Reactive Synthesis of ZrB<sub>2</sub>-based Ultra High Temperature Ceramics

Hai-Tao Liu and Guo-Jun Zhang†
State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai 200050, China
(Received May 22, 2012; Accepted June 28, 2012)

ABSTRACT

Reactive processing, such as reactive hot pressing (RHP) and reactive spark plasma sintering (R-SPS), is effective densification method to prepare ZrB<sub>2</sub>-based ultra high temperature ceramics (UHTCs). The present paper reviewed some typical reactive processing of ZrB<sub>2</sub>-based UHTCs. All the reactions from the starting materials in the reactive processing are thermodynamically favorable, which generate enough energy and driving force for the densification of the final products under a relatively low temperature. Besides, compared with non-reactive processing, anisotropic ZrB<sub>2</sub> grains, such as ZrB<sub>2</sub> platelets, can only be obtained in the reactive processing, resulting in an improvement of the mechanical properties.

Key words : Zirconium diboride (ZrB<sub>2</sub>), Ultra high temperature ceramics (UHTCs), Reactive processing, Reactive hot pressing (RHP), Platelet

1. Introduction

With the development of hypersonic aerospace vehicles and re-usable atmospheric re-entry vehicles, ultra high temperature ceramics (UHTCs) has attracted lots of interests and attentions during the past few years.1-7 The UHTCs consists of several borides, carbides and nitrides of the group IVB and VB transition metals, whose melting temperatures are in excess of 3000°C. Among these materials, ZrB<sub>2</sub>-based ceramics are important member of the UHTCs family.8-12 Owing to a unique combination of chemical stability, high electrical and thermal conductivities, and resistance to erosion/corrosion, ZrB<sub>2</sub>-based UHTCs are considered to be suitable for the extreme chemical and thermal environments for high temperature structural applications.

On the other hand, however, because of the high refractoriness, the densification of ZrB<sub>2</sub>-based UHTCs becomes a difficult task. Recent studies have focused on different densification techniques together with some additives which promote the densification process. Nowadays, there are four typical densification approaches: pressureless sintering (PLS),10,13-17 hot pressing (HP),17-20 reactive processing and spark plasma sintering (SPS).4,17,21-24 Besides, there are also some processing combining these approaches, such as reactive hot pressing (RHP reactive processing + HP),8,15,21,23-35 and reactive spark plasma sintering (R-SPS, reactive processing + spark plasma sintering).36,37 Among these methods, it should be noted that the reactive processing, also including the RHP and R-SPS processing, is an effective densification method which can produce UHTCs at a relatively lower temperature, along with novel and controlled microstructures, with high chemical compatibility of the in-situ formed individual phases and phase distribution uniformity, which has been attracted plenty attentions in recent years.

The reactive processing, which combines the synthesis routes and densification process together, can produce the in-situ formed thermodynamic stable phases from some available starting powders and gain the final densified UHTCs by one step.6,8,20 The chemical reactions in the reactive process are highly exothermic and thermodynamically favorable, generating a mass of heat which can reduce the densification temperature to a great degree.27,30 Also, the in-situ formed phases are highly chemically reactive and have unique ability to form anisotropic morphology, which provide a wide range for microstructure tailoring and property improvements of the UHTCs.26,28,33-35

In the present paper, preparation of ZrB<sub>2</sub>-based UHTCs via reactive processing is reviewed. The article starts with the thermodynamic consideration, and then discusses some typical reactive processing of ZrB<sub>2</sub>-based ceramics. Although the paper only focus on the ZrB<sub>2</sub>-based ceramics, yet the reactive process is also suitable for the Ti and Hf-based ceramics, which also belong to the borides of IVB transition metal group.

2. Thermodynamic Consideration

Usually, the starting materials for the ZrB<sub>2</sub>-based UHTCs via reactive process are some commercially available powders. The Zr sources are commonly dependent on elemental Zr or ZrH<sub>x</sub> while the B sources come from some compound, such as B<sub>4</sub>C and BN, along with elemental B. It should be
noted that although ZrO$_2$ is a much available source for Zr, it is usually used for synthesis ZrB$_2$ powders by the boro/carbo-thermal reduction, owing to the high content of oxygen in ZrO$_2$. Moreover, because ZrB$_2$-based ceramics also contain other phases, such as SiC, ZrC and MoSi$_2$, so the B sources, B$_4$C and BN, are also the C or N sources for the final products. The reactions to prepare ZrB$_2$ monolithic or ZrB$_2$-based ceramics are as follows:

\[
\begin{align*}
Zr + 2B &= ZrB_2 & (1) \\
3Zr + B_4C &= 2ZrB_2 + ZrC & (8) \\
Zr + 2B + xMo + 2xSi &= ZrB_2 + xMoSi_2 & (9) \\
Zr + 2Al + 2BN &= ZrB_2 + 2AlN & (11)
\end{align*}
\]

Reactions (1) and (2) are used to prepare monolithic ZrB$_2$ ceramics, while the others are used to prepare ZrB$_2$-based composites. The Gibbs’ free energies of these reactions are summarized in Fig. 1. It can be seen that all these reactions are highly exothermic and thermodynamically favorable, which is suitable for reactive processing.

3. Preparation of ZrB$_2$-based UHTCs Via Reactive Processing

3.1. ZrB$_2$ monolithic ceramics

ZrB$_2$ monolithic ceramics can be prepared by the simple reaction:

\[
Zr + 2B = ZrB_2
\]

Chamberlain et al. once prepared the monolithic ZrB$_2$ ceramics by RHP and studied the reaction mechanism that formed ZrB$_2$ from elemental Zr and B.$^{29}$ Powder mixtures were examined before and after heating to 1700°C for reaction. Analysis concluded that B diffused into the Zr granules to form ZrB$_2$. This behavior has also been observed in diffusion couple experiments in which polished Zr was heated to 1450°C in contact with B. Given this reaction path, the size and shape of the Zr precursor determined the size and shape of the resulting ZrB$_2$ and Fig. 2 demonstrates a simple schematic of the possible reaction path, which is very similar to the case occurred in the reactive synthesis of ZrB$_2$-SiC composite (Fig. 3).

In view of that the final ZrB$_2$ particle size dependent on the starting Zr metal particles, later, they began to try to prepare monolithic ZrB$_2$ ceramics using finer starting materials.$^{31}$ By attrition milling of the precursors, nanosized (less than 100 nm) Zr metal particles were available to react with B to form ZrB$_2$. As low as 600°C, ZrB$_2$ can be obtained with an average particle size of less than 100 nm. The nano-crystalline ZrB$_2$ exhibited significant coarsening and densification between 600°C and 1450°C, which was result of the fine particle size and possibly a high defect concentration. Significant particle coarsening below 1650°C decreased the sinterability of the ZrB$_2$. As a result, processing temperatures of 2100°C were required to achieve full density. However, consolidation of RHPed ZrB$_2$ at 2100°C resulted in large grains (~12 µm), leading to a relative lower flexure strength.

3.2. ZrB$_2$-SiC-(third phase) ceramics

In practical applications, ZrB$_2$-SiC-(third phase) ceramics is an important member, where the SiC and the third phase can improve the densification process and the properties of the final products. Therefore, the ZrB$_2$-SiC-(third phase) ceram-
ics system has been paid the most attentions in the ZrB$_2$-based UHTCs fields.

Zhang et al. once prepared ZrB$_2$-SiC composites by RHP using Zr, Si and B$_4$C as starting powders, according to the following reaction$^{26}$:

$$2Zr + B_4C + Si = 2ZrB_2 + SiC$$  \hspace{1cm} (3')

The volume contents of the composite formed from the above-mentioned reaction are 74.85 vol% ZrB$_2$ and 25.15 vol% SiC. A formation mechanism of this composite in the reactive hot pressing process were proposed as shown in Fig. 3. It can be seen that, in the reactive hot-pressing process, the B and C atoms in B$_4$C will diffuse into the Zr and Si sites, respectively, and then form ZrB$_2$ and SiC in situ. Because the diffusion of Zr and Si atoms is slow, the formed agglomerates of synthesized ZrB$_2$ and SiC possess the features of the starting powders. Owing to the RHP process, the grain sizes of both the phases are relatively small, resulting in an improvement of the mechanical properties, compared with the same composites prepared by other methods. Furthermore, according to the model, it is believed that a ZrB$_2$-SiC composite with a fine and homogeneous microstructure and better mechanical properties can be obtained by using starting powders with a fine particle size, providing an approach to optimize the microstructures and properties.

Subsequently, using the same starting powders, Wu et al.$^{20}$ developed an extended reaction to prepare ZrB$_2$-SiC-ZrC composites via RHP based on the above work:

$$(2+x)Zr + B_4C + (1-x)Si = 2ZrB_2 + (1-x)SiC + xZrC$$  \hspace{1cm} (5')

When $x=0$, reaction (5) reduces to reaction (3). For reaction (5), through increasing the amount of Zr and reducing Si, a third phase ZrC, which is also one kind of UHTCs can be obtained. When taken $x=0.20$, the calculated volumetric composition of final product is (vol%) 73.6%ZrB$_2$+20SiC+6.4ZrC.

Further investigation on the reaction revealed that reaction (5) may consist of two sub-reactions, which take place in steps as follows:

$$3Zr + B_4C = 2ZrB_2 + ZrC$$  \hspace{1cm} (8')

$$2ZrC + B_4C + 3Si = 2ZrB_2 + 3SiC$$  \hspace{1cm} (12)

This means that in the reactive process, ZrC first formed at a relatively low temperature and with the temperature increase, ZrB$_2$ become the main phase; in addition, SiC appeared and the amount of ZrC decreased at the same time according to reaction (12). In view of these reaction steps, Wu optimized the reaction model of the phase formation sequence during RHP when using starting materials of Zr, Si and B$_4$C (Fig. 4). Besides, from the SEM images (Fig. 5), it can be speculated that the ZrC seems to promote the growth of the ZrB$_2$ platelets, which should have improved the fracture toughness of the composites. The same RHP process can also be used to prepare HfB$_2$-SiC ceramics using Hf, Si and B$_4$C as starting materials.$^{20}$

As discussed above, reaction (5) is thermodynamic favorable, so Wu et al.$^{27}$ developed the RHP process, where an SHS reaction can be ignited instead of reaction in two steps (reaction (8) and (12)) : after planetary ball milling with a high rotation speed, the starting powders can be not only mixed efficiently, but also reduced the particle size by the effect of friction and high-energy collisions, resulting in a homogeneous mixture with fine and high reactive powders. Then with a heating rate of 10$^\circ$C/min, the SHS reaction was ignited. The as-obtained fine powders with fresh surfaces have high reactivity, and thus provide a high driving force in densification. Besides, the heat generated in the SHS reaction can also remove the oxide impurities. Both the high reactive powders and the low oxygen impurities can promote the mass transport during the heating process, which result in a sintering temperature as low as 1600$^\circ$C (relative density: 97.3%).

Besides ZrB$_2$-SiC and ZrB$_2$-SiC-ZrC, Wu et al.$^{21}$ also prepared ZrB$_2$-SiC-ZrN and ZrB$_2$-SiC-AlN composites when adding BN and Al into the original starting materials of Zr, Si and B$_4$C, according to the reaction:

$$(1+x)Zr + (0.5 – 0.25x)Si + (0.5 – 0.25x)B_4C + xBN = ZrB_2 + (0.5 – 0.25x)SiC + xZrN$$  \hspace{1cm} (6')

$$Zr + (0.5 – 0.25x)Si + (0.5 – 0.25x)B_4C + xBN + xAl = ZrB_2 + (0.5 – 0.25x)SiC + xAlN$$  \hspace{1cm} (7')

![Fig. 4](image)

**Fig. 4.** Microstructure formation mechanism of the ZrB$_2$-ZrC-SiC composite in the reaction-synthesis process, depicting the conversion from (a) the powder compact to (b) the intermediate state, and (c) the final microstructure of the composite.$^{26}$

![Fig. 5](image)

**Fig. 5.** Backscattered electron images of a polished surface of the reactive hot-pressed composite. The gray phase is ZrB$_2$, the dark phase is SiC, and the white phase is ZrC.$^{20}$
Wu prepared these composites by both RHP and R-SPS. There results show that there are not remarkable differences in the ZrB\textsubscript{2}-SiC and ZrB\textsubscript{2}-SiC-ZrC systems in both the RHP and R-SPS conditions. While it is not the same case in the ZrB\textsubscript{2}-SiC-ZnN and ZrB\textsubscript{2}-SiC-AlN composites: According to the XRD patterns, the phases existing in the two systems are ZrB\textsubscript{2}, SiC and a solid solution of Zr(C,N) instead of ZnN and AlN. And the Zr(C,N) phase in the R-SPS process is much higher than that in RHP process. It is known that ZrC acts as an intermediate phase during sintering of the ZrB\textsubscript{2}-SiC-ZrC composite.\textsuperscript{28} It can be deduced that the Zr(C,N) in the current work acted in the same way as ZrC did. Unlike the RHP process, however, the R-SPS process had very high heating rate and short holding time. The intermediate Zr(C,N) cannot transfer to ZrB\textsubscript{2} and SiC completely, so the reaction proceeds far away from the equilibrium state, and the content of Zr(C,N) will be higher in the R-SPS composites. Besides the Zr(C,N) phase amounts, the R-SPS process tends to form a more homogeneous and finer microstructure because of its high heating rate and short holding time, while the RHP process is likely to form coarse microstructures due to the high holding time long enough for grain-growth to proceed. The short holding time and finer microstructure of the final products in the SPS process also gives the advantage of the densification of the materials.

ZrB\textsubscript{2}-SiC composites also prepared by R-SPS process using the same starting material as Zhang’s\textsuperscript{36} at 1450°C for a 3-min dwelling time under 30 MPa by Zhao et al.\textsuperscript{37} The results show that both intergranular and intragranular SiC grains are found in the micrographs of the composite, and a number of SiC grains (<0.5 \textmu m) are entrapped within the ZrB\textsubscript{2} grains. The reason for the formation of this microstructure was possibly based on the following two factors:

(i) Some of the SiC grains may not form directly from the initial Si, but from intermediate phases. The following chemical reactions are proposed to occur:

\begin{align*}
3\text{Zr} + \text{B}_2\text{C} & = 2\text{ZrB}_2 + \text{ZrC} \quad (8') \\
\text{xZrC} + \text{ySi} & = \text{ZrSi}_x \quad \text{y/x = 1/2, 2} \quad (13) \\
2\text{ZrC} + \text{B}_2\text{C} + 3\text{Si} & = 2\text{ZrB}_2 + 3\text{SiC} \quad (12') \\
\text{ZrSi}_x + \text{B}_2\text{C} + \text{ZrC} & = 2\text{ZrB}_2 + 2\text{SiC} \quad (14) \\
\text{ZrSi}_x + \text{B}_4\text{C} & = 2\text{ZrB}_2 + \text{SiC} \quad (15) \\
\text{ZrSi}_x + 3\text{B}_2\text{C} + 3\text{Zr} & = 6\text{ZrB}_2 + 3\text{SiC} \quad (16)
\end{align*}

Reactions (14)–(16) describe the delayed formation of SiC.

(ii) The shortened sintering time and lowered sintering temperature, as a high sintering temperature and a long sintering time, could induce grain growth. With lowered sintering temperature and a shortened sintering time, the SiC nanophase can be retained. It is speculated that the reaction nucleation and grain growth rate of ZrB\textsubscript{2} is much faster than that of SiC. During sintering and consolidation processes, some of the SiC grains (<0.5 \textmu m) remain located intragranularly. Also, it was discovered that density increases with holding time and applied pressure.\textsuperscript{38}

Furthermore, also using Zr, B\textsubscript{2}C and Si, Qu prepared ZrB\textsubscript{2}-SiC-ZrC composites by in situ reactive synthesis at different temperatures (from 1750°C to 1900°C).\textsuperscript{39} The results showed that the relative density and average grain size of the composites increased with the increase of sintering temperature. There also found some platelet ZrB\textsubscript{2} grains in the microstructure and the fracture toughness has remarkable improved owing to the anisotropic grains. Then a contrast experiment was done that ZrB\textsubscript{2}-SiC-ZrC composites were fabricated using ZrB\textsubscript{2}, SiC and ZrC as raw powders for HP and Zr, B\textsubscript{2}C and Si for RHP.\textsuperscript{40} The results show that the ZrB\textsubscript{2} grains were equiaxed in the HP sample while a mixture of equiaxed and plate-like ZrB\textsubscript{2} grains were found in the RHP samples. So, it could be concluded that the reactive process is a unique method to prepare ZrB\textsubscript{2}-based ceramics with anisotropic ZrB\textsubscript{2} grains.

Besides using B\textsubscript{2}C as B source and starting material, Chamberlain once used elemental Zr, B, SiC and small amount of B\textsubscript{4}C (to remove oxygen impurities) as starting materials to prepare ZrB\textsubscript{2}-SiC ceramics by RHP.\textsuperscript{41} Samples with relative densities in excess of 95% can be produced at temperature of 1650°C. the reaction of the RHP is as follows:

\[ \text{Zr} + 2\text{B} + x\text{SiC} = 2\text{ZrB}_2 + x\text{SiC} \]  \hspace{1cm} (17)

In fact, the reaction just started between Zr and B just like the preparation of monolithic ZrB\textsubscript{2} ceramics:

\[ \text{Zr} + 2\text{B} = 2\text{ZrB}_2 \]  \hspace{1cm} (1')

Because reaction (1) is thermodynamically favorable, the SiC phase can not only be an important second phases for the final product, but also play a role as an inert diluent to reduce the potential for a self-propagating reaction to ignite. Besides SiC diluent, the in situ reaction/densification process also used a slow heating rate (~1°C/min below 600°C) and an extended isothermal hold in the reaction temperature range (~6 h at 600°C) to avoid initiating a self-propagating reaction.

Owing to the attrition milling for the starting materials, the particle size of Zr metal was reduced. The nanometer-sized precursors lead to the reaction between Zr and B proceed to completion at 600°C, resulting in nanosized crystallites of ZrB\textsubscript{2} products. And even after heating to 1000°C, the ZrB\textsubscript{2} crystallites are still as small as ~50 nm. Then the crystallite size increased significantly upon heating to 1450°C to about 300 nm. Measurement of geometric densities of specimens produced at 1000°C or 1450°C showed an increase in the relative density from 37% to 40%, further verifying that coarsening and densification were possible at these temperatures. From this analysis, it can be concluded that the use of a low-temperature reaction to form ZrB\textsubscript{2} allowed for retention of nanometer-size particles from the milling process through the conversion to ZrB\textsubscript{2}. It can be concluded that the grain coarsening observed at these moderate temperatures suggests that the driving force for densification was significantly higher in the RHP materials than in conventional...
powders. Besides using Zr, B and SiC as starting materials, Zimmerrmann also fabricated ZrB$_2$-SiC ceramics by in-situ RHP from ZrH$_2$, B$_4$C and Si$^{(3)}$. Fully dense ZrB$_2$–27 vol% SiC ceramics were fabricated by RHP at 1890°C for 10 min according to the reaction:

$$2ZrH_2 + B_4C + Si = 2ZrB_2 + SiC + 2H_2(g)$$ (4')

The reaction was studied using two processes, (1) powder reactions at temperatures from 1150 to 1450°C and (2) reactive hot pressing between 1600 and 1900°C.

For the stoichiometric composition according to reaction (4), the products included the expected ZrB$_2$ and SiC phases with some minor secondary products including ZrC, ZrO$_2$ and Si. The presence of ZrC and Si in the final composition indicated that the precursors were deficient in boron compared to Reaction (4). The boron deficiency probably resulted from the presence of oxide impurities (as B$_2$O$_3$) on the surface of the B$_4$C powder. Because it is a more reactive metal than Si, any free Zr will preferentially react with B, C or O species present to form a Zr compound and leave unreacted Si. In addition, ZrC is not stable in the presence of boron or B$_4$C as reaction (18) is favorable at 1150°C. Thus, ZrB$_2$ and SiC should form if additional B$_4$C were added to the system. Because of the boron (B$_4$C) deficiency, ZrB$_2$ and ZrC form and are stable with silicon as indicated by the positive change in Gibbs’ free energy of Reactions (19) and (20) at 1150°C.

$$2ZrC + B_4C + 3Si = 2ZrB_2 + 3SiC$$ (18)

$$ZrC + Si = SiC + Zr$$ (19)

$$2ZrB_2 + Si = SiB_4 + 2Zr$$ (20)

When heated to 1300°C, there are no silicon peaks, together with an apparent increase in the amount of SiC, a decrease in the amount of ZrC, and the formation of ZrO$_2$. The reduction in the amount of ZrC and Si, relative to the sample reacted at 1150°C, may be due to reactions involving B$_2$O$_3$ that become favorable in a flowing gas atmosphere that would keep the activity of SiO low (Reaction 21). The loss of SiO as a gaseous phase is consistent with the total mass loss of 1.5% observed at 1300°C, compared to 1.3% for the sample reacted at 1150°C and 1.49% predicted from Reaction 1. Reactions between ZrC and B$_2$O$_3$ could also result in the formation of ZrO$_2$. The XRD analysis and mass loss of the composition heated to 1300°C were consistent with the consumption of ZrC and B$_2$O$_3$ described by Reactions 21 and 22.

$$ZrC + B_2O_3 + 4Si \rightarrow ZrB_2 + SiC + 3SiO$$ (21)

$$5ZrC + 2B_2O_3 + 5Si \rightarrow 2ZrB_2 + 5SiC + 3ZrO_2$$ (22)

The higher mass losses were attributed to volatilization of unreacted B$_2$O$_3$ and SiO, which was formed due to Reaction 21.

In order to eliminate the undesired ZrO$_2$ and ZrC phases, a second powder batch was formulated with excess B$_4$C and Si. Excess B$_4$C supplied a sufficient amount of boron to react with all of the zirconium to minimize the formation of ZrC. This formulation also increased the zirconium to silicon molar ratio from 2:1 to 2:1.16 to accommodate Si loss due to SiO formation. Based on XRD analysis, the products of the reaction included ZrB$_2$, β-SiC and excess B$_4$C. Neither ZrC nor ZrO$_2$ peaks were observed in the X-ray diffraction patterns.

The excess B$_4$C provided sufficient boron to react with all of the zirconium to produce ZrB$_2$, thus eliminating the formation of ZrC. In addition, excess Si was added based on the lower-than-expected SiC content. Reactive hot pressing of the B$_4$C-rich composition produced ZrB$_2$ with 27 vol% SiC and less than 1 vol% excess B$_4$C. Reactively hot pressed samples with excess B$_4$C also appeared to decrease the ZrB$_2$ grain size from ~5 to ~2 μm and the mean SiC particle size from ~3.5 to ~1 μm compared to samples reactively hot pressed with a stoichiometric powder mixture.

Using the same Zr source, ZrH$_2$, together with B, SiC and B$_4$C (1.0wt%, to remove any ZrO$_2$ impurity), Ran prepared fully densified ZrB$_2$-20vol%SiC composites by reactive pulsed electric current sintering (PECS) within a total thermal cycle time of only 50 min$^{(3)}$. In view of that when metal Zr reacts with B, the B dissolves and diffuses into the metal Zr to form ZrB$_2$. Therefore, the size and shape of the ZrB$_2$ product will be strongly influenced by the Zr starting powder. Since metal Zr is ductile and difficult to be milled down to small particle sizes, the use of brittle ZrH$_2$ is thought to be a suitable alternative to easily obtain small starting powders. It should be noted that the same starting material, TiH$_2$, had been also used to prepare TiB$_2$-based ceramic.$^{30-40}$ Metal Zr is also considered to be more prone to self-ignition or oxidation in air compared to ZrH$_2$. Moreover, the particle size can be further decreased by the decomposition of ZrH$_2$. They investigated the reaction process and reveal that ZrH$_2$ first decomposed into metal Zr before reacting with B to form ZrB$_2$. Therefore, it can be concluded that the reaction between ZrH$_2$ and B is basically the same as the reaction of Zr and B with a super-imposed dehydrogenation of ZrH$_2$. The reactions in this experiment are as follow, one is for the reaction process and the other is for removing oxygen impurities:

$$ZrH_2 + 2B + SiC = ZrB_2 + SiC + H_2(g)$$ (23)

Which can be reduced to reaction (2):

$$ZrH_2 + 2B = ZrB_2 + H_2(g)$$ (2')

$$5B_4C + 7ZrO_2 = 7ZrB_2 + 3B_2O_3(g) + 5CO(g)$$ (24)

In their study, a heating rate of 50°C/min was used to in situ synthesize and sinter ZrH$_2$-B-SiC-B$_4$C powders in one step using PECS. During the PECS process, the changes in temperature, pressure, vacuum level, shrinkage and shrinkage rate were recorded to allow elucidating the reactive synthesis and densification process. In the experiments, results show that an abrupt exothermic reaction has occurred. Since
the reaction between metal Zr and B is reported to be highly exothermic with an adiabatic temperature of 3050°C, a self-propagating high temperature synthesis (SHS) reaction can be ignited by a current pulse. From the PECS experiments and particle size of the powder grades, it can be concluded that the critical particle size of ZrH and particle size of the powder grades, it can be concluded that the critical particle size of ZrH for ignition SHS reaction under the applied experimental conditions was between 1.3 and 0.5 µm.

Besides densification, another interesting phenomenon should be reported is the orientation of ZrB₂ grains. The XRD patterns indicate that the peaks of (00l) have a higher intensity than those of (100) in the TS surface, which are different from the reference ZrB₂ pattern. This implies that the hexagonal ZrB₂ grains have grown in a preferred direction. XRD patterns of a top (TS) and side surface (SS), respectively perpendicular and parallel to the pressing direction as well as the current flow direction, are compared in Fig. 6. It is clear that the relative intensity of the (001) plane is much higher than that of the (100) plane and comparable to the (101) plane on the TS surface (Fig. 6(b)), whereas the (100) plane is the most intense on the SS surface (Fig. 6(c)). (001) planes are perpendicular to the c-axis of the grains, therefore ZrB₂ grains grew with an aligned c-axis.

The mechanism of orientation of ZrB₂ grains can be attributed to an anisotropic Ostwald ripening process under pressure. The crystal structure of ZrB₂ is primitive hexagonal. It is possible for ZrB₂ powders to grow in a certain direction due to anisotropic interfacial energies. It is well known that a liquid phase is the key factor in Ostwald ripening. In the present study, B₂O₃ and SiO₂ are the potential liquid phases, which originate from the B, B₄C and SiC starting powder particle surfaces. During PECS, there is always a minimum contact pressure, 4 MPa in the present case, on the powders that can promote preferential growth of ZrB₂ particles with respect to the pressure direction. Although B₂O₃ begins to evaporate at 1750°C, SiO₂ glass originating from the SiC starting powder can serve as a liquid phase at higher temperature.

According to the Ostwald ripening mechanism, the small grains will dissolve in the liquid and the appropriate constituents diffuse towards the surface of larger grains to re-precipitate. The grains are initially randomly oriented, but some large grains with certain orientation tend to grow during sintering at the cost of smaller grains. Since the liquid phases in the current study originate from the oxide layer on the starting powders, the amount is limited. Therefore, only those grades with very fine particles, i.e., the attritor milled powder based grades, are susceptible to this mechanism. With a higher temperature and higher pressure, the preferred orientation of ZrB₂ grains increased significantly.

3.3. ZrB₂-ZrC ceramics

In 1989, Johnson et al. had reported that using the directed reaction of a liquid metal with boron carbide to yield platelet-reinforced carbide matrix materials. By this method, ZrB₂-ZrC-Zr system can be obtained according to the reaction:

\[(2.2+x)\mathrm{Zr} + 0.6\mathrm{B}_4\mathrm{C} = 1.2\mathrm{ZrB}_2 + \mathrm{ZrC}_{3x} + x\mathrm{Zr} \quad (25)\]

In the final product, the composites are composed of platelets of ZrB₂ distributed uniformly within a matrix of equiaxed grains of \(\mathrm{ZrC}_3\), while the residual Zr metal is generally situated at the grain triple points (Fig. 7). The researcher demonstrated a proposed reaction mechanism as follows:

1. Molten zirconium reacts with \(\mathrm{B}_4\mathrm{C}\) to form \(\mathrm{ZrB}_2\) and \(\mathrm{ZrC}\). Concurrently boron and carbon can dissolve into the liquid zirconium and graphite may precipitate at the interface with the \(\mathrm{B}_4\mathrm{C}\).

2. The high heats of these reactions raise the local temperature well above the nominal furnace temperature of 1900°C.

3. A B-rich liquid forms at the reaction interface with the \(\mathrm{B}_4\mathrm{C}\) as a result of this temperature rise. The first B-rich liquid in the system outside of molten boron occurs at 2165°C from the eutectic reaction of \(\mathrm{B}_4\mathrm{C}\), \(\mathrm{C}\), and \(\mathrm{ZrC}\). Upon further local heating (T>2220°C), a continuous B-rich liquid can form between pure boron and the eutectic liquid. The exact composition of the B-rich liquid is unknown, but the presence of graphite implies that it lies somewhere within the triangle formed by \(\mathrm{B}_4\mathrm{C}\), \(\mathrm{C}\), and \(\mathrm{ZrB}_2\).

4. The two-phase boride/carbide layer described in (1) moves downward as the boron-rich liquid below it is drawn into the porous boron carbide by capillary action. Boron and carbon rapidly diffuse through this thin B-rich liquid layer, causing the two-phase layer to thicken as the directed reaction proceeds.

It should be also emphasized that these platelet-reinforced ceramics exhibit an attractive combination of high strength (800-1030 MPa), high fracture toughness (11-23 MPa·m\(^{1/2}\)), and high thermal conductivity (50-70 W/m·K), which displayed the advantages of the ceramics prepared by reactive process. However, a small amount of residual Zr metal will be remained in the composites.
Zhang prepared ZrB$_2$-ZrC ceramics using Zr, B$_4$C as starting materials, according to the reaction:

$$2Zr + B_4C = 2ZrB_2 + ZrC$$  \hspace{1cm} (8')$$

In the final ZrB$_2$-ZrC composite, there are large ZrC agglomerates surrounded by fine ZrB$_2$ and ZrC particles. The reason is that in Zr-B$_4$C system for preparing ZrB$_2$-ZrC composite, due to the diffusion coefficient of carbon being much faster than that of boron in zirconium, only carbon can reach the center of the large Zr particles, which results in the microstructure with large ZrC agglomerates surrounded by fine ZrB$_2$ and ZrC particles.

### 3.4. ZrB$_2$-MoSi$_2$ ceramics

ZrB$_2$-MoSi$_2$ ceramics is another important member of the ZrB$_2$-based UHTCs family. Using elemental Zr, B, Mo and Si as starting materials, Wu first prepared ZrB$_2$-MoSi$_2$ ceramics via RHP according to the reaction$^{28}$:

$$Zr + 2B + xMo + 2xSi = ZrB_2 + xMoSi_2$$  \hspace{1cm} (9')$$

RHP temperature of 1800°C is essential to densify the composites, which is nearly the same with other densification process, such as PLS, which means that the RHP process in the ZrB$_2$-MoSi$_2$ system can not reduce the densification temperature.

It has been reported that due to the ductility of MoSi$_2$ at temperatures over 1000°C, the shape of the MoSi$_2$ grains could deform to fill the voids in the ZrB$_2$ skeleton, thus favoring the formation of a porosity-free material, however, the densification temperature is still as high as 1800°C during the RHP process. The unusual phenomenon is attributed to the “unusual” ZrB$_2$ morphology in the microstructure of the composites: the ZrB$_2$ grain is platelet, not globular. As we all know that ZrB$_2$ is primitive hexagonal (AlB$_2$-type, P6/mmm space group), so it seems possible to form platelet grains, though there have been only a few reports in the literature on this phenomenon in UHTCs. So it is interesting to find the anisotropic ZrB$_2$ grains in the ZrB$_2$-MoSi$_2$ prepared by RHP. It should also noted that the anisotropic ZrB$_2$ platelets grains in the ZrB$_2$-MoSi$_2$ system were only found during the RHP process, and there were no platelets formed during the PLS, HP and SPS process. So the RHP process has the unique ability to form anisotropic morphology of the ZrB$_2$-based UHTCs. HRTEM images of ZrB$_2$ showed that at the rim of the particles, there were some amorphous phases which enclosed the grain surface, and the same “core-rim” structure also existed in MoSi$_2$ phase. On the other hand, EDS analysis also showed that there were some amorphous phase (particles) of Mo-Si-B, as well as a small amount of Zr-B-O and Mo-Si-O. The surface energy on the (001) planes of ZrB$_2$ crystal is higher than other planes, such as (100) and (110), so the low activation energy diffusion paths are along <210> and <100> direction, respectively. Therefore, it can be concluded that the in situ formed liquid phase imposed the catalysis effect on the growth of ZrB$_2$ grains. With the increase of the temperature, the liquid phase can wet the grain boundary, and the Zr and B atoms in the liquid phase will easily transport to the low surface energy planes ((100) or (110) planes) of ZrB$_2$ grains, which favors in the elongation of ZrB$_2$ grains along the a- and b-axis resulting from the Ostwald ripening at higher temperature.$^{49}$

In view of the platelet ZrB$_2$ grains in the composites, Liu et al. used RHP and subsequent hot forging method to realize the microstructure tailoring of the ceramics.$^{50}$ The result is that textured and platelet-reinforced ZrB$_2$-based UHTCs were obtained. During the hot forging process, the platelet ZrB$_2$ grains grow larger and simultaneously, under the applied pressure, the platelet grains rotate and rearrange to align along the top surface of the specimen. With the more orderly realignment of the grains, more (001) planes of the grains are distributed on the top surface, resulting in the intensity increase of the (001) peaks and a highly textured

---

**Fig. 7.** Backscattered electron images of the cross section of a typical ZrB$_2$-platelet-reinforced ZrC product taken 2 mm from the top (a) and bottom (b) of a 12.7-mm-thick part. The darkest phase is ZrB$_2$, the gray phase is ZrC, and the lightest phase is zirconium metal.$^{48}$
microstructure. The textured composites with high Lotgering orientation factor showed a remarkable improvement in mechanical properties compared with untextured composites, and also demonstrated obvious anisotropic properties (Fig. 8).

3.5. Other ZrB₂-based UHTCs

Using Zr and BN as starting material, Zhang also prepared ZrB₂-ZrN and ZrB₂-AlN (together with Al as starting material) ceramics, according to the following reaction:

\[
2Zr + 2BN = ZrB_2 + 2ZrN \quad (10')
\]
\[
Zr + 2Al + 2BN = ZrB_2 + 2AlN \quad (11')
\]

Both the final composites show homogeneous microstructure with fine grain size. The researchers reveal that in Zr-BN system for preparing ZrB₂-ZrN composite, the diffusion coefficient of N is smaller than that of C but close to that of B. Accordingly, homogeneous microstructure can be obtained by the inter-constraint of grain growth of the formed two phases. Abnormal grain growth of ZrB₂ and ZrN can also be effectively restrained. And in Zr-Al-BN system for preparing ZrB₂-AlN composite, Al will melt at temperature as low as 660°C and the maximum solubilities of Al in α-Zr and β-Zr are as large as 11.5 and 26 at.% respectively. Accordingly, redistribution process of Zr and Al is remarkable in this system, thus fine and homogeneous microstructure can be obtained. Schematic illustration of the microstructural features of the obtained ZrB₂-containing composites. ZrB₂-ZrC and ZrB₂-ZrN composites correspond to the case I and II, respectively. ZrB₂-SiC and ZrB₂-AlN composites correspond to the case III and IV, respectively. The dotted circles in case I represent the size of Zr starting powder (outside one) and the agglomerate size of ZrC (inside one), respectively. The dotted circles in case III represent the size of Zr starting powder, also the size of ZrB₂ agglomerates.²⁵

Fig. 8. (a) TEM image of the ZrB₂ platelet grains, (b) HRTEM image of the ZrB₂ platelet grains in (a) with larger magnification, (c) selected-area electron diffraction pattern of the ZrB₂ platelet grains of (b), (d) and (e) SEM images of polished P-surface for sample before and after hot forging, respectively, (f) and (g) SEM images of fractured P-surface for sample before and after hot forging, respectively.

Fig. 9. Schematic illustration of the microstructural features of the obtained ZrB₂-containing composites. ZrB₂-ZrC and ZrB₂-ZrN composites correspond to the case I and II, respectively. ZrB₂-SiC and ZrB₂-AlN composites correspond to the case III and IV, respectively. The dotted circles in case I represent the size of Zr starting powder (outside one) and the agglomerate size of ZrC (inside one), respectively. The dotted circles in case III represent the size of Zr starting powder, also the size of ZrB₂ agglomerates.²⁵
4. Summary

The present paper reviewed some typical ZrB$_2$-based UHTCs prepared via reactive processing, such as RHP, R-SPS and R-PECS, etc. Using the available starting materials, such as elemental powders or simple compounds, the final ZrB$_2$-based UHTCs can be obtained by only one step, which combine the synthesis routes and densification process together, resulting in the in-situ formed thermodynamic stable phases under relative low temperature compared with the non-reactive processing. Besides, an interesting phenomenon that anisotropic grain growth of ZrB$_2$ grain occurred during the densification process is a unique advantage of the UHTCs prepared via reactive processing, which is a novel approach for mechanical properties improvements and microstructure tailoring.

Acknowledgments

The authors express their gratitude to financial supports from the National Natural Science Foundation of China (No. 50632070 and 91026008), the bilateral project of NSFC-JSPS (No. 40310103), the Program for Recruiting Outstanding Overseas Chinese (No. 51111140017), the Chinese Academy of Sciences under the Program for Recruiting Outstanding Overseas Chinese, and the State Key Laboratory of High Performance Ceramics and Superfine Microstructures of Shanghai Institute of Ceramics are gratefully acknowledged.

REFERENCES


