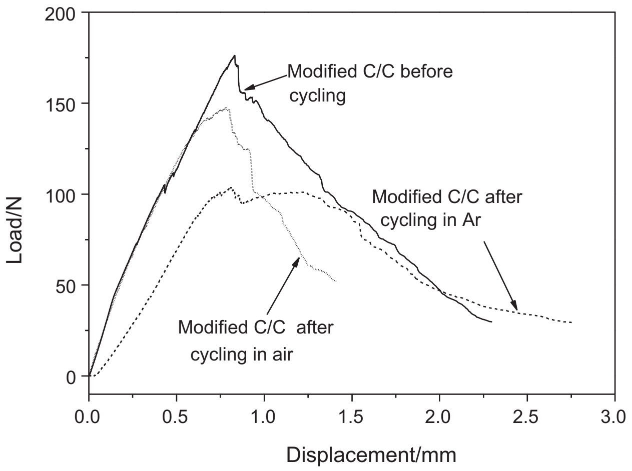

Fig. 5. The load–displacement curves of the samples after flexural tests.

no sign of obvious oxidation can be found in C/C substrate since the samples were exposed to Ar environment. Fig. 4(d) shows the cross-section of modified samples after 20-time thermal cycles in air. A penetration microcrack can be seen in the coating, which will create a free path for oxygen penetration, causing protection failure of the coating. During thermal cycling between 1773 K and room temperature in air, oxygen would diffuse into C/C substrate through the penetration crack in the coating and react with C/C substrate, causing some defects in C/C substrate and resulting in the weight loss of modified C/C samples. It can be clearly observed that C/C substrate was oxidized seriously and some big holes or voids are existent in C/C substrate. Some coating materials have also been separated from the C/C substrate. In addition, some carbon fibers also can be seen clearly, inferring that carbon substrate was oxidized primarily by oxygen diffusion through the penetration cracks. The phenomenon above indicates that penetration cracks would be formed during thermal cycling, which resulted in the partial oxidation of C/C substrate after thermal shock test in air.

Table 1
Flexural properties of the as-tested samples.

Samples	Flexural strength (MPa)	Modulus (GPa)
Modified C/C	70.84	7.07
Modified C/C after cycling in Ar	67.24	6.86
Modified C/C after cycling in air	53.29	4.47

The flexural property parameters of the samples were shown in Table 1. After thermal cycling in Ar for 20 times, the strength of modified C/C samples decreased from 70.84 to 67.24 MPa, and the corresponding modulus reduced from 7.07 to 6.84 GPa. That is, the percentages of remaining strength and modulus of modified samples after 20 times thermal cycles in Ar are 94.92% and 96.75%, respectively, indicating that thermal cycling in Ar has little effect on the flexural properties of modified C/C samples. However, after 20-time thermal cycles in air, the strength and modulus of modified samples are only 53.29 MP and 4.47 GP, respectively, and the percentages of remaining strength and modulus are only 75.22% and 63.22%, respectively. Therefore, it was inferred that the partial oxidation of the C/C samples was the major reason for the decrease of the flexural properties after 20-time thermal cycles in air.

Fig. 5 shows the load–displacement curves of the samples. It can be seen that the modified C/C samples exhibited an obvious brittle fracture mode. After 20-time thermal cycles in Ar, the modified C/C samples still exhibited a brittle fracture mode. While the modified C/C samples exhibited a bit pseudo-plastic fracture behavior and their toughness was improved evidently after 20-time thermal cycles in air.

Fig. 6 shows the fracture surface of the samples after flexural tests. From Fig. 6(a), the modified C/C samples have an even fracture surface and no obvious pull-out fibers can be found, accordant with its brittle fracture characteristic. As is well known, large numbers of defects, such as holes and cracks, are generally existent at the interface between carbon fiber and carbon matrix [6]. After being modified by the coating, these defects will be eliminated partially, as shown in Fig. 2(b), and the interface bonding between

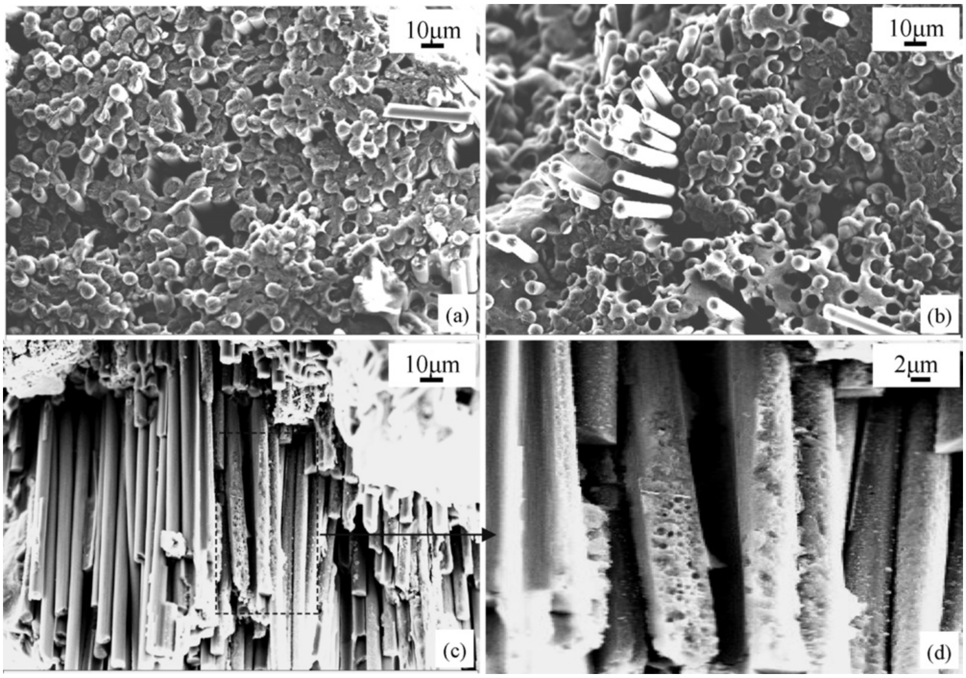

Fig. 6. Fracture surface SEM micrographs of modified C/C samples after flexural tests. (a) Before thermal cycling, (b) after thermal cycling in Ar, (c) after thermal cycling in air at low-magnification view, (d) after thermal cycling in air at high-magnification view.

fiber and matrix will be improved largely [6]. Therefore, the fracture mode of modified C/C samples exhibits a brittle one. Once modified C/C samples experienced 20-time thermal cycles in Ar, the interfaces among carbon fibers, pyrolytic carbon and coating were partially destroyed during the quick thermal shock between 1773 K and room temperature due to their different thermal expansion coefficients, which would lead to the decrease of mechanical properties of modified C/C samples. Accordingly, despite the fact that modified C/C samples had an even fracture surface, a small quantity of pull-out fibers could be found on the even fracture surface (Fig. 6(b)). After thermal cycling in air for 20 times, large numbers of defects were formed in modified C/C samples due to the oxidation of C/C substrate (Fig. 4(d)), and the interface bonding between fiber and matrix would be decreased largely. Consequently, carbon fibers pulled out from pyrolytic carbon can be seen evidently in Fig. 6(c), which is advantageous to the ductility of the samples. Moreover, some oxidation of carbon fibers can be observed obviously, as shown in Fig. 6(d), which is the primary reason for the decreasing of the flexural properties of modified C/C samples after thermal cycles in air.

4. Conclusions

C/C composites were modified by SiC–$MoSi_2$–$CrSi_2$ multiphase coating by pack cementation. The coating materials can infiltrate into C/C substrate deeply and reduce the defects in C/C composites, resulting in excellent mechanical properties and obvious brittle fracture characteristic. After the modified C/C samples experienced 20-time thermal cycles in Ar, their flexural strength and modulus were decreased lightly. While their flexural strength and modulus decreased obviously after thermal cycling in air for 20 times. The fracture mode of the modified C/C samples changed from a brittle behavior to a pseudo-plastic one as the service environment transformed from Ar to air. Partial oxidation of the modified C/C samples was the primary reason for the decrease of the flexural properties.

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