

HfB₂-SiC-MoSi₂ oxidation resistance coating fabricated through in-situ synthesis for SiC coated C/C composites

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Abstract

A brand new HfB₂-SiC-MoSi₂ coating was fabricated to protect carbon/carbon (C/C) composites with inner SiC coating from oxidation, which was prepared by in-situ synthesis. In this paper, the C/C substrate with the protection of the HfB₂-SiC-MoSi₂/SiC coating could resist oxidation in 1773 K air for 408 h. The double coating also presented expected oxidation protection performance at dynamic oxidation environment. In the test process, the surface coating was oxidized to form a self-sealing silicate glass layer containing HfO₂ and HfSiO₄, which could hinder crack propagation in coating.

Keywords: C/C composites; Oxidation; Surface analysis; Heat treatment

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1. Introduction

In the fields of aeronautics and astronautics, carbon/carbon (C/C) composites are a kind of the most promising thermal structural materials [1-4], which are noted for their outstanding mechanical properties from low temperature to very high temperature, for instance, high creep resistance, low coefficient of thermal expansion and suitable resistance to thermal shock [5-7]. Just because there are so many special characteristics, they are preferable material for aeronautical and space application, such as turbine engines, leading edges of reentry vehicles, rocket nozzle and so on [8]. But their wide applications are limited owing to the easy oxidation above 723 K in atmospheric conditions [9-10]. The multilayer protective layer is a pivotal strategy to solve the problem [11-12]. SiC coating has low thermal expansion coefficient and appropriate compatibility with C/C composites. It can also form dense and continuous SiO₂ glass layer during oxidation, so SiC is considered to be the inner coating of C/C composites. However, SiO₂ glass layer is volatile more than 1500, which can form some defects in the glass layer.

Recently, UHTCs of borides have attracted many attentions because of their high melting point, high hardness, excellent oxidation resistance performance and good chemical stability [13-15]. In addition, their oxides also present as the inlay in SiO₂ glass, which will improve the stability of the silicate glass and block oxygen into substrate [16-17]. It is helpful to decrease the generation of the cracks, and lessen the penetration of oxygen, which are all conducive to increase the anti-oxidation of the sample and then protect C/C substrate better. Therefore, introducing transition-metal borides into the SiC coatings is promising to broaden their application prospect.

Among the transition metal borides ceramic, hafnium diboride (HfB_2) [18-20] as one of promising candidates has attracted much attention in recent years, which has a series of unexceptionable performances, for instance, excellent resistance to oxidation and thermal shock. The method of in-situ synthesis is easy to fabricate the UHTCs borides at the lower temperature [21]. During the preparation process, many reactions may occur to generate the desired phases.

In this research, the Si, C, B_2O_3 , HfO_2 and Mo powders as raw materials prepared the UHTCs HfB_2 -SiC- MoSi_2 oxidation protective layer through in-situ synthesis on the surface of C/C composites with SiC coating. Furthermore, the dynamic anti-oxidation of HfB_2 -SiC- MoSi_2 coating from room temperature to 1673 K had been investigated. Meanwhile, the microstructure, oxidation protection behavior and mechanism of the samples at 1773 K also were investigated.

2. Experimental procedures

The oxidation protective coatings were applied on 2-D C/C composites substrates, which were cut into little specimens ($8 \times 8 \times 8 \text{ cm}^3$). The density of the C/C substrate was 1.70 g/cm^3 . Before applying the coatings, the specimen was polished first and then ultrasonically cleaned. The coating contained SiC layer and HfB_2 -SiC- MoSi_2 layer was applied on the C/C substrate. The pack cementation technique with Graphite (20-40 wt.%) and Si (60-80 wt.%) as raw materials were used for fabricating the inner SiC coating [21]. While the raw materials of B_2O_3 (10-25 wt.%), graphite (3-15 wt.%), HfO_2 (25-40 wt.%), Mo (5-10 wt.%) and Si (40-60 wt.%) powders could fabricate the outer HfB_2 (30 wt.%) - SiC (58 wt.%) - MoSi_2 (12 wt.%) coating through in-

situ synthesis. All the specimens and raw powders were placed in the graphite crucible with a heat treatment of heating up 5-10 K/min, then thermal insulation for 2 hours at 2373 K in normal argon atmosphere.

The isothermal oxidation test and thermo gravimetric analysis (TGA) test was used for researching the oxidation resistance of the samples. An isothermal oxidation test was implemented in 1773 K air and the samples were placed in an oxidation furnace. The samples were weighed by an analytical balance whose sensitivity is ± 0.1 mg. The samples were taken out of the oxidation furnace at set intervals during oxidation. As time went on, the accumulated weight alterations rates were calculated. The TGA test with the heating rate of 10 K/min measured the dynamic oxidation resistance of the specimens whose weight alterations were recorded by thermogravimetry mode in air atmosphere from room temperature to 1673 K. The crystalline structure, microstructures and elemental distribution could be analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively. And the time taken of each point for EDS data collection was 60 s.

3. Experimental results and discussion

3.1 Microstructure of the coatings

An illustration diagram of the preparation process of outer HfB₂-SiC-MoSi₂ layer is shown in Fig.1 and it can be divided into four steps. At first, according to a certain proportion, the raw materials of Si, C, HfO₂, B₂O₃ and Mo powders were used for packing the C/C with inner SiC coating, thereby making the samples surrounded by these powders in all directions. Then, during the heat-treatment of the samples at 2373 K, carbothermal reduction reaction as well as the solid reaction would occur among the raw materials, which would form the HfB₂, SiC and

MoSi₂ particles. Next, during the process of the in-situ reaction, due to the low melting point of silicon, molten silicon was formed, which would be helpful to form the outer HfB₂-SiC-MoSi₂ coating. In addition, owing to the fluidity of the silicon melt, the formed coating materials were carried to penetrate into the inner coating, thus strengthening the bonding between inner and outer coating. Finally, the HfB₂-SiC -MoSi₂/SiC double coating was prepared on C/C substrates.

The XRD pattern of HfB₂-SiC-MoSi₂ coating is shown in Fig.2. The HfB₂-SiC-MoSi₂ coating comprises HfB₂, β-SiC, α-SiC and MoSi₂ phases, they are all the desired products. The HfB₂ phase is obtained by the in-situ carbothermal reduction reaction to reduce HfO₂ using B₂O₃ and graphite. The SiC phase is made by Si and C powders, while the MoSi₂ phase is made by Si and Mo powders with the solid reaction. All phases are acquired in the process of heat-treatment, which proves the superiority of this method. The reactions can be drawn as follows:



The backscatter micrographs of the HfB₂-SiC-MoSi₂ coating are shown in Fig.3. As shown in Fig.3 (a), the outer coating is dense with a lot of white and grey particles distributed on its surface. Fig.3 (b) shows a higher magnification than Fig.3 (a), from which the coating includes of three kinds of grains (white, black and grey phases). Through XRD and spot analyses of EDS (Fig.3 (c)), the different grains are confirmed as HfB₂ (white phase), SiC (black phase)

and MoSi₂ (grey phase). The SiC grains bond closely and few gaps can be seen among them.

In addition, the HfB₂ and MoSi₂ grains mainly exist in the interspaces among SiC grains, which indicates that the outer coating is formed by the combination of the three kinds of grains. The close bonding among the grains is conducive to establish a barrier to effectively hinder the penetration of oxygen, thus decreasing the possibility of oxidation occurred at the C/C substrate.

In Fig.4 (a), the cross-section backscatter micrograph of the HfB₂-SiC-MoSi₂/SiC coated C/C is analyzed. The double layer coating has a thickness about 200-310μm, and no penetrating crack or obvious hole appears. In addition, some coating materials actually penetrate into substrate through the defects, and the bonding strength of the matrix and coating is enhanced. The high magnification of Fig.4 (a) is shown in Fig.4 (b). No distinct interface of double coating can be observed, which shows a close combination between two coatings. Furthermore, some white HfB₂ particles can be found in the inner coating owing to the penetration of the outer coating materials during preparing outer coating. Therefore, the penetration of outer coating materials into the inner coating will contribute to pad the defects of the inner coating and build a strong combination between the double coatings. As shown in Fig.4 (c), the inner SiC coating combines closely with C/C substrate and no distinct gap was observed between them. Owing to the penetration of the coating materials into the voids of substrate, some carbon fibers were wrapped as Fig.4 (d). Through spot EDS analyses (Fig.4 (e)), the materials can be confirmed as SiC. Fig.4 (f) presents the line analyses of HfB₂-SiC-MoSi₂ coating. Four elements are detected which present different trends, and the curves can be divided into two parts. The Si element is widespread in the inner and outer coating and most of the C element exists in the inner part, the Hf and Mo element is mainly present in 130-330 μm. In summary, the coating

presents HfB₂-SiC-MoSi₂/SiC double layer structure, and it is coincident with our prospective coating.

3.2 The 1773 K isothermal oxidation test of HfB₂-SiC-MoSi₂/SiC coating

The 1773 K isothermal oxidation test in air was carried out to survey the oxidation resistance of the HfB₂-SiC-MoSi₂/SiC coated C/C composites as shown in Fig.5. The oxidation curve of C/C with SiC coating exhibits a rapid increase trend. The weight loss of the samples reaches to 4.15 % after testing 54 h, which presents a finite oxidation resistance. While after applying the outer HfB₂-SiC-MoSi₂ coating, the weight loss rate of the samples drops to 0.76 % after testing 408 h, which indicates that the oxidation resistance of the coating is further improved. Furthermore, The C/SiC/MoSi₂-Si coatings prepared by Zhang et al. [23] can protect C/C for 300 h under the same conditions with weight loss 1.4 %. It proves the introduction of HfB₂ phase to effectively increase the oxidation resistance of silicon-based ceramic coating.

XRD pattern of C/C with HfB₂-SiC-MoSi₂/SiC coating after oxidation 408 h is shown in Fig.6.

After a period of time of oxidation, many oxidation products are generated. Strong SiO₂ peaks are detected in XRD, which means the generation of the silicate glass. Because of the self-sealing performance, the formed silicate glass can fill some flaws of coating and protect C/C substrate. HfO₂ peaks appear, which is the solid oxidation product of HfB₂. HfO₂ is a stable transition metal oxide, whose presence will improve the glass layer stability and viscosity. Except SiO₂ and HfO₂ peaks, HfSiO₄ peak can also be found, which is generated due to the

reaction of SiO_2 and HfO_2 . HfSiO_4 phase is thermal stable with a high melting point (>2900), whose formation will enhance the oxidation protection of the glass layer effectively.

According to Fig.7 (a), the surface backscatter micrograph of $\text{HfB}_2\text{-SiC-MoSi}_2/\text{SiC}$ coated C/C after oxidation 408 h at 1773 K is shown. During experiment, the specimens were removed at set intervals, which would generate great temperature difference, and create micro-cracks. Although an intact silicate glass layer over the coating, some micro-cracks can still form owing to the thermal expansion coefficients difference with coating, it can provide a way for oxygen into substrate, so increasing the likelihood of oxidation occurred at inner. And a small amount of bubbles exist in the glass layer. In addition, a mass of white grains consist in the silicate glass layer. The magnification of the white particles is shown in Fig.7 (b). Parts of the white particles are in fact embedded in the black glass layer. By EDS analyse (shown in Fig.7 (d)), the black layer is confirmed as SiO_2 glass, and the white particles are composed of HfO_2 and HfSiO_4 . Since the SiO_2 glass possesses fluidity at high temperature and the HfSiO_4 phase is formed owing to the reaction between the SiO_2 and HfO_2 , the HfO_2 and HfSiO_4 grains are embedded in the silicate glass through a close chemical bonding, which presents as immiscible phases in SiO_2 glass and increases its viscosity. As shown in Fig.7 (c), crack deflecting or termination appears in the surrounding of the white grains, it might be caused by the “pinning effect” played by HfO_2 and HfSiO_4 grains, thus beneficial to expending the cracks energy, and effectively promoting the oxidation resistance of samples.

Fig.8 shows the cross-section backscatter micrograph of $\text{HfB}_2\text{-SiC-MoSi}_2/\text{SiC}$ coating after testing for 408 h. In Fig.8 (a), no penetration crack can be observed in the section, which proves

its good oxidation resistance. Fig.8 (b) presents the magnification of Fig.8 (a) after oxidation. Although some holes are existed because of the coating being oxidized, a large part of the coating is still very dense. Besides, plentiful white grains can still be found on the surface. Through EDS analysis (Fig.8 (f)), the white particles in the outer part of the coating can be recognized as the solid oxidation products of HfSiO_4 , while the white particles in the inner part of the coating are the un-reacted HfB_2 . Therefore, the external of the coating is oxidized primarily. The magnification of the outer part of the coating is shown in Fig.8 (c). The outer part of the coating consists of two zones. One zone is the loose and porous region, caused from oxidation. Another near the substrate is the fine and close region, thus shows an un-reacted zone. Fig.8 (d) shows the magnification of Fig.8 (a) part B. Part of the carbon fibers wrapped by coating materials can be found from it. Through EDS analyses (Fig.8 (f)), O element is detected in the SiC coating materials, which manifests SiC being oxidized due to the penetration of oxygen. However, owing to the protection of SiC, the wrapped carbon fibers are not oxidized. In Fig.8 (e), due to the oxidation of carbon, many holes exist in the substrate. According to the different oxidation levels, the substrate is divided into two oxidation zones, one zone is higher oxidation zone, and another is lower oxidation zone. In the former, the substrate is very dense, mainly composed of carbon fibers and pyrolytic carbon, therefore, more voids can be observed due to the fast oxidation of carbon. While in the lower oxidation zone, many coating materials appears in the substrate because of the penetration of them during preparing the inner SiC coating, which can be good for protecting the C/C substrate, therefore, fewer voids are formed.

3.3 Dynamic oxidation test of $\text{HfB}_2\text{-SiC-MoSi}_2$ coating

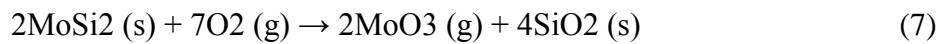
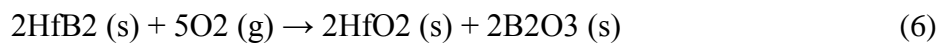
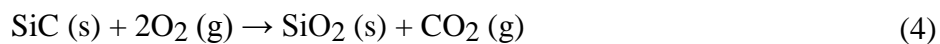
The Dynamic oxidation test of the $\text{HfB}_2\text{-SiC-MoSi}_2/\text{SiC}$ coated C/C is investigated in a wide temperature range from room temperature to 1673 K with the heating rate of 10 K/min as shown

in Fig.9. After the TGA experiment, the weight losses rates of the C/C substrates coated with single coating and double coating are 19.65 % and 10.29 %, respectively. The coated samples in the oxidation process of a wide temperature range can be divided into three stages as shown in Fig.9 (a): A stage (room temperature-800K), B stage (800 K-1400 K) and C stage (1400 K-1673 K). At A stage, neither of two kinds of samples loses weight, but shows a slight weight gain phenomenon. The high magnification of B stage is shown in Fig.9 (b). The single SiC coating displays weak oxidation resistance above 800 K, but with the modification of HfB₂ and MoSi₂ phases, whose oxidation protection is observably promoted, it reveals the remarkable oxidation resistance of HfB₂ in a wide temperature range. In general, silica-based coating can form fluid SiO₂ glass at temperature above 1400 K, thus it has the expected oxidation protective effect in this temperature range, but the SiO₂ glass layer cannot protect substrates effectively from 800 K to 1473 K, which causes large weight loss. Owing to the oxidation of HfB₂ phase, B₂O₃ is a crucial oxidation product in the range from 800K to 1400 K, which can heal some defects in the coating and provide effective oxidation protection before the generation of the SiO₂ glass. The high magnification of C stage is shown in Fig.9 (c). When the temperature reaches the oxidation protection range of silicon-based ceramic, the vast defects have existed in the coating and substrate, thus the SiC coated sample continues losing weight. However, the TGA curve of HfB₂-SiC-MoSi₂/SiC coated C/C flattens out gradually owing to the formation of Hf-Si-O glass. In addition, the existence of MoSi₂ phase is conducive to form denser SiO₂ glass layer and reduce the consumption of SiO₂ glass [22], which can preferably inhibit the

entrance and spread of oxygen. Therefore, with the coexistence of HfB₂ and MoSi₂ phases, the samples present anticipant oxidation resistance in the TGA test.

3.4 Anti-oxidation mechanism of the HfB₂-SiC-MoSi₂/SiC coating

In order to analysis of oxidation mechanism, a schematic diagram of the HfB₂-SiC-MoSi₂/SiC coated C/C is shown as Fig.10. Before oxidation, the double coatings including SiC and HfB₂-SiC-MoSi₂ coating are applied on C/C specimens to prevent oxidation (Fig.10 (a)). The C/C substrates covers with coatings are exposed to the oxygen atmosphere at 1773 K. Under the attack of the oxygen, the coating materials can react with oxygen firstly, basing on the reactions (4)-(11).



As shown in Fig.10 (b), at the initial period of oxidation, although many kinds of solid products generate, such as SiO₂, B₂O₃ and HfO₂, they can't form a complete protective layer to block oxygen into the coating. In addition, some gas byproducts are also generated, which will be released from the sample and result in the weight loss. The SiC inner coating is oxidized to produce SiO gas (reaction (9)), which can consume the SiO₂ protective layer, and cannot be removed quickly enough by the bubble migration. Moreover, it will prompt that the SiO₂ glass generates bubbles and defects, which cannot completely self-cure. The oxidation of MoSi₂

phase can produce more SiO_2 , which means the formation of more dense of SiO_2 glass layer offering the expected self-cure ability. Accompanied by the longer test time, more SiO_2 glass are generated due to the oxidation of SiC and MoSi_2 , thus rapidly forming a continuous silicate glass layer, which can cover the defects and block the diffusion path of oxygen [23-24]. Owing to the fluidity of the SiO_2 glass layer, the formed HfO_2 particles are embedded in the silicate glass, thereby presenting as immiscible phases in it and increasing its viscosity and stability. Based on reaction (8), HfSiO_4 particles are formed by the reaction of SiO_2 and HfO_2 (Fig.10 (c)), which will serve as the reinforcing phase with HfO_2 in the silicate glass layer. In Fig.10 (d), because the volume change of coating and glass layer is different under unit temperature variation, some micro-cracks are formed [25-26]. However, because of the “pinning effect” of HfO_2 and HfSiO_4 particles in the silicate glass layer, the formed microcracks are forced to deflect and terminate, which decreases the size of cracks and effectively increase the oxidation protection of glass layer [27-28]. After a long time oxidation (Fig.10 (e)), some oxygen penetrates matrix and C/C is oxidized, accordingly some voids are formed. Moreover, some carbon fibers wrapped by the penetrated coating materials are protected from the oxidation. However, although a fraction of substrate is oxidized, the weight loss of the sample is only 0.76% after oxidation 408 h at 1773 K in air and 10.29% after TGA test, which shows its remarkable oxidation protection ability.

4. Conclusions

The in-situ synthesis was used for fabricating outer $\text{HfB}_2\text{-SiC-MoSi}_2$ coating to apply on C/C with inner SiC coating. The double layer coating with the thickness about 200-310 μm could

protect C/C composites 408 h at 1773 K with 0.76 % weight loss. The dense and continuous silicate glass layer concluding HfO₂ and HfSiO₄ particles was formed during the oxidation. The HfO₂ and HfSiO₄ particles were inlaid in SiO₂ glass, they could enhance its stability and viscosity and decrease the flaw size. By the end of oxidation test, the oxidation of the coating primarily occurred in coating external, and C/C was intact protected.

Acknowledgements

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Figure captions

Fig.1 Illustration diagram of the preparation of the outer $\text{HfB}_2\text{-SiC-MoSi}_2$ coating;

Fig.2 XRD pattern of the outer $\text{HfB}_2\text{-SiC-MoSi}_2$ coating;

Fig.3 (a) Low magnification and (b) high magnification backscatter micrographs of the $\text{HfB}_2\text{-SiC-MoSi}_2$ coating; (c) spot EDS analyses of (b);

Fig.4 (a) Low and (b) high magnification cross-section backscatter micrographs of the coated C/C composites; (c) high magnification backscatter micrograph of the interface between C/C composites and the inner SiC layer; (d) magnification of part A in Fig.4 (a); (e) spot EDS analyses of Fig.4 (d); (f) EDS element line analyses of the coating;

Fig.5 Isothermal oxidation of the coated C/C composites in air at 1773 K;

Fig.6 XRD pattern of the double layer coated C/C composites after oxidation at 1773 K in air for 408 h;

Fig.7 (a) Surface backscatter micrograph of the double layer coated C/C composites after oxidation at 1773 K in air for 408 h; (b) magnification of part A in Fig.7 (a); (c) magnification of part B in Fig.7 (a); (d) spot EDS analyses of (b);

Fig.8 (a) Low and (b) high magnification cross-section backscatter micrograph of the coated C/C composites after oxidation; (c) magnification of part A in Fig.8 (b); (d) magnification of part B in Fig.8 (a); (e) magnification of part C in Fig.8 (a); (f) spot EDS analyses of Fig.8 (b) and (d);

Fig.9 TGA curves of coated C/C composites from room temperature to 1673 K;

Fig.10 Oxidation protection schematic diagram of the $\text{HfB}_2\text{-SiC-MoSi}_2/\text{SiC}$ coating for C/C composites.

Figures

Fig.1

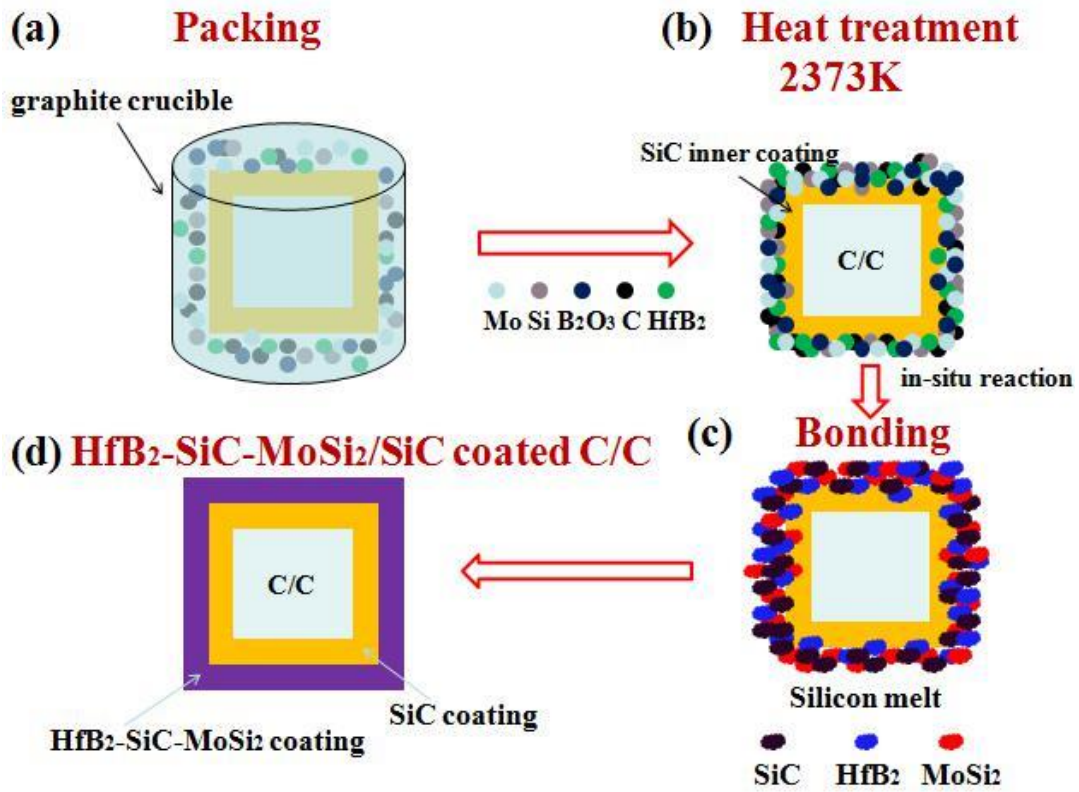


Fig.2

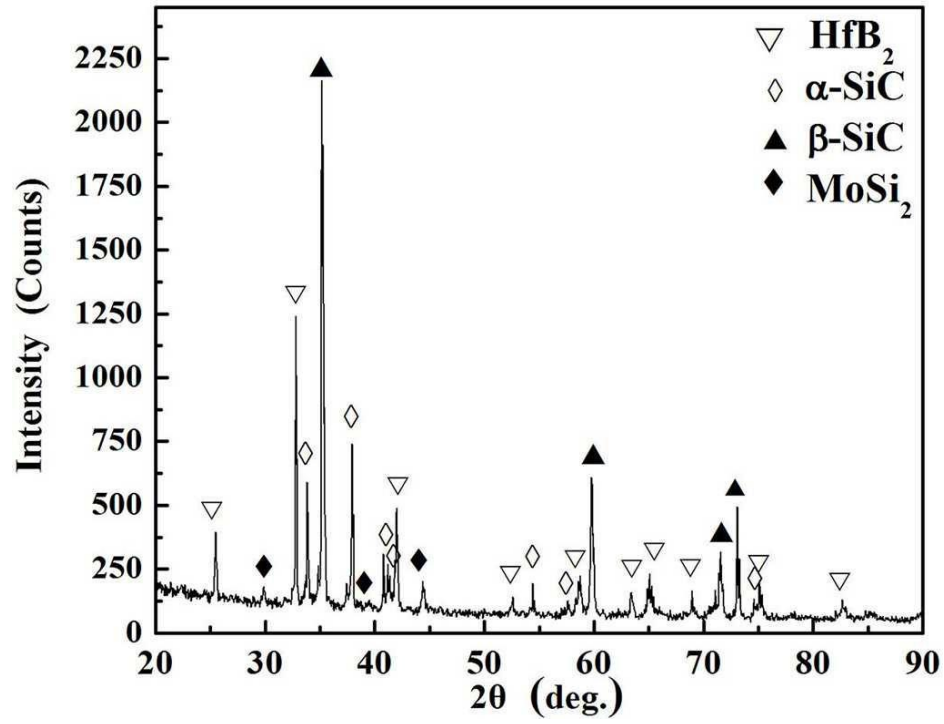


Fig.3

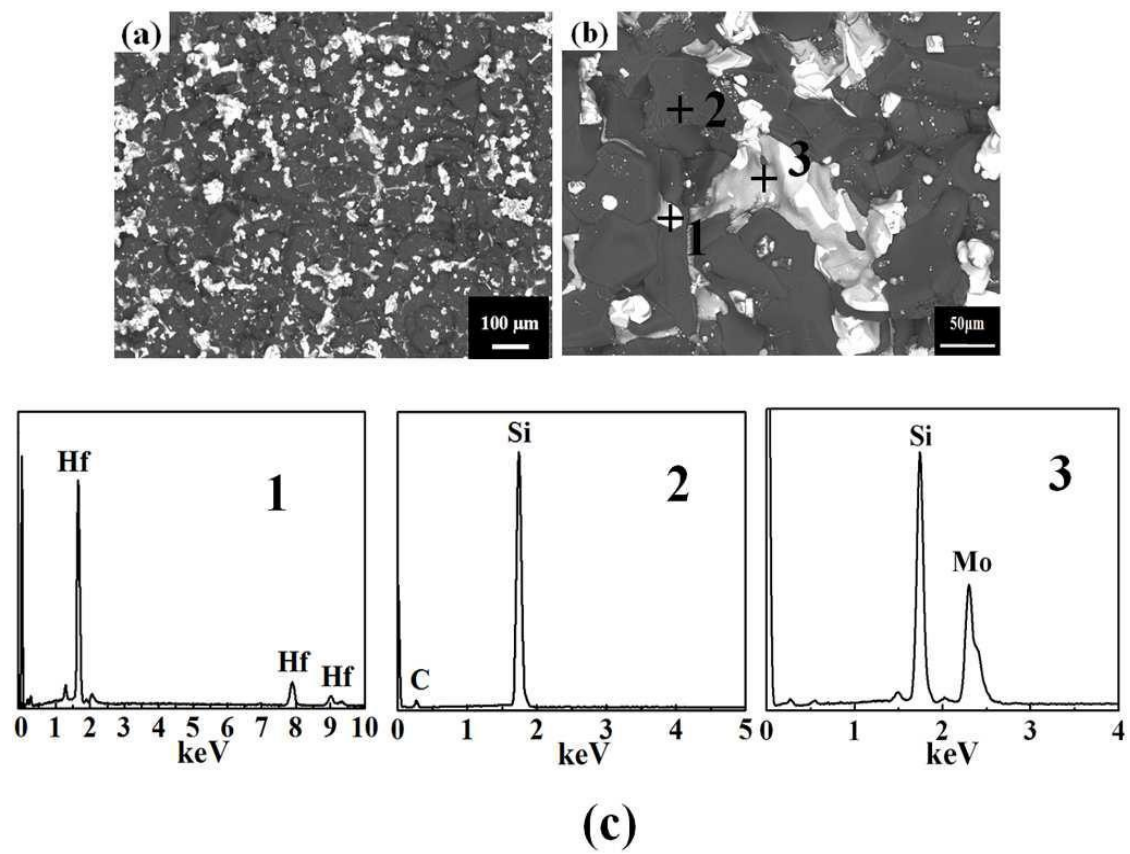


Fig.4

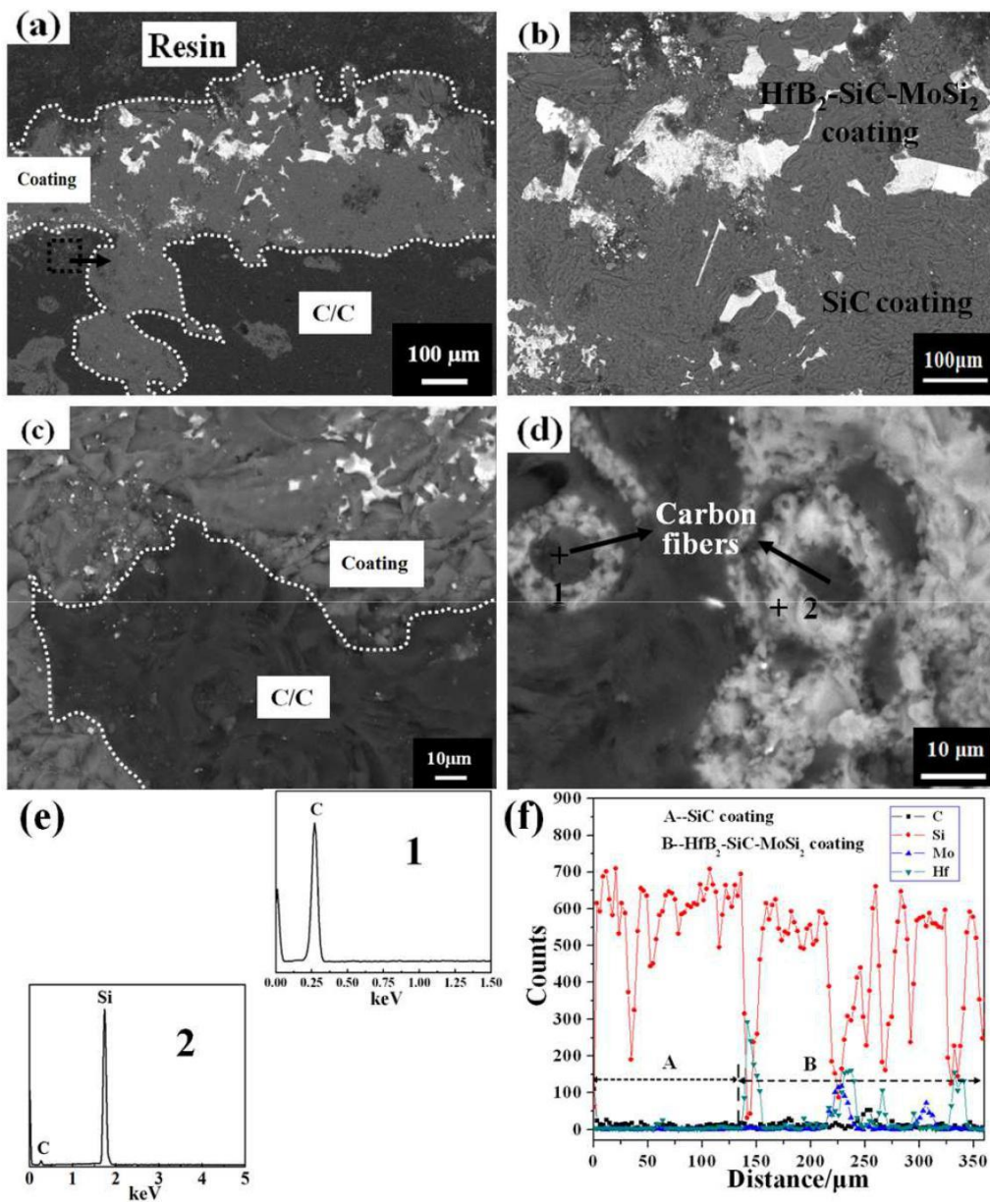


Fig. 5

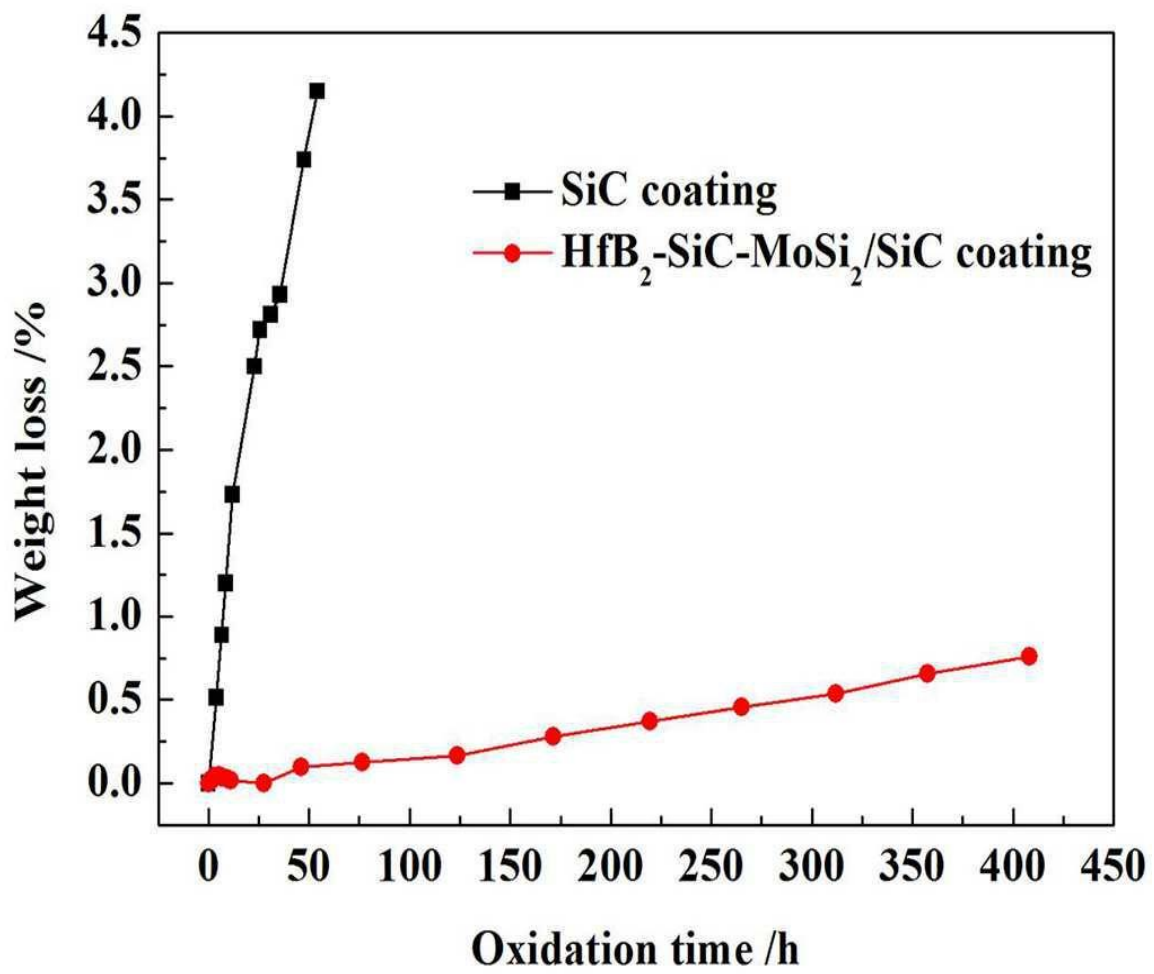


Fig. 6

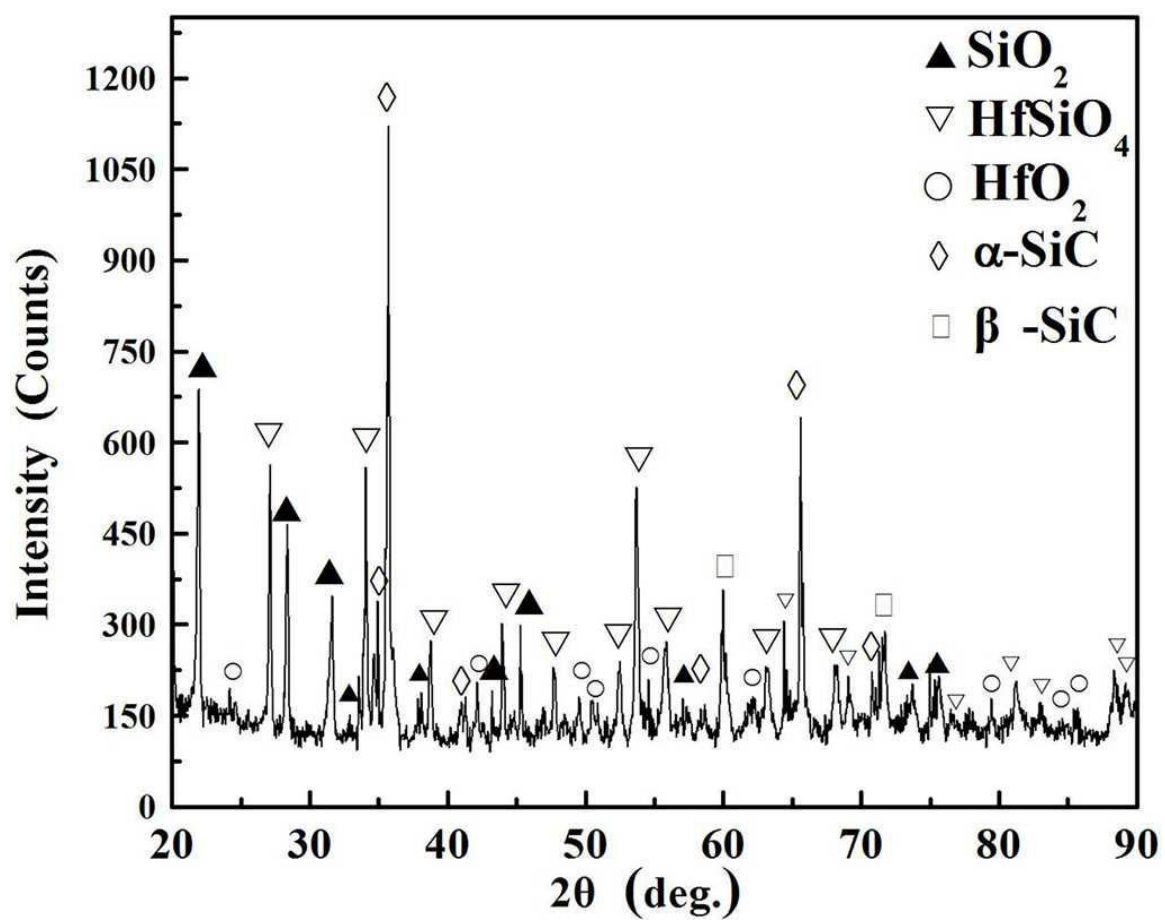


Fig.7

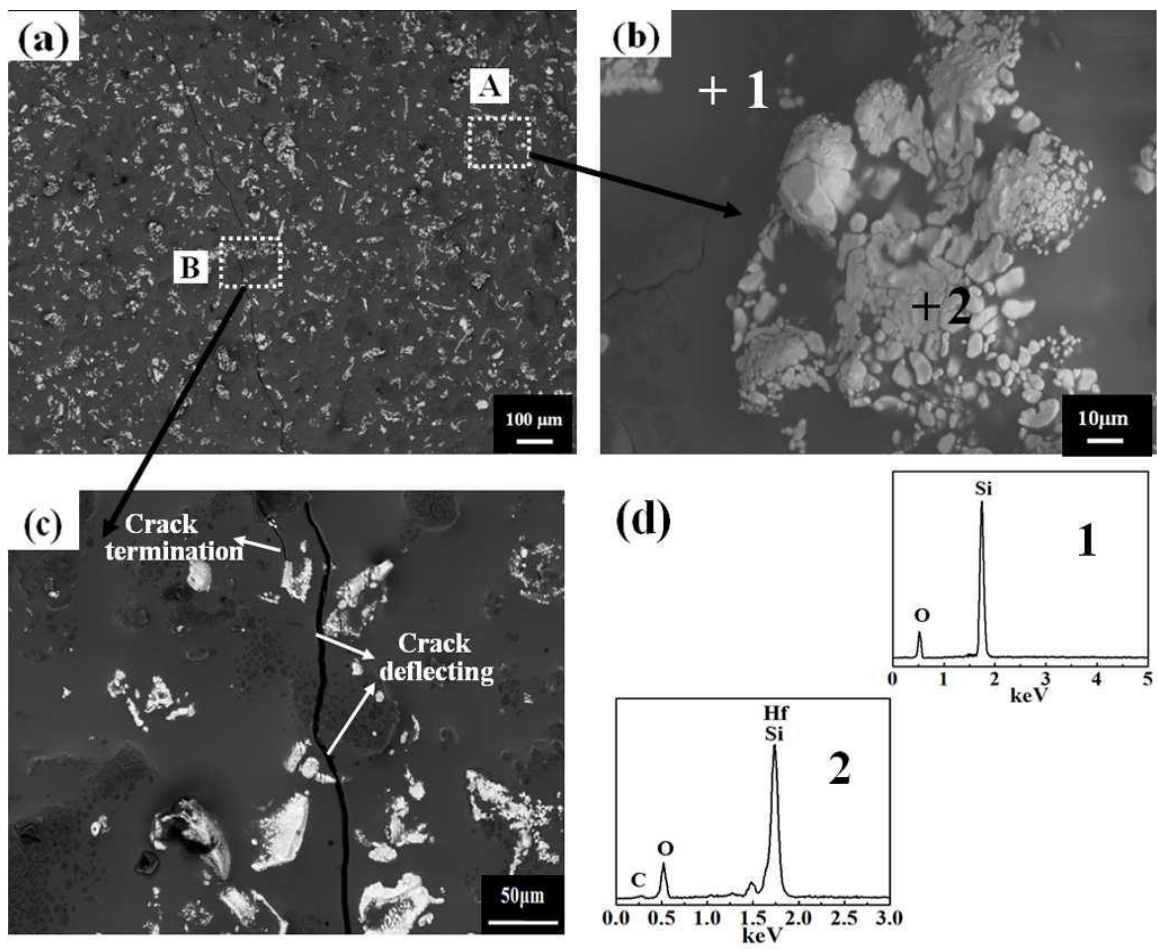


Fig.8

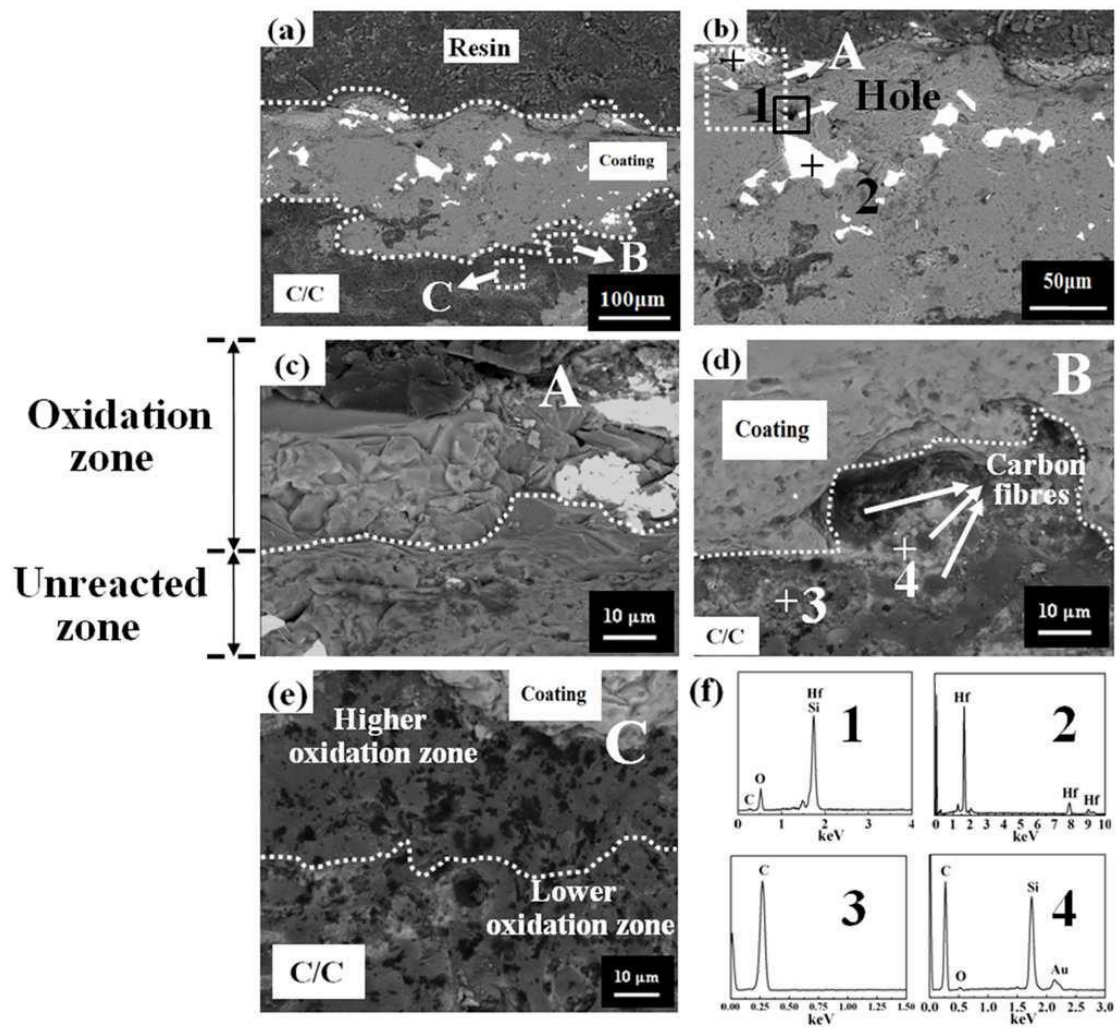


Fig.9

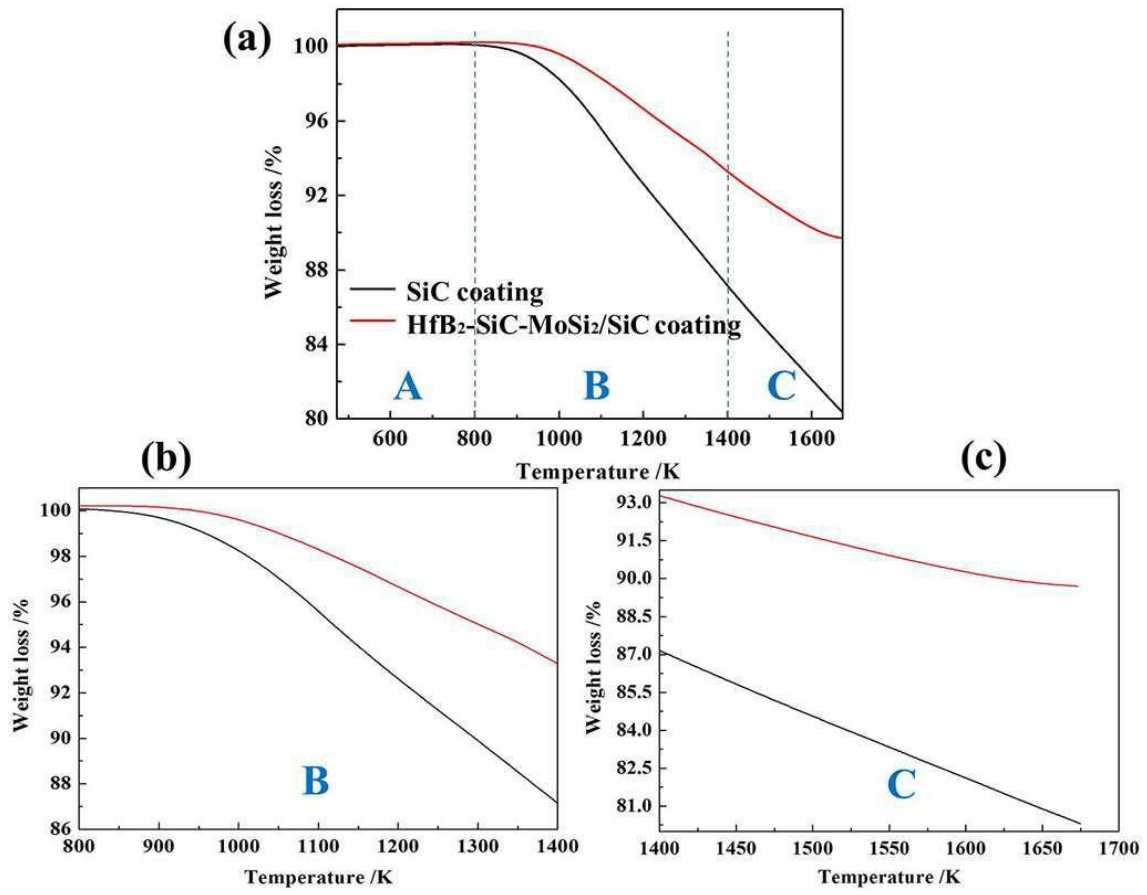
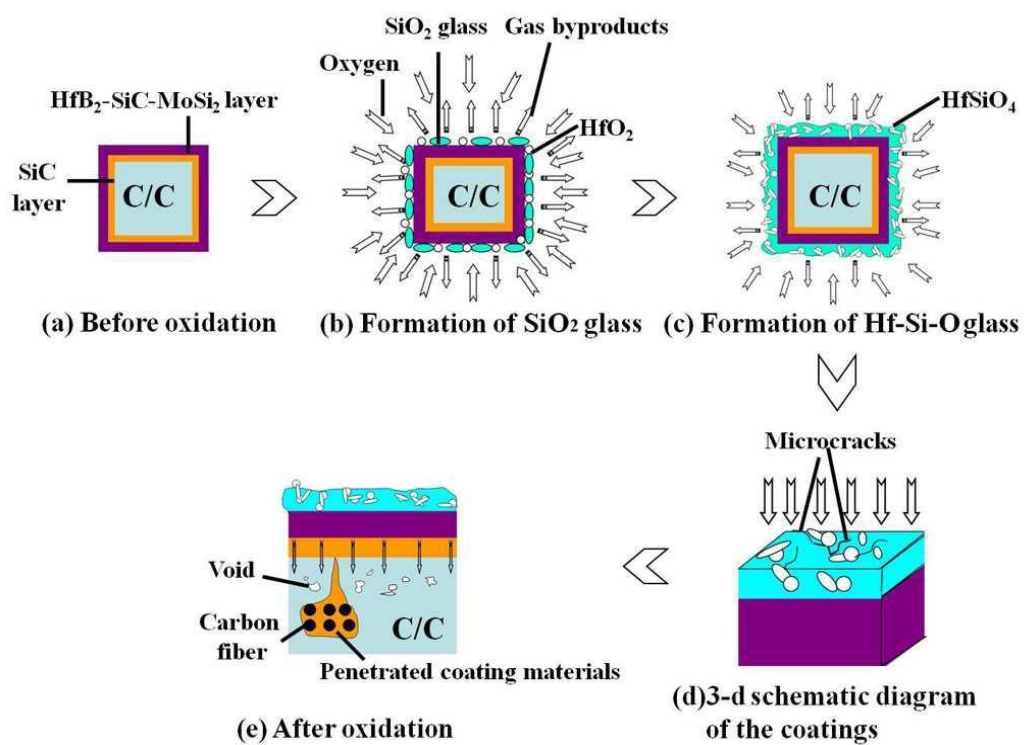


Fig.10



Highlights

1. The UHTCs HfB₂-SiC-MoSi₂ coating was fabricated through in-situ synthesis.
2. The coating could protect C/C for 408 h with only 0.76% mass loss in 1773K air.
3. The SiO₂ glass layer offered the expected self-cure ability.
4. The Hf-Si-O glass layer was responsible for the good oxidation resistance.