Mechanical and oxidation behavior of spark plasma sintered ZrB$_2$–ZrC–SiC composites

Ipek AKIN and Gultekin GOLLER$^1$

Istanbul Technical University, Department of Metallurgical and Materials Engineering, 34469 Maslak Istanbul Turkey

ZrB$_2$–ZrC–SiC composites were prepared by spark plasma sintering (SPS) at temperatures of 1750°C for 300 s under a pressure of 40 MPa. Densification, microstructural, mechanical properties and oxidation behavior of the composites were investigated. Fully dense ZrB$_2$–ZrC–SiC composites with a relative density of more than 99% were obtained at 1750°C for 300 s. Vickers hardness of ZrB$_2$–ZrC–SiC composites decreased with increasing ZrC content from 20 to 40 vol %, and composite containing 60 vol % ZrB$_2$, 20 vol % ZrC and SiC sintered at 1750°C for 300 s had the highest value of 21.1 GPa. The crack mode for the same composite was zigzag, and resulted in remarkable crack deflections and the highest fracture toughness value of 5.5 MPa·m$^{1/2}$. Oxidation of composites resulted in formation of protective layered oxide structures consisted of ZrO$_2$ and Si–O rich layer in the form of SiO$_2$ or SiO, and normalized mass change results increased with increasing oxidation temperature.

©2012 The Ceramic Society of Japan. All rights reserved.

Key-words : Sintering, Carbides, Mechanical properties, Densification

1. Introduction

Diborides and carbides of zirconium belong to a class of materials with extremely high melting temperatures, and defined as ultra-high temperature ceramics. Zirconium diboride (ZrB$_2$) is a candidate material of this group because of its high melting temperature (3027°C), high hardness (23 GPa), low theoretical density (6.1 Mg/m$^3$), high thermal (60–120 W/mK) and electrical (~10$^7$ S/m) conductivity and excellent chemical and physical stability at high temperatures.$^{1,2}$

ZrB$_2$–SiC composites are known to have higher strength, fracture toughness and oxidation resistance than monolithic ZrB$_2$, and the addition of SiC particles has been found to improve the oxidation resistance and fracture toughness of ZrB$_2$.3–5) Also, studies have shown that the addition of both SiC and ZrC increased the strength and fracture toughness of ZrB$_2$.5,6) However, fully dense composites without sintering additives have been hardly obtained because of high melting temperature and strong covalent bonding of ZrB$_2$, SiC and ZrC.1–3)

Spark plasma sintering (SPS) makes possible to densify ZrB$_2$–ZrC–SiC composites at a lower temperature and in a shorter time compared with conventional techniques.$^{1,7}$–10) In the SPS technique, a pulsed direct current passes through graphite punch and dies simultaneously with a uniaxial pressure. Thus, the grain growth can be suppressed by rapid heating and the densification is accelerated at high temperature. Furthermore, the microstructure can be controlled by a fast heating rate and shorter processing times.$^{2,7}$–11)

Ternary ceramic composites of ZrB$_2$–ZrC–SiC have been prepared by several researchers using spark plasma sintering,$^{1,2,14}$ hot-pressing, and reactive hot-pressing.$^{3,5}$ However, comparatively, there have been few studies on the ternary spark plasma sintered composites consisted of high amount of ZrC.

In this study, ZrB$_2$–ZrC–SiC composites having high amounts of ZrC were produced using SPS method at different compositions, and densification, microstructural, mechanical properties and oxidation behavior of the composites were characterized.

2. Experimental procedure

ZrB$_2$ (Grade B, H.C. Starck Corp., an average particle size of 2 μm), ZrC (Grade B, H.C. Starck Corp., an average particle size of 2 μm) and α-SiC (Grade UF-10, H.C. Starck Corp., an average particle size of 1 μm) powders were used as starting materials (Table 1). Throughout the text, samples were designated by their component volume fractions; for example, the designation of 603010 indicates a composite with ZrB$_2$, ZrC and SiC volume fractions of 60, 30 and 10%, respectively. The raw materials were weighed in appropriate quantities, ball milled in ethanol for 24 h and then dried.

A graphite die 50 mm in inner diameter was filled with the mixture, followed by sintering using SPS apparatus (SPS-7.40 MK-VII, SPS Syntex Inc.) at 1750°C for 300 s with a heating rate of 100°C/min in a vacuum. The entire sintering processes completed in 25 min including 300 s holding time. A uniaxial pressure of 40 MPa and a pulsed direct current (12 ms on, 2 ms off) were applied during the entire SPS process.

The temperature of the die was measured by an optical pyrometer and sintering of composites was conducted under temperature controlled mode by monitoring the shrinkage behavior of the specimens during SPS process. The crystalline phases were identified by X-ray diffractometry (XRD; MiniFlex, Rigaku Corp.) in the 2θ range of 10–80° with Cu Kα radiation. The bulk densities of the specimens were determined by the Archimedes’ method and converted to relative densities according to the Eq. (1):

$$D_R = \left( \frac{D_R}{D_T} \right) * 100$$

where $D_R$ is the relative density, $D_B$ is the bulk density (Mg/m$^3$) of the sintered sample, and $D_T$ is the theoretical density (Mg/m$^3$) of the composite. The value of theoretical density depends on the composition and calculated using theoretical densities and volume fractions of ZrB$_2$ (6.1 Mg/m$^3$), ZrC (6.7 Mg/m$^3$) and SiC (3.2 Mg/m$^3$).
The fracture surfaces of the specimens were observed by scanning electron microscopy (FESEM; JSM7000F, JEOL Ltd.), Vickers hardness \((H)\) was measured under loads of 9.8 N and fracture toughness \((K_{IC})\) was evaluated by a microhardness tester (VHMOT, Leica Corp.), under loads of 19.6 N from the half-length of a crack formed around the indentations by using the following equations.

\[
K_{IC} = 0.016(E_c/H)^{1/2}(P/c^{3/2})
\]

(2)

\[
K_{IC} = 0.028H^{1/2}(E_c/H)^{1/2}(c/a)^{-3/2}
\]

(3)

\[
K_{IC} = 0.0309(E_c/H)^{1/2}(P/c^{3/2})
\]

(4)

Eq. (2) was derived from Anstis et al.\(^{15}\) which is based on the results of Lawn et al.\(^{16}\) Eq. (3), Equation (4) was derived from Niihara et al.\(^{17}\) for \(c/a \geq 2.5\) median cracks. In these equations, \(E_c\) is Young’s modulus (GPa) of composites calculated assuming a mixture rule, \(H\) is Vickers micro-hardness (GPa), \(P\) is load (N), \(c\) is half of the average crack length, and \(a\) is half of the average diagonal length of indentation.\(^{15-17}\) The average value of the 20 measurements for each sample was used for the evaluations of hardness and toughness.

In the oxidation studies, ZrB\(_2\)–ZrC–SiC composites were exposed to stagnant air at temperatures of 1400, 1500 and 1600°C for 180 min. The samples with size of 12 mm \(\times\) 7 mm \(\times\) 6 mm were heated and cooled at 10°C/min. A MoSi\(_2\) resistance-heated furnace (Nabertherm C42) was used to heat the samples. Sample weights were measured before and after oxidation and the dimensions were measured to \(0.01\) mm to calculate the surface area of the samples during SPS process was indicated a dense microstructure and the morphology of the phases, respectively. The distribution of the grains was homogenous which was consistent with previous studies.\(^{2,5,6}\) The grain size of ZrC and ZrB\(_2\) were similar, about 2–4 \(\mu m\), whereas that of SiC was smaller, which was about 1 \(\mu m\). The fracture surface of the ZrC particles showed features of cleavage and the effect of this structure on the mechanical properties of the composites will be discussed in the following section.

### 3. Results and discussion

#### 3.1 Densification behavior and crystalline phases

The densification of the specimens during SPS process was evaluated by the displacement of punch rods due to the shrinkage of the composites. **Figure 1** shows the displacement of ZrB\(_2\)–ZrC–SiC composites of 603010, 603020, 503020 and 504010 at 1400–1750°C and isothermal shrinkage at 1750°C for 300 s. The shrinkage of the composites started below 1400°C. The shrinkage completion temperature for 504010 composite was higher than that of other composites. For the 603010 and 602020 composites, shrinkage completed at 1730°C, for the composites of 503020 and 504010, shrinkage completion temperatures were determined as 1720 and 1750°C, respectively.

The highest shrinkage (2.69 mm) was observed for the composites containing 60 vol % ZrB\(_2\), 20 vol % ZrC and SiC (602020) at temperatures between 1400 and 1750°C. For the same temperature interval, the shrinkages were 2.47, 2.34 and 2.20 mm for the composites 504010, 603010 and 503020, respectively. So, the highest rate of shrinkage was observed for the 602020 composites.

A relative density of more than 99% was obtained for the composites sintered at 1750°C for 300 s. The density results (Table 1) were in agreement with the shrinkage results presented in Fig. 1.

**Figure 2** shows the XRD patterns of ZrB\(_2\)–ZrC–SiC composites sintered at 1750°C for 300 s. Characteristic peaks of ZrB\(_2\) (JCPDS: 65-3389), ZrC (JCPDS: 65-8704) and α-SiC (JCPDS: 49-1428) were identified and no chemical reaction was detected between phases for all compositions at 1750°C.

#### 3.2 Microstructure

**Figure 3** shows cross section of ZrB\(_2\)–ZrC–SiC composites sintered at 1750°C for 300 s, where black areas represents the SiC particles, darker and lighter gray areas show ZrB\(_2\) and ZrC phases, respectively. The distribution of the grains was homogenous for all composites. The fracture surface morphology indicated a dense microstructure and the morphology of the grains was mainly equiaxed which was consistent with previous studies.\(^{2,5,6}\) The grain size of ZrC and ZrB\(_2\) were similar, about 2–4 \(\mu m\), whereas that of SiC was smaller, which was about 1 \(\mu m\). The fracture surface of the ZrC particles showed features of cleavage and the effect of this structure on the mechanical properties of the composites will be discussed in the following section.

#### 3.3 Hardness and fracture toughness measurements

Table 1 summarizes the effect of composition on the Vickers hardness and fracture toughness of the ZrB\(_2\)–ZrC–SiC composites at load of 9.8 and 19.6 N. The ranges of hardness were...
measured to be as 19.6–21.1 GPa. In the case of the same amount of ZrB₂ (50 vol%) containing composites (504010 and 503020), the hardness values were 19.6 and 20.4 GPa, respectively. The hardness of the composites increased with increasing ZrB₂ as well as SiC content, but decreased with increasing ZrC addition. The sample containing 60 vol% ZrB₂ and same amounts of ZrC and SiC (602020) had higher hardness than the others. The hardness of the composites decreased from 21.1 to 19.6 GPa when the amount of ZrC increased from 20 to 40 vol%.

Cao et al.⁴ produced ZrB₂–40ZrC–12SiC (vol%) composition at 1800°C with a holding time of 10 min by the combination of self-propagating high temperature synthesis (SHS) and spark plasma sintering technique, and reported the Vickers hardness as 16.9 GPa. It is obvious that the hardness result obtained in this study is similar. The hardness of the ZrB₂–20SiC–6.05ZrC (vol%) composite prepared by reactive hot pressing at 1750 and 1900°C by Qiang et al.⁷ were 14 and 19.8 GPa, respectively. Qu et al.⁵ have prepared the same composition by hot pressing and reported a relative density of 98% and hardness of 19 GPa. Wu et al.⁶ have studied ZrB₂–20SiC–6.4ZrC (vol%) composites produced by reactive hot pressing. They have reported relative density of 97% and hardness of 16.7 GPa. In another study, Qiang et al.¹³ have prepared ZrB₂–20SiC–6.05ZrC (vol%) with raw materials of Zr–B₄C–Si through the gradual heating in situ reactive processing by using hot pressing at 1900°C for 60 min and reported a relative density of 99.6% and hardness of 20.2 GPa. ZrB₂-based composites prepared by spark plasma sintering technique in this study exhibited higher hardness than those prepared by conventional sintering.

For a full dense composite, Young’s modulus of the composite can be described by the rule of mixture as follows:

$$E_c = \sum_{i=1}^{n} E_i \cdot f_i$$

Fig. 2. XRD patterns of ZrB₂–ZrC–SiC composites of 504010 (a), 603010 (b), 602020 (c), 503020 (d) sintered at 1750°C for 300 s.

Fig. 3. SEM images of fracture surfaces of ZrB₂–ZrC–SiC composites of 603010 (a), 602020 (b), 503020 (c), 504010 (d) sintered at 1750°C for 300 s.
where $E_i$ is Young’s modulus of $i$th constituent phase, and $f_i$ is volume fraction of $i$th constituent phase, and $n$ is total number of constituent phases. With the values of $E_1 = 540$ GPa (ZrB$_2$), $E_2 = 400$ GPa (ZrC), $E_3 = 480$ GPa ($\alpha$-SiC), Young’s modulus of the composites in Eq. (5) yields 478, 492, 500 and 486 GPa for the 504010, 603010, 602020, and 503020 composites, respectively. These theoretical Young’s modulus values for dense structures were multiplied by the relative densities of the composites and calculated values of $E_i$ were used in the measurements of fracture toughness [Eqs. (2)–(4)]. The optimized values of Young’s modulus of composites ($E_1$) were 474.37, 489.34, 498.25 and 483.13 GPa for 504010, 603010, 602020, and 503020 composites, respectively.

The fracture toughness values were in the range of 4.6–5.5 MPa·m$^{1/2}$. The $K_{IC}$ was calculated by the three equations showed almost the same trend, although the $K_{IC}$ calculated from Eq. (4) was the highest. For the samples containing the same amount of ZrB$_2$ (603010 and 602020), fracture toughness was measured as 5.3 and 5.5 MPa·m$^{1/2}$, respectively. For the composites having 50 vol% ZrB$_2$ (504010 and 503020), lower values of fracture toughness were obtained. The results indicated that fracture toughness values increased with increasing ZrB$_2$ and SiC content, but decreased with increasing ZrC content and the lowest fracture toughness was obtained with the highest ZrC containing samples (504010).

The fracture toughness of the composites having 60 vol% ZrB$_2$ were higher than that of the others and the maximum toughness was obtained for 602020 composites at load of 19.6 N.

The $K_{IC}$ of the ZrB$_2$–20SiC–6.05ZrC (vol%) composite prepared by reactive hot pressing at 1750 and 1900°C by Qiang et al.18) were 5.6 and 6.5 MPa·m$^{1/2}$, respectively. Qu et al.23) have prepared the same composition by hot pressing and reported a relative density of 98% and fracture toughness of 5.6 MPa·m$^{1/2}$. Wu et al.9) have studied ZrB$_2$–20SiC–6.4ZrC (vol%) composites produced by reactive hot pressing. They have reported relative density of 97% and fracture toughness of 5.1 MPa·m$^{1/2}$. Guo et al.24) have studied the spark plasma sintered ZrC–ZrB$_2$–SiC composites with different compositions and reported the hardness and fracture toughness values in the range of 18.8–21.5 GPa and 4.6–6.1 MPa·m$^{1/2}$, respectively. Cao et al.25) reported the fracture toughness of ZrB$_2$–40ZrC–12SiC (vol%) composition as 5.9 MPa·m$^{1/2}$ prepared by the combination of SHS/SPS technique.

In order to determine the toughening mechanisms, interaction between propagating crack and microstructure was analyzed. The fracture surface of the ZrC particles exhibited features of cleavage as shown in Fig. 3. The cleavage of ZrC particles implied that when the propagating crack met a ZrC particle, the crack most frequently crossed through the ZrC rather than propagated around the particle and this is consistent with the observation on the crack path of 504010 composites as shown in Fig. 4(a).

The crack mode for 602020 composite was more likely to have zigzag crack mode and resulted in a remarkable crack deflections as indicated by white arrows and D in Fig. 4(b). The crack deflection became more severe as more SiC was present in the crack path. For the composites of 504010 and 602020, the crack propagated along the ZrC grains and showed trans-granular tendency. In the SiC phases, crack propagated along the grain-borders and in ZrB$_2$ phases deflected an angle, and thus the crack path became more tortuous [shown as TC in Fig. 4(a)] and according to the crack deflection model,19) the energy consumption increased. The zigzag crack pattern in combination with local crack bridging [shown as CB in Fig. 4(b)] caused by SiC could be the reason of higher fracture toughness of 602020 composite than the others.

The results indicated that both the hardness and fracture toughness of the composites depended on the compositions of the composites. Although some deflections in ZrB$_2$/SiC and ZrB$_2$/ZrC grain boundaries were detected in the composite of 504010, their frequency was so low to be determined the main toughening mechanism as due to crack deflection. Also the propagated crack did not form any deflection in ZrC phases and crack directly propagated through the ZrC phase. So, the fracture toughness values of the composites were prone to decrease with increasing ZrC content. Therefore, the high amount of ZrC could be the reason of lower fracture toughness of this study than the previous studies.12–14,18)

### 3.4 Oxidation studies

Several studies have been done on the oxidation behavior of monolithic ZrB$_2$, ZrB$_2$–SiC system,21–23) and ZrB$_2$–SiC–ZrC(21,23) composites containing 6 vol% ZrC at oxidizing temperatures. In this section, the oxidation behavior of spark plasma sintered ZrB$_2$–ZrC–SiC composites containing high amount of ZrC (20 to 40 vol%) at different temperatures and compositions were investigated.

The oxidation behavior of the ZrB$_2$–ZrC–SiC composites mainly depend on the oxidation behavior of the individual components. At around 800°C, monolithic ZrB$_2$ starts to oxidize and forms an oxide scale composed of crystalline ZrO$_2$ and liquid B$_2$O$_3$ [Eq. (6)].21–23)

$$ZrB_2(s) + \frac{5}{2}O_2(g) \rightarrow ZrO_2(s) + B_2O_3(l) \tag{6}$$
Above 1400°C, the oxidation rate of monolithic ZrB₂ increases and results in a porous, non-protective ZrO₂ and is described with rapid linear kinetics. With the addition of SiC to ZrB₂, the oxidation resistance of the composite above 1200°C increases due to the formation of a SiO₂ rich layer on the exposed surface when SiC part of the composite starts to oxidize [Eq. (7)].

As it is well known, the oxidation of SiC is divided into two regimes. One of them is passive oxidation with the formation of a SiO₂ layer on the surface according to Eq. (7). When SiC oxidizes to SiO₂ in the passive regime, there is a net mass gain.

\[ \alpha \text{SiC(s)} + 3/2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{SiO}_2(s) \]  

This reaction may also be written with oxidation to gas phase CO₂ as follows;

\[ \alpha \text{SiC(s)} + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{SiO}_2(s) \]  

The other type of oxidation is active oxidation. The active oxidation results in the formation of SiO according to Eqs. (8)-(9) at higher temperatures and weight loss.21-26

\[ \text{SiC(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{SiO}_2(s) \]  

Above 600°C, ZrC oxidized by the reaction given below [Eq. (9)]. The atomic oxygen displaces carbon in the interstitial vacancies of the ZrC lattice. The initial weight increase is due to the formation of an intermediate, Zr(CO)₂.27 Ordan’yan et al.28 have studied the oxidation behavior of dense ZrB₂-40 mass % ZrC composite prepared by cold pressing under 100 MPa and reported no weight change up to 500°C.

\[ \text{ZrC(s)} + 2 \text{O}_2(g) \rightarrow \text{ZrO}_2(s) + \text{CO}_2(g) \]  

Table 2 shows the normalized mass change (mg/mm²) results of the composites oxidized at 1400, 1500 and 1600°C for 180 min. For all four composites, normalized mass change results increased with increasing oxidation temperature and the mass gain for 503020 was significantly greater than other specimens for all oxidation temperatures. When we compare the mass gain data for composites at oxidation temperatures of 1400 and 1500°C, the highest and lowest mass gain results were observed with 503020 and 602020 composites, respectively. These results indicated that oxidation stability of the materials increased with increasing ZrB₂ and SiC content at 1400 and 1500°C.

On the other hand, the mass gain of 504010 was the lowest at 1600°C. The mass change of this composite was a combination of mass loss due to the removal of carbon in the form of CO₂ and mass gain due to the formation of ZrO₂ and SiO₂ layers. The amount of removal of carbon in the form of gas phase CO₂ became much more pronounced with increasing ZrC content. Therefore, corresponding low mass gain at high temperature could be related to the high amount of ZrC.

Figure 5 shows the cross sectional morphology and EDS mapping of the oxide scale at 1600°C for the composite of 602020. Mapping of oxygen (O) and silicon (Si) concentration using EDS showed that the surface layer was Si and O rich. The analysis revealed that, oxidation of specimen at 1600°C produced a silicon oxide-rich outer surface layer with a thickness of 10 µm. The silicon-depleted ZrO₂-rich layer with a thickness of 15 µm remained below the outer silicon-oxide layer. Corresponding layer was observed in the previous studies, both at high temperatures and low oxygen partial pressures. This SiC-depleted layer could have been caused by the active oxidation of α-SiC to form gas phase of SiO according to the reaction 9.

Above 1100°C, α-SiC oxidized by the reaction given above in Eq. (7) and resulted in a formation of outer surface layer of Si and O rich. The silica containing scale was stable at 1400°C than the B₂O₃ due to lower volatility of liquid SiO₂ compared with liquid B₂O₃ at that temperature.27 The formation of ZrO₂ layer with a thickness of 15 µm was attributed to the oxidation of ZrB₂ and ZrC to form ZrO₂ according to the reactions given in Eq. (6) and Eq. (10), respectively.

Cross sectional microstructure of 503020 oxidized at 1600°C for 180 min and elemental composition maps of each composite are shown in Figure 6. Oxidation of 503020 composite at 1600°C resulted in a formation of three-layered structure. Mapping of oxygen and zirconium showed that the porous surface layer (Layer 1) with a thickness of 1 mm was ZrO₂-rich layer and formation of this thick layer was due to the oxidation of ZrB₂ and ZrC according to the Eq. (6) and Eq. (10), respectively. Also, the formation of thick and porous outer ZrO₂ layer was attributed to the presence of high amount of ZrC in this system. The carbon rich layer (Layer 2) with a thickness of 40 µm remained below the outer ZrO₂ rich layer.
The formation of solid phase carbon is possible under certain conditions. One of them is active oxidation of SiC by the reaction given in Eq. (9). The formation of silicon-depleted layer was observed, so the possible reason of formation of solid phase carbon (Layer 2) could be related to the active oxidation of α-SiC. Also, some of the gas phase of CO and/or CO₂ formed as a result of the oxidation of SiC and ZrC might have been trapped under the outer thick layer. It was clear that the amount of porosity was low at the bottom of the Layer 1 in Fig. 6. The formation of this thin layer labeled as 2 might have been assigned to the condensation of the trapped gas during cooling stage.

Although the amount of SiC is same for 602020 and 503020 composites, the formation of solid phase carbon was not observed for 602020 (Fig. 5). The oxidation products of ZrC are ZrO₂ and carbon oxides, and oxidation of ZrC occurs more aggressively than that of ZrB₂. So, the oxygen rich layer was thicker in Fig. 6(e) where the content of ZrC was higher, 30 vol%. The formation of oxide layer could begin to occur at lower temperatures due to the low oxidation resistance of pure ZrC, and the formation of thick oxide layer could inhibit removal of carbon. The high C distribution below Layer 1 in Fig. 6 may support this hypothesis.

For the composite 602020, the oxygen rich layer was thinner and C distributed freely in a wide range as well as Zr. These two micrographs shown in Figs. 5 and 6 are in agreement with the mass gain results given in Table 2.

The layer 3 in Fig. 6 with a thickness of 225 μm consisted of silicon, carbon, boron, zirconium and oxygen elements. In this layer, the oxygen concentration was lower than the layers 1 and 2 and the concentration of elements except oxygen increased. Under these three-layered oxide structures, formation of unoxidized region was observed.

**Figure 7** shows the cross sectional morphology and EDS mapping of oxide scales at 1600°C for the composite of 603010. As shown in the image, the oxidation layer can be divided into two parts. Mapping of oxygen (O), silicon (Si) and zirconium (Zr) concentration showed that the outer surface layer with a thickness of 360 μm was porous and rich of Si–O and Zr–O. Beneath this outer layer, formation of another one with a thickness of 90 μm was observed. This layer was composed of zirconium, oxygen, carbon and could be related to the formation of ZrCxOy. The analysis of the EDS observations demonstrated that this layer was also Si-depleted. As reported in previous studies, the formation of silicon-depleted layer is related to the active oxidation of SiC and is necessary in order to protect further oxidation. The silicon concentration increased below this carbon rich layer, and the amount of oxygen gradually decreased from upper to bottom layer. High amount of oxygen was detected in the upper side of the cross sectional image in the thickness of 360 μm. In the second layer with a thickness of 230 μm, the amount of oxygen decreased and the unoxidized region formed below these layers.

In the present study, the surface of the ZrB₂–ZrC–SiC composites was covered by silicon oxide and zirconium oxide rich layers. The concentration of oxygen gradually decreased from upper to bottom layer and formation of unoxidized region can be achieved for all samples. The formation of oxide scales
strongly dependent on several factors. One of them is the composition of the samples. Oxidation of composites containing 30 vol% ZrC (603010 and 503020) resulted in the formation of thick oxide layers and samples were completely coated by a white color oxide scale at the end of the oxidation process. The other critical component in the oxidation behavior of the samples was SiC. Previous studies related to the oxidation of ZrB2–SiC composites reported that the formation of SiO2-rich glass layer was insufﬁciently due to the presence of high amount of ZrC and resistance to oxidation. In this study, oxidation occurred more aggressively due to the presence of high amount of ZrC and formation of SiO2-rich glass layer was insufficient to prevent the further oxidation compared with samples without ZrC.

4. Conclusions

ZrB2–ZrC–SiC composites were prepared by SPS at 1750°C for 300 s. The results of this study showed that fully dense ZrB2–ZrC–SiC composites with a relative density of more than 99% were obtained at 1750°C. Vickers hardness of ZrB2–ZrC–SiC composites decreased with increasing ZrC content, and composite containing 60 vol% ZrB2, 20 vol% ZrC and SiC sintered at 1750°C for 300 s had the highest value of 21.1 GPa. The crack mode for the same composite was zigzag, and resulted in remarkable crack deflections and the highest fracture toughness value of 5.5 MPa m1/2. Oxidation of composites resulted in formation of protective layered oxide structures consisted of ZrO2 and Si–O rich layer in the form of SiO2 or SiO, and normalized mass change results increased with increasing oxidation temperature.

Acknowledgements This work was supported by the Scientiﬁc Research Project Funds of Istanbul Technical University (Project number: 32770). The authors thank H. Dincer for his contribution in SPS studies, H. H. Sezer and T. T. Alpak for SEM studies.

References

5) X. Zhang, Q. Qu, J. Han, W. Han and C. Hong, Scr. Mater., 59, 753–756 (2008).