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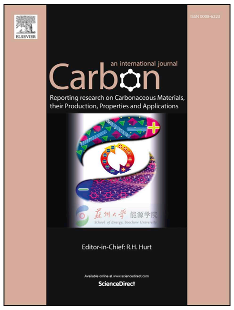

Effect of carbon fiber crystallite size on the formation of hafnium carbide coating and the mechanism of the reaction of hafnium with carbon fibers

Hui Zhu, Xuanke Li, Zhijun Dong, Guozhi Ma, Fei Han, Ye Cong, Guanming Yuan, Zhengwei Cui, Aidan Westwood

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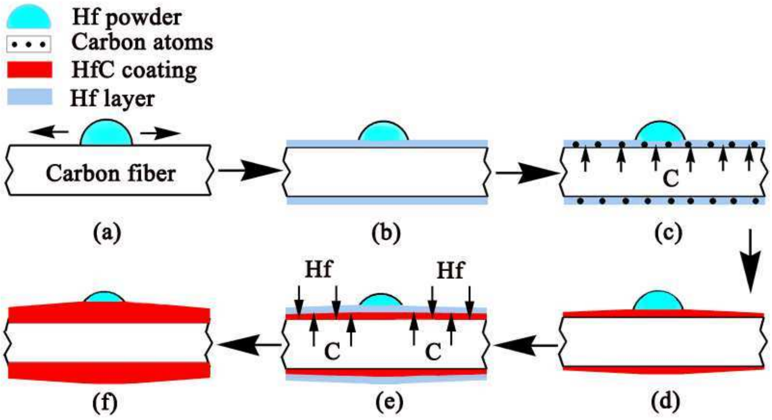
Graphical abstract

The effect of carbon source crystallite size on the formation of hafnium carbide (HfC) coating was investigated via direct reaction of hafnium powders with mesophase pitch-based carbon fibers (CFs) heat-treated at various temperatures. The carbide synthesis temperature and the sizes of crystallites in the CFs have a remarkable influence on the integrity and thickness of the coatings. The effect of carbon fiber crystallite size on the formation of carbide coating was systematically investigated and the mechanism of the reaction of hafnium with carbon fibers involved in the processes of surface diffusion and bi-directional diffusion was also confirmed.



Effect of carbon fiber crystallite size on the formation of hafnium carbide coating and the mechanism of the reaction of hafnium with carbon fibers

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Abstract

The effect of carbon source crystallite size on the formation of hafnium carbide (HfC) coating was investigated via direct reaction of hafnium powders with mesophase pitch-based carbon fibers (CFs) heat-treated at various temperatures. X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy analyses reveal that uniform and dense HfC coatings are preferentially formed on CFs containing larger and more ordered graphite crystallites. The carbide synthesis temperature and the sizes of crystallites in the CFs have a remarkable influence on the integrity and thickness of the coatings. The formation the HfC coatings can be attributed to the surface diffusion of hafnium and the bi-directional diffusion of hafnium and carbon sources inside the HfC coating. The reaction of HfC coated carbon fibers with zirconium powders leads to the growth of ZrC on the HfC coating and this has been shown to occur by the diffusion of carbon from the carbon fiber core through the carbide coating to its surface.

1. Introduction

Ultra-high-temperature-ceramics (UHTCs) offer the highest potential as thermal protection materials for high-temperature structural applications in oxidizing environments and they have been widely investigated in the past decades [1,2]. In particular, HfC, which possesses one of the highest melting points (3890 °C), excellent phase stability, as well as good thermomechanical and thermochemical properties, is therefore the most attractive candidate for application as a thermal protection barrier, withstanding high temperatures exceeding 2000 °C in severely oxidizing atmospheres [3-5]. HfC is often introduced into C/C composites to enhance oxidation and ablation performance, which can efficiently prolong the lifetime of C/C composites in severely ablative environments [6,7].

So far, several attempts have been made to prepare HfC coatings on C/C composites, mainly involving the methods of conventional chemical vapor deposition [8-11], precursor infiltration and pyrolysis [12], reactive melt infiltration (RMI) [13] and

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vacuum plasma spraying [14,15]. All of them can be considered successful because of the achievement of remarkable resistance to oxidation and ablation in such C/C composites due to the formation of high temperature carbide coatings, such as HfC, SiC, ZrC and TaC etc. However, the chemical vapor deposition process for the synthesis of HfC coating commonly requires a special carrier system to constantly supply powdered or vaporized $HfCl_4$ and rigorous control of the gas flow rates. Moreover, it is worth noting that this process is of low efficiency with respect to the growth rate of the coating and generally unfriendly to the environment due to the generation of toxic gases [8-11]. Similarly, the precursor infiltration and pyrolysis method suffers from the disadvantage of low efficiency because of the tedious infiltration process cycle [12]. On the other hand, the otherwise convenient and efficient vacuum plasma spray process requires the input of very large amounts of energy to melt HfC powders which form a HfC coating with thickness of 110 μm in 8 min. [14]. A further problem is that the mismatch of thermal expansion coefficient between HfC coating and C/C composite formed by high temperature annealing may result in delamination of the protective layer from the C/C composite [14,15]. RMI is also suitable for preparing HfC coating via the introduction of Hf alloy into a C/C composite at relatively low temperature and serves as an efficient, controllable and economical method [13]. Often, the syntheses of carbide ceramic coatings via the RMI process involve reacting metal with C/C composite at high temperature. However, the influence of crystallite size and microstructure in C/C composites composed of carbon fiber and carbon matrix (often derived from pyrolytic carbon and/or resin/pitch based carbon) on the formation of carbide coating is not clear.

Our previous work [16,17] confirmed that the microstructure of carbon sources has an influence on the formation and growth of carbide nanofibers. However, few studies have given sufficient attention to the effect of the carbon source’s crystallite size on the morphology and crystal phase composition of HfC formed by the carbon’s reaction with hafnium.

Hence in order to study the synthesis of HfC via reaction of hafnium powder with carbon fibers at high temperature in the present work, mesophase pitch based carbon fibers treated at various temperatures and hafnium powders are used as carbon and hafnium sources, respectively. The structure and crystalline parameters of the mesophase pitch-based carbon fibers as they vary with heat-treatment temperature have already been fully characterized [17]. Consideration of the remarkable differences in crystallite size and microstructure of the carbon fiber and the matrix carbon in C/C composite will be helpful to elucidate the possible formation mechanism of HfC, in order to understand the influence of carbon fiber crystallite size on the formation and growth of HfC coating on carbon fibers. More generally, this work offers a possible optimal process for the pretreatment of C/C composites and the synthesis of HfC on C/C composites for high temperature applications via directional reaction of hafnium powder with such C/C composites.

2. Experimental

2.1 Preparation of mesophase pitch-based carbon fibers

Commercial naphthalene-derived synthetic mesophase pitch purchased from Mitsubishi Gas Chemical Corporation, was used directly as raw material for the preparation of round-shaped anisotropic pitch fibers by a melt-spinning method. The as-spun carbon fibers were oxidatively stabilized at 240-250 ºC for 10-20 h in a flowing oxygen atmosphere, then heat-treated at 450 ºC for 1 h and subsequently carbonized at 1000 ºC for 1h under nitrogen atmosphere in a tube furnace with a heating rate of 1 ºC/min. The carbonized fibers were finally heat-treated at 2000 or 3000 ºC for 15 min with a heating rate of 15 ºC/min. The carbon fibers heat treated to 1000, 2000 and 3000 °C were labeled as AF1000, AF2000 and AF3000, respectively.

2.2 Synthesis of HfC-coated carbon fibers

Hafnium powders (ca.300 mesh and purity of 99.9%) were purchased from Beijing New Material Technical Co. Ltd. in China. Carbon fibers and hafnium powder at a 2:1 (C/Hf) molar ratio were used as raw materials. Carbon fibers with length of 3 cm were placed in a covered graphite crucible and covered by hafnium powder in alternating layers to facilitate reaction to form HfC. The covered graphite crucibles were placed in a vertical graphitizing furnace, vacuum purged to 3 Pa and filled with argon to a pressure of 0.1 MPa. Purging and filling was then repeated to eliminate residual air. The furnace was heated to either 1000, 1200 or 1400 °C and held for 2 h under argon atmosphere.

2.3 Characterization of HfC-coated carbon fibers

The crystalline structures of the carbon fibers, before and after HfC coating were analysed by an X-ray diffraction (XRD) instrument (Philips X'Pert Pro MPD) using

Cu-K$_\alpha$ radiation (λ=1.54056 Å). The working voltage and current of the Cu target were 40 kV and 40 mA, respectively. A NOVA400 NANOSEM field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS) for X-ray microanalysis was used to analyse reactant and product surface morphology, and element content and the coating thickness of the HfC-coated fibers.

3. Results and discussion

3.1. Characterisation of mesophase pitch-based carbon fiber precursors

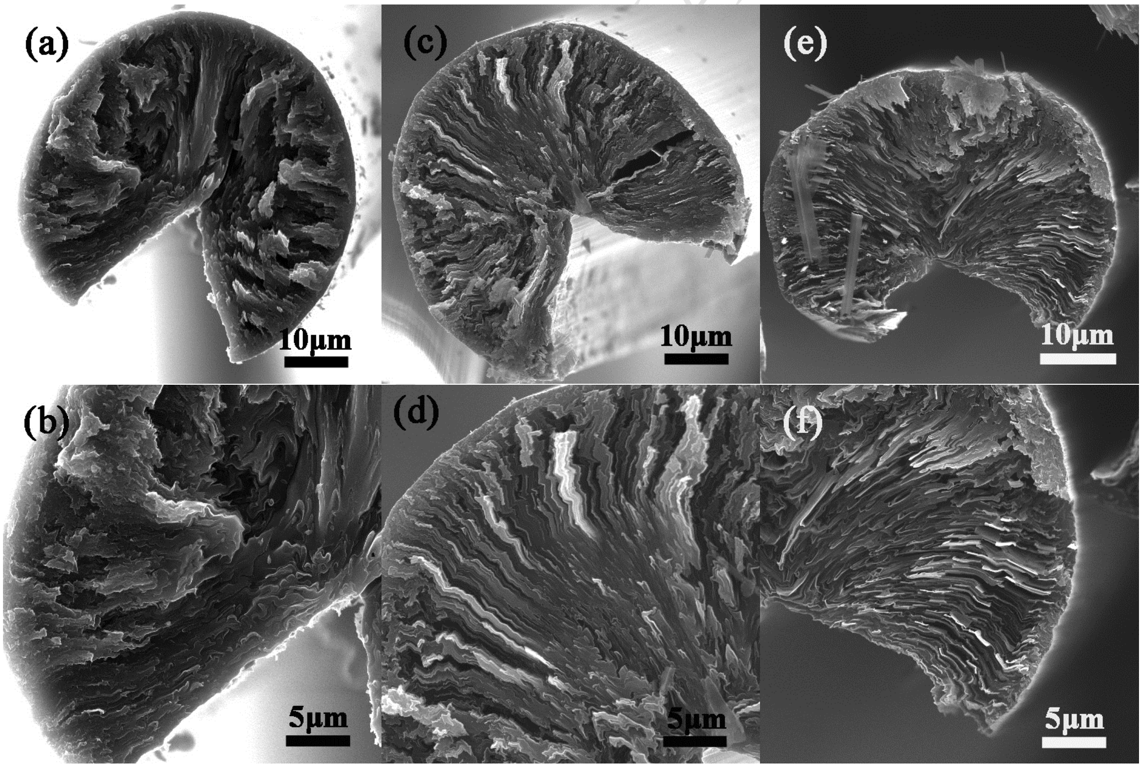

Fig. 1 Typical SEM images of mesophase pitch-based carbon fibers treated at (a,b) 1000, (c,d) 2000 and (e,f) 3000 °C.

Fig. 1 shows typical SEM images of mesophase pitch-based carbon fibers heat-treated at various temperatures. The transverse section of these carbon fibers in Fig. 1(a, c and e) presented typical radial open wedge textures. The carbon fibers' cross-sectional split angles expand from about 60° to 120° with increasing heat-treatment temperature. These are caused by the internal stresses within the highly oriented carbon fibers, resulting from circumferential shrinkage during preferential orientation of crystallites in the fiber during heat treatment [18,19]. A high magnification view in Fig. 1b shows embryonic radial structure in the cross-section of AF1000, implying oriented growth of graphite crystals even at the relatively low temperature of 1000 °C. As the heat treatment progresses, typical flake graphite layers in the cross-section of the carbon fibers are clearly developed from the surface to the center. The transverse cross-sectional texture of the carbon fiber entirely transforms into flake graphite layers after graphitization at 3000 °C (Fig. 1(d and f)). This reveals the perfect growth and highly preferred orientation of the graphite crystals in the carbon fiber with increasing heat treatment temperature and this is consistent with comprehensive crystalline structure analyses from X-ray diffraction and transmission electron microscopy [17].

The crystalline parameters and graphitization degree, calculated from XRD results [17], are listed in Table 1. It can be seen that the coherence length and graphitization degree of carbon fiber increase markedly upon heat treatment temperature. This indicates that heat treatment facilitates the growth and ordering of graphite crystals and much bigger and ordered graphite crystals can develop in carbon fibers at higher temperature, quantitatively illustrating the observed differences in microstructure between these carbon fibers to some extent.

Table 1 Crystalline parameters and graphitization degree of carbon fibers heat-treated at various temperatures

Sample	d_{002}/nm[a]	$Lc_{(002)}$/nm[a]	d_{100}[a]	$La_{(100)}$ /nm[a]	g/%[b]
AF1000	0.3529	1.4	0.2079	5.1	-
AF2000	0.3422	13.6	0.2115	13.4	20.9%
AF3000	0.3368	39.7	0.2130	78.9	83.7%

[a] The crystalline parameters of carbon fibers quoted from [17].

[b] Degree of graphitization (g) was calculated by the expression $g=(0.3440-d_{002})/(0.3440-0.3354)$ [20] where the figures are quoted in nm.

3.2. Effect of carbon fiber-hafnium reaction temperature

Fig. 2 illustrates the XRD patterns of the un-coated carbon fibers and of the products obtained from them. As shown in Fig. 2(a), relatively strong peaks at about 26° are assigned to graphite crystals which for the majority of the carbon fibers. The intensity of (002) plane diffraction peaks increased with the synthesis temperature being highest at 1200 ºC due to the growth of graphite crystal of carbon fibers. The magnified XRD patterns shown in Fig. 2(b), from the shaded area of Fig. 2(a), show weak HfC and HfO_2 diffraction peaks indicating that HfC is formed at 1000 °C. With increase of synthesis temperature to 1400 ºC, the intensity of the graphite (002) diffraction peak decreases, and five sharp diffraction peaks at approximately 33.4°, 38.8°, 56.1°, 66.9° and 70.3°, corresponding respectively to the (111), (200), (220), (311) and (222) planes of cubic phase HfC (JCPDS 03-065-0975), are clearly observed. This suggests the formation and growth of HfC coating on the carbon fibers. The drastic jump of the relative intensity of HfC's characteristic peak observed in Fig. 2(a) is similar to that in Blum's work, which suggests the important role of the reaction temperature [21].

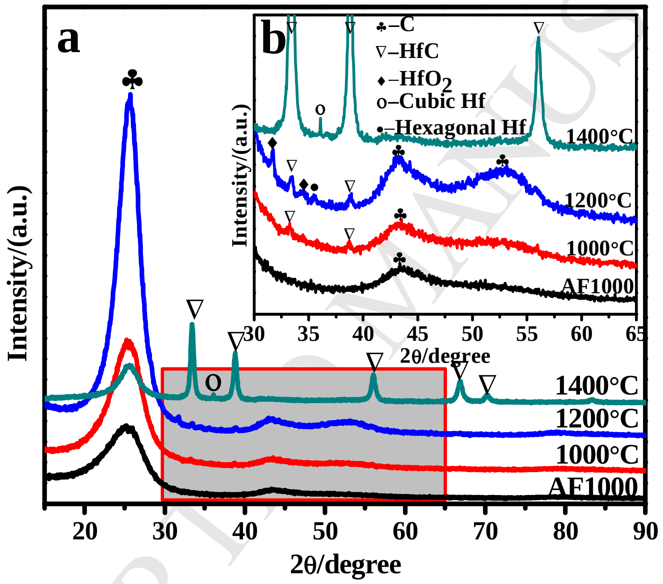

Fig. 2 XRD patterns of (a) AF1000 and HfC-coated fibers prepared at various temperatures on AF1000 for 2 h and (b) magnified XRD patterns from the shaded area in Fig. 2(a).

Furthermore, hexagonal phase and cubic phase hafnium were detected in the samples synthesized at 1200 °C and 1400 °C, respectively. It indicates that the hexagonal phase residual hafnium transfers to cubic phase with the increase in synthesis temperature from 1200 °C to1400 °C. The existence of weak HfO_2 peaks can be assigned to the slight oxidation of residual Hf in the as-prepared product during the storage.

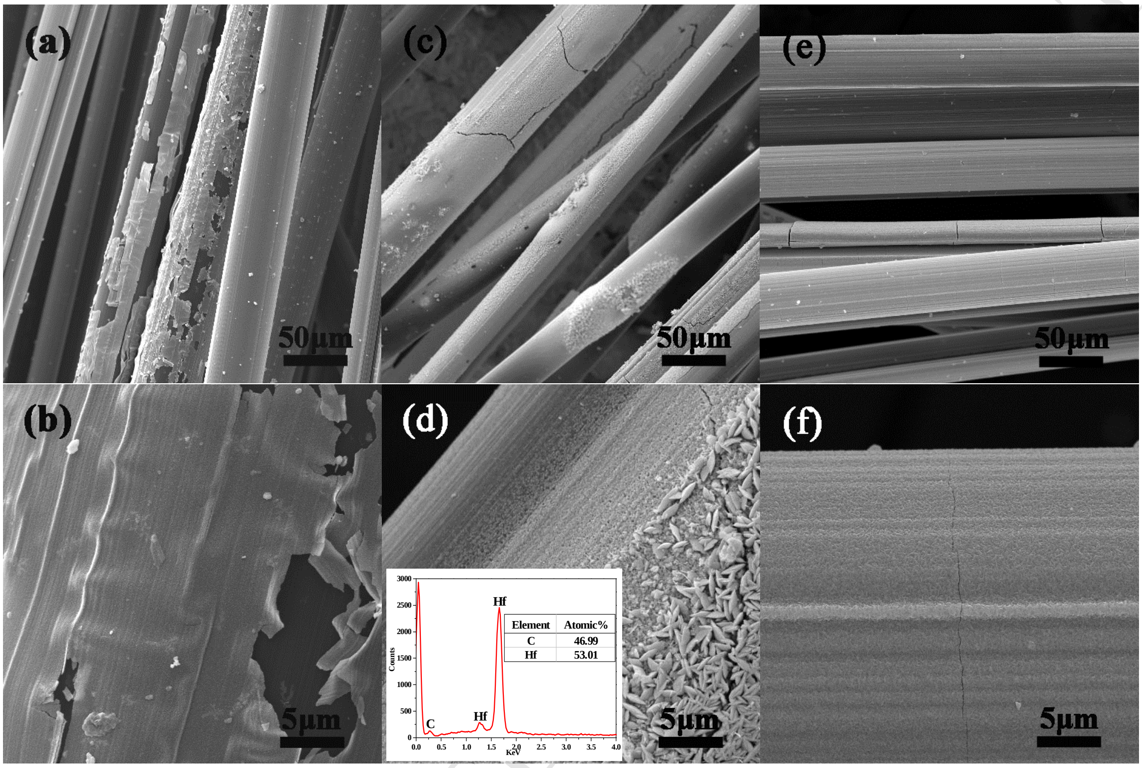

Fig. 3 SEM images of HfC-coated carbon fibers prepared for 2 h at 1000 °C (a and b), 1200 °C (c and d) and 1400 °C (e and f) on AF1000; the inset in (d) is the carbon and hafnium composition of the particles shown in (d) as measured by semi-quantitative SEM-EDX analysis.

To further study the influence of reaction temperature on the formation of HfC on the carbon fibers, the morphologies of products prepared at different temperatures were investigated by SEM observation as shown in Fig. 3. This reveals that HfC coatings were formed on the surface of carbon fibers. Some cracks and exfoliated coatings can be seen in the products synthesized at 1000 °C and 1200 °C shown in Fig. 3(a-b) and Fig. 3(c-d), respectively. The inset in Fig. 3(d) shows the semi-quantitative carbon and hafnium EDX elemental analyses of the particles shown in Fig. 3(d), showing that hafnium is more abundant than carbon in these particles. These heterogeneous coatings may result from uncompleted reaction of Hf and HfO_2 in the coating. This result agrees well with the XRD profiles shown in Fig. 2(b).

In comparison with the products prepared at 1000-1200 °C, relatively smooth and uniform HfC coatings on the carbon fibers are clearly observed in Fig. 3(e-f) as the temperature increased to 1400 °C, although a few cracks still can be seen. The differences in both the XRD and SEM results for these product synthesized at various temperatures indicates that reaction temperature has significant influence on the composition, morphology and microstructure of the HfC coating.

3.3. Effect of carbon fiber pre-heat treatment temperature on carbon fiber-hafnium reaction at 1400 °C

Fig. 4 shows the XRD patterns of HfC coatings prepared on carbon fibers previously heat treated to various temperatures. Carbon and HfC diffraction peaks can be observed distinctly in these patterns. It can be observed that the relative intensity of the graphite (002) plane diffraction peak from carbon fibers AF1000, AF2000 and AF3000 shows clear variations, suggesting the rapid growth of graphite microcrystal size and apparent enhancement of crystal ordering in the carbon fibers with the increase of heat-treatment temperature. The relative intensity of HfC’s characteristic peaks also increases at the same time, which may result from an increase in HfC coating thickness and grain size. This clearly indicates that a carbon fiber substrate with higher graphitization degree and crystallinity favours the growth of HfC coating.

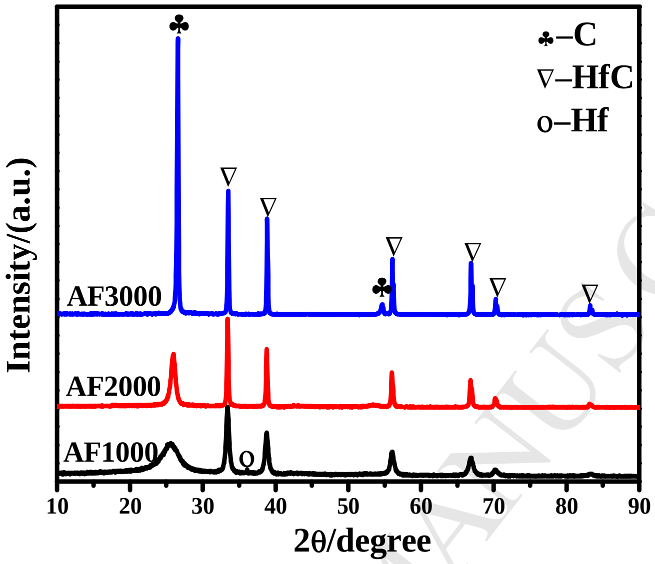

Fig. 4 XRD patterns of HfC-coated carbon fibers prepared for 2 h at 1400 °C on mesophase pitch-based carbon fibers previously heat-treated at different temperatures.

Fig. 5 shows the typical cross-sectional morphologies of HfC coatings prepared on various carbon fibers. From these SEM images, it can be seen that all coatings formed on the carbon fibers are relatively uniform and continuous. With the increase of carbon fiber graphitization and degree of crystallinity as shown in Fig. 4 and Table 1, the coating thicknesses on carbon fibers AF1000, AF2000 and AF3000 increase from about 0.7 to 3.5 and then 9.0 μm, respectively. These results are consistent with those of the XRD profiles in Fig. 4.

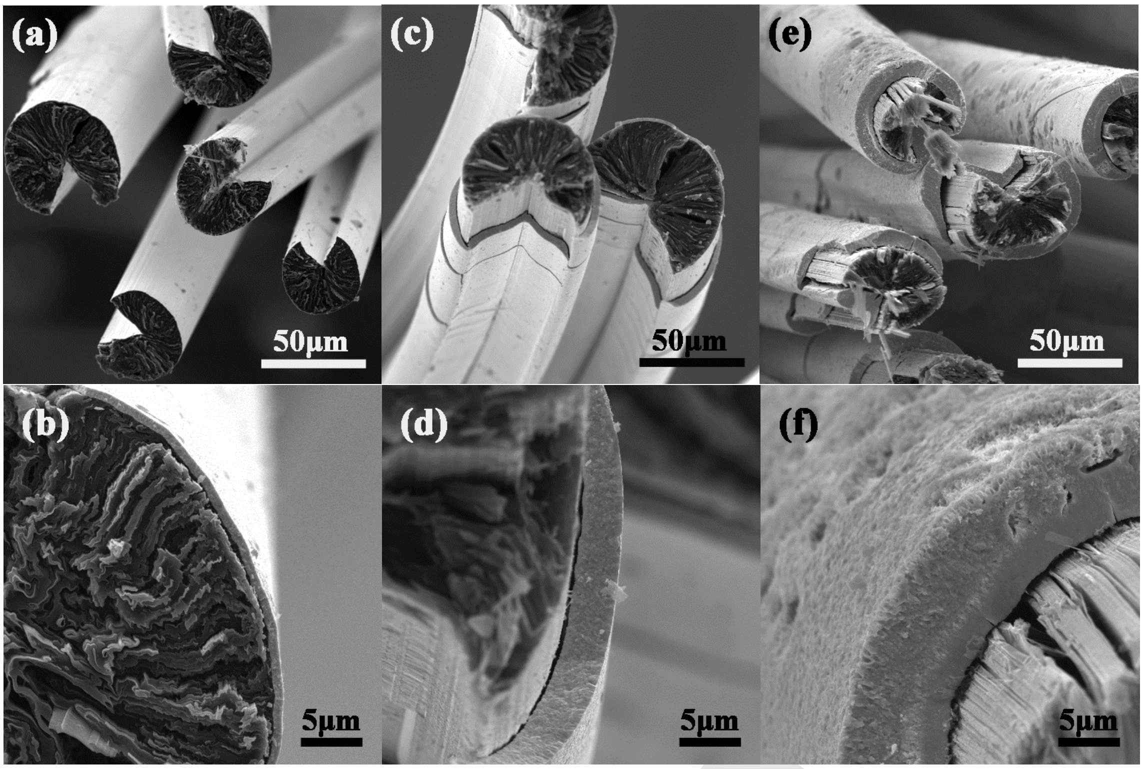

Fig. 5 SEM images of HfC-coated carbon fibers prepared at 1400 °C for 2 h on mesophase pitch based fibers previously heat treated at various temperatures (a-b) AF1000, (c-d) AF2000 and (e-f) AF3000.

3.4. Hafnium diffusion along carbon fiber surface during hafnium-carbon reaction

Only a small portion of the Hf powders is actually in intimate contact with the carbon fibers during the synthesis of HfC. Therefore, the HfC may initially form at (and adjacent to) contact areas between Hf and C, and the formation of an integrated HfC coating may involve the diffusion of Hf and/or carbon. For this diffusion-based formation of HfC coating on the surface of the carbon fibers, the synthesis temperature and the crystallite size of the carbon may be the main factors to affect the diffusion rate of both Hf and C sources.

Knözinger [22] reported that the motion of atoms within their lattice can occur at temperatures around half of their melting point (0.5Tm), often termed the ‘‘Tammann’’ temperature, which can even be as low as around 0.3Tm for the migration of atoms on the surface of materials. It has been recognised that metal salts, oxides and metals can spontaneously migrate onto surfaces of other supports at temperatures that are approximately half of the melting point of these dispersants [21,22,23]. Since Hf metal’s 0.5Tm is about 1100 °C, the diffusion of Hf on the surface of carbon fiber or on the surface of a HfC layer to form HfC coating appeared to be a possibility above such temperatures.

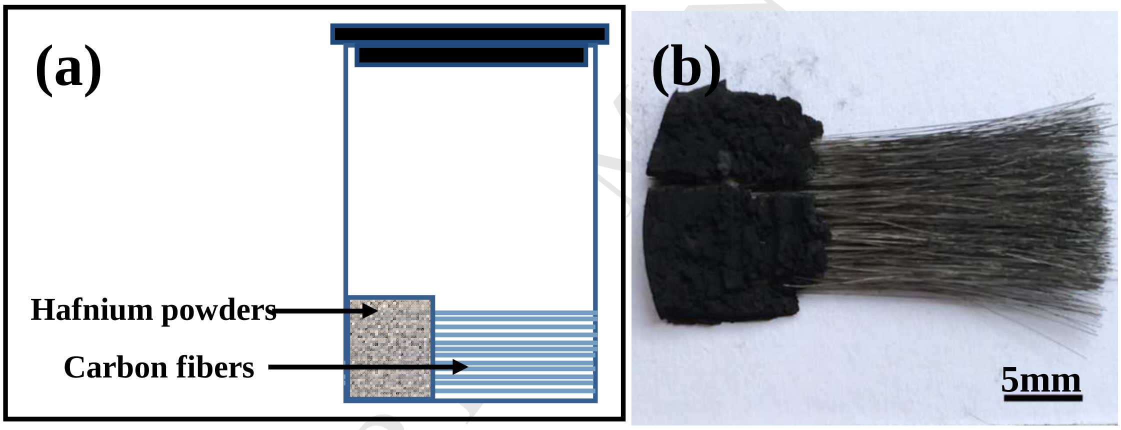

Fig. 6 Schematic diagram of the confirmatory experiment (a) and photograph of the as-prepared sample (b).

To verify the diffusion-based formation of HfC coating on the surface of carbon fibers, based on the spreading of Hf atoms, a confirmatory experiment was carried out. The schematic diagram of this experiment is shown in Fig. 6(a). One end of a bundle of AF1000 carbon fibers was embedded in Hf powder to maintain sufficient contact and then heated at 1400 °C for 2 h. A photograph of the as-prepared sample is shown in Fig.

6(b). After reaction, the aggregated Hf powders at the end of the carbon fiber bundle could be seen, suggesting the partial melting of Hf powders.

Fig. 7(a) and (b) respectively show the hafnium powder before and after reacting with carbon fibers AF1000. The Hf powder after the reaction is clearly observed to have melted, at least partially. According to Aminikia’s work [24], the adiabatic temperature (T_{ad}) for the reaction of hafnium with carbon can be calculated using the following relation:

$$-\Delta H^{o}_{298} = \int_{To}^{Tad} \Delta CpdT$$

where ΔH_{298} is the enthalpy changes at 298 K and Cp is the heat capacities of the products. The T_{ad} for the reaction between hafnium and carbon was calculated to be 3900 K, i.e. 3627 °C, a value which is much higher than the temperature giving rise to the melting of Hf powders as shown in Fig. 7(b).

Fig. 7(c) and (d) show the representative morphology of the product obtained along the longitudinal direction of the carbon fibers and the corresponding line scanning EDX profiles are shown in Fig. 7(e) and (f). From the SEM and EDX results, it can be seen that HfC coating formed on the surface of carbon fibers even where Hf was not previously present, indicating the spreading of Hf along the surface of the carbon fibers. In addition, the linear EDX spectra illustrate the variation of Hf and C content near the surface along the scanning line, from which the diffusion distance of Hf is estimated to be ca. 3 mm in the longitudinal direction (Fig. 7(e and f)), although the initial constant abundance of Hf tails-off after the first ca. 1.5 mm. By comparing it with the coating thickness in Fig. 5(b), the growth rate of HfC coating along the

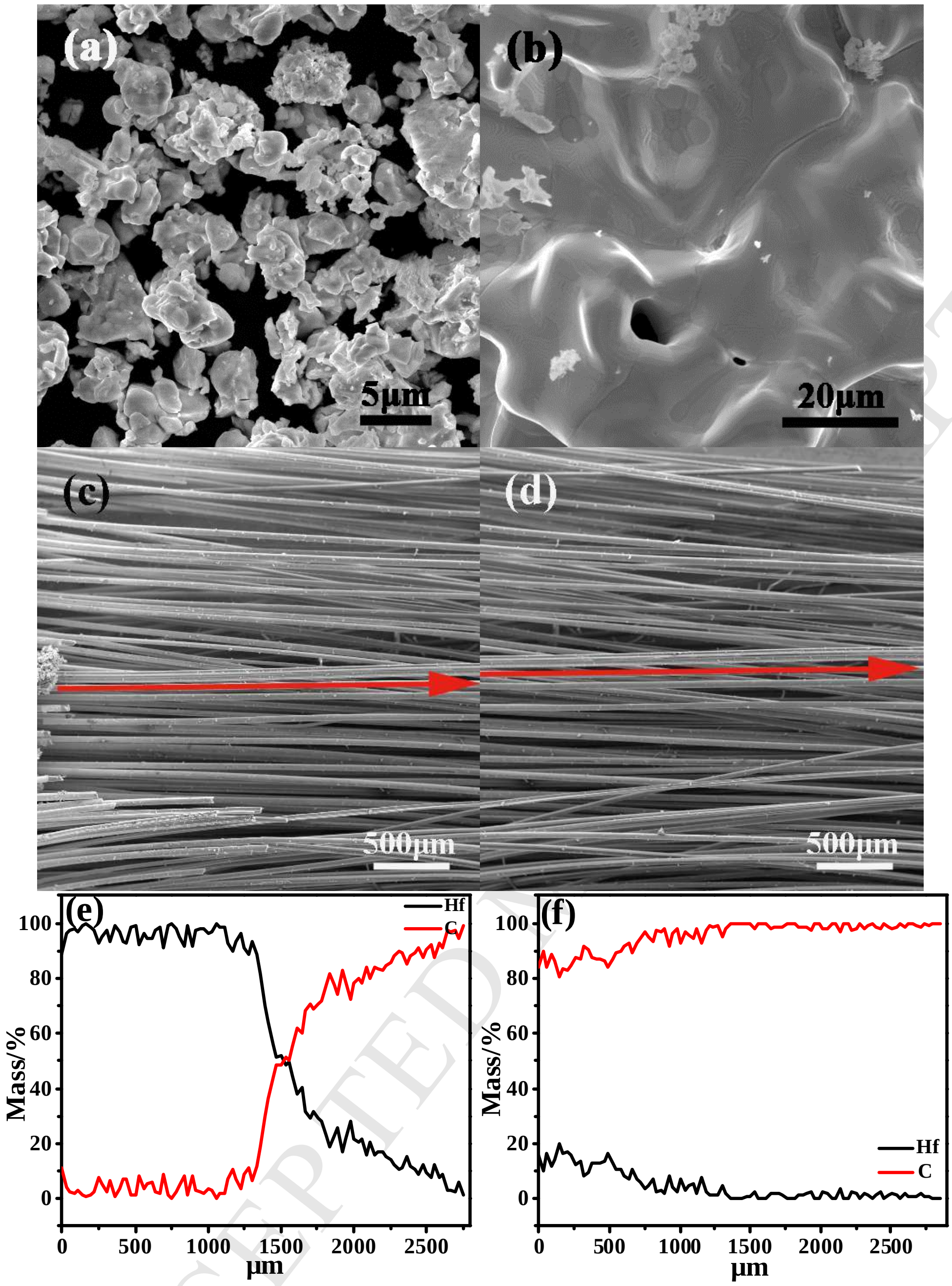

Fig. 7 SEM images of hafnium powders (a) before and (b) after reaction with carbon fibers AF1000, HfC-coated carbon fibers (c) close to and (d) farther from Hf powders, and the corresponding line scanning EDX spectra (e) and (f) of HfC coating along the red arrow in Fig. 7(c) and (d), respectively.

longitudinal direction is found to be much faster than in the radial direction of the carbon fiber, and this may be attributed to the surface diffusion process.

The above verification demonstrates that the rapid diffusion of Hf atoms on the surface of materials makes it possible to form a continuous HfC coating on carbon fibers. From the drastic jump in the relative intensity of the HfC XRD peaks (Fig. 2) and the changing integrity of the HfC coating (Fig. 3), it is believed that increase of reaction temperature coupled with the polymorphic crystalline transformation of hafnium strongly favours the spreading of Hf on the surface of carbon fiber. This markedly facilitates the reaction between C and Hf, leading to the rapid formation of a uniform and dense HfC coating.

3.5. Influence of carbon structure on the formation of HfC coating

As carbon fiber pre-heat treatment temperature increases, the resulting HfC coating thickness also increases suggesting that the carbon microstructure affects the surface diffusion of Hf, considering the diffusion limited condition. The heat treatment of carbon fibers promotes the growth and preferred orientation of radial-like graphite crystals, thus decreasing the occurence of structural defects and crystal boundaries [17,19]. Moreover, the growth of carbide on the surface of carbon substrate is generally a template reaction process [25] and, in this work, the obtained carbide inherits the outline of the carbon fibers. This means that the HfC coating formed on AF3000 may be less defective than those formed on AF1000 and AF2000. The less defective surface created by preferred orientation of radial-like graphite crystals in the carbon fiber or HfC coating may provide a more expedient path for the transport of hafnium to distant areas, resulting in better supply of Hf and thus leading to the formation of thicker HfC coating.

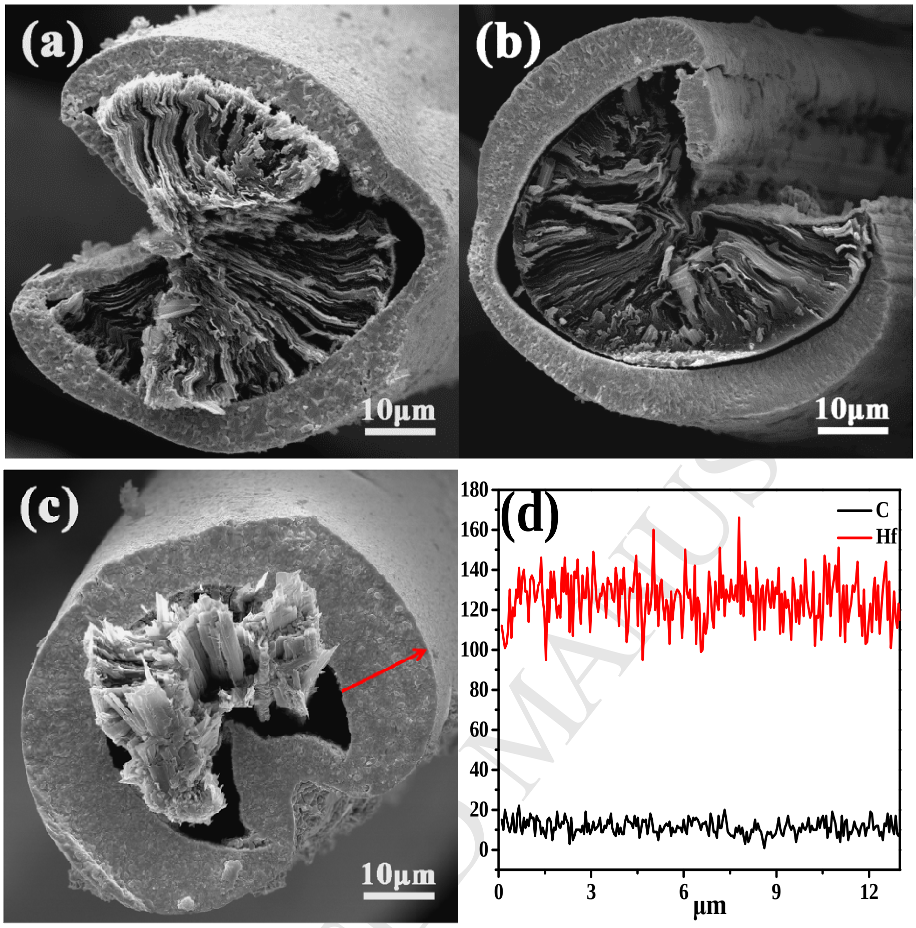

Fig. 8 SEM images of cross sections of HfC-coated carbon fibers based on (a) AF1000, (b) AF2000 and (c) AF3000 prepared by embedding one end of the carbon fiber in Hf powders at 1400 °C for 2 h, and the line scanning EDX spectra (d) of HfC coating along the red arrow in Fig. 8(c).

In order to further study the influence of carbon structure on the formation of HfC coating, homogeneous reaction between the variously heat treated carbon fibers and Hf powders was carried out by embedding one end of the carbon fibers in Hf powders. The representative cross sections of individual HfC-coated carbon fibers prepared by this embedding process are shown in Fig. 8. In comparison with the coating in Fig. 5(b, d and f), the corresponding thicknesses of coatings increase apparently from 0.7 to 3.5 and 9.0 μm, respectively, to 8.2, 9.2 and 13.5 μm using the same reaction temperature and time. This reveals that the coating thicknesses in Fig. 5(b, d and f) are strongly restricted by the supply of Hf source which is controlled by surface diffusion.

This further study also corroborates the previous findings with respect to the effect of crystallite size of carbon fibers on the surface diffusion of Hf; the differences in coating thickness are still observed in Fig. 8(a-c) even with a sufficient supply of Hf source. Carbon fiber which possesses more extensive crystalline structure and more preferred orientation with its graphite crystals favours the growth of HfC coating. Interestingly, it was found that the $Lc_{(002)}$ and $La_{(100)}$ values of the carbon fibers listed in Table 1 obviously increase with heat-treatment temperature, and the coating thickness on the corresponding carbon fibers (Fig. 8(a-c)) also increases, again suggesting that the crystallite size and microstructure of carbon source may be a key factor affecting the growth of HfC coating.

3.6. Correlation between graphitic crystallite size and metal carbide coating thickness

To clarify the correlation between graphitic crystallite size and metal carbide coating thickness, the reactions between various carbon fibers and Hf, Ta and Zr powders were carried out along the same lines as the experiment shown in Fig. 6(a) at 1400 °C but, on this occasion, for 3 h. The variation of carbide coating thickness on corresponding carbon fiber with respect to the crystalline parameters ($La_{(100)}$ and $Lc_{(002)}$) of isotropic carbon fiber (IF) and anisotropic carbon fiber (AF) heat-treated at various temperatures is shown in Fig. 9. This shows that the $Lc_{(002)}$ and $La_{(100)}$ values of carbon fibers increase as expected with the heat-treatment temperature. Compared with corresponding isotropic carbon fibers, the crystal size of anisotropic carbon fibers is larger and, with heat treatment, the graphite crystals in the latter increase in size more markedly. The various carbide coating thicknesses on the corresponding carbon fibers also increase (Fig.9 (a) and (b)), albeit more and more slowly, with increasing crystal size in the carbon fibers, confirming that the crystallite size and microstructure of carbon source are a key factor affecting the growth of HfC and other carbide coatings.

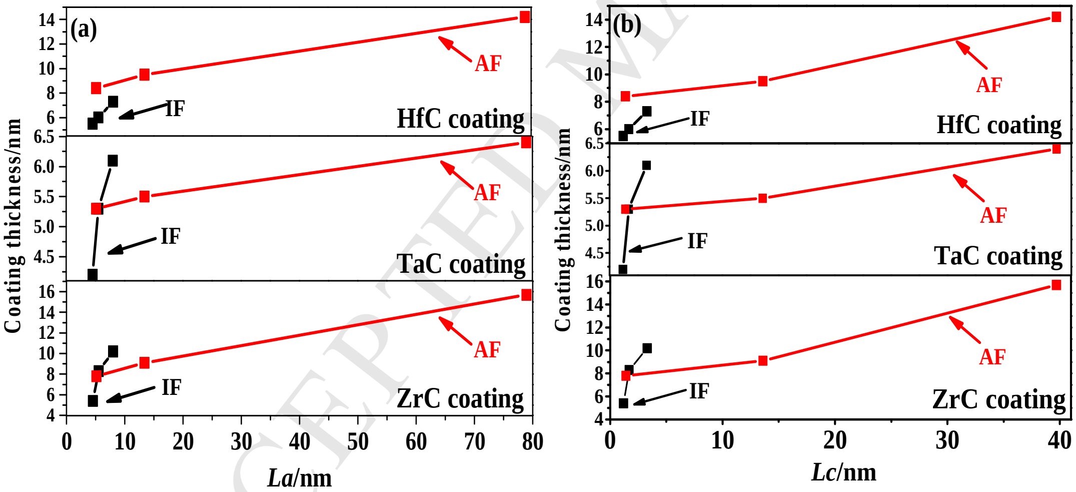

Fig. 9 The variation of carbide coating thickness on corresponding carbon fiber with respect to the crystalline parameters [17] (a) $La_{(100)}$ and (b) $Lc_{(002)}$ of IF and AF heat-treated at 1000, 2000 and 3000 ºC, respectively.

This significant effect of carbon fiber crystallite size on the formation of HfC coating may be caused by the templated reaction process. This process leads to the formation and growth of more ordered carbide crystals on carbon sources with larger crystal size and better ordering, and thus the formation of more ordered grain boundaries between the carbide crystals which is more favourable for the diffusion of C and Hf in the HfC interlayer and hence the formation of a thicker HfC coating due to grain boundary diffusion.

3.7. Radial diffusion during carbide formation on carbon fibers

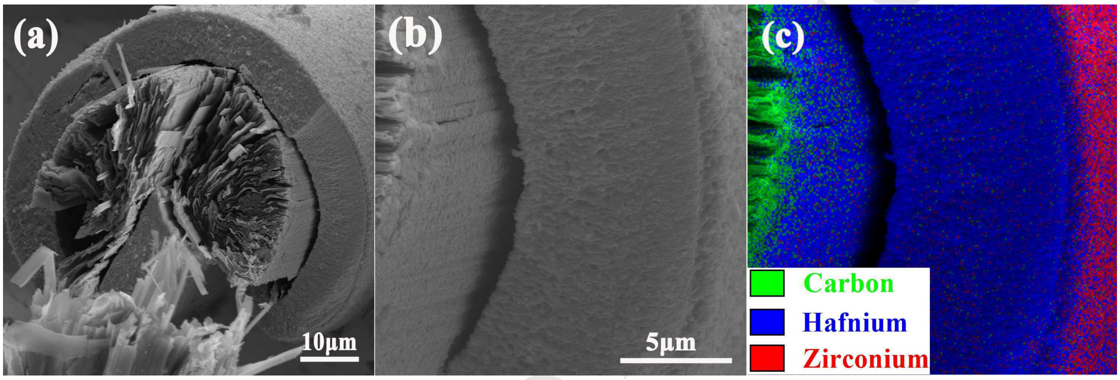

Fig. 10 SEM image of the cross-section of (a,b) ZrC/HfC coating prepared by reacting zirconium powder with HfC-coated AF3000 (as shown in Fig. 5(e)) at 1400 °C for 0.5 h and (c) its corresponding elemental mapping image.

As shown in Fig. 8(a-c), the diameter of carbon fiber core decreases as the thickness of the HfC coating increases but some thin HfC coatings, which are prone to spallation from the carbon fiber core, can be seen in Fig. 8(a) and (b). This exfoliation of the coating will prevent the bi-directional diffusion of hafnium and carbon sources through the HfC coating both to the surface of the HfC coating and to the interface between the HfC and carbon fiber core. This is important because the formation and growth of HfC coating via a bi-directional diffusion process is implied by the elemental abundances of C and Hf in Fig 8(d), as measured by semi-quantitative SEM-EDX line scanning analysis through the thickness of the HfC, because these are almost constant rather than showing a gradient distribution.

To further confirm the diffusion of carbon from the carbon fiber core to the surface of the HfC coating, HfC-coated AF3000 carbon fibers were reacted with zirconium powder at 1400 °C for 0.5 h. The SEM image shown in Fig. 10(a) illustrates the cross-sectional morphology of the carbide coating. A thin additional coating formed on the surface of the HfC coating can be clearly distinguished in Fig. 10(b). The mapping image shown in Fig. 10(c) corresponding to elemental distribution of C, Zr, and Hf reveals the formation of a ZrC coating on the surface of the HfC coating. This indicates that the C diffuses from the carbon core to the surface of HfC coating. These results reveal the bi-directional diffusion of carbon and metal atoms leading to the formation and growth of carbide coatings.

3.8. Formation and growth mechanism of HfC coating on carbon fiber

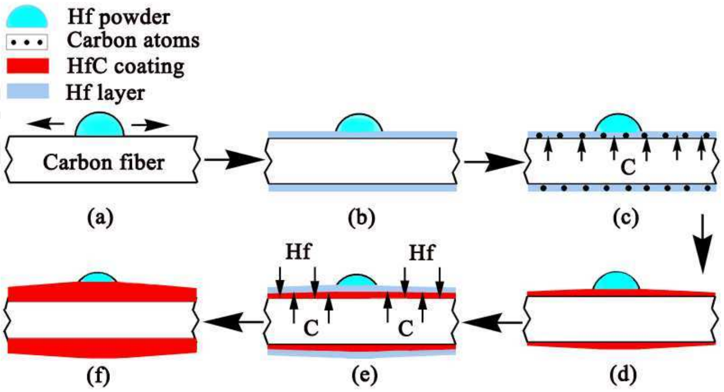

Fig. 11 Schematic illustration of the growth of HfC coating on carbon fiber.

To assist understanding of the formation and growth mechanism of the HfC coating on carbon fiber, Fig. 11 illustrates the growth process schematically. Initially, carbon fiber is partially in intimate contact with Hf powder shown in Fig. 11(a). The increase of reaction temperature supplies sufficient energy for the crystalline polymorphic transformation of hafnium, which promotes the spreading of Hf atoms across the surface of the carbon fiber from the contact areas between Hf and carbon fiber as shown in Fig. 11(b). Subsequently, the reaction of the spread Hf with carbon leads to the rapid formation of an initial HfC coating as shown in Fig. 11(c) and (d). Further growth of the HfC coating proceeds by the process of bi-directional diffusion of Hf and C across the HfC layer to the reaction interface to form the thicker coating shown in Fig. 11(e) and (f). In comparison with the diffusion of carbon through the HfC coating, it seems that the diffusion of Hf is the controlling factor in the formation and growth of HfC coating and for the increase of HfC coating thickness. If the reverse were true, the coating would be expected to stop growing and separate from the carbon fiber due to consumption of carbon. In addition to the expected effect of reaction temperature, the coating growth process can be strongly accelerated by prior development of the carbon fiber structure and a systematic study of this will be carried out in a future investigation.

4. Conclusions

Continuous and uniform HfC coatings were successfully prepared on carbon fibers by reaction of hafnium powders with pitch-based carbon fibers at 1400 °C. Increasing the reaction temperature coupled with the crystalline transformation of hafnium from Fcc to Hcp structure strongly promotes the surface diffusion of Hf along carbon fibers, which is beneficial for the rapid formation of integrated and dense HfC coating. It was also found that HfC coating preferred to grow on the surface of carbon fibers having larger crystal size and more graphitic order because the formation of HfC coating on carbon fiber arises via a template reaction process. The carbon fibers heat-treated at higher temperature have more ordered crystalline structure with less defects and grain boundaries as well as more preferred orientation of radial-like graphite crystals and this favours the surface diffusion of Hf and the bi-directional diffusion of Hf and C sources within the HfC coating through grain boundary diffusion. The results obtained in this work therefore confirm the feasibility of fabrication of refractory ceramic coatings on the surface of C/C composites at relatively low temperature by controlling the structure of the carbon source.

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