Ablation properties of ZrC-SiC-HfB₂ ceramic with different amount of carbon fiber under an oxyacetylene flame

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Abstract
In the present work, a carbon fiber reinforced ZrC-20 vol% SiC-15 vol% HfB₂ composite was produced by pressureless sintering method. Carbon fiber with various weight percentages (0, 10, 20, 30) was added to the milled ZrC-SiC-HfB₂. The mixed powders were pressed and sintered at 2200 °C for 2 h. The microstructure and mechanical properties of the specimens were investigated by Scanning Electron Microscope (SEM) equipped with EDS spectroscopy, XRD analysis and hardness and toughness tests. The ablation resistance of the composites was performed by oxyacetylene torch. The results showed that as the carbon fiber content was increased, the porosity and toughness were increased as well, while the hardness and density were decreased. During the ablation test, the outer surface of the composite underwent a sintering process and formed a dense layer of Zr-Hf-Si-O on the surface. ZrSiO₄ and HfSiO₄ were also created after cooling, so these phases played a pinning effect and prevented the crack propagation. The results also showed that linear and mass ablation rates were increased with increasing the weight percentage of the carbon fiber. SEM analysis with EDS further revealed that with increasing the carbon content, the defects in the formed oxide layer on the composite surface were increased due to the evaporation of SiO₂ and the decrease in the pinning effect of ZrSiO₄ and HfSiO₄ phases as well as the phase transformation of the remained ZrO₂ and HfO₂. As a result, as the carbon fiber was increased, the ablation resistance of the composite was decreased.

1. Introduction

C/C and C/SiC composites because of good thermo-mechanical properties, low thermal expansion, low density and good thermal shock resistance currently used in aerospace applications. In C/C composites the carbon fibers are oxidized below 500 °C, Whereas in C/SiC or SiC/SiC the SiO₂ protective layer prevents the oxidation of SiC matrix up to 1650 °C [1–3]. Several approaches have been used to increased ablation and oxidation resistance of these composites as follow:

The reinforcing of C/C composites with UHTC particles.

The coating of C/C composites with a layer of UHTC phase [4, 5].

However, all the mentioned approaches introduce only a little amount of the UHTC particles in the matrix. The materials used in temperature protection systems (TPS) need to be stable at high temperature oxidation (>2000 °C). So, there has been a growing demand for advanced structural materials with sustainability at high temperatures [6]. Recently, the ultra-high temperature ceramics (UHTCs) used in temperature protection systems and other components of hyper sonic aerospace vehicles have attracted much attention [7, 8]. UHTCs are carbides, nitrides and borides of group IV and V transition metals such as ZrB₂, HfB₂, ZrC, TaC, HfC, HfN and ZrN [9]. Zirconium carbide (ZrC) is an extremely hard and refractory ceramic material due to its high melting point (3420 °C), it has been placed in the UHTCs class [10]. ZrC, like other compounds of this class, has interesting properties such as high corrosion resistance to acidic and alkaline environments, low thermal conductivity (20.5 Vm⁻¹ K⁻¹), high electrical conductivity (78 × 10⁻⁶ Ω cm) due to the presence of metal bands, high hardness (25 GPa) owing to the presence of strong ZrC covalent bonds, great young module (440 GPa),...
lower density, as compared with other transition metal carbides like WC, TaC or HfC, mechanical strength in corrosive environments even at temperatures higher than 3000 °C and suitable dimensional stability at high temperatures (1900 °C–2500 °C) [11–13]. The main drawback of all the transition metal borides and carbides, are their poor oxidation resistance. ZrC oxidation begins at the low temperature of about 600 °C, depending on the partial pressure of oxygen. A dense layer of C-ZrO2 is formed preventing further carbon oxidation in the ZrC matrix. At temperatures above 800 °C, when the partial pressure of oxygen is increased, ZrC is rapidly oxidized to monoclinic or tetragonal ZrO2. As a result, a porous and cracked layer is formed on the surface [14]. One way to improve the oxidation and ablation resistance of ZrC is to prepare composites with additives such as ZrB2, SiC or silicids to prevent the diffusion of oxygen through the formation of the B2O3 layer filled with ZrO2 or the formation of a SiO2 or ZrSiO4 protective layer [15]. Researches have also shown that by increasing SiC the strength and toughness of ZrC ceramics can be improved; however, it does not influence the hardness and elasticity modulus [15]. Adding a higher capacity cation is another way to improve the oxidation and ablation resistance of ZrC ceramics. The addition of higher capacity cations causes the oxygen vacancies in ZrO2 to be filled, resulting in the stability of the ZrO2oxide layer in the tetragonal structure. Also, the addition of higher capacity cations increases the viscosity of the glass phase, thereby raising the glass boiling point [10]. Another drawbacks of UHTCs are their low fracture toughness and high density. Simple method is proposed to fabricate UHTC based composites with short carbon fibers as both a reinforcing and mass-lightening phase [16]. Some works have been done on UHTCs reinforced with carbon spheres or short fibers [17–21]. There are few works concerning the performance of UHTC-rich matrix under oxidizing atmospheres. Sciti and Zoli have successfully obtained carbon fiber reinforced UHTCs via slurry infiltration and hot pressing [22, 23]. Preliminary studies on these materials have shown their promising mechanical properties and oxidation resistance at 1500 °C [24]. Recent studies on the kinetics of oxidation of a carbon fibre reinforced ZrB2 composite doped with 10 vol% SiC have shown that the critical temperature for these composites is below 1000 °C [25]. Silvestroni studied ablation properties of functionally graded composite based on ZrB2 with 0–50 vol% of short carbon fibers at 2500 °C under oxyacetylene torch for 60 s [16]. Elsewhere, ZrB2/SiBCN composites containing carbon fibers coated with BN were prepared using combination of sol-gel and spark
plasma sintering (SPS) techniques by Miaoa et al. Theses researchers compared ablation behavior of ZrB$_2$/SiBCN with and without Cfs for 10−30 s under oxyacetylene torch [26]. Inoue et al studied architecture of the carbon fibers on the oxidation behaviors of the composites by oxidation tests by an oxyhydrogen burner at 1700 °C for 10 min. The experimental results showed that the oxidation of both composites significantly depended on the microstructural parameters and properties of the constituent materials [27]. The effect of short carbon fiber addition on the oxidation behavior of the ZrB$_2$–20vol%SiC–2vol%B$_4$C composite studied by Das et al. Oxidation study was carried out at 1600 °C for 2 h. After the oxidation test, the carbon fiber reinforced composite showed formation of SiO$_2$ rich, continuous and protective top layer of about 30 μm. On the other hand, the base composite showed the formation of a discontinuous SiO$_2$–rich top layer of about 20–30 μm after the same oxidation treatment [28].

Figure 2. SEM images of (a) ZSH0, (b) ZSH10, (c) ZSH20, (d) ZSH30, (e) and (f) high magnification of (c) and (d) of mixed powders after ball milling.
Also, it has been shown that HfB₂ and HfO₂ have higher oxidation resistance and melting point than ZrB₂ and ZrO₂. There is still no literature on the ablation behavior of ZrC-SiC-HfB₂ composites reinforced with carbon fibers. In this study, therefore, a carbon fiber reinforced ZrC-20 vol% SiC-15 vol% HfB₂ composite with different weight percentages of fiber, from 0% to 30%, was fabricated by the pressureless sintering method (PLS). The main purpose of this paper was, in fact, to study the ablation resistance of the prepared composite.

2. Material and methods

In this research, a carbon fiber reinforced ZrC-20 vol% SiC-15 vol% HfB₂ composite was prepared by the pressureless sintering method. Accordingly, ZrC powder with the particle size less than 10 μm was used as the matrix. SiC (<4 μm), HfB₂ (<5 μm), and chopped carbon fibers (with 1.5 μm diameter and the average length of 1 mm) were used as the reinforcement. The SEM images of the raw materials used in this study are shown in figure 1. Initially, the raw materials were milled by planetary ball mill using zirconium balls and ethanol. 1 ml of ethanol was added for every 5 g of powders. The ball to powder weight ratio was 10:1 and the speed of ball milling was set at 200 rpm for 3 h. The carbon fibers (0, 10, 20 and 30 wt%) were then added to the ZrC-20 vol% SiC-15 vol% HfB₂ slurry, and again ball milled for 3 min to obtain a homogeneous mixture. The obtained slurry was then dried in an oven. After that, the mixture was compressed at a pressure of 30 MPa using the uniaxial press. The specimens were then compressed at a pressure of 200 MPa using CIP to increase the green body strength. The pressureless sintering process was also carried out in a high-temperature graphite furnace at 2200 °C under an argon atmosphere for 2 h with heating and cooling rates of 10 °C min⁻¹. In the present work, the prepared composites were labeled as ZSH0, ZSH10, ZSH20 and ZSH30.

2.1. Ablation test

The oxyacetylene ablation test was used to determine the ablation resistance of the specimens. The oxyacetylene flame was consisted of a mixture of oxygen and acetylene gases with a pressure of 1.6 bar and 2 bar, respectively; also the oxygen and acetylene gas flow rates were 1 Nm³ h⁻¹ and 2 Nm³ h⁻¹, respectively. The surface of the specimens was vertically exposed to the flame up to 3000 °C at a distance of 10 mm of the nozzle tip. The test time was 60 s and the surface temperature of the samples was measured using an infrared thermometer. After the ablation test, the samples were cooled at room temperature. The ablation efficiency was measured based on the linear ablation rate and the mass ablation rate. The mass and thickness of the samples were determined before and after the ablation test.

Figure 3. X-ray diffraction of (a) ZSH0, (b) ZSH10, (c) ZSH20 and (d) ZSH30 composites.
The formulas of the mass ablation rate ($R_m$) and the linear ablation rate ($R_l$) were as follows:

$$R_m = \frac{(m_0 - m_t)}{t}$$

$$R_l = \frac{(l_0 - l_t)}{t}$$

Where $m_0$ and $l_0$ are the mass and thickness of the samples before the ablation test, respectively, and $m_t$ and $l_t$ are the mass and thickness of the samples after the ablation test, respectively; also, $t$ is the time of the ablation test.

Figure 4. SEM images of (a) ZSH0, (b) ZSH10, (c) ZSH20 and (d) ZSH30 composites after sintering.
2.2. Characterization

In order to obtain the bulk density and the amount of open porosity, the Archimedes principle was used. The formulas used were as follows:

\[
\frac{1}{D} = \frac{1}{M_{1}} - \frac{1}{M_{2}} - \frac{1}{M_{3}}
\]

Where \( P \) is the open porosity of the sample, \( D \) is the density of the sample, \( M_{1} \) is the weight of the dried sample, \( M_{2} \) is the weight of the immersed sample in water and \( M_{3} \) is the weight of the wet sample. The average results of

![Figure 5. Agglomeration of carbon fibers in (a) ZSH10, (b) ZSH20 and (c) ZSH30 composites.](image)

| Sample  | Theoretical density (g cm\(^{-3}\)) | Relative density (g cm\(^{-3}\)) | Bulk density (g cm\(^{-3}\)) | Open porosity (%) | Hardness (GPa) | Toughness MPa m\(^{1/2}\) |
|---------|-------------------------------------|----------------------------------|-----------------------------|-------------------|----------------|---------------------|
| SZH0    | 6.69                                | 95.6                             | 6.4                         | 3.8               | 12.3           | 4.2                 |
| SZH10   | 5.37                                | 91.4                             | 4.91                        | 5                 | 11.2           | 4.6                 |
| SZH20   | 4.59                                | 89.5                             | 4.11                        | 7.6               | 10.4           | 4.7                 |
| SZH30   | 4.12                                | 87.2                             | 3.59                        | 8                 | 8.6            | 4.9                 |

| Sample  | Ablation time (s) | Ablation surface temperature (°C) | Liner ablation (mm/s) | Mass ablation (g/s) |
|---------|-------------------|----------------------------------|----------------------|---------------------|
| SZH0    | 60                | 2873                             | 1.64 \times 10^{-4}  | 1.73 \times 10^{-4} |
| SZH10   | 60                | 2826                             | 1.05 \times 10^{-5}  | 1.22 \times 10^{-5} |
| SZH20   | 60                | 2822                             | 2.49 \times 10^{-5}  | 1.62 \times 10^{-5} |
| SZH30   | 60                | 2810                             | 3.51 \times 10^{-5}  | 2.46 \times 10^{-5} |

Table 1. The compositions, densities and mechanical properties of the composites.

Table 2. Linear and mass ablation rates of the composites after ablation.
the three samples were selected as the final result. According to the law of mixtures, theoretical density values for the composites was calculated. In order to calculate the theoretical density values of the composites, the values of 6.73 g cm\(^{-3}\), 3.22 g cm\(^{-3}\), 10.2 g cm\(^{-3}\), and 1.8 g cm\(^{-3}\) were used as the density of ZrC, SiC, HfB\(_2\) and carbon fiber (Cf), respectively. The crystalline phases were identified by x-ray diffraction (XRD). A scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) was also used to investigate the morphology and microstructure of the samples before and after the ablation test. The hardness of the composites was measured by the Vickers method, according to the ASTM 0327-08. The standard applied load was 2 kg with the holding time of 10 s on the polished surface. The fracture toughness (\(K_{IC}\)) was measured by the direct crack measurement method (DCM), using the Vickers indentor and the applied load was 30 kg with the holding time of 15 s.

3. Results and discussion

Figure 2 shows the scanning electron microscope image of the mixed powders used for composite preparation after ball milling for 3 h. As shown in figure 2, the particle size of the powder decreased after ball milling for 3 h. Also, after the addition of chapped carbon fibers and ball milling for 3 min, the fiber length was decreased by 200 \(\mu\)m, but the fibers were not damaged.

It was found that the chapped fibers were randomly and uniformly dispersed in the powders without any clumps in the resulting mixed powders. The absence of the clumps fibers suggested that the short fibers were uniformly dispersed in the matric slurry after ball milling. This indicated that the mixing method used in this study was effective in uniformly dispersing short fibers in ceramic slurry, although the mixing time was very short (only 3 min). Short mixing time greatly reduced the damage to the fibers.

Figure 3 shows the XRD patterns of the prepared composites. In all samples there were peaks associated with ZrC, SiC and HfB\(_2\) phases. No additional phases were formed during the sintering process.

Figure 4 shows the SEM images of the polished cross-section of the composites are shown. According to XRD and EDS, it shown that the light phase was ZrC, and the light gray phase and the dark gray phase were HfB\(_2\) and SiC, respectively. The isolated pores were formed and uniformly distributed in the ZrC matrix. EDS results revealed the presence of chapped fibers in the ZrC matrix.

On the other hand, with the increase of carbon fiber in each composition, agglomeration of fiber increases (figure 5) and this prevents complete sinterability of composites. According to figure 5(c), it could be seen that the length of the fibers on the polished cross-section of the composite was less than that of the primary fibers. In
other words, it indicated that the length of the fibers was changed after the ball milling and pressing process. The reduction in the fiber length can be explained as follows:

First, the fibers were broken during the ball milling process. Second, some fibers were broken due to the volumetric shrinkage of the green body during the pressing process [21].

In table 1, the measured densities and mechanical properties of the dense composites made by the pressureless sintering method are presented. As can be seen, by increasing the carbon fiber, the porosity was increased. The porosities were derived from the difference of thermal expansion coefficient (CTE) between the carbon fiber, SiC and HfB$_2$ and ZrC matrix [29].

The mismatch between the matrix and the reinforcement phase caused tensile and compressive stresses in the matrix and the second phase. These stresses caused the separation of the matrix/reinforcement interface, as a result, porosity was created. On the other hand, as the carbon fiber was increased in the composite, agglomeration was also increased (figure 5); as a result, complete sintering of the composites was prevented.

Density was also decreased with the increase in the carbon fiber content. Two main reasons for the decrease in relative density are as follows:

1. Agglomeration of primary powder particles during ball milling accelerated coarse aggregation before densification was complete.

When the carbon fibers were agglomerated and separated at the grain boundaries, the diffusion at the grain boundaries was prevented.
boundaries was decreased; in other words, the diffusion at the ZrC grains was increased. Therefore, when large amounts of the carbon fiber was used, the grain growth was increased.

(2) In the presence of oxide impurities, densification was prevented.

As can be seen, slight changes in the hardness were seen as a function of the amount of the short carbon fiber. A similar result has also been observed in other research [29]. Furthermore, sintered composites showed that fracture toughness was improved due to the use of the carbon fibers in the composite matrix (table 1). Composite fracture toughness changed in the range of 4.2–5.4 MPa m$^{1/2}$, when the amount of the fiber was varied from 0 to 30%. Obviously, this improvement was related to the deflection or bridging of the crack.

Table 2 presents the linear and mass ablation rates of the samples after ablation. The rate of ablation could be controlled by the oxidation reactions of C [30, 31], ZrC [31], SiC [32–36], HfB$_2$ [37] and the diffusion of oxygen through the surface [38]. The linear and mass ablation rates of the samples showed possess similar variations [39]. As the carbon fiber content was increased, the composites showed higher linear and mass dissipation rates due to the higher percentage of carbon fiber and porosity [38,40–44].

As the amount of the carbon fiber was increased, the porosity in the composite was increased, so the channels of oxygen penetration into the matrix were increased. As a result, the endothermic oxidation reactions were accelerated and the surface temperature was decreased after ablation. In the first stage, ZrC and HfB$_2$ were

Figure 8. Surface morphologies and EDS analysis of ZSH10 composite in the ablation (a) center, (b) transition and (c) brim region after ablation.
oxidized; therefore, an increase in the composite weight was expected. However, the severe evaporation of SiO2 and burning carbon fiber played an important role in determining the weight loss.

Figure 6 shows the XRD patterns of the composite after ablation. It can be seen that all patterns were similar and the major oxides were ZrO2 and HfO2. The melting point of ZrO2 and HfO2 is 2810 and 2800 °C, respectively [18]. It indicates that the dissipation of ZrO2 and HfO2 was low during ablation.

In the XRD patterns, no diffraction peaks related to SiO2 were observed. The melting point of SiO2 is about 1673 °C, showing that SiO2 was melted and evaporated during ablation. Also, scouring flame was high which could easily spread SiO2 around. In addition, the samples were cooled rapidly at room temperature after ablation and prevented the crystallization of SiO2. At the same time, in the XRD pattern, some diffraction peaks of HfSiO4 and ZrSiO4 could also be observed [45]. In the XRD patterns of ZSH0, no carbon peak was observed, which means that the surface of the sample was well covered by ZrO2 coating and no carbon material was burnt [39].

Three regions could be found on the ablated surface of the composites: center region, transition region and brim region.

The SEM images of the composites surface after ablation are shown in figures 7–10. It can be seen that the grains were interconnected. The stacked oxide particles began to sinter at the ablation temperature [46]. During the sintering process, a dense layer was formed on the surface which could prevent oxygen penetration. In addition, this structure was derived from the high melting points of HfO2 and ZrO2 and their high viscosity and resistivity to the spread particles at the high flux of the oxyacetylene flame; these prevented to help the surface from burning and oxidizing [47].
However, there were still some pinholes distributed on the surface. These pinholes were generated by the evaporation of gases generated by oxygen diffusion channels. In the sample ZSH0, no micro-cracks were observed on the surface; this could be related to the new HfSiO4 and ZrSiO4 phases formed during the ablation process [48] (figure 7). EDS analysis (figures 7–10) also showed that the amount of Si was lower than the initial amount in the precursor powder, indicating that some SiO2 formed during the ablation process had been evaporated. In addition, some of the remaining SiO2 could be reacted with ZrO2 and HfO2, generating HfSiO4 and ZrSiO4 stable phases; so, these could play the pinning effect to prevent cracking [49].

The formation of the porous oxide layer was related to the generation of SiO, CO2, CO and B2O3 gases, as well as the active oxidation of SiC and the carbon fiber.

Increasing the amount of carbon fiber in the composite increased the porosity and consequently, oxygen penetration into the matrix, leading to the production of more gaseous products. According to the EDS analysis of the ablated carbon fiber in the composite, this may lead to further reduction in the generated HfSiO4 and ZrSiO4, resulting in the weakening of the pinning effect.

In addition, the remaining ZrO2 and HfO2 can undergo a phase transformation during the cooling process leading to the formation of cracks due to the volumetric effect [50–52]. Furthermore, cracks could appear due to the CTE mismatch of the ablation layer and the composite matrix [52]. These resulted in increasing the porosities and cracks in the oxide layer formed on the composite surface during the ablation process. With

![Figure 10. Surface morphologies and EDS analysis of ZSH30 composite in the ablation (a) center, (b) transition and (c) brim region after ablation.](image-url)
increasing the porosity in the composite and enhancing oxidation reactions, the partial pressure of oxygen in the ablation environment was decreased. This could encourage the active oxidation of SiC and the coarser porosities formed in the oxide layer [6].

In general, these defects became transition channels for the oxidizing species thereby increasing the composite ablation.

SEM images of the ablated cross-section of the composite with different percentages of the carbon fiber in the three ablation zones are shown in figures 11–14.

Although the ablation surface temperature is lower than the melting temperature of HfO₂ and ZrO₂, the SiO₂ product in HfO₂ and ZrO₂ could cause the lower melting point of HfO₂ and ZrO₂. It resulted in a continuous field consisting of oxide (HfO₂ and ZrO₂) and carbide (ZrC) compounds in which HfO₂ and ZrO₂ grains were scattered (figure 6).

The dense structure also revealed that the oxide layer containing oxide and carbide particles effectively acted as a layer against heat and prevented further oxidation of the matrix.

SEM images of the ablation cross-section of the sample ZSH10 (figure 12) showed that due to the relatively high surface temperature, the oxide layer was sintered and some porosity and micro-cracks were observed. These defects were caused by the evaporation of SiO₂ and the decrease in the pinning effect of HfSiO₄ and ZrSiO₄ phases.

SEM images of the ablation cross-section of the sample ZSH20 (figure 13) showed that the oxide grains were stacked together with clear boundaries and the structure of the stacked grains was loose. The cracks and pinholes in the oxide layer were generated by the gaseous products, and the severe evaporation of SiO₂ created channels for the penetration of oxygen into the matrix, which could not be beneficial to prevent the passage of oxygen.

The cross-section of the sample ZSH30 oxide layer, as shown in figure 14, represented a coral-like oxide structure consisting of ZrO₂, HfO₂ and ZrC formed after the ablation.

According to figure 14, the oxidation layer was loose and brittle with a number of pores and spalls. Thus, one would expect a lack of proper adhesion between the oxide layer and the composite, so it could not effectively prevent base oxidation.
3.1. Ablation mechanism

The ablative behavior of the composite can be described by the following three processes:

1. Oxidation of matrix, ZrC, SiC, HfB$_2$ and carbon fiber.
2. Oxygen penetration through oxide species.
3. Evaporation of SiO$_2$.

Depending on the XRD patterns, the following chemical reactions might occur:

\[
\begin{align*}
2 \text{ZrC}(s) + 3\text{O}_2(g) & \rightarrow 2\text{ZrO}_2(s) + 2\text{CO}(g) \\
2\text{SiC}(s) + 3\text{O}_2(g) & \rightarrow 2\text{SiO}_2(1) + 2\text{CO}(g) \\
2\text{HfB}_2(s) + 5\text{O}_2(g) & \rightarrow 2\text{HfO}_2(s) + 2\text{B}_2\text{O}_3(s) \\
2\text{C}(s) + \text{O}_2 & \rightarrow 2\text{CO}(g) \\
\text{C}(s) + \text{O}_2(g) & \rightarrow \text{CO}_2(g) \\
\text{SiO}_2(1) & \rightarrow \text{SiO}_2(g) \\
\text{B}_2\text{O}_3(1) & \rightarrow \text{B}_2\text{O}_3(g) \\
\text{HfO}_2(s) + \text{SiO}_2(1) & \rightarrow \text{HfSiO}_4(s) \\
\text{ZrO}_2(s) + \text{SiO}_2(1) & \rightarrow \text{ZrSiO}_4(s) \\
\text{SiO}_2(1) + \text{C} & \rightarrow \text{SiO}(g) + \text{CO}(g) \\
\text{ZrO}_2(s) & = \text{ZrO}_2(1)
\end{align*}
\]
Reactions (1)–(10) can occur in all regions of the ablation surface, and the reactions (11) and (12) may occur in high temperature regions, especially in the surface ablation layer [53]. When ablation begun, the carbides, HfB$_2$ and C were oxidized, forming a Zr-Si-Hf-O layer on the surface. A massive amount of gaseous products was developed by carbon fiber, ZrC, HfB$_2$ and SiC oxidation reactions (reactions (1)–(5)). Also, SiO$_2$ (l) and B$_2$O$_3$ (l) were transformed to gaseous products that were rapidly evaporated to CO (g) and CO$_2$ (g) (reactions (6) and (7)). In addition, the reaction (10) also occurred at the high temperature ablation.

Release gaseous products at all stages of ablation represent an endothermic process absorbing heat. This could result in lower surface temperatures [54]. The higher mass and linear ablation rate of the composite caused the higher evaporation of the gaseous products, resulting in the increased composite porosity, more oxygen penetration to the base; then, with the increase in carbon fiber, oxidation reactions are accelerated [54]. Due to the oxidation of carbon fibers and the matrix and evaporation of gaseous products, a porous oxide species was formed on the surface.

According to the HfO$_2$-ZrO$_2$ binary phase diagram, HfO$_2$ could form a continuous solid solution with ZrO$_2$ in the heating process, so it could accelerate the sintering process [54, 55].

In addition, SiO$_2$ could react with HfO$_2$ and ZrO$_2$ (reactions 8 and 9), forming the new stable phases HfSiO$_4$ and ZrSiO$_4$ during the cooling process, which could prevent the propagation of cracks. However, with the increase of the carbon fiber in the composite, oxide species were formed with further and larger pinholes and a large number of micro-cracks on the surface due to the phase transition of HfO$_2$ and ZrO$_2$ and further reduction of SiO$_2$. 

$$\text{HfO}_2(s) = \text{HfO}_2(1)$$  \hspace{1cm} (12)
4. Conclusions

ZrC-SiC-HfB₂ composites with different weight percentages of carbon fiber were prepared by free pressureless sintering at 2200 °C for 2h. As the amount of carbon in the composite was increased, the porosity and toughness were improved, while hardness and density were declined. The ablation characteristic of the composites was investigated with an oxyacetylene torch for 60s. The rates of linear and mass ablation were raised with increasing the carbon content. Structural evaluation of the formed oxide layer also showed that a dense layer was formed on the composite surface. Due to the reaction of SiO₂ with ZrO₂ and HfO₂, stable phases of ZrSiO₄ and HfSiO₄ were formed. With increasing the carbon content, the defects were increased on the oxide layer surface and the Si element was decreased. Thus, by reducing the amount of ZrSiO₄ and HfSiO₄ phases, due to the locking effect and the phase transformations of the remained ZrO₂ and HfO₂, the crack formation in the Zr-Hf-Si-O oxide layer was increased. As a result, oxygen penetration channels to the composite were increased and the ablation resistance of the composite was decreased with increasing the carbon fiber content.

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