A facile route for graded conversion of carbon fabric to silicon carbide fabric and its oxidation kinetics study in atmospheric high-temperature environment

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Abstract. Silicon carbide fabric converted from carbon fabric was prepared by a facile halide-activated pack cementation method. The XRD, SEM and EDS analyses confirm the formation of SiC fibres with graded conversion of carbon to SiC from surface to core of individual carbon fibres of carbon fabric. The graded conversion of carbon fibre to SiC was uniform and homogeneous throughout the fabric dimension. The thermokinetics of oxidation in atmospheric environment was studied by TGA analysis. The reaction kinetics and governing mechanism for oxidation of bare carbon fabric and silicon carbide fabric were calculated using Kissinger and Ozawa methods. It was observed that the activation energy for bare carbon fabric and silicon carbide fabric converted from carbon fabric are 62 and 174 kJ mol^{-1}, respectively. Further, it was observed that the silicon carbide fabric converted from carbon fabric follows the second-order surface reaction oxidation mechanism.

Keywords. Carbides; vapour deposition; thermogravimetric analysis; surface properties.

1. Introduction

The materials for extreme applications, such as space aircraft [1], rocket shields [2] and braking systems [3] require high strength as well as thermal and oxidative resistances. Currently, high strength requirement is met by using carbon fibre-reinforced composites owing to their high aspect ratio and good strength [4]. It was observed that irrespective of type of carbon fibres, its rapid oxidation takes place at the operation temperature of above 673 K in oxidative environment [5], which makes it unsuitable even for oxidative low temperature atmospheric application. This limitation has given rise to modification of the composition in carbon fibre-based composites. To overcome this issue, two major ways with its own limitation are used, i.e., (i) impregnating carbon-fibre preform with ceramic matrix [6] and (ii) applying preventive layer coating on C/C composite [7]. The other possible way is to coat/convert individual carbon fibres with protective layer before incorporating them into the composite [8–10]. The potential materials used for this purpose are silicon carbide (SiC) [5], boron carbide [11] and other materials [2]. There are few reports based on carbothermal reduction [12], precursor infiltration pyrolysis (PIP) [13], sol–gel [8] and chemical vapour deposition [14] methods on the protective layer coating of individual fibres before using them in composites. Ke-dong Xia *et al* [8] have reported

silicon oxycarbide ceramic coating on carbon fibres using sol precursor. However, it was observed that debonding of coatings and surface cracks led to a reduction in tensile strength. Recently, Pillai *et al* [10] have reported deposition of crystalline silicon carbide on the carbon fibre substrate using plasma-enhanced chemical vapour deposition process. It was concluded that deposited coating was crystalline and the coating was uniform throughout the fibre tow. Further, dendrite growth was observed, which suggests non-homogeneity and rough surface. This implies that the deterioration occurs due to the collisions of the charged particles of plasma. Therefore, the challenges remain, i.e., homogeneous coating along the length of fibre, uniform coating on entangled carbon fibres in carbon-fibre preform, stability/performance of preventive layer coating in oxidative environment.

To address these issues, a facile method, i.e., halide-activated pack cementation (HAPC) was reported in the present work. In the present method, silicon metal was activated with ammonium fluoride to form active gaseous silicon fluoride intermediates. These diffuse through carbon-fibre substrate and convert carbon to silicon-carbide phase at high-temperature environment. The carbon fibres in loose form or in entangled carbon-fibre preform can be effectively converted to SiC uniformly throughout their length. There is graded conversion of carbon to SiC from top surface of carbon fibre to the core of carbon fibre. In addition, phase,

microstructure and oxidation kinetics of such SiC-converted carbon fibres were studied in detail.

2. Materials and methods

Carbon-fabric substrates (density: 0.90 g cc^{-1}) with the dimensions of 10 mm × 10 mm × 2 mm were prepared. The carbon fabric was prepared by weaving carbon fibres in desired pattern. The carbon fabric was porous in nature. The samples were ultrasonically cleaned with acetone and dried at 373 K. The carbon fibres in carbon fabric were converted to SiC using HAPC method. The detailed pack cementation experimental procedure was reported earlier [15]. The HAPC experiment was carried out at temperature 1773 K for 10 h. The pack comprising of 20 wt% Si–2.5 wt% NH_4F–77.5 wt% Al_2O_3 was used for this study. After the HAPC experiment, the specimens were cleaned under the water jet followed by ultrasonic cleaning and drying. The SiC fabric converted from carbon-fabric sample (termed as SiC fabric) was characterized for thickness, microstructure and composition using scanning electron microscopy (SEM)—Camscan MV2300CT/100, UK, equipped with energy dispersive spectroscopy (EDS) (Oxford, X-Max 80). The crystalline structures of SiC converted surface on carbon fibres were characterized by X-ray diffraction (XRD) — Philips Xpert pro XRD unit using CuK α radiation at an accelerating voltage of 40 kV, current of 35 mA and scanning rate of 0.05° s^{-1}.

Non-isothermal oxidation tests were conducted at four heating rates of 5, 8, 12, 15 K min^{-1} up to 1473 K for carbon fabric and SiC fabric using a thermogravimetric (TG) (Setsys Evolution, Setaram, France) equipment in static air environment. The weight changes of the specimens corresponding to oxidation were recorded continuously in TG mode.

The kinetics of solid-state oxidation reactions can be described by various equations taking into account the special features of their mechanism. In kinetic study of oxidation of carbon fabric and SiC fabric, Ozawa and Kissinger, Akahira and Sunose (KAS) equations were used to determine the activation energy (E_α) and pre-exponential factor (A) of the oxidation reaction. These methods are well described and widely used in the literatures [16], which provide reliable results. Therefore, these methods are selected for kinetic analysis of the oxidation of the prepared composite. The equations used for E_α calculation are as follows:
Ozawa equation:

$$\ln\beta = \ln\left(\frac{0.0048AE_\alpha}{g\left(\alpha\right)R}\right) - 1.0516\left(\frac{E_\alpha}{RT}\right). \quad (1)$$

KAS equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{g\left(\alpha\right)E_\alpha}\right) - \left(\frac{E_\alpha}{RT}\right), \quad (2)$$

$g(\alpha)$ is the integral form of $f(\alpha)$, which is the reaction model that depends on the reaction mechanism. According to the above-mentioned equations, the plots of ln β *vs.* 1000/T (equation (1)) and ln (β/T^2) *vs.* 1000/T (equation (2)) corresponding to different extents of conversion α can be obtained by a linear regression of the least-squares method. The activation energy E_α can be evaluated from the slopes of the straight lines with better linear correlation coefficients (r^2), respectively. The activation energy values were calculated at the heating rates of 5, 7.5, 10 and 12.5 K min^{-1} via the mentioned methods in the α range of 0.03–0.32. The mechanism function $g(\alpha)$ value was determined for most probable mechanism using the following equation [17]:

$$\ln g(\alpha) = \left(\ln\left(\frac{AE_\alpha}{R}\right) + \ln\frac{e^{-x}}{x^2} + \ln h\left(x\right)\right) - \ln\beta;$$

$$x = \frac{E_\alpha}{RT}$$

and

$$h\left(x\right) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120}. \quad (3)$$

The plots of ln $g(\alpha)$ *vs.* ln β were carried out using a linear regression of the least-squares method. To determine the most probable mechanism function, the degrees of conversion α corresponding to four heating rates taken at the same temperature were substituted into the left side of equation (3) for all the 28 types of mechanism functions. If the mechanism functions according to equation (3) exhibit the slope and the linear correlation coefficient r^2 close to 1.0000 and unity, respectively, then the function $g(\alpha)$ is the most probable mechanism function.
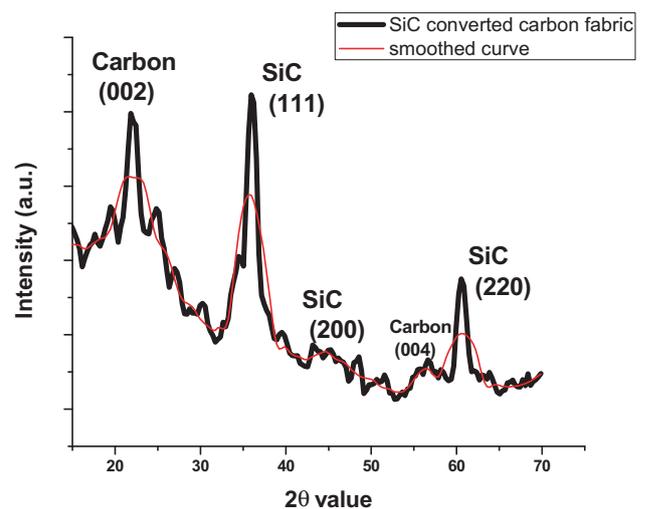

Figure 1. XRD pattern of the surface of as-prepared SiC fabric sample.
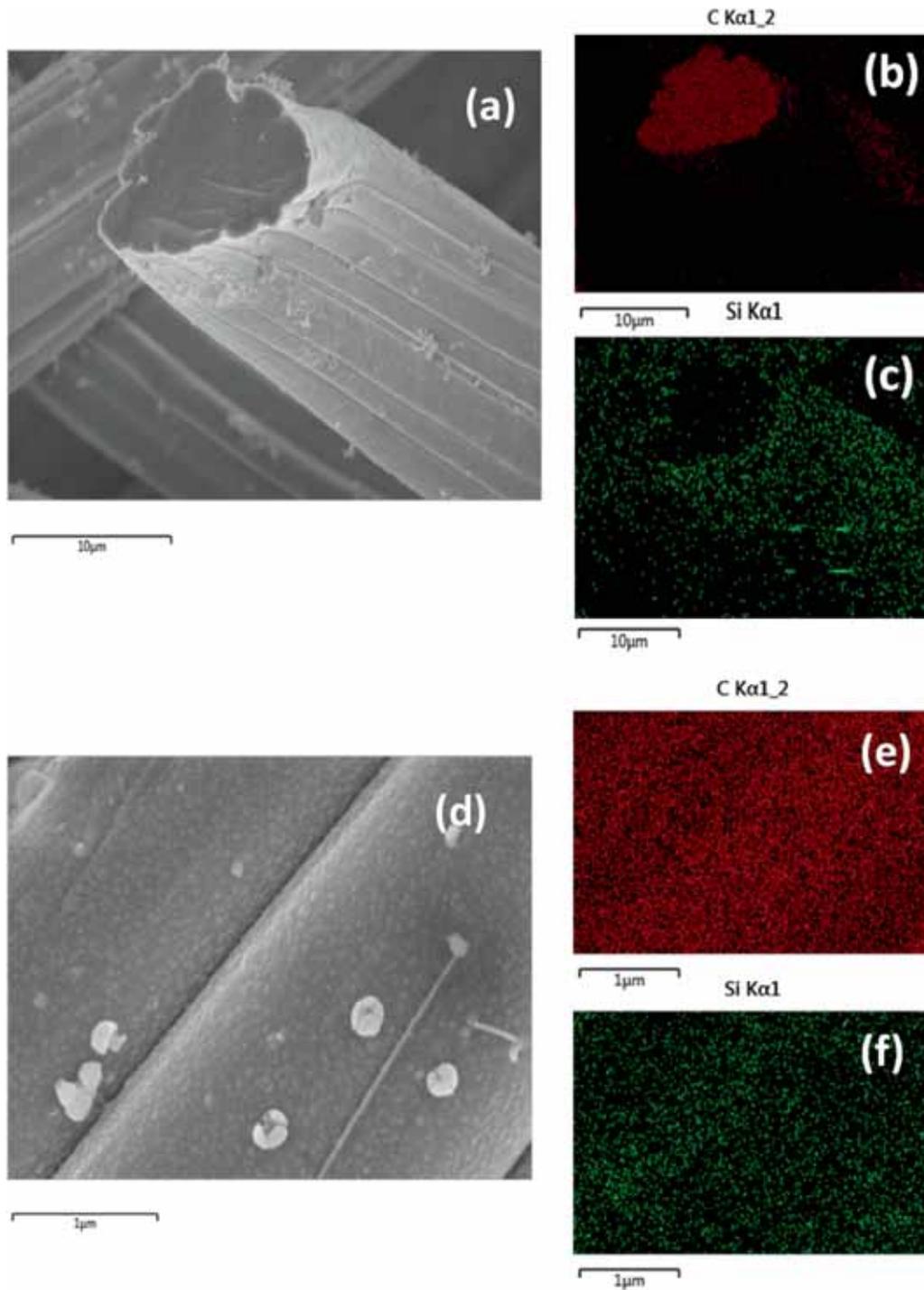
Figure 2. SEM images of the SiC fabric: (**a**) individual SiC fibre, (**b** and **c**) elemental mapping on the SiC fibre surface, (**d**) image of top surface of individual SiC fibre and (**e** and **f**) elemental mapping on top surface of SiC fibre (red colour: carbon and green colour: silicon).

3.   Results and discussion

The SiC fabric was prepared by HAPC method. One of the advantages of this method was that the SiC was formed uniformly on each surface of carbon fibres present in carbon fabric. This leads to the uniform and homogeneous conversion of carbon fibre surface to SiC. The XRD profile of SiC fabric is shown in figure 1. It was observed that there were distinguished diffraction peaks corresponding to carbon and crystalline cubical SiC phase in SiC-converted carbon fabric. The SEM micrograph (figure 2) of SiC fabric shows that each carbon fibre surface is homogeneously and
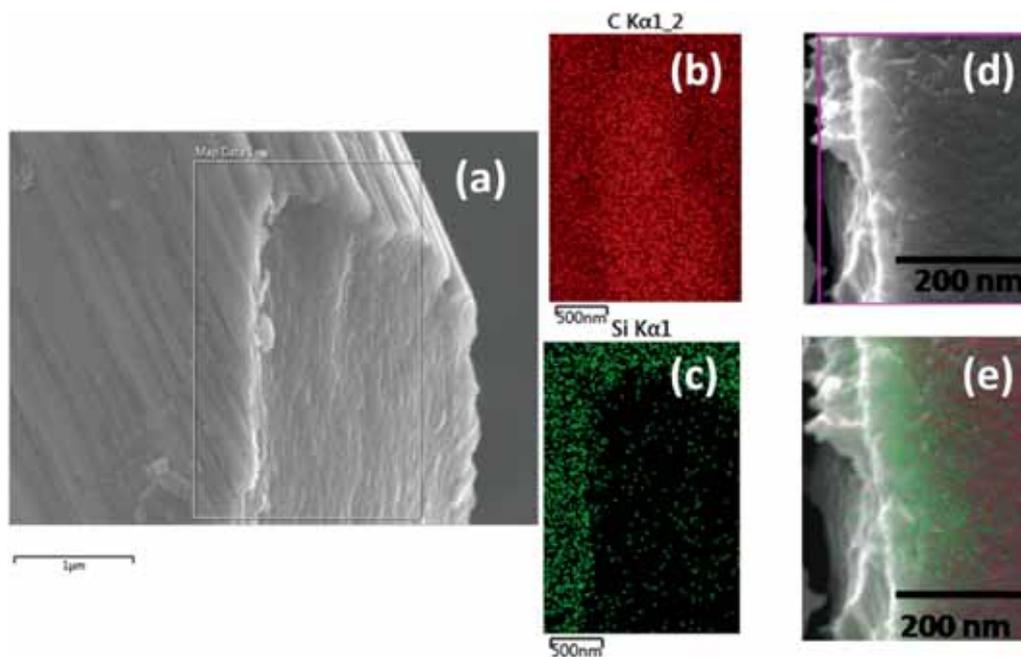
Figure 3. (**a**) Magnified SEM image of cross-section of individual SiC fibre, (**b** and **c**) elemental mapping on cross-section of SiC fibre, (**d**) magnified image of top surface in cross-section of individual SiC fibre and (**e**) elemental mapping on top surface in cross-section of individual SiC fibre (red colour: carbon and green colour: silicon).

uniformly converted to SiC along the length and the diameter. The cross-section images of individual SiC converted from carbon fibre (figure 3a–c) shows that there is gradient conversion of carbon to SiC when we move from the surface of carbon fibre to the core of carbon fibre. The top surface of carbon fibres are completely converted to SiC up to 100 nm (figure 3d and e). It was reported that SiF2 [15] is the main gaseous constituent responsible for conversion of carbon to SiC in HAPC process. In HAPC process, the chemical potential gradient is the main driving force for diffusion of silicon fluoride vapours from the surroundings to the substrate surface in the pack. There are four major steps involved with the HAPC method, i.e., (i) gaseous reactive species (such as SiF2) formation; (ii) transportation of reactive species to the surface of substrate; (iii) dissociation of the silicon fluoride; (iv) absorption, diffusion and chemical reaction; and (v) desorption of gaseous by products. In the present case, absorption, diffusion and chemical reaction of SiF2 decide the degree of conversion of carbon from surface to core of carbon fibre. For the present duration of reaction, i.e., 10 h up to 200 nm of top carbon surface of carbon fibre completely converted to SiC phase and then, moving towards the core of carbon fibre, there is drastic decrease in SiC phase due to low diffusion of SiF2. The solid-state diffusion of vapour species, i.e., SiF2 from surface to bulk of carbon substrate limit the conversion rate. It was observed that with the partial conversion of carbon fibre to SiC, the flexibility of carbon fibre remains same in comparison with the coated carbon fibre. Normally, the CVD-coated

carbon fibres tend to get stiff due to extra layer formation over the carbon fibre surface. This can hamper the further processing of fibre to composite. But in the present case, the processing of SiC fabric can be easily done to make composites of desired characteristics.

The thermogravimetric analysis (TGA) and differential-TGA curves of carbon fabric and SiC fabric are shown in figure 4a and b, respectively. From TGA curves (figure 4a, table 1), it was observed that the oxidation process of carbon fabric began from 865 K, but that of SiC fabric started from 1008 K. The carbon fabric was burnt at 1029 K and 23–24% weight of SiC fabric was retained at 1164 K. From TGA curves (figure 4a), it was observed that the oxidation of SiC began from 1164 K and weight gain was observed in the TGA curve. The weight gain indicated the formation of SiO_2 layer over the SiC surface due to the oxidation of the exposed SiC surface. From differential-TGA curve (figure 4b), it was observed that the oxidation reaction rate (da/dT) of SiC fabric was maximum when it was burnt off 33%. It was observed from differential-TGA that there are two peaks at 1060 and 1107 K. At the first peak temperature of 1060 K, oxidation of carbon from fibre occur due to the diffusion of oxygen through micropores/cracks generated on surface at high temperature. At this point, the surface reaction rate is exceeded when compared to diffusion rate of oxygen gas due to the availability of more active sites. Hence, overall reaction should be controlled by gas diffusion. But the generation of second peak around 1107 K indicated that the diffusion control reaction was not the rate-limiting step. The second peak at 1107 K

can be attributed to the competitive oxidation of carbon and silicon carbides. The oxidation of SiC leads to the formation of inert silica layer, which reduces the number of active carbon sites. So, the oxidation rate reduces and gas diffusion rate exceeds with respect to surface reaction. In this scenario, the overall oxidation reaction of SiC fabric could be controlled by the chemical reaction.

To determine the oxidation kinetics of SiC fabric sample, well known KAS and Ozawa methods were used. The

Figure 4. (**a**) Thermogravimetric and (**b**) derivative analyses of bare carbon fabric and SiC fabric in atmospheric environment.

calculated results from Ozawa and KAS methods according to four TG measurements are presented in table 2.

The average activation energy values of SiC fabric calculated from Ozawa and KAS methods are 184 and 164 kJmol^{-1}, respectively. Further, average activation energy values of bare carbon fabric calculated from Ozawa and KAS methods are 64 and 59 kJ mol^{-1}, respectively. The activation energy of the oxidation is reliable via the small difference of the calculated values from the two methods ($\sim$ 20 kJ mol^{-1}). The results of the most probable mechanism functions during the oxidation process are tabulated in table 2. The calculated mechanism function shows that the oxidation of SiC fabric follow 3D diffusion (Zhuravlev–Lesokhin–Tempel'man—ZLT model) below the reaction temperature of 1060 K and follows second-order reaction mechanism at the reaction temperature of 1107 K and above. Therefore, it can be stated that the mechanism function with differential form $f(\alpha) = 1.5(1 - a)4/3[(1 - a) - 1/3 - 1] - 1$ and integral form $g(\alpha) = [(1 - a) - 1/3 - 1]2$ belong to the mechanism of 3D diffusion reaction following the ZLT equation below the reaction temperature of 1060 K. In the similar way, mechanism function with differential form $f(\alpha) = 2(1 - a)3/2$ and integral form $g(\alpha) = [1 - (1 - a)2]$ belong to the mechanism of second-order reaction at and above reaction temperature of 1107 K. This is in consent with our oxidation results, i.e., presence of two troughs as shown in figure 4b. Presence of two troughs in differential TGA curve represents two kinds of oxidation reactions. In the present case of oxidation of SiC fabric, oxidative gas can diffuse from the exposed surface due to the micropores/cracks generated on the surface at high temperature oxidative environment. If one looks at the possibility of different steps in oxidation process, it was observed that in the first step, carbon exposed due to formation of pores/cracks on the surface of individual fibre of SiC fabric, initially gets oxidized. This initiation of oxidation process leads to the formation of more active carbon sites. So, the diffusion is rate-limiting step. Whereas in the second step, the diffusion of oxygen through these micro cracks/pores to carbon active sites inside carbon fibre is limited due to healing of micropores/cracks. The reaction of reactant oxygen, carbon and SiC will lead to the formation of products (such as silica, CO, CO_2, etc.) and the diffusion of the products out of the system. Thus, the second trough represents the
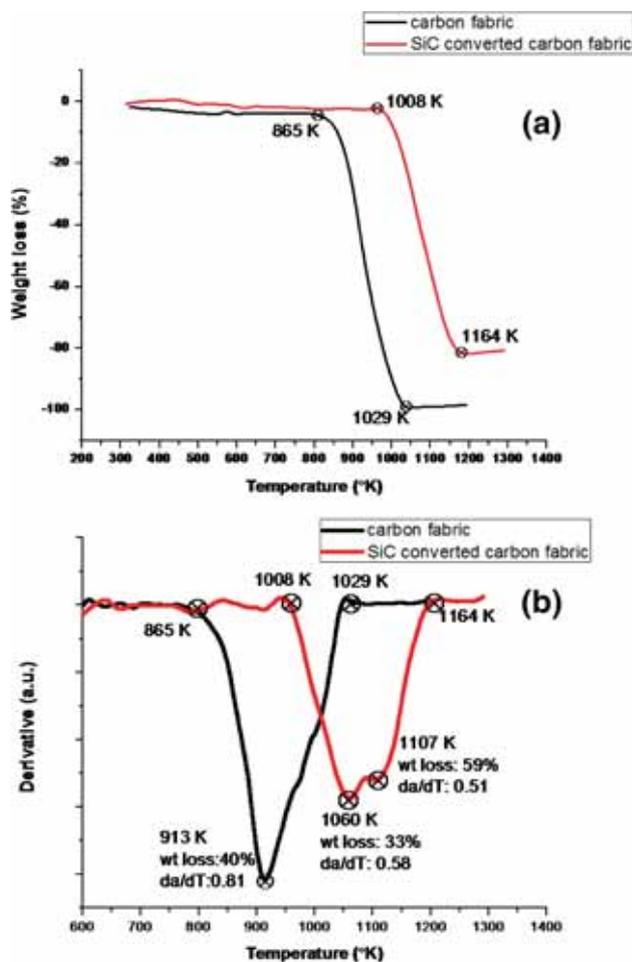
Table 1. The values derived from TG curve of the oxidation of bare carbon fabric and SiC fabric in static air atmosphere.

Environment	Sample	Onset temperature (K)	Temperature at which different weight losses (%) occurred (K)	Residual yield (%) (particular temperature)
Static atmospheric condition	Bare carbon fabric	865	900 (29%) 938 (57%)	0 (1040 K)
	SiC fabric	1008	1037 (15%) 1091 (46%)	23–24% (1164 K)

Table 2. Results of activation energy and most probable mechanism functions during the oxidation process.

Sample	Activation energy (kJ mol^{-1})	Temperature (K)	Reaction mechanism
Carbon fabric	64 (Ozawa), 59 (KAS)	865–1040	3D diffusion (anti-Zhuravlev–Lesokhin–Tempel'man model)
SiC fabric	184 (Ozawa), 164 (KAS)	1008–1060 1107–1211	3D diffusion (Zhuravlev–Lesokhin–Tempel'man model) Second-order reaction mechanism

competitive oxidation of carbon and SiC. Due to non-availability of active carbon surface, the reaction mechanism is governed by the surface reaction. Further temperature increase after 1164 K leads to weight gain, it represents oxidation of SiC and formation of silica phase. The formation of silica phase leads to the complete healing of pores/microcracks and further prevents the oxidation of the carbon fibre.

4. Conclusion

The SiC fabric was prepared from carbon fabric using facile and simple HAPC method. The graded conversion of carbon fibres to SiC in carbon fabric was carried out uniformly and homogeneously throughout the length of the fibre. Even, bent area of carbon fibres in carbon fabric was also converted to SiC effectively. In comparison to CVD/PIP/sol–gel methods, the present reported method has shown better uniformity in conversion of carbon fibre to SiC. Such graded conversion of carbon fabric to SiC leads to the enhancement of oxidative performance in static air environment. Use of such SiC fabric in place of simple carbon fabric in preparation of advance composite will lead to the extraordinary performance of composites in extreme environment. Further, such study of oxidation mechanism is essential to simulate and design a good oxidation-resistant high strength composite for commercial applications.

References

[1] Hopkins A R, Labatete-Goeppinger A C, Kim H and Katzman H A 2016 *Carbon* **107** 77

[2] Tang S and Hu C 2017 *J. Mater. Sci. Tech.* **33** 117

[3] Wu S, Yi M, Ge Y, Ran L and Peng K 2017 *Carbon* **117** 279

[4] Li Y, Cai S and Huang X 2017 *Compos. Sci. Tech.* **143** 89

[5] Prakash J, Venugopalan R, Paul B, Bahadur J, Ghosh S K and Sathiyamoorthy D 2013 *Corros. Sci.* **67** 142

[6] Tai N and Chen C 2001 *J. Am. Ceram. Soc.* **84** 1683

[7] Smeacetto F, Salvo M and Ferraris M 2002 *Carbon* **40** 583

[8] Xia K, Lu C and Yang Y 2015 *New Carbon Mater.* **30** 236

[9] Yuanjian T, Xiaoqian W, Hua S and Lianghua X 2011 *Corros. Sci.* **53** 2484

[10] Pillai R, Batra N, Manocha L M and Machinewala N 2017 *Surf. Interfaces* **7** 113

[11] Das M, Ghosh J and Basu A K 2010 *Ceram. Int.* **36** 2511

[12] Das M, Basu A K and Ghatak S 2009 *J. Eur. Ceram. Soc.* **29** 2129

[13] Tong D, Wang H, Wang L, Chen L and Li Z 2017 *Surf. Coat. Technol.* **319** 335

[14] Li J S, Zhang C R and Li B 2011 *Appl. Surf. Sci.* **257** 7752

[15] Paul B, Prakash J and Sarkar P S 2015 *Surf. Coat. Technol.* **282** 61

[16] Vlaev L, Nedelchev N, Gyurova K and Zagorcheva M 2008 *J. Anal. Appl. Pyrol.* **81** 253

[17] Pérez-Maqueda L A and Criado J M 2000 *J. Thermal Anal. Cal.* **60** 909