ACERP: Vol. 4, No.1, (Winter 2018) 18-23

Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Oxidation of ZrB_2-SiC Composites at 1600°C: Effect of Carbides, Borides, Silicides, and Chopped Carbon Fiber

Z. Balak*, M. Azizieh

Department of Materials Science and Engineering, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran.

PAPER INFO

Paper history:
Received 29 April 2018
Accepted in revised form 21 August 2018

Keywords:
Oxidation Resistance
Spark Plasma Sintering
ZrB_2-SiC
Carbides
Borides
Chopped Carbon Fiber

ABSTRACT

The aim of this work is to optimize the oxidation resistance of ZrB_2-SiC-based composites with different additives. Effect of nine factors including SiC, C_f, $MoSi_2$, HfB_2 and ZrC contents, milling time of C_f (M.t) and SPS parameters such as temperature, time and pressure on oxidation resistance in four levels was investigated. Taguchi design was applied to explore effective parameters for achieving the highest oxidation resistance. Spark plasma sintering (SPS) was used for sintering. Oxidation resistance tests were carried out on all composites using box furnace at 1600°C for 1 hr holding time. Then Taguchi design was applied to determine effect of each factor on it. It has been concluded that ZrC by 45% has the most significant the effect on the oxidation resistance and oxidation resistance decreases by ZrC ascent while HfB_2 has positive effect on oxidation resistance of ZrB_2-based ceramics. Among the SPS parameters, the temperature has the most effect on microstructure and eventually oxidation resistance. Pressure by 2.3% and M.t by 3.4% have the least effect on the oxidation resistance. Other factors such as SiC, C_f, temperature, HfB_2, $MoSi_2$ and time have 12.8%, 8.3%, 7.7%, 6.2%, 5.9% and 5.6% on the oxidation resistance respectively.

1. INTRODUCTION

ZrB_2 ceramic is belonged to the family of ultra high temprature ceramics (UHTC). This material is an attractive candidate for high temprature andstructural application due to their unique properties such as ultra-high melting temperature [≥ 3000 °C], high hardness and strength, and high thermal and electrical conductivity [1]. In this condition, the material should be able to bear the existing enviroment at high temprtaure and be stable thermally and chemically [2].

When ZrB_2 is exposed to air at high temperatures, it reacts with O_2 to form crystalline ZrO_2 and liquid B_2O_3. [3]. According to different studies, oxidation behavior can be classified to three temperature regimes as below:

Less than 1100 °C (1)

Between 1100 °C and 1400 °C (2)

Higher than 1400 °C (3)

At temperatures less than 1100°C, the B_2O_3 forms a continuous liquid layer which limits the transport of oxygen to the ZrB_2 surface, and as a consequence diffusion controlled, passive oxidation behavior with parabolic mass gain kinetics are observed [4].

At temperatures above 1100°C, the B_2O_3 evaporates due to high vapor pressure. The removal of B_2O_3 by vaporization leaves behind a porous ZrO_2 scale which does not protect underlying ZrB_2 from more oxidation. So, the oxidation rate increases and exhibits para-linear kinetics between 1100 °C and 1400 °C [4].

In this temperature range, the overall rate of mass change is a combination of mass gain due to formation of B_2O_3 and ZrO_2 and mass loss due to B_2O_3 (l) vaporization[4, 5].

At temperatures higher than 1400 °C, linear mass gain kinetics ensue due to rapid evaporation of B_2O_3, and a non-protective porous ZrO_2 scale is formed [4]. Because the rate of B_2O_3 vaporization is rapid compared to its rate of formation. Thus, the high-temperature applications of monolithic ZrB_2 will be limited by its poor oxidation resistance [3].

Many additives have been used to improve the oxidation resistance of ZrB_2-based materials such as $MoSi_2$, SiC, graphite /B_4C [5]. SiC not only improves oxidation resistance but has a positive effect on sinter-ability, flexural strength, fracture toughness and hardness of

*Corresponding Author's Email: zbalak1983@gmail.com (Z. Balak)

ZrB_2. Therefore most studies were conducted on ZrB_2-SiC composites. Up to date, the oxidation resistance of ZrB_2 with different SiC contents, in various temperatures were investigated by different methods. The main techniques for the evaluation of the oxidation resistance include methods involving arc-jet, furnace and oxyacetylene torch treatment [6].

In our previous works, ZrB_2-based composites with different additives such as SiC, C_f, $MoSi_2$, HfB_2 and ZrC were produced under different SPS conditions (temperatures, times and pressures). Effect of each factor on densification, hardness, flexural strength and fracture toughness were investigated and discussed. The aim of this work is to study the effect of each factor oxidation resistance behavior and its importance. Also oxidation resistance optimization is conducted by Taguchi method. This research has two major differences with other researches in this field. At first, in all previous researches, the effect of additives, process conditions or manufacturing producer was evaluated on one or more properties (such as densification, hardness, flexural strength, fracture toughness, etc.) separately and then their optimum values were obtained. But in this research, the optimum levels of each factor to reach composite with desired or defined mechanical properties and oxidation resistance are obtained simultaneously using Qualitek-4 software. At second, it is possible to specify the optimum values of each factor and SPS conditions for one or more combined properties which lie in the range of this work.

2. EXPERIMENTAL

Starting powders and their characters were given in later our works[7-9]. Taguchi design was applied to explore effective parameters for achieving the highest oxidation resistance. Nine variables including contents of silicon carbide, short carbon fiber, molybdenum disilicide, hafnium diboride and zirconium carbide, milling time of C_f (M.t) and SPS parameters such as temperature, time and pressure in four levels were considered through the Taguchi technique. Experimental design was explained in previous work in details [7-9]. L_{32} orthogonal array was chosen to determine the optimum conditions [7-9]. Concerning the L_{32} orthogonal array, conditions for the preparation of each sample were given in our later works[7-9].

According to Taguchi design [9], the powders were mixed together by wet ball-milling. Then the mixed powders were put in a graphite die and were sintered by SPS apparatus at different temperatures, pressures and holding times. For oxidation evaluation, the surface of the samples was polished before oxidation. Oxidation resistance was carried out in a box furnace at 1600 °C for 1 hr.

3. RESULT AND DISCUSSION

To determine composite oxidation, weight changes of samples before and after of oxidation were measured. Images of all samples were prepared before and after oxidation (Fig. 1). To ensure about data accuracy, the test was conducted three times by sampling from three positions of the disk (A, B and C) for each composite (Fig. 2). According to Fig. 1, it can be observed that the composite 27, 19, 30 and 21 have the worst oxidation resistance and in contrary, composites 16, 24, 25, 26 and 32 indicate any oxidation in 1600 °C for 1 hr holding time.

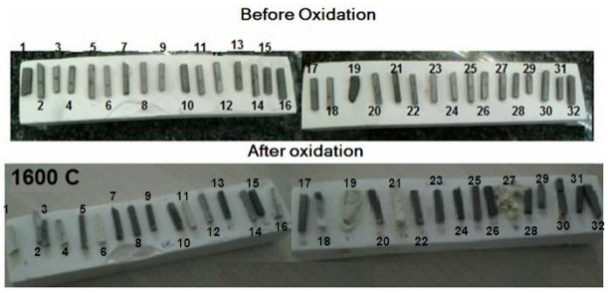

Figure. 1. Images of all samples before and after oxidation

Since the composites are different with each other, at least in 6 factors, so to specify importance and influence of each factor on oxidation, the data were entered to Qualitek-4 software (version 14.5). There are three different quality characteristics in standard analysis, namely, "Larger the better", "Smaller the better", and "On-target, minimum-variation" which was explained in details in thr previous study [8]. In this situation, "Smaller the better" will be chosen.

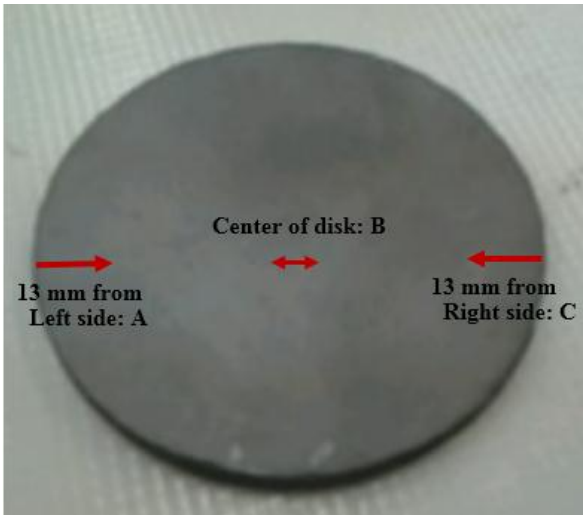

Figure. 2. Positions sampling from disk for each composite

The results of ANOVA (analysis of variance) analysis are given in Fig. 3. It is clear that ZrC with 45%, SiC with 13% temperature with 8% and C_f with 8% have the most

effect on oxidation resistance, respectively and M.t with 3% and pressure with 2% have the least influence. Other factors, such as HfB_2, $MoSi_2$ and time have a nearly equal portion, 6%, on oxidation resistance. The error of DOE is 2.7%. It means the design of the experiment was done correctly. Finally, to study and discuss the behavior of each factor, the standard analysis was applied.

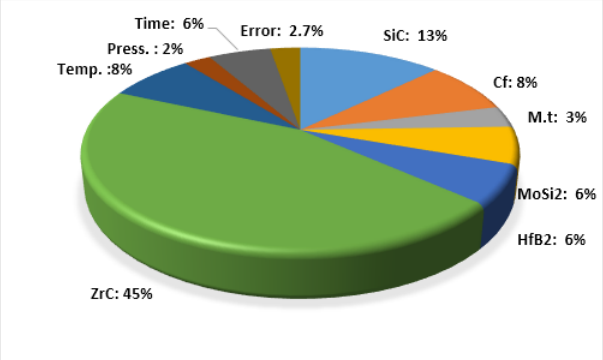

Figure. 3. Results of ANOVA for each factor

3.1. Effect of SiC, Cf and M.t. on the oxidation resistance

SiC addition resulted in more oxidation resistance according to Fig. 4 which is consistent with other researches reports. The addition of silica scale formers, such as SiC or $MoSi_2$, has been shown to improve oxidation resistance above 1100 °C [10]. In fact, SiC improves oxidation resistance by glassy layer formation. Below 1100 C, ZrB_2 oxidizes rapidly and the formed liquid B_2O_3 acts as a barrier to oxygen diffusion resulting in passive oxidation of ZrB_2 ceramic. Above 1300 C, B_2O_3 becomes non-protective because of rapid evaporation. SiC significantly improves the oxidation resistance of the composites due to the formation of the more viscous silica-containing glass, which has a higher melting temperature, a lower vapor pressure, and is a barrier to oxygen diffusion. Indeed, SiC-containing ZrB_2 based UHTCs are resistance to oxidation up to high temperatures of 1700–1800 °C [6].

Also, it is observed that more SiC addition induced better oxidation resistance (Fig. 4). Many research have investigated the oxidation behavior of ZrB_2–SiC ceramics[11-15]. Fahrenholtz et al. have studied the structure of oxide scales on ZrB_2–SiC ceramics after oxidation at temperatures up to 1500 °C [12-15]. They indicated that the typical scale is composed of three layers: (1) a SiO_2-rich glassy layer; (2) a thin ZrO_2–SiO_2 layer; (3) a SiC-depleted layer. Guo and et al. [3] were studied SiC content effect on oxidation behavior of ZrB_2-based composites with 10 vol% and 30 vol% SiC(ZB30S). They found although even with 10 vol% SiC (ZB10S), an outer glassy layer was formed, it had different microstructural features on ZB10S and ZB30S. ZrO_2 inclusions were observed in the layer on ZB10S, whereas very few ZrO_2 were found in the glassy layer on ZB30S. Also, the B_2O_3 concentration of the glassy layer in the ZB30S is lower than that of ZB10S.

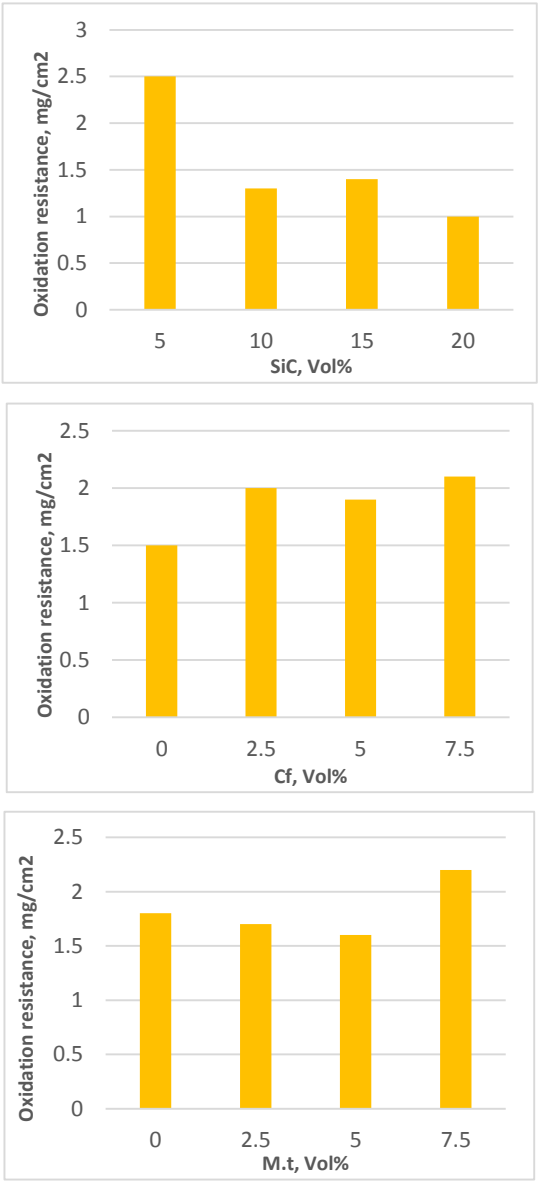

Figure. 4. Effect of SiC, C_f and M.t. on the oxidation resistance

The lower B_2O_3 concentration induced the higher viscosity of glassy layer of the ZB30S, which should retard oxygen diffusion. Finally, the higher viscosity and fewer ZrO_2 inclusions in the glassy layer resulted in better oxidation resistance of the ZB30S to ZB10S. Also, oxidation kinetics deviate from parabolic behavior (n = 2) for ZB10S, tending toward a logarithmic relationship (n= 3) for ZB30S, indicated that the glassy layer in ZB30S was more protective than that of ZB10S. Hence,

we conclude that more SiC addition induced better oxidation resistance.

All ZrB_2–SiC composites from 20 to 80 vol% SiC form a continuous layer of SiO_2 after oxidation in air for 50 h at 1773 K. For compositions from 20 to 80 vol% SiC there is a systematic trend for the SiO_2 layer thickness to decrease. Over the same composition range the SiC-depletion layer thickness also decreases systematically and becomes undetectable at 65 vol% SiC [16].

C_f has the detrimental effect on oxidation resistance, as expected according to its performance during exposure in the oxidizing atmosphere. Generally, the oxidation resistance of C_f in 350 °C to 450 °C range can be improved by controlling impurities that catalyze the oxidation [16]. So, oxidation increases by the addition of C_f. Although the knowledge about its detrimental effect on oxidation, it is used to improve fracture toughness in this study. Fracture toughness data will be expressed and discussed in another our work.

M.t has no significant effect on oxidation resistance up to 5 hr, but more M.t resulted in oxidation ascent. According to the previous study [17], surface destruction of C_f occurs in 7.5 hr milling time. It seems, this destruction decreases the stability of C_f and suspends it to more oxidation. Moreover, it can be related to a more activated C_f surface to react with oxygen due to more M.t.

3.2. Effect of $MoSi_2$, HfB_2 and ZrC on the oxidation resistance

Metal silicides, are often utilized ,to enhance high-temperature oxidation resistance for refractory ZrB_2 ceramics or coatings owing to the capability to form glassy silica layer.

As shown in Fig. 5, $MoSi_2$ improves oxidation resistance of ZrB_2. Although its low content compares with other additives such as SiC and HfB_2, it has a significant effect on it (Fig. 3). Only 6 vol% $MoSi_2$ addition in composites such as 4, 7, 10, 13, 20, 23 and 26 with different additives and SPS conditions, resulted to low oxidation (1.25) except in composite 4-four which its oxidation is 3. It can be related to its high ZrC (15 vol%) content which will be discussed in following.

The MoB, the oxidation product of element Mo in $MoSi_2$, could help to support the integrity of the silica layer. MoB played the role defending the wholeness of the silica layer and reducing the evaporation of B_2O_3 and MoO_3 at the same time[18].

HfB_2 improves oxidation resistance of ZrB_2-SiC- based composites in 15 vol% and has no sensitive effect in lower content, as shown in Fig. 3. Both HfB_2 and ZrB_2 are refractory materials which oxidize in high temperatures and creates HfO_2 and ZrO_2 oxide films respectively as follow equations:

$$ZrB_2+5/2\ O_2=ZrO_2+B_2O_3$$

$$HfB_2+5/2\ O_2=HfO_2+B_2O_3$$

Since both of these oxides have an equal melting point, 2715 °C, their oxidation resistance is the same approximately.Of course in studious was done by M. Malik, degradation appears more severe in isothermally oxidized ZS rather than HS due to phase transformations in ZrO_2[19].

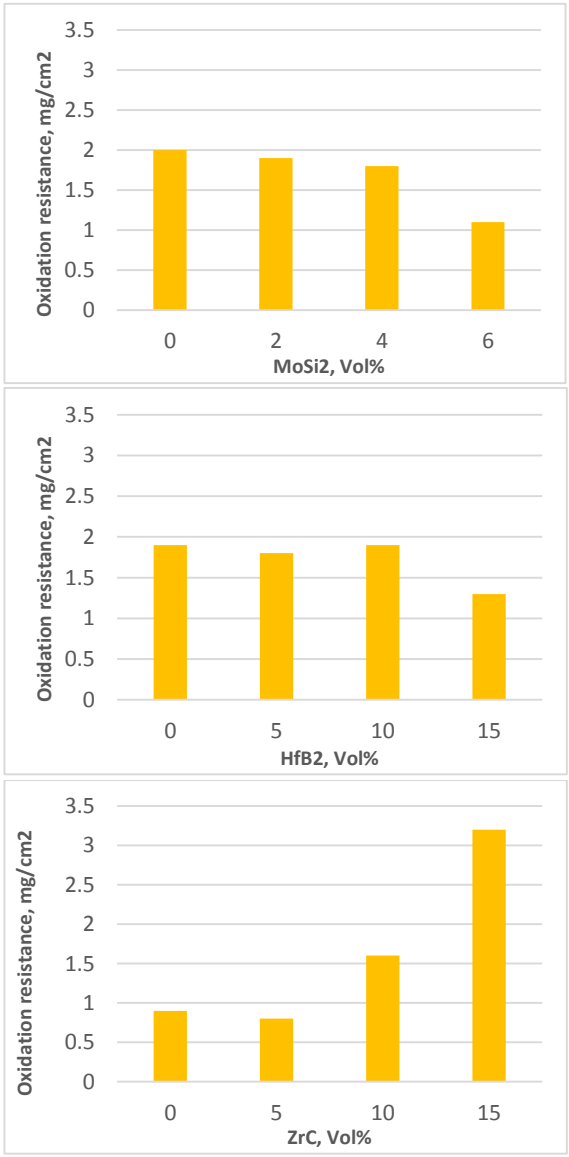

Figure. 5. Effect of $MoSi_2$, HfB_2 and ZrC on the oxidation resistance

Effect of ZrC on oxidation of ZrB_2-SiC-based composites are shown in Fig. 5. ZrC addition till 5 vol% does not have any significant effect on oxidation but in a higher content, has a detrimental effect and oxidation increases very sharply in 1600 °C. ZrC decreases oxidation resistance by three mechanisms: 1) Guo et al. [20] reported oxide structure of ZrB_2–SiC with the addition of 15vol%ZrC at 1500 °C and observed one ZrO_2 layer with large voids. This layer could not

effectively prevent oxygen diffusion, compared with the borosilicate glass layer on the surface of ZrB_2–SiC [21]. 2) The SiO_2-rich layer was much thinner with 10 vol% ZrC (5–20 μm) and disappeared at 20 vol% ZrC. 3) The obvious static oxidation of ZSZ was attributed to the non-protective oxidation of ZrC above 400 °C and the large volume expansion during the conversion of ZrC to ZrO_2 (about 32%). The oxidation of baseline ZS and low content of ZrC (10 vol%) obeyed parabolic kinetics while that containing 20 vol% ZrC followed linear kinetics[22].

3.3. Effect of temperature, time and pressure on the oxidation resistance

SPS parameters effect on is shown in Fig. 6. It is obvious that the temperature has the most influence among them.

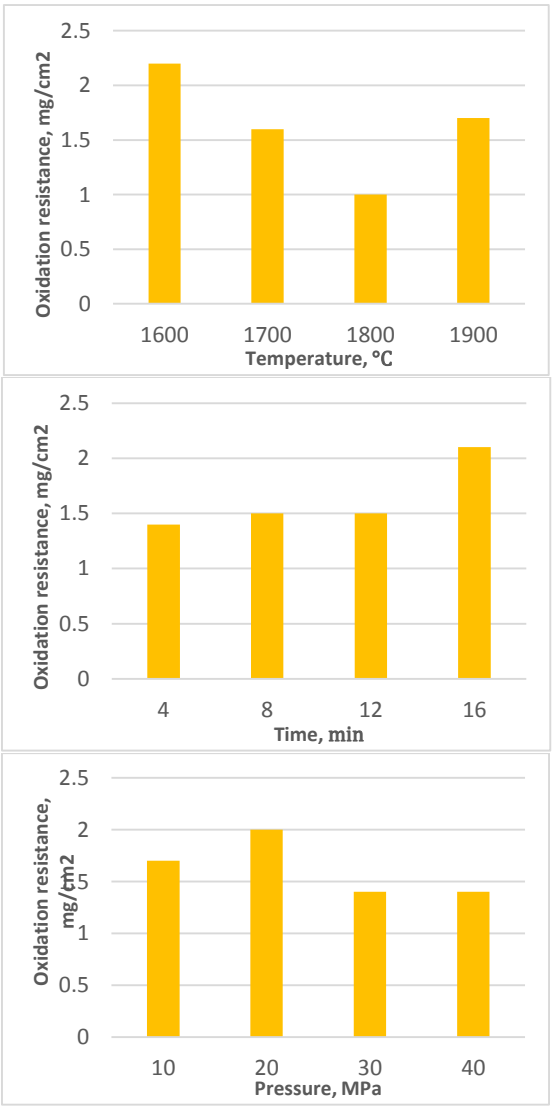

Figure. 6. Effect of temperature, time and pressure on the oxidation resistance

On the other hand, time and pressure have a negligible effect on it which may be related to their low effect on grain size based on previous study. Also, although temperature ascent up to 1800 °C induces oxidation reduction, more increase has an inverse effect. According to temperature effect data [8] on grain size, significant grain size ascent is observed in 1900°C. So, it seems that the finer microstructure has better oxidation resistance which of course is needed to investigate in details and prove by logical reason. It will be done in our next study.

3.4. Validation test with an optimum level for oxidation resistance

To validate the obtained results, the Taguchi method is used. Optimum levels to reach the best oxidation resistance is shown in table 1. So, for results validation, a composite was prepared with optimum levels (table 1). Then oxidation test was done. No oxidation effect was observed which was completely consisted of perdition result of Taguchi method.

TABLE 1. Optimum values to reach the best oxidation resistance

Factor	SiC	C_f	M.t	$MoSi_2$	HfB_2	ZrC	T	P	t
	Vol%						C	MPa	min
optimum level to reach the best oxidation resistance	20	0	0	6	15	0	1800	30	8

4. CONCLUSION

4.1. HfB_2 has the positive effect on oxidation resistance of ZrB_2-based ceramics.
4.2. It has been concluded that ZrC by 45% has the most significant effect on the oxidation resistance and oxidation resistance decreases by ZrC ascent.
4.3. Among the SPS parameters, the temperature has the most effect on microstructure and eventually oxidation resistance.
4.4. Pressure by 2.3% and M.t by 3.4% have the least effect on the oxidation resistance.
4.5. Other factors such as SiC, C_f, temperature, HfB_2, $MoSi_2$ and time have 12.8%, 8.3%, 7.7%, 6.2%, 5.9% and 5.6% on the oxidation resistance respectively.
4.6. Optimum values to fabricate ZrB_2- based composite with the best oxidation resistance are as below:

SiC	**C_f**	**M.t**	**$MoSi_2$**	**HfB_2**	**ZrC**	**T**	**P**	**t**
20 vol%	0 vol%	5 hr	6 vol%	15 vol%	10 vol%	1800 C	30 MPa	8 min

5. ACKNOWLEDGEMENTS

This article has been extracted from the research project in the name of "Optimization of Effective Parameters on Thermal Shock Resistance and oxidation of ZrB_2 Ceramic Prepared by SPS" which was supported by Islamic Azad University of Ahvaz.

REFERENCES

1. Shahedi Asl, M., Ghassemi Kakroudi, M., Nayebi, B., Nasiri, H., "Taguchi analysis on the effect of hot pressing parameters on density and hardness of zirconium diboride", ***International Journal of Refractory Metals and Hard Materials,*** Vol. 50, (2015), 313-320.
2. George, M.R., "Studies of ultra-high temperature ceramic composite components: synthesis and characterization of HfO_xC_y and Si oxidation in atomic oxygen containing environments", P.H.D Thesis, Vander Bilt university, (2008).
3. Guo, W.M., Zhang, G.J., "Oxidation resistance and strength retention of ZrB_2–SiC ceramics", ***Journal of the European Ceramic Society,*** Vol. 30, (2010), 2387-2395.
4. Sarin, P., Driemeyer, P.E., . Haggerty, R.P., Kim, D. K., Bell, J.L., Apostolov, Z.D., Kriven, W.M., "In situ studies of oxidation of ZrB_2 and ZrB_2–SiC composites at high temperatures", ***Journal of the European Ceramic Society,*** Vol. 30, (2010), 2375-2386.
5. Rezaie, A.R., . Fahrenholtz, W.G., Hilmas, G.E., "The effect of a graphite addition on oxidation of ZrB_2–SiC in air at 1500 ◦C", ***Journal of the European Ceramic Society,*** Vol. 33, (2013), 413-421.
6. Han, J., Hu, P., Zhang, X., Meng, S., Han, W., "Oxidation-resistant ZrB_2–SiC composites at 2200 °C", ***Composites Science and Technology,*** Vol. 68, (2008), 799-806.
7. Balak, Z., Zakeri, M., Rahimipour, M.R., Salahi, E., "Taguchi design and hardness optimization of ZrB_2-based composites reinforced with chopped carbon fiber and different additives and prepared by SPS", ***Journal of Alloys and Compounds,*** Vol. 639, (2015), 617-625.
8. Balak, Z., Zakeri, "exural strength of ZrB_2-based composites prepared by spark plasma sintering", ***International Journal of Refractory Metals and Hard Materials,*** Vol. 55, (2016), 58-67.
9. Balak, Z., Zakeri, M., Rahimipour, M.R., Salahi, E., Kermani, M., "Investigation of Effective Parameters on Densification of ZrB_2-SiC Based Composites Using Taguchi Method", ***ACERP,*** Vol. 2, No. 2, (2016), 7-15.
10. Monteverde F., "The thermal stability in air of hot-pressed diboride matrix composites for uses at ultra-high temperatures", ***Corrosion Science,*** Vol. 47, (2005), 2020-2033.
11. Li, J., Lenosky, T.J., Först, C.J., Yip, S. "Thermochemical and mechanical stabilities of the oxide scale of ZrB_2 + SiC and oxygen transport mechanisms", ***Journal of the American Ceramic Society,*** Vol. 91, (2008), 1475-1480.
12. Rezaie, A., Fahrenholtz, W.G., Hilmas, G.E., "Oxidation of zirconium diboridesilicon carbide at 1500 ◦C at a low partial pressure of oxygen", ***Journal of the American Ceramic Society,*** Vol. 89, (2006), 3240-3245.
13. Monteverde, F., Bellosi, A., "Oxidation of ZrB_2-based ceramics in dry air", ***Journal of the Electrochemical Society,*** Vol. 150, (2003), 552-559.
14. Rezaie, A., Fahrenholtz, W.G., Hilmas, G.E., "Evolution of structure during the oxidation of zirconium diboride-silicon carbide in air up to 1500 °C", ***Journal of the European Ceramic Society,*** Vol. 27, (2007), 2495-2501.
15. Fahrenholtz, W.G., "Thermodynamic analysis of ZrB_2–SiC oxidation: formation of a SiC-depleted region", ***Journal of the American Ceramic Society,*** Vol. 90, (2007),143-148.
16. Peter, A., Williams, A., Ridwan, S., John, H., Perepezko, P.R., "Oxidation of ZrB_2–SiC ultra-high temperature composites over a wide range of SiC content", ***Journal of the European Ceramic Society,*** Vol. 32, (2012), 3875-3883.
17. Buckley, J.D., Edie, D.D., "Carbon-Carbon materials and composites", (1993).
18. Wang, Z., Niu, Y., Hu, C., Li, H., Zeng, Zheng, X., Sun, "High temperature oxidation resistance of metal silicide incorporated ZrB_2 composite coatings" , ***Prepared by Vacuum Plasma Spray Ceramics International,*** Vol. 41, (2015),14868-14875.
19. Mallik, M., Ray, K.K. ,Mitra, R., "Oxidation behavior of hot pressed ZrB_2–SiC and HfB_2–SiC composites", ***Journal of the European Ceramic Society,*** Vol. 31, (2011), 199-215.
20. Guo, W.M.,, Zhou X.J., Zhang, G.J., Kan, Y.M., Li, Y.G, Wang, P.L., "Effect of Si and Zr additions on oxidation resistance of hot-pressed ZrB_2–SiC composites with polycarbosilaneasa precursor at 1500°C", ***Journal of Alloys and Compounds,*** Vol. 471, (2009), 153-156.
21. Ni, D.W., Zhang, G.J., Xu, F.F., Guo, W.M., "Initial stage of oxidation process and microstructure analysis of HfB_2-20 vol% SiC composite at 1500°C", ***Scripta Materialia,*** Vol. 64, (2011), 617-620.
22. Liu, H. L., Liu, J.X., Liu, H.T., Zhang, G.J., "Changed oxidation behavior of ZrB_2–SiC ceramics with the addition of ZrC", ***Ceramics International,*** Vol. 41, (2015), 8247-8251.