

Available online at www.synsint.com

Synthesis and Sintering

ISSN 2564-0186 (Print), ISSN 2564-0194 (Online)



Research article

Oxidation response of ZrB_2 -SiC- ZrC composites prepared by spark plasma sintering



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ABSTRACT

Considering the importance and application of ultrahigh temperature ceramics in oxidizing environments, in this research, the effect of ZrC content and spark plasma sintering parameters (temperature, time and pressure) on the oxidation response of ZrB_2 -SiC composites has been investigated. After fabricating the ternary composite samples in different SPS conditions and with different amounts of ZrC , the post-sintering oxidation process was carried out in a box furnace at the temperature of 1400 °C. Increasing the time and temperature of the SPS process caused the decrease in the oxidation resistance of the samples. The reason for such observations was attributed to the extreme growth of grains with increasing the temperature and time of the sintering process despite the better densification of the samples. This research did not reach a clear result about the effect of SPS pressure on composites oxidation behavior. Increasing the amount of ZrC also did not have a positive effect on the oxidation resistance of the samples because this phase itself undergoes oxidation at low temperatures.

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KEYWORDS

Ultrahigh temperature ceramics
Oxidation behavior
Spark plasma sintering
Processing parameters
Additive content



1. Introduction

Some parts of hypersonic vehicles and aircraft must be made of special materials that are resistant to oxidation at elevated temperatures. Ultrahigh temperature ceramics (UHTCs) have been scrutinized extensively as proper candidates for such applications [1–5]. It was elucidated that the UHTCs reinforced with a silicon carbide-like binary system of ZrB_2 -SiC have excellent oxidation resistance [6]. Besides the binary system, ternary composites have also been investigated to boost the resistance of binary systems [7–9].

Opeka et al. [10] oxidized the ZrB_2 -SiC- ZrC composites up to 1500 °C for 5 h in the Ar/O_2 and found that the gained weight intensifies with increasing the amount of ZrC additive. Wu et al. [11] studied the influence of surface oxidation on the thermal shock performance of ZrB_2 -SiC- ZrC composites. They reported that the generation of the oxide layers on the surface of the samples results in an enhancement in thermal shock resistance. In addition, Shi et al. [12] found that the surface oxidation trick is favorable for enhancing the

flexural strength of these ternary ceramic composites. Wang et al. [13] oxidized the ZrB_2 -SiC- ZrC composites for 30 min at 1750 °C and investigated the oxidation kinetics and microstructure of the oxide layers. They detected that the oxidized area is composed of a glassy SiO_2 -rich layer, a thin ZrO_2 - SiO_2 layer, and a SiC-depleted ZrB_2 and/or ZrO_2 layer.

Arai et al. [14] fabricated several ZrB_2 -SiC- ZrC composites by spark plasma sintering (SPS) and examined the role of the ZrB_2/ZrC ratio on the oxidation performance using the thermogravimetric test. They also performed an in-situ observation above 1500 °C through a high-temperature observation system. Protective oxide layers were formed on the composites containing lower amounts of ZrC , but the samples with higher ZrC levels were completely oxidized below 1500 °C. Kubota et al. [15] studied the oxidation behavior of ZrB_2 -SiC- ZrC composites under low oxygen partial pressure at 1700 °C. The oxide layers composed of ZrO_2 and SiO_2 formed on the surface of the samples and thickened by increasing the ZrC amount. They also

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Received 4 December 2022; Received in revised form 30 December 2022; Accepted 31 December 2022.

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<https://doi.org/10.53063/synsint.2022.24134>

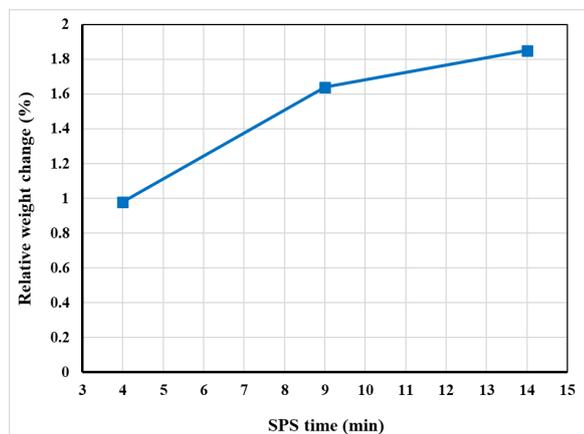


Fig. 1. Relative weight changes as a function of SPS time.

compared the oxidation behavior of such ternary ceramics in an oxygen-hydrogen torch environment at 1700 °C [16].

Recently, Inoue et al. [17] examined the initial oxidation response of ZrB₂-SiC-ZrC ternary ceramics above 2000 °C. They found that the amount of ZrC can control the morphology of the oxide layers because of the volume expansion over the oxidation of ZrC into ZrO₂.

The objective of this research is to determine the role of ZrC additive as well as the effects of SPS parameters such as time, temperature, and pressure in boosting the resistance of ZrB₂-SiC UHTCs against oxidation at 1400 °C.

2. Materials and methods

Commercially accessible SiC (purity: 98.7%, particle size: 15 μm, supplier: Northwest Institute for Non-Ferrous Metal Research from China), ZrC (purity: 98.5%, particle size: 20 μm, supplier: Alfa Aesar Co. from the United States), and ZrB₂ (purity: 99.5%, particle size: 20 μm, supplier: Northwest Institute for Non-Ferrous Metal Research from China) powders were employed as the starting ceramic particles. Several ZrB₂-30 vol% SiC-based composites samples were fabricated by spark plasma sintering with different ZrC additives and various SPS parameters to investigate the role of ZrC content and SPS time, temperature, and pressure on the subsequent oxidation resistance of the ZrB₂-SiC-ZrC UHTCs.

The initial ceramics were weighed and mixed via high-energy wet-ball-milling in ethanol for 3 h to prepare mixtures with 4, 8, and 12 vol%

Table 1. Microstructural and densification characteristics of composites after SPS for different times.

SPS time (min)	4	9	14
ZrB ₂ grain size (μm)	2.8	4.8	5.9
SiC grain size (μm)	1.6	3.8	5.3
Relative density (%)	87.2	90.1	92.1
Open porosity (%)	8.5	7.9	6.3

ZrC additives. The as-mixed powders were fully dried on a magnetic stirrer (Heidolph MR 3001 K, Germany) for 2 h at 150 °C. Each prepared batch was loaded into a die made of graphite appropriate for sintering processes. The sintering step was completed using an SPS machine (20T-10, China) in a 15 Pa vacuum. The processing conditions of the samples were not the same, and for this purpose, different temperatures (1650, 1725, and 1800 °C), times (4, 9, and 14 min), and pressures (20, 30, and 40 MPa) were used. The fabricated samples were ground to clean the graphite contaminations. The post-sintering oxidation process was performed in a box furnace at 1400 °C. The relative density and percentage of open porosity of the as-sintered samples were estimated with the help of Archimedes' principles and relations. The average size of ZrB₂ and SiC grains in the microstructure of sintered composites was measured using ImageJ software. The relative mass changes over time were calculated to compare and evaluate the oxidation response of the samples. Microstructural observation of the oxidized layers was done using a field emission Mira3 SEM facility (Made in Czechia, Tescan Co.).

3. Results and discussion

In general, the surface of a non-oxide ceramic sample oxidizes when exposed to air, which can be accelerated at high temperatures [18–20]. For example, ZrB₂ transforms into ZrO₂ and B₂O₃ at temperatures above 800 °C [21, 22], SiC into SiO₂ and CO at temperatures above 900 °C [23, 24], and ZrC into ZrO₂ and CO at temperatures above 450 °C [13, 25]. Therefore, by placing the ZrB₂-SiC-ZrC composites in oxidation conditions at 1400 °C, the following chemical reactions are expected:

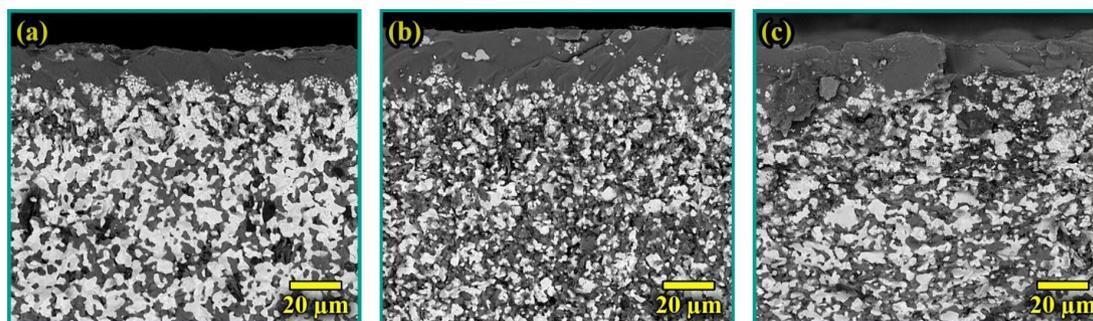


Fig. 2. FESEM images of the oxidized cross-section of ZrB₂-30 vol% SiC-8 vol% ZrC composites SPSed for different holding times: a) 4 min, b) 9 min, and c) 14 min.

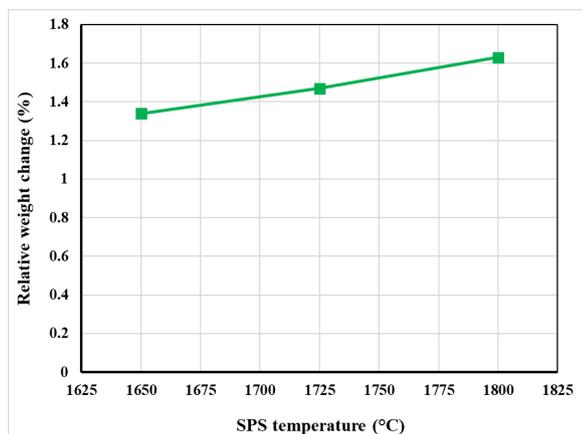


Fig. 3. Relative weight changes as a function of SPS temperature.

The formation of the SiO_2 oxide layer causes the consumption of silicon in the lower layer and hence a Si-depleted zone appears [26–28]. The formed SiO_2 oxide phase creates a sticky glass layer that increases the oxidation resistance [29–31]. Therefore, the presence of SiC reinforcement in ZrB_2 -based ceramic composites reduces their oxidation rate. This is due to the formation of the B_2O_3 - SiO_2 glass shell, which is more viscous and stable compared to a single B_2O_3 and has a lower vapor pressure [32–36].

The diffusion of oxygen in this silica-rich amorphous shell is low due to its high viscosity, and it is resistant to a minimum temperature of 1600 °C in oxidizing environments [37–39]. Another advantage of this shell is its sufficient fluidity to fill the voids or discontinuities (empty spaces) in the ZrO_2 layer and, as a result, completely cover the surface of the sample due to its excellent wettability. The diffusion of dissolved oxygen in semi-solid B_2O_3 - SiO_2 present in porous ZrO_2 has been proposed as the limiting factor for oxidation up to 1400 °C [29, 40, 41].

3.1. Effect of sintering time on the oxidation behavior

The graph of the relative changes in weight of the ZrB_2 -30 vol% SiC-8 vol% ZrC composites after oxidation for 18 h at 1400 °C as a function of the sintering time is presented in Fig. 1. If a composite with this composition is sintered for 4 min, the weight change percentage reaches 0.98% due to its oxidation. By increasing the SPS time to 9 min and 14 min, the weight changes reach 1.64% and 1.85%,

Table 2. Microstructural and densification characteristics of composites after SPS at different temperatures.

SPS temperature (°C)	1650	1725	1800
ZrB_2 grain size (μm)	4.7	5.9	7.8
SiC grain size (μm)	3.5	3.9	5.1
Relative density (%)	89.2	91.8	92.2
Open porosity (%)	8.3	7.1	6.7

respectively. In other words, by increasing the duration of holding the composite at the maximum sintering temperature from 4 min to 14 min, the amount of weight change due to oxidation of the part has doubled. Increasing the sintering time caused an increase in weight changes, which means a decrease in the oxidation resistance of the sample.

Because the chemical composition was constant in these three samples, it can be concluded that the only factor influencing the amount of weight changes affected by oxidation is the microstructural evolutions of the composite with the time of the sintering process. The data relating to the microstructural characteristics and densification of the samples made at different SPS times are given in Table 1. These results show that the relative density of the composites increases with the increase of the holding time at the maximum SPS temperature, and subsequently, the number of open porosities in the parts decreases. Such an outcome seems strange at first comparison because it is expected that the oxidation resistance of a sample that is denser will be higher. But by comparing the size of ZrB_2 and SiC grains in different samples, this enigma can be solved. As it can be clearly seen, with the increase of SPS time, the grain size of both phases has increased significantly. Although increasing the holding time of the sample during the sintering process leads to better densification of the composite, but the oxidation resistance is weakened due to excessive grain growth.

For a more detailed examination, FESEM images of the cross-section of the oxidized samples are shown in Fig. 2. With the increase of the sintering time, the thickness of different layers affected by oxidation has increased, which indicates a decrease in resistance to oxidation. The reason for this observation can be attributed to the coarsening of grain size with increasing sintering time, which is in complete harmony with the data presented in the graph related to weight changes due to oxidation (Fig. 1) and the microstructural results reported in Table 1.

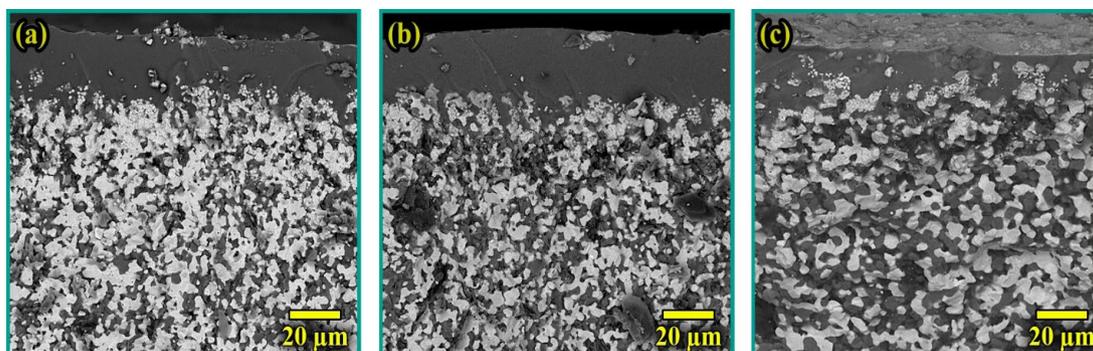


Fig. 4. FESEM images of the oxidized cross-section of ZrB_2 -30 vol% SiC-12 vol% ZrC composites SPSed at different temperatures: a) 1650 °C, b) 1725 °C, and c) 1800 °C.

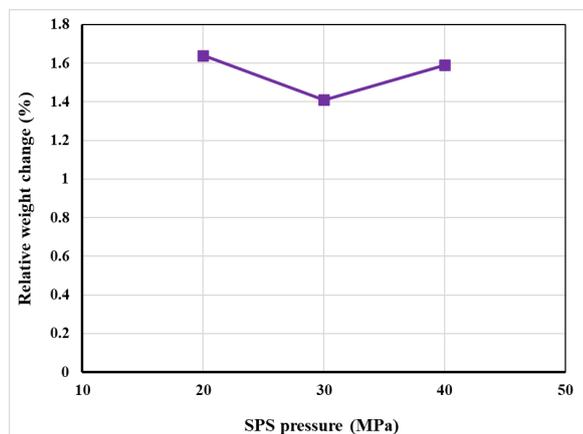


Fig. 5. Relative weight changes as a function of SPS pressure.

3.2. Effect of sintering temperature on the oxidation behavior

Fig. 3 shows the graph of relative weight changes based on SPS temperature for three samples subjected to oxidation treatment at 1400 °C for 18 h. The composition of all composite samples was constant and 30 vol% SiC and 12 vol% ZrC were added to the ZrB₂ matrix. The composite that was sintered at 1650 °C showed the lowest relative weight changes of 1.34% after oxidation. As the SPS temperature increased to 1725 °C and then to 1800 °C, the relative weight changes increased almost linearly and reached 1.47% and 1.63%, respectively. Therefore, it seems that increasing the sintering temperature from 1650 °C to 1800 °C causes the relative weight changes to increase by about 20%, which can be interpreted as a decrease in oxidation resistance with an increase in SPS temperature.

The effect of sintering temperature on the microstructural evolution caused by subsequent oxidation of these composites can be compared in Fig. 4. As the increase in SPS temperature from 1650 °C to 1800 °C has linearly intensified the relative weight changes, it has also resulted in an increase in the thickness of the layers affected by oxidation. Considering that the chemical composition of these composites is the same and all of them have 12 vol% ZrC, it seems that the microstructure of the samples developed at different SPS temperatures is the most important factor affecting their oxidation behavior. The microstructural characteristics (grain size and porosity) of these

Table 3. Microstructural and densification characteristics of composites after SPS under different pressures.

SPS pressure (MPa)	20	30	40
ZrB ₂ grain size (μm)	4.8	3.9	5.2
SiC grain size (μm)	3.8	2.4	4.5
Relative density (%)	90.1	92.9	94.1
Open porosity (%)	5.8	4.3	3.9

UHTCs are presented in Table 2 and as can be seen, increasing the sintering temperature has led to a continuous and significant increase in the size of ZrB₂ and SiC grains. The significant growth of grains at 1800 °C is clearly seen in Fig. 4c. However, sintering at a higher temperature has partially helped to increase the relative density and reduce the number of open porosities. But it should be noted that the growth of the grains has been so high that it has finally led to a drop in the oxidation resistance of the composite.

3.3. Effect of sintering pressure on the oxidation behavior

Fig. 5 shows the relative weight changes due to the oxidation of composite samples sintered under different pressures of 20, 30, and 40 MPa. The composition of all three samples was constant and equal to ZrB₂-30 vol% SiC-8 vol% ZrC. After the oxidation test for 18 h at 1400 °C, the sample that was sintered under 20 MPa pressure experienced a 1.64% relative weight increase. The composite that was produced under a pressure of 30 MPa showed a relative weight increase of 1.41%, which had fewer weight changes than the sample sintered under lower pressure. The sample prepared under 40 MPa pressure showed a different trend and the relative weight changes in this sample increased compared to the previous one. Therefore, unlike the specific trends that were claimed about the effects of sintering time and temperature on the oxidation behavior, it is not possible to make a definite statement about the influence of SPS pressure on the performance of composites whether increasing the pressure improves or weakens the oxidation resistance.

For additional investigations, FESEM microstructures taken from the cross sections of the oxidized layers in three samples are shown in Fig. 6. Moreover, the grain size, relative density, and amount of open porosity in the sintered samples, before the oxidation test, are given in Table 3. As expected, by applying more pressure during the sintering process, better densification is provided, and the relative density

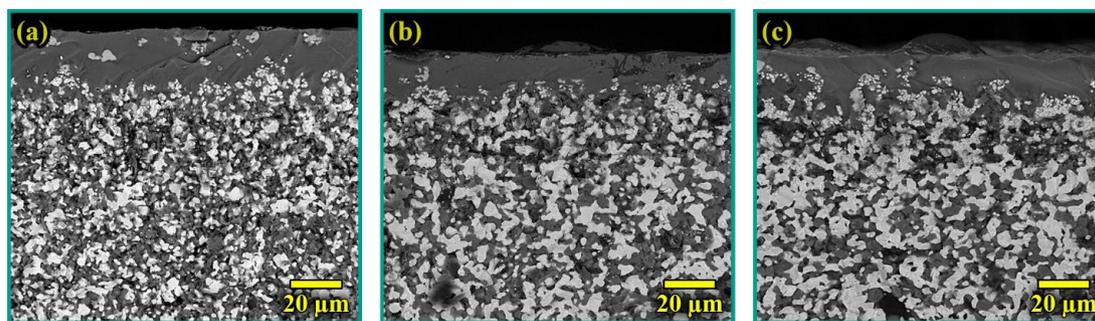


Fig. 6. FESEM images of the oxidized cross-section of ZrB₂-30 vol% SiC-8 vol% ZrC composites SPSed under different pressures: a) 20 MPa, b) 30 MPa, and c) 40 MPa.

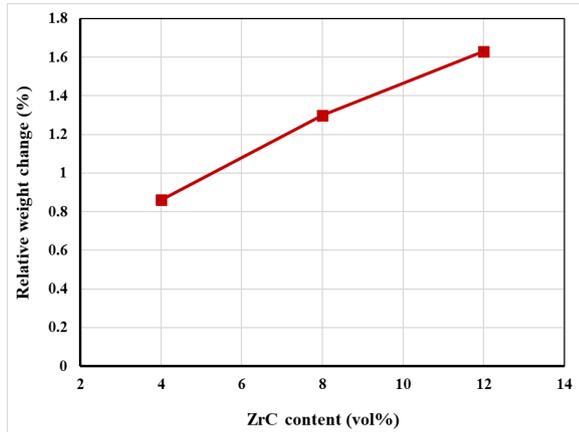


Fig. 7. Relative weight changes as a function of ZrC content.

increases. Higher pressure causes a better rearrangement of the powder particles, increases the probability of the powder being fragmented into smaller particles and generally enhances the sinterability of the powder.

Table 4. Microstructural and densification characteristics of composites after SPS with different ZrC content.

ZrC content (vol%)	4	8	12
ZrB ₂ grain size (μm)	4.2	6.1	7.8
SiC grain size (μm)	1.8	4.0	5.1
Relative density (%)	94.1	93.1	92.2
Open porosity (%)	4.4	7.6	7.9

The results obtained about the relative density and percentages of open porosity in Table 3 are in full agreement with these expectations. Even the smaller grain size in the sintered sample at 30 MPa compared to the composite processed under 20 MPa can be justified and attributed to the role of pressure on the fragmentation of the powder particles. Unfortunately, the authors do not have a justification for the contradictory and unexpected observation about the grain size with the application of more pressure up to 40 MPa. Maybe there was a test or measurement error, or another parameter is involved that was out of the authors' knowledge due to the available test facilities.

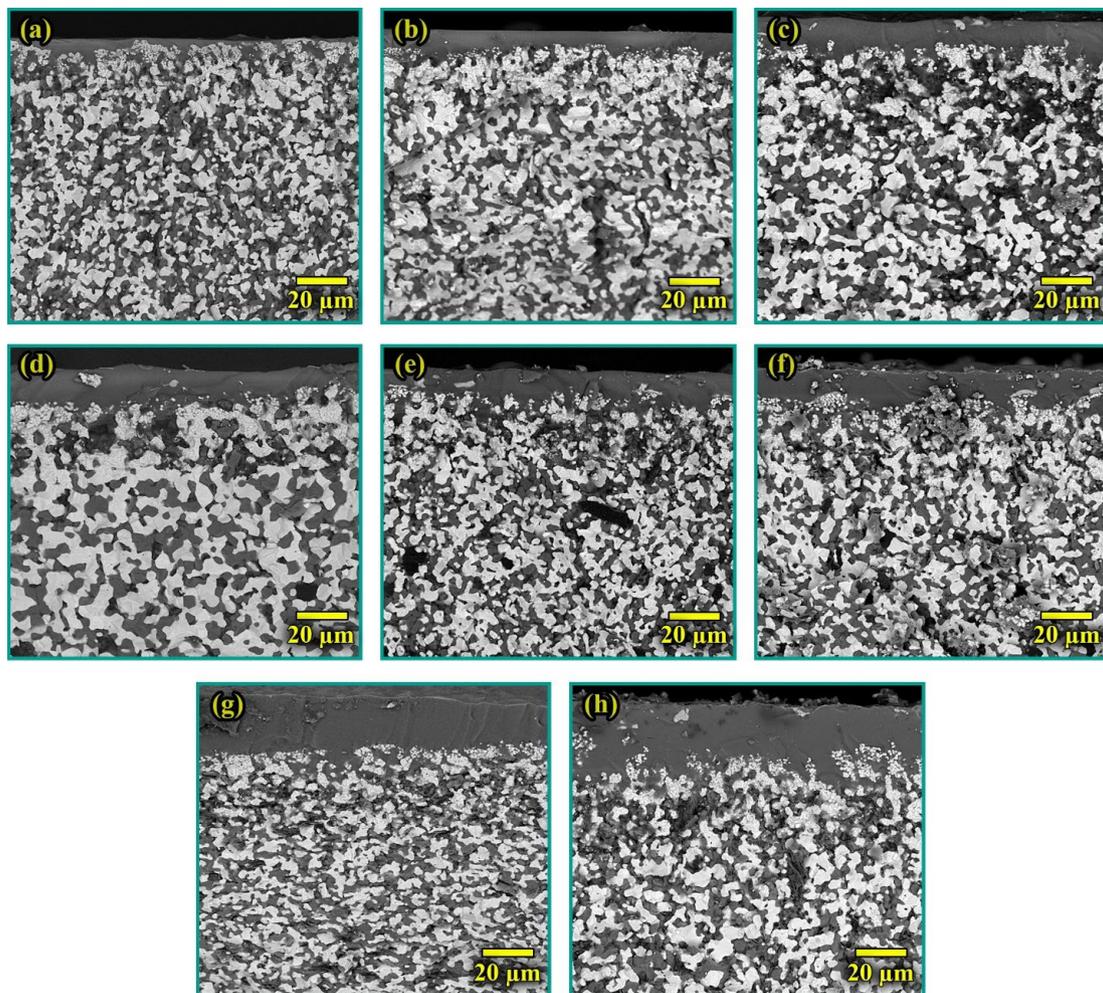


Fig. 8. Cross-sectional FESEM images of ZrB₂-30 vol% SiC-12 vol% ZrC composites oxidized at 1400 °C for different durations a) 1 h, b) 2 h, c) 5 h, d) 6 h, e) 7 h, f) 10 h, g) 15 h, and h) 18 h after prepared by SPS at 1800 °C for 9 min under 30 MPa.

3.4. Effect of ZrC content on the oxidation behavior

Fig. 7 shows the relative changes of weight in terms of ZrC content in ZrB₂-30 vol% SiC composites sintered at 1800 °C for 9 min under 30 MPa pressure after oxidation for 18 h at 1400 °C. It can be seen that with the increase of ZrC amount, the relative weight change increases which leads to a decrease in oxidation resistance. In the composite that only 4 vol% ZrC was added, the relative weight changes reached 0.86%. As the amount of carbide additive increases, the relative weight change also intensifies, so with the addition of 8 vol% and 12 vol% ZrC, the relative changes in weight have reached 1.3% and 1.63%, respectively. Considering that the starting temperature of ZrC oxidation is much lower than those of the ZrB₂ matrix and SiC additive, increasing its amount causes a drop in the oxidation resistance of the composite, which can be clearly seen in Fig. 7.

The data presented in Table 4, which shows the microstructural and densification characteristics of the SPSeD composites with different amounts of ZrC addition, can provide further information about the relative weight changes after oxidation. As can be compared, with the addition of more ZrC, the grain size of ZrB₂ and SiC has shown significant growth. Therefore, this additive has not only progressed the densification of the samples but also caused the extreme growth of the grains. The drop in relative density and the increase in the amount of open porosity with the addition of more ZrC is evidence for this claim.

3.5. Oxidation mechanism

In order to show how the oxidation process progresses via the formation and thickening of the oxide layers, the sample sintered at 1800 °C for 9 min under 30 MPa and containing 12 vol% ZrC, which showed a weak resistance to oxidation, was investigated. FESEM images of its cross-section after oxidation at 1400 °C for different times are shown in Fig. 8. By increasing the duration of exposure of the sample in oxidizing conditions, the intensity and extent of oxidation naturally increase, because exposing the sample for a longer period, oxygen diffusion to the surface of the sample increases, and as a result, the thickness of the oxidized layers and the area affected by oxidation increases. Therefore, it seems that the rate of oxygen diffusion to the underlying layers is a key parameter in the oxidation behavior of these composites. What can be clearly seen in these figures is that with increasing the oxidation time, the thickness of the upper layer, which is SiO₂, increases.

4. Conclusions

Several ZrB₂-SiC composites with different amounts of ZrC additive were fabricated by SPS technology at different temperatures for various holding times under different pressures. The role of these variables (ZrC content and SPS conditions) on the oxidation performance of ternary ZrB₂-SiC-ZrC composites were studied and discussed. The post-sintering oxidation process was completed inside a box furnace at 1400 °C up to 18 h. No clear result was found for the effect of applied pressure during the SPS step on the post-sintering oxidation behavior of the samples. Increasing the SPS temperature, the SPS time, and the ZrC content led to a drop in the oxidation performance due to the fanatic grains growth in the as-sintered microstructures. According to the obtained data and results, the reasons for these observations were justified.

CRediT authorship contribution statement

Mohsen Ghasilzadeh Jarvand: Investigation, Funding acquisition.
Zohre Balak: Conceptualization, Formal Analysis, Supervision, Writing – original draft, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

Funding and acknowledgment

The content of this article has been derived from the research project titled “Fabrication of ZrB₂-SiC-ZrC composite and investigation of its oxidation resistance” supported by Islamic Azad University of Ahvaz.

References

- [1] D. Ni, Y. Cheng, J. Zhang, J.-X. Liu, J. Zou, et al., Advances in ultra-high temperature ceramics, composites, and coatings, *J. Adv. Ceram.* 11 (2022) 1–56. <https://doi.org/10.1007/s40145-021-0550-6>.
- [2] R. Savino, M. De Stefano Fumo, D. Paterna, M. Serpico, Aerothermodynamic study of UHTC-based thermal protection systems, *Aerosp. Sci. Technol.* 9 (2005) 151–160. <https://doi.org/10.1016/j.ast.2004.12.003>.
- [3] X. Jin, R. He, X. Zhang, P. Hu, Ablation behavior of ZrB₂-SiC sharp leading edges, *J. Alloys Compd.* 566 (2013) 125–130. <https://doi.org/10.1016/j.jallcom.2013.03.067>.
- [4] H. Istgaldi, M. Mehrabian, F. Kazemi, B. Nayebi, Reactive spark plasma sintering of ZrB₂-TiC composites: Role of nano-sized carbon black additive, *Synth. Sinter.* 2 (2022) 67–77. <https://doi.org/10.53063/synsint.2022.22107>.
- [5] T. Cheng, W. Li, W. Lu, Y. Shi, Heat Transfer and Failure Mode Analyses of Ultrahigh-Temperature Ceramic Thermal Protection System of Hypersonic Vehicles, *Math. Probl. Eng.* 2014 (2014) 412718. <https://doi.org/10.1155/2014/412718>.
- [6] I.G. Talmy, J.A. Zaykoski, M.M. Opeka, High-temperature chemistry and oxidation of ZrB₂ ceramics containing SiC, Si₃N₄, Ta₅Si₃, and TaSi₂, *J. Am. Ceram. Soc.* 91 (2008) 2250–2257. <https://doi.org/10.1111/j.1551-2916.2008.02420.x>.
- [7] S. Haghgooye Shafagh, S. Jafargholinejad, S. Javadian, Beneficial effect of low BN additive on densification and mechanical properties of hot-pressed ZrB₂-SiC composites, *Synth. Sinter.* 1 (2021) 69–75. <https://doi.org/10.53063/synsint.2021.1224>.
- [8] H. Sahasrabudhe, A. Bandyopadhyay, Additive Manufacturing of Reactive In Situ Zr Based Ultra-High Temperature Ceramic Composites, *JOM.* 68 (2016) 822–830. <https://doi.org/10.1007/s11837-015-1777-x>.
- [9] Z. Bahararjmand, M.A. Khalilzadeh, F. Saberi-Movahed, T.H. Lee, J. Wang, et al., Role of Si₃N₄ on microstructure and hardness of hot-pressed ZrB₂-SiC composites, *Synth. Sinter.* 1 (2021) 34–40. <https://doi.org/10.53063/synsint.2021.1113>.
- [10] M.M. Opeka, I.G. Talmy, E.J. Wuchina, J.A. Zaykoski, S.J. Causey, Mechanical, thermal, and oxidation properties of refractory hafnium and zirconium compounds, *J. Eur. Ceram. Soc.* 19 (1999) 2405–2414. [https://doi.org/10.1016/S0955-2219\(99\)00129-6](https://doi.org/10.1016/S0955-2219(99)00129-6).
- [11] Z. Wu, Z. Wang, G. Shi, J. Sheng, Effect of surface oxidation on thermal shock resistance of the ZrB₂-SiC-ZrC ceramic, *Compos.*

- Sci. Technol. 71 (2011) 1501–1506.
<https://doi.org/10.1016/j.compscitech.2011.06.008>.
- [12] G. Shi, Z. Wang, X. Sun, Z. Wu, Effect of the surface oxidation on the flexural strength of the ZrB₂-SiC-ZrC ceramic, *Mater. Sci. Eng. A*. 546 (2012) 162–168. <https://doi.org/10.1016/j.msea.2012.03.044>.
- [13] Z. Wang, Z. Wu, G. Shi, The oxidation behaviors of a ZrB₂-SiC-ZrC ceramic, *Solid State Sci.* 13 (2011) 534–538. <https://doi.org/10.1016/j.solidstatesciences.2010.12.022>.
- [14] Y. Arai, R. Inoue, H. Tanaka, Y. Kogo, K. Goto, In-situ observation of oxidation behavior in ZrB₂-SiC-ZrC ternary composites up to 1500°C using high-temperature observation system, *J. Ceram. Soc. Jpn.* 124 (2016) 890–897. <https://doi.org/10.2109/jcersj2.16043>.
- [15] Y. Kubota, H. Tanaka, Y. Arai, R. Inoue, Y. Kogo, K. Goto, Oxidation behavior of ZrB₂-SiC-ZrC at 1700 °C, *J. Eur. Ceram. Soc.* 37 (2017) 1187–1194. <https://doi.org/10.1016/j.jeurceramsoc.2016.10.034>.
- [16] Y. Kubota, M. Yano, R. Inoue, Y. Kogo, K. Goto, Oxidation behavior of ZrB₂-SiC-ZrC in oxygen-hydrogen torch environment, *J. Eur. Ceram. Soc.* 38 (2018) 1095–1102. <https://doi.org/10.1016/j.jeurceramsoc.2017.11.024>.
- [17] R. Inoue, Y. Arai, Y. Kubota, Y. Kogo, K. Goto, Initial oxidation behaviors of ZrB₂-SiC-ZrC ternary composites above 2000 °C, *J. Alloys Compd.* 731 (2018) 310–317. <https://doi.org/10.1016/j.jallcom.2017.10.034>.
- [18] E. Wang, X. Hou, Y. Chen, Z. Fang, J. Chen, et al., Progress in cognition of gas-solid interface reaction for non-oxide ceramics at high temperature, *Crit. Rev. Solid State Mater. Sci.* 46 (2021) 218–250. <https://doi.org/10.1080/10408436.2020.1713047>.
- [19] A.N. Astapov, B.E. Zhestkov, Y.S. Pogozhev, M.V. Zinovyeva, A.Y. Potanin, E.A. Levashov, The oxidation resistance of the heterophase ZrSi₂-MoSi₂-ZrB₂ powders – Derived coatings, *Corros. Sci.* 189 (2021) 109587. <https://doi.org/10.1016/j.corsci.2021.109587>.
- [20] E.P. Simonenko, N.P. Simonenko, A.F. Kolesnikov, A.V. Chaplygin, A.S. Lysenkov, et al., Modification of HfB₂-30% SiC UHTC with Graphene (1 vol %) and Its Influence on the Behavior in a Supersonic Air Jet, *Russ. J. Inorg. Chem.* 66 (2021) 1405–1415. <https://doi.org/10.1134/S003602362109014X>.
- [21] R. Ghelich, R. Mehdinavaz Aghdam, M.R. Jahannama, Elevated temperature resistance of SiC-carbon/phenolic nanocomposites reinforced with zirconium diboride nanofibers, *J. Compos. Mater.* 52 (2018) 1239–1251. <https://doi.org/10.1177/0021998317723447>.
- [22] E.M. Alosime, M.S. Alsuhybani, M.S. Almeataq, The oxidation behavior of ZrB₂-SiC ceramic composites fabricated by plasma spray process, *Materials (Basel)*. 14 (2021) 392. <https://doi.org/10.3390/ma14020392>.
- [23] X. Li, A. Ermakov, V. Amarasinghe, E. Garfunkel, T. Gustafsson, L.C. Feldman, Oxidation induced stress in SiO₂/SiC structures, *Appl. Phys. Lett.* 110 (2017) 141604. <https://doi.org/10.1063/1.4979544>.
- [24] D. Seo, M. Sayar, K. Ogawa, SiO₂ and MoSi₂ formation on Inconel 625 surface via SiC coating deposited by cold spray, *Surf. Coat. Technol.* 206 (2012) 2851–2858. <https://doi.org/10.1016/j.surfcoat.2011.12.010>.
- [25] S. Shimada, T. Ishil, Oxidation kinetics of zirconium carbide at relatively low temperatures, *J. Am. Ceram. Soc.* 73 (1990) 2804–2808. <https://doi.org/10.1111/j.1151-2916.1990.tb06678.x>.
- [26] G. Ouyang, P.K. Ray, M.J. Kramer, M. Akinc, High-temperature oxidation of ZrB₂-SiC-AlN composites at 1600 °C, *J. Am. Ceram. Soc.* 99 (2016) 808–813. <https://doi.org/10.1111/jace.14039>.
- [27] M. Sakvand, M. Shojaie-Bahaabad, L. Nikzad, Effect of graphite addition on the microstructure, mechanical properties and oxidation resistance of HfB₂-SiC composites prepared by the SPS method, *Int. J. Eng.* 35 (2022) 1867–1876. <https://doi.org/10.5829/IJE.2022.35.10A.06>.
- [28] N. Petry, A.S. Ulrich, B. Feng, E. Ionescu, M.C. Galetz, M. Lepple, Oxidation resistance of ZrB₂-based monoliths using polymer-derived Si(Zr,B)CN as sintering aid, *J. Am. Ceram. Soc.* 105 (2022) 5380–5394. <https://doi.org/10.1111/jace.18473>.
- [29] M. Mallik, K.K. Ray, R. Mitra, Oxidation behavior of hot pressed ZrB₂-SiC and HfB₂-SiC composites, *J. Eur. Ceram. Soc.* 31 (2011) 199–215. <https://doi.org/10.1016/j.jeurceramsoc.2010.08.018>.
- [30] A. Buyakov, V. Shmakov, S. Buyakova, Dual composite architectonics: Fracture toughness and self-healing of ZrB₂-SiC-TaB₂ based UHTC, *Ceram. Int.* 49 (2022) 13648–13656. <https://doi.org/10.1016/j.ceramint.2022.12.241>.
- [31] S. Torabi, Z. Valefi, N. Ehsani, The effect of the SiC content on the high duration erosion behavior of SiC/ZrB₂-SiC/ZrB₂ functionally gradient coating produced by shielding shrouded plasma spray method, *Ceram. Int.* 48 (2022) 1699–1714. <https://doi.org/10.1016/j.ceramint.2021.09.249>.
- [32] E. Dodi, Z. Balak, H. Kafashan, Oxidation-affected zone in the sintered ZrB₂-SiC-HfB₂ composites, *Synth. Sinter.* 2 (2022) 31–37. <https://doi.org/10.53063/synsint.2022.21111>.
- [33] L. He, Y. Sun, Q. Meng, B. Liu, J. Wu, X. Zhang, Enhanced oxidation properties of ZrB₂-SiC composite with short carbon fibers at 1600 °C, *Ceram. Int.* 47 (2021) 15483–15490. <https://doi.org/10.1016/j.ceramint.2021.02.114>.
- [34] S.M. Arab, M. Shahedi Asl, M. Ghassemi Kakroudi, B. Salahimehr, K. Mahmoodipour, On the oxidation behavior of ZrB₂-SiC-VC composites, *Int. J. Appl. Ceram. Technol.* 18 (2021) 2306–2313. <https://doi.org/10.1111/ijac.13858>.
- [35] M. Dehghanzadeh Alvari, M. Ghassemi Kakroudi, B. Salahimehr, R. Alaghmandfard, M. Shahedi Asl, M. Mohammadi, Microstructure, mechanical properties, and oxidation behavior of hot-pressed ZrB₂-SiC-B₄C composites, *Ceram. Int.* 47 (2021) 9627–9634. <https://doi.org/10.1016/j.ceramint.2020.12.101>.
- [36] S.A.A. Shalmani, M. Sobhani, O. Mirzaee, M. Zakeri, Ablation resistance of graphite coated by spark plasma sintered ZrB₂-SiC based composites, *Bol. Soc. Esp. Cerám. Vidr.* 61 (2022) 604–610. <https://doi.org/10.1016/j.bsecv.2021.05.004>.
- [37] W.G. Fahrenholtz, Thermodynamic analysis of ZrB₂-SiC oxidation: formation of a SiC-depleted region, *J. Am. Ceram. Soc.* 90 (2007) 143–148. <https://doi.org/10.1111/j.1551-2916.2006.01329.x>.
- [38] X.-H. Zhang, P. Hu, J.-C. Han, Structure evolution of ZrB₂-SiC during the oxidation in air, *J. Mater. Res.* 23 (2008) 1961–1972. <https://doi.org/10.1557/JMR.2008.0251>.
- [39] N. Li, P. Hu, X. Zhang, Y. Liu, W. Han, Effects of oxygen partial pressure and atomic oxygen on the microstructure of oxide scale of ZrB₂-SiC composites at 1500°C, *Corros. Sci.* 73 (2013) 44–53. <https://doi.org/10.1016/j.corsci.2013.03.023>.
- [40] D. Sciti, M. Brach, A. Bellosi, Oxidation behavior of a pressureless sintered ZrB₂-MoSi₂ ceramic composite, *J. Mater. Res.* 20 (2005) 922–930. <https://doi.org/10.1557/JMR.2005.0111>.
- [41] E.S. Dedova, A.G. Burlachenko, Y.A. Mirovoy, A.S. Buyakov, S.P. Buyakova, Oxidation behavior of ZrB₂-ZrC-SiC-ZrO₂ ceramics, *AIP Conf. Proc.* 2310 (2020) 020071. <https://doi.org/10.1063/5.0034147>.