The Effect of the Mg Content on Mechanosynthesis of ZrB_2–SiC–ZrC Composite in the $Mg/ZrSiO_4/B_2O_3/C$ System

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ABSTRACT

The influence of the magnesium content on the mechanosynthesis of ZrB_2–SiC–ZrC composite in the $Mg/ZrSiO_4/B_2O_3/C$ mixture was investigated. Thermodynamic evaluations revealed that the amount of Mg played a main role and, as a consequence, the overall reaction enthalpy and adiabatic temperature (Tad) changed by the variation of the magnesium content. According to the differential thermal analysis (DTA) results, after 45 min of milling, the temperature of the combustion reaction decreased to 576 ◦C and all the reactions occurred simultaneously. The experimental findings indicated that the type of reactions in the mixture powder with stoichiometric ratio (7mol Mg) was mechanically induced self-sustaining reaction (MSR). When the Mg content was within the range of 6-7mol, the magnesiothermic reduction occurred in the MSR mode and the carbothermal reaction was activated; hence, the carbon acted not only as a carbide former agent but also as a reductant. The MSR mode magnesiothermic reduction and gradual carbothermal reduction occurred when the Mg value was 11/2-6 mol. At lower Mg contents in the mixture (5mol), the reduction reaction proceeded through a gradual mode and no carbothermal reaction occurred.

1. Introduction

The borides and carbides of the early transition metals, such as ZrB_2, ZrC, HfB_2, and HfC, are often referred to as ultrahigh-temperature ceramics (UHTCs) which are promising candidates for structural applications exceeding 2250 ◦C [1]. These materials have strong covalent bonding characteristics, high melting points, high strength and hardness, good thermal conductivity and thermal shock resistance [1-3]. However, the use of these ceramic materials for high-temperature applications is constrained by their poor oxidation, thermal shock, as well as poor damage tolerance [3]. Tsuchida and Yamamoto [4] synthesized ZrB_2–ZrC composite by mechanically activated self-propagating high temperature synthesis (MA-SHS) from the powder mixtures of Zr/B/C=1/1/1. Moreover, it is well known that the addition of appropriate amounts of SiC to these materials strongly improves their oxidation resistance at high temperature [1]. Zhang et al. [5] synthesized ZrB_2–SiC composite powders by combustion

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synthesis in air, using a mixture of Zr, B4C and Si as raw materials.

ZrB_2–SiC–ZrC composites have also been developed by a number of researchers through various methods such as reactive hot pressing in the Zr/Si/B_4C system [1], self-propagating high-temperature synthesis (SHS) of Zr, B_4C, Si [6], graphite, liquid precursors (one-pot reaction of polyzirconoxanesal with boric acid and poly ethynylene) [7] and mechanochemical synthesis [8]. Besides these techniques, there have been various studies on the use of active metals like Al and Mg as reducing agents to generate a great amount of heat, which can be used as a heat source for the activation of synthesis reactions with using cheaper raw materials compared to the other synthesis routes [9, 10]. In this regard, the reaction mechanism of ZrB_2 formation by the SHS process from mixture containing H_3BO_3, ZrO_2 and Mg was studied by Khanra [11].

Mechanochemical activation as a type of in-situ method is a solid state powder processing that involves inducing chemical reactions in a mixture of as-received powders at room temperature or at least much lower temperatures. An increase in the kinetic of reactions during high energy milling can be a result of microstructural refinement, repeated cold deformation and fracture of particles [12, 13]. In recent years, the mechanochemical technique has been widely used to fabricate interpenetrating phase composites with nanosized microstructures. Mechanochemical process was proposed by Jalaly et al. [8] to prepare ZrB_2–SiC–ZrC nanocomposite powder via metallothermic reduction of zircon ($ZrSiO_4$) as a principal economic source of zirconium and silicon. They reported that Mg content plays a key role in the mechanochemical behavior of Mg/$ZrSiO_4$/B_2O_3/C system.

The main aim of this study is to provide information about the influence of the Mg value in the Mg/$ZrSiO_4$/B_2O_3/C mixture mechanism of reactions during ball milling. In addition, thermodynamic calculations and thermal analysis were performed to get an insight about the probable reactions.

2. Experimental

2. 1. Explanation

The chemical reaction for the Mg–$ZrSiO_4$–B_2O_3–C system can be expressed as Eq. (1):

$$7Mg + B_2O_3 + ZrSiO_4 + C = 7MgO + ZrB_2 + SiC \quad [1]$$

It is known [8, 11] that this reaction comprises two steps: a highly exothermic B_2O_3– $ZrSiO_4$ –Mg thermite reaction (magnesiothermic reaction) and, consequently, weakly exothermic synthesis reactions. To investigate the influence of the Mg content on the mechanochemical behavior of this system, the milling process took place through the following stoichiometric compositions:

A. Stoichiometric Mg content: For this purpose, the powders were mixed with starting compositions according to reaction (1).

B. Under - stoichiometric Mg content: The powders were mixed to give the following desired under-stoichiometric composition:

$$(7-x)Mg + B_2O_3 + ZrSiO_4 + (1+x)C = ZrB_2 + SiC + (7-x)MgO + xCO \quad [2]$$

In the above reaction, x is a variable which gradually influences the primary carbon and magnesium values (mole).

2. 2. Procedure

The precursor materials were magnesium (Merck, 99.7% purity, mean particles size 40 ± 5 μm), Zircon (Aldrich, 99.95% purity, mean particles size 44 ±5 μm), boron oxide (Merck, 99.95% purity, mean particles size 30 ±5 μm) and graphite (Merck, 99.5% purity, mean particles size 50 μm).

The precursor materials were milled in a planetary ball mill for various durations at room temperature. Details of the ball mill machine and milling conditions are given in Table 1. To prevent oxidation, the container vessel of milling was filled with high purity argon gas before ball milling.

In this study, the amounts of the remained B_2O_3 and C were calculated to understand the reaction mechanism. For calculation of the remained B_2O_3 value, firstly, the obtained powder from the milling process was weighed and considered as W_1. Then, the powder was washed by hot water (60 – 70 °C) for 1h with magnetic stirrer and then the solution was

Table 1. Details of the ball mill machine and milling conditions.

Rotation speed of container vessel (rpm)	500
Diameter of container vessel (mm)	100
Container vessel material	Hardened chromium steel
Ball material	Hardened carbon steel
Diameter of balls (mm)	20
Number of balls	5
Balls to powder weight ratio	20:1
Total powder mass (g)	7

filtered and the residue on the filter was dried at the 90 °C for 2 h, and then weighed as W_2. The difference $W_1 - W_2 = W_3$ is the amount of the remained B_2O_3. For removing probable Mg and MgO, the obtained powder was leached with 18% hydrochloric acid for 1 h. The solution was filtered after leaching and the purified products were washed several times by distilled water to eliminate the extra HCl acid until the pH value was about 7. Again, the residue on the filter was dried at the 90 °C for 2 h and weighed as W_4. At the end, the obtained powder was oxidized at 700°C for 30 min in the air and then was weighed as W_5. The difference $W_4 - W_5 = W_6$ yields the amount of free carbon. Finally, to report changes in data as percentage change, the following formula was used: [(the obtained value/initial value) ×100]. In an attempt to reduce errors, the reported data were average of three experimental values.

2. 3. Testing methods

XRD analysis was carried out using Cu-Kα radiation to identify different phases of the starting powders and the mechanically alloyed powders. The diffractometer (Philips X-ray diffractometer) was operated at 40 kV and 30 mA. Scans were performed between $10^\circ < 2\theta < 90^\circ$. "PANalytical X'Pert HighScore" software was also used for the analysis of different peaks. The diffraction patterns of the products were compared to proposed standards by the Joint Committee on Powder Diffraction and Standards (JCPDS). The reaction process and features were also investigated by thermal analyses (STA; BÄHR 503). A small amount of the reactants weighing about 50±5mg were held in an alumina crucible and heated under argon flow (flow rate: 50 ml/min) at a heating rate of 10 °C/min up to 1100 °C.

3. Results and Discussion

3. 1. Thermodynamic evaluations

Considering the basis of reaction thermodynamic can contribute to understand the basic information about reactions and to estimate their behavior and formation of the possible phase compositions during the mechanochemical process.

According to the ΔG°-Mg value plot in Fig. 1, the sample with 1mol of $ZrSiO_4$, 1mol of B_2O_3 and 8mol of C (without Mg) has a big positive value of ΔG° (+1755.93 kJ). The ΔG° value was found to decrease rapidly by increasing the amount of Mg and became zero at Mg = 4.38 mol. Thereafter, negative values were found, suggesting high possibility and favor for the reaction. The maximum negative ΔG° value was obtained for a mixture containing 1mol of B_2O_3 and $ZrSiO_4$, 1mol of C and 7mol of Mg (the stoichiometric ratio).

The ΔH°-Mg value plot also revealed that by increasing the Mg content, the samples tend to abruptly change the behavior from endothermic to exothermic (Mg= 4.32). This is to say that for the mixture without Mg, ΔH° has a high positive value (+2129.03 kJ), which means that this reaction is sensitively endothermic. When the mass content of Mg became 7mol (the stoichiometric ratio), ΔH° achieved its maximum negative value (-1307.97 kJ), resulting in extreme heat generated by the exothermic reaction.

Depending on the milling conditions and the

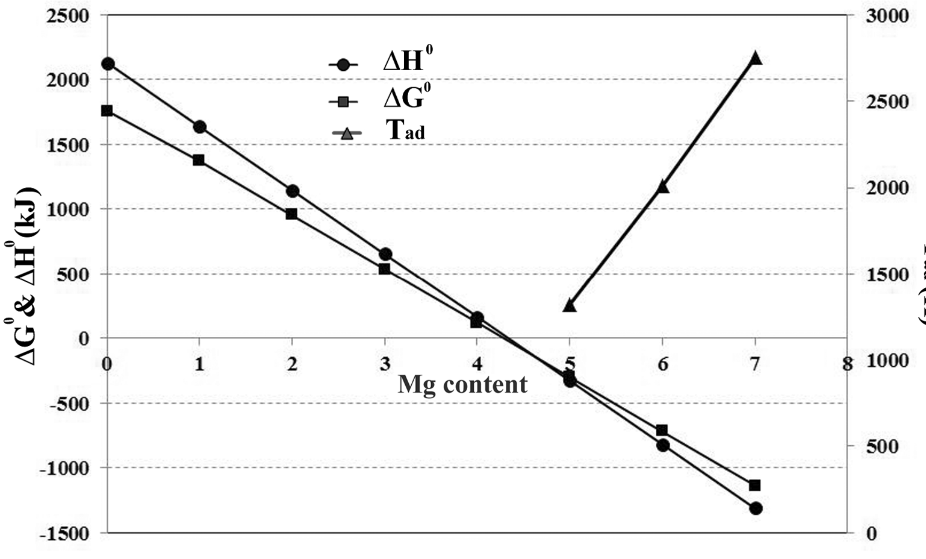

Fig. 1. The ΔG°, ΔH° and T_{ad} curves versus value of Mg

enthalpy of the reactions, mechanochemical reactions are divided into two categories: progressive reaction and mechanically induced self-sustaining reaction (MSR). In the first type, the synthesis of the final products extends to a very small volume slowly during each collision between the milled material and the grinding medium that contributes to the comminution, mixing, and defect formation [12, 14]. In the second type, a self-propagating combustion reaction is initiated after a definite amount of the milling process. During the milling, the intimate contact between the reactant phases is an essential requirement for the self-propagating synthesis. Therefore, the occurrence of the combustion reaction causes a rapid rise in temperature at the wall of the mill vial, and provides the conditions for quick transformation [12, 14]. This type of reaction mechanism can be predicted by calculating the adiabatic temperature (T_{ad}) or by describing this property ($-\Delta H_{298}/\sum C_p$). For self-sustaining mode reaction to take place it is necessary that these quantities be at least $T_{ad} > 1800$ K and $-\Delta H_{298}/\sum C_p > 2000$ K [12].

The value of T_{ad} would be calculated using the equation below:

$$\Delta Q = -\Delta H^0_{298} + \int_{298}^{Tm} \sum C_p(Solid).dT + \Delta H_m + \int_{Tm}^{Tad} \sum C_p(Liquied).dT = 0 \quad [3]$$

Where C_p, and ΔH^0_{298} and ΔQ are specific heat capacity, standard enthalpy changes of formation at 298K and heat of reaction, respectively. Thermodynamic calculations were carried out based on the main assumption that milling container vessel was sealed and isolated.

The calculated T_{ad} values as a function of Mg contents in the blends are shown in Fig. 1. As can be seen, the T_{ad} values significantly increased by increasing the Mg contents and reached over 1800 K at Mg=5.72mol which met the empirical criterion for the MSR mode reaction. It can be concluded that the mode of the reactions with the Mg content ranging between 5.72-7mol would be MSR.

3. 2. Experimental findings

3. 2. 1. Stoichiometric Mg content

The general form of the reactions taking place in the Mg–$ZrSiO_4$–B_2O_3–C system is represented in reaction (1).The possible reduction reactions that may occur in this system are described as follows:

$3Mg + B_2O_3 = 2B + 3MgO$ [4]

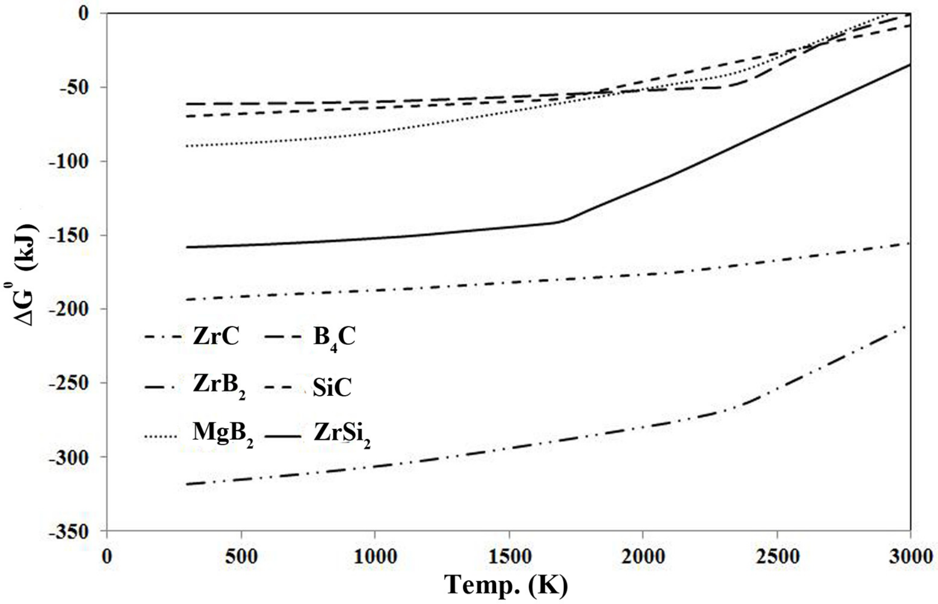

Fig. 2. The diagram of ΔG◦ of possible compounds between Zr, Si, B and C elements

ΔH^0_{298} = - 531.3 kJ/mol ΔG^0_{298} = - 513.5 kJ/mol

$4Mg + ZrSiO_4 = 4MgO + Zr + Si$ [5]

ΔH^0_{298} = -382.59 kJ/mol ΔG^0_{298} = -368.18 kJ/mol

According to the thermodynamic data [15], both reduction reactions (4) and (5) can be thermodynamically possible to occur and extremely exothermic. It should be mentioned that the enthalpy change of reaction (4) is significantly more negative than reaction (5); therefore, the magnesiothermic reduction of the boron oxide is most favorable and exothermic compared to the zircon reduction.

In the next step, the elemental boron, silicon and zirconium produced from magnesiothermic reductions are presented. Fig. 2 exhibits the standard free energy of the formation of various possible compounds containing these elements. It is worth mentioning that reaction (6) is more negative than the others, and hence the formation of the ZrB_2 phase directly from the reaction between Zr and B is most favorable. In addition, the ZrC and SiC phases are more stable in thermodynamics than other possible phases, which implies that the formation of a small amount of zirconium carbide through the reaction among zirconium, silicon and carbon appears to be inevitable. Therefore, the presumed reactions could be written as follows:

$Zr + 2B = ZrB_2$ [6]

$Zr + C = ZrC$ [7]

$Si + C = SiC$ [8]

3. 2. 2. Thermal behavior (DTA analysis)

DTA technique was utilized to study the reaction mechanism and to investigate the effect of the activation time on thermite reactions behavior and the initial reaction temperature. For this purpose, the $Mg–ZrSiO_4–B_2O_3–C$ (according to the stoichiometric ratio) powder mixtures were milled for 0 (unmilled sample), and 45 min and then subjected to DTA analysis at a heating rate of 10 deg. min^{-1} (Fig. 3).

The endothermic peak at ~190°C in the DTA curve of both samples is related to disintegration of dehydration of B_2O_3 reactants. The second endothermic peak at about 650°C in the curve of the unmilled sample was related to the melting of Mg. There were two exothermic peaks after melting of Mg, approximately between 700 and 950°C. In order to make clear the reactions which occurred within exothermic peaks, after DTA analysis, the coarse samples were ground into powder and then characterized by XRD. The X-Ray diffraction result of the unmilled sample at 830°C, before the second exothermic reaction, (Fig.4- a) indicated the sharp peaks of

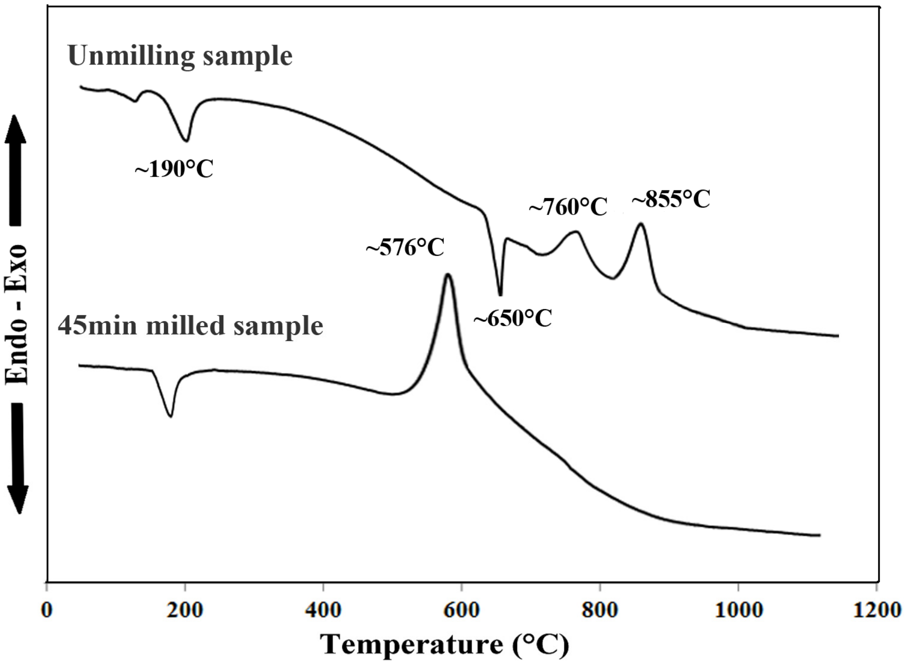

Fig. 3. DTA curves for the $7Mg + B_2O_3 + ZrSiO_4 + C$ mixtures milled for 0 and 45min (heating rate 10 deg. min^{-1}).

MgO and magnesium borate ($Mg_3(BO_3)_2$) phases and low amount of remained unreacted powders (remained Mg, $ZrSiO_4$ and C). As expected by the thermodynamics evaluations (section 3.1), the first exothermic peak at 760°C is attributed to the initiation of reduction of B_2O_3 by Mg (magnesiothermic reaction) according to reaction (4). $Mg_3(BO_3)_2$ appears as the major by-product in the Mg–B_2O_3 system [9,10]. Based on the results, in thermal process, once the combustion reaction is initiated, the magnesiothermic reaction will make a rapid raise in the temperature of the system which is favorable for the formation of magnesium borate as a competing reaction to the synthesis reactions according to the following:

$3MgO + B_2O_3 = Mg_3(BO_3)_2$ [9]

With regard to the XRD analysis of this specimen at 1100°C (Fig.4-b), the peaks corresponding to raw materials have significantly been diminished, and several new peaks appear to emerge beside the sharp peaks of MgO, corresponding to the formation of magnesium borate ($Mg_3(BO_3)_2$), zirconium boride (ZrB_2) and zirconium carbide (ZrC). As a result, it is concluded that later exothermic peak is related to the following reactions: (i) reaction between the remained Mg (from reaction 4) and $ZrSiO_4$ powders started at about 855 °C (5) (ii) direct reaction between produced zircon and elemental boron (formed from reaction 4 and 5) and carbon to form ZrB_2 and ZrC, respectively according to reaction (6) and (7). Based on reaction (1), ZrC is not expected to be present among the products, but as can be seen in Fig. 2, it is an inevitable (but valuable) by-product in this system. This result is related to the standard free energy of the formation of ZrC as explained in thermodynamics evaluation section. Concurrent formation of ZrB_2 and ZrC has also been reported by other researchers [8].

The DTA curve of the 45min-milled sample displays the only strong and wide exothermic peak at 576°C, revealing this is a complex exothermic reaction. This indicates that all the mentioned reactions simultaneously began prior to the melting of Mg (650 °C). The heat generated during the reduction and synthesis reactions is much larger than the fusion heat of Mg (+8.48 kJ/mol). Therefore, the endothermic peak related to the Mg melting overlapped with the exothermic reactions peak.

Decreasing the temperature of the exothermic

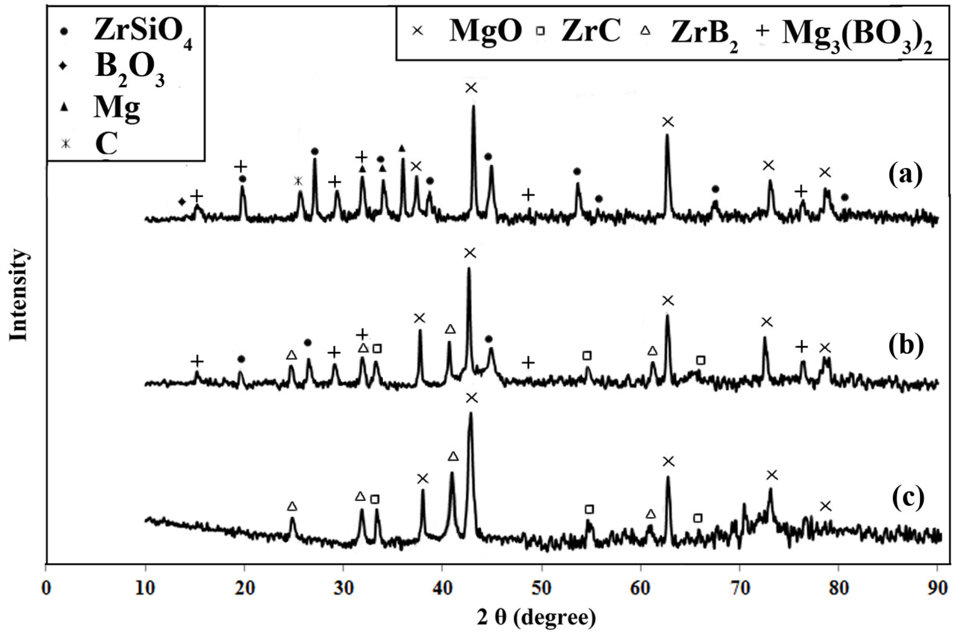

Fig. 4. XRD patterns for the DTA samples: (a) unmilled sample and heated up to 830°C (b) unmilled sample and heated up to 1100°C (c) sample milled for 45min and heated up to 1100°C.

reactions may be attributed to the uniform distribution of the reactants which can reduce the diffusion distance and degrade the magnesiothermic reaction temperature. Moreover, mechanochemical processing can make the reactions simultaneous via: (i) large amount of reaction heat, (ii) high active boron atoms produced by the magnesiothermic reaction, and (iii) uniform distribution of the reactant powders due to milling process [9, 12]. A similar behavior was reported in the mechanochemical process of the $Al:B_2O_3:AlN$ [16], $Al:B_2O_3$: C [9], $Mg:B_2O_3$: C [10] and $Al–WO_3$-C ternary systems [17].

The absence of the Mg and $ZrSiO_4$ peaks and developing of the sharp MgO and ZrB_2 peaks in the XRD pattern of the sample milled for 45 min at 1100 °C (Fig. 4-c) verified that the magnesiothermic reduction of B_2O_3 (4) is responsible for activating the reduction reaction of $ZrSiO_4$ (5) and subsequently occurring reactions (6) and (7). Although silicon carbide (SiC) was detected in the XRD pattern, this cannot be taken as proof of their absence due to low amount and poor peaks. After 45 min of milling process, the intensity of the peaks at around $2\theta= 14.51°$, $2\theta= 29.06°$, $2\theta= 31.70°$ and $2\theta= 75.37°$ extremely decreased (Fig. 4-c), indicating that increase in the milling time decreased the tendency of magnesium borate formation. The quantity of magnesium borate mainly depends on excess B_2O_3 in the system and is affected by the size of the B_2O_3 powder [9,10].The excellent dispersion of powder during the mechanochemical process at higher milling times helps consume the whole amount of B_2O_3, and decrease the particle size of B_2O_3 powder to prevent the formation of $Mg_3(BO_3)_2$. The result is in good agreement with the report by Khanra [11] on the SHS process of the $H_3BO_3–ZrO_2–Mg$ system.

3. 2. 3. Phase detection (XRD analysis)

Fig. 5 shows the XRD patterns of the stoichiometric mixture of $Mg–ZrSiO_4–B_2O_3–C$ mechanically alloyed for 0.5, 1 and 3 hours. In the case of the sample milled for 30 min, all the sharp peaks correspond to Mg and zircon and those corresponding to B_2O_3 and C have low intensity. Low intensity of the boron oxide peaks in this sample could be related to transformation of the crystal state of B_2O_3 into amorphous state as reported in some investigations [10]. After 1h of milling, the

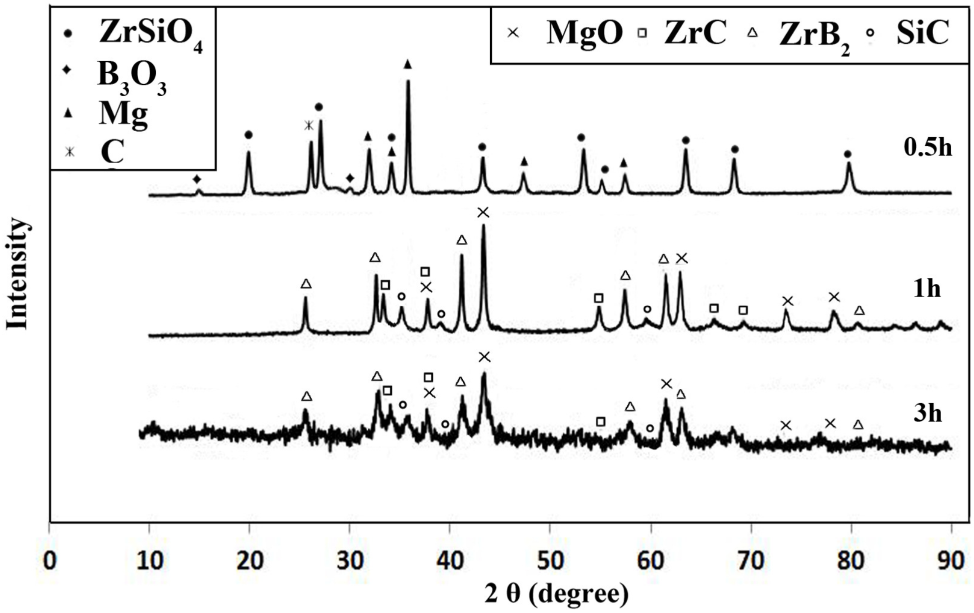

Fig. 5. XRD patterns of typical samples containing 7mol of Mg ($7Mg + B_2O_3 + ZrSiO_4 + C$) after several milling times.

Table 2. Calculated amount of the remained B_2O_3 and free carbon for the stoichiometric Mg content (7mol) during various milling times.

$X = 0 \rightarrow 7Mg + B_2O_3 + ZrSiO_4 + C = 7MgO + ZrB_2 + SiC$

$Mg : B_2O_3 : ZrSiO_4 : C = 39.10 : 15.99 : 42.13 : 2.76$ (Wt.%)

Milling time (h)	Remained B_2O_3 (%)	Free carbon (%)
0.5	~ 99	~ 99
1	Trace	Trace
3	Trace	Trace

peaks of the as-received materials completely disappeared; meanwhile, new peaks appeared to emerge, corresponding to the formation of MgO, ZrB_2, ZrC and SiC. Based on thermodynamics evaluations and thermal analysis, it can be concluded that the reaction comprises two steps which occurred simultaneously: reduction of B_2O_3 and $ZrSiO_4$ by Mg (reactions 4 and 5) to release large amount of heat, followed by the synthesis reactions including the formation of ZrB_2, ZrC and SiC (reactions 6, 7 and 8). The result is in good agreement with the report by Jalaly et al. [8].

Further milling process up to 3h shows no change except the broadening of the Bragg peaks which is attributed to a decrease in the crystallite size as well as the lattice strain induced in the powder particles [9, 10]. It should be mentioned that in Fig. 5, no traces of undesirable phases (such as $Mg_3(BO_3)_2$) were observed in the XRD patterns during milling.

To confirm the XRD analysis, the amount of the remained B_2O_3 and C were calculated as explained in section (2.2) and provided in table 2. As can be seen, there is no tangible change in these values after 0.5h of milling process. However, for the sample milled for 1h, the value of the remained $B_2O_3$and C became about zero, which reveals that the whole of them were used. This fact together with quick transformation in the XRD pattern observations (Fig.5) and high calculated T_{ad} (2751 K) revealed that the reaction mode of the

Table 3. Calculated amount of the remained B_2O_3 and free carbon for under - stoichiometric Mg content (x= 1) during various milling times.

$X = 1 \rightarrow 6Mg + B_2O_3 + ZrSiO_4 + 2C = 6MgO + ZrB_2 + SiC + CO$

$Mg : B_2O_3 : ZrSiO_4 : C = 34.5 : 16.46 : 43.36 : 5.68$ (Wt.%)

Milling time (h)	Remained B_2O_3 (%)	Free carbon (%)
0.5	~ 98	~ 98
1	Trace	Trace
3	Trace	Trace

stoichiometric mixture of Mg–$ZrSiO_4$– B_2O_3–C is MSR. These results are also in agreement with the DTA analysis observations (section 3.2-C).

In this case (the stoichiometric ratio reaction), it is assumed that all amount of carbon is used to form the ZrC and SiC compounds as a carbon agent and there is no excess value of carbon to play the role of a carbothermal reduction agent. As a result, in the next step, lower Mg values, compared to the stoichiometric ratio, were selected to investigate the effect of magnesiothermic reaction on the progression of the other reduction reactions.

3. 3. Under stoichiometric Mg content

Generally, in these samples, the Mg values are insufficient for reduction of whole B_2O_3 and $ZrSiO_4$; however, the C contents are more than what is needed for carbide formation (according to reaction 2).

For better discussion and understanding, the samples are categorized into three groups as follows.

3. 3. 1. 6< Mg (mol) <7 or 0 <x<1

With regard to table 3, the specimen containing 6mol Mg (x =1) milled for 1h indicated a rapid change in the remained B_2O_3 and C values which referred to the occurrence of magnesiothermic reductions similar to the stoichiometric ratio sample.

The XRD patterns of some samples of this group are presented in Fig. 6. Same as stoichiometric ratio, sudden changes in the XRD pattern of the milled powder after 1h indicated that the reaction mode is MSR. Calculated T_{ad} (Fig.1) and the rapid changes in the remained B_2O_3 and C values (table 3) confirmed this notion. The Absence of free carbon coupled with consumption of whole boron oxide verified that the heat resulted from magnesiothermic reductions provided enough energy for the occurrence of carbothermal reduction (by 1mol excess C). By considering the fact that the carbothermal reduction of $ZrSiO_4$ needs a lot of energy due to big positive value of ΔG° (+1581.63 kJ), the carbothermal reduction of B_2O_3 (+941.83 kJ) is most favorable. Therefore, based on the thermodynamic analysis and DTA results, presumed reduction reactions could be written as follows:

$$6Mg + \frac{2}{3}B_2O_3 + ZrSiO_4 = 6MgO + \frac{4}{3}B + Zr + Si + Q \qquad [10]$$

$$\frac{1}{3}B_2O_3 \text{ (remained)} + C + Q \text{ (generated by reaction 10)} = \frac{2}{3}B + CO(g) \qquad [11]$$

3. 3. 2. 11/2< Mg (mol) <6 or 1 <x<3/2

Based on the calculated T_{ad} (Fig. 1) and considering Table 4, magnesiothermic reaction in the sample with lower Mg content (Mg : B_2O_3 : $ZrSiO_4$: C = 11/2: 1: 1: 5/2 by mole fraction (x=3/2)) also occurred in MSR mode. It is worth mentioning that the consumed carbon value ($W_{used} = W_{total} - W_{free} \sim 59\%$) after 1h of milling was more than what is required for carbide compositions formation (~ 41%). As expected, the heat produced by the magnesiothermic reaction (12) could activate the carbothermal reaction (reaction 13). By further milling process up to 3h, the remained carbon content became about zero, which could

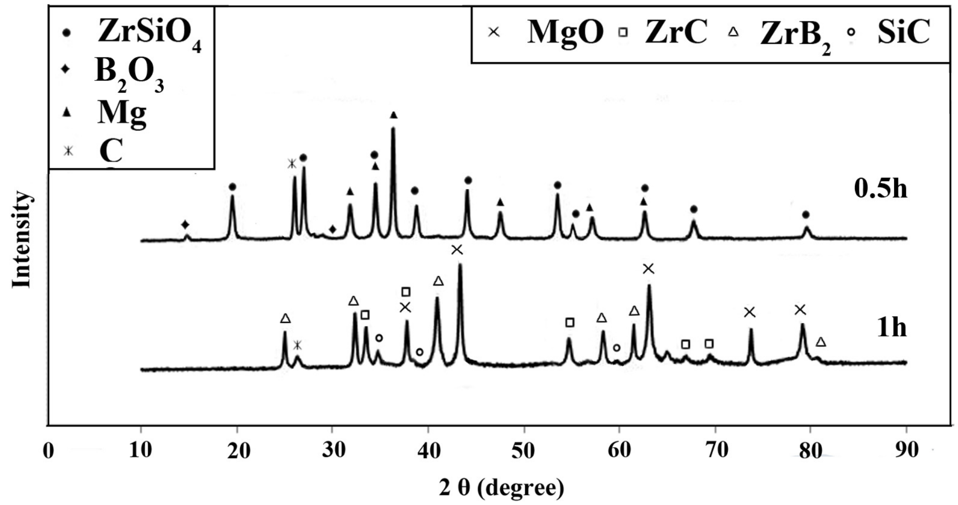

Fig. 6. XRD patterns of typical samples containing 6mol of Mg ($6Mg + B_2O_3 + ZrSiO_4 + 2C$) after several milling times.

Table 4. Calculated amount of the remained B_2O_3 and free carbon for under - stoichiometric Mg content (x= 3/2) during various milling times.

$X = 3/2 \rightarrow 11/2Mg + B_2O_3 + ZrSiO_4 + 5/2C = ZrB_2 + SiC + 11/2MgO + 3/2CO$

$Mg : B_2O_3 : ZrSiO_4 : C$ = 33.04 : 17.20 : 45.30 : 7.42 (Wt.%)

Milling time (h)	Remained B_2O_3 (%)	Free carbon (%)
0.5	~ 98	~ 98
1	~ 32.1	~ 40.6
2	~ 16.5	~ 19.7
3	Trace	Trace

be attributed to the fact that boron oxide was partially reduced by excess carbon as a reducing agent. As a result, the presumed reactions could happen:

$$\frac{11}{2}Mg + \frac{1}{2}B_2O_3 + ZrSiO_4 = \frac{11}{2}MgO + B + Zr + Si + Q \qquad [12]$$

$$\frac{1}{2}B_2O_3 \text{ (remained)} + \frac{3}{2}C + Q \text{ (generated by reaction 12)} = B + \frac{3}{2}CO(g) \qquad [13]$$

Incomplete carbothermal reaction was due to the fact that the heat produced by the magnesiothermic reductions was low compared to the previous samples (more Mg content). On the other hand, the continuous decrease in free carbon content together with the steady decline in the remained B_2O_3 value (Table 4) confirmed that the carbothermal process continued progressively by increasing the milling time up to 3h. Gradual increase in carbothermal reduction may be related to the following reasons: (i) decrease in the diffusion distances by accumulation of defects and creation of fresh surface and distribution of particles during the ball milling process (ii) local temperature increase caused by the heat generated from magnesiothermic reaction, and (iii) uniform distribution of C powder [8, 12].

3. 3. 3. 5< Mg (mol) <11/2 or 3/2 <x<2

Fig. 7 shows the XRD patterns of powder mixture with the composition $Mg : B_2O_3 : ZrSiO_4 : C$ = 5 : 1: 1 : 3 by mole fraction (x=2) and after different milling times. After 1h of milling, the heights of Mg and $ZrSiO_4$ peaks decreased and new peaks indicating MgO,

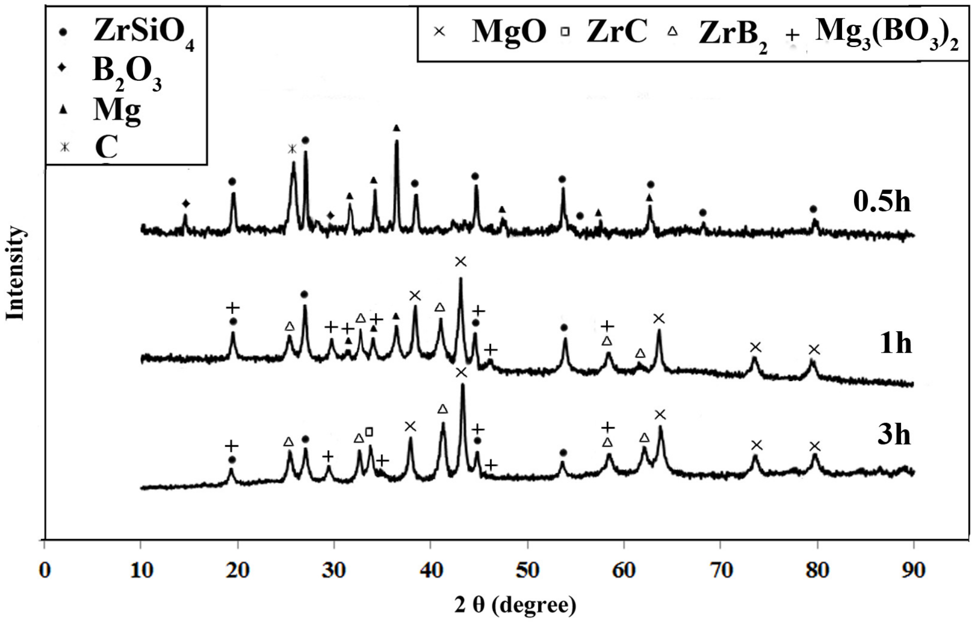

Fig. 7. XRD patterns of typical samples containing 5mol of Mg ($5Mg + B_2O_3 + ZrSiO_4 + 3C$) after several milling times.

Table 5. Calculated amount of the remained B_2O_3 and free carbon for under - stoichiometric Mg content (x= 2) during various milling times.

$X = 2 \rightarrow 5Mg + B_2O_3 + ZrSiO_4 + 3C = ZrB_2 + SiC + 5MgO + 2CO$

$Mg : B_2O_3 : ZrSiO_4 : C = 29.60 : 16.95 : 44.66 : 8.78$ (Wt.%)

Milling time (h)	Remained B_2O_3 (%)	Free carbon (%)
0.5	~ 98	~ 98
1	~ 80	~ 97
2	~ 52.4	~ 96.5
3	~ 29	~ 91.7

$Mg_3(BO_3)_2$ and ZrB_2 appeared. This shows that magnesiothermic reduction of B_2O_3 and consequently $ZrSiO_4$, according to the following reactions, has been initiated.

$$5Mg + \frac{1}{3}B_2O_3 + ZrSiO_4 = 5MgO + \frac{2}{3}B + Zr + Si + Q \quad [14]$$

The presence of the Mg and $ZrSiO_4$ peaks in this sample milled for 1h (Fig.7) suggested that the magnesiothermic reductions took place gradually. This can be verified by both low calculated T_{ad} (Fig. 1) and low amount of used B_2O_3 (Table 5) after 1h of milling (lower than needed to complete magnesiothermic reaction~ 67%).

In this group, the carbon value increased by decreasing the Mg content, while the carbothermic reaction did not proceed as can be seen obviously in table (5). Negligible carbon consumption after 1h of milling should be related to the formation of carbide compounds (ZrC and SiC) as a carbon agent. Therefore, a gradual magnesiothermic reaction did not supply the required temperature for the occurrence of carbothermic reaction. It should be noted that MgO provided from reaction (14) had an adequate opportunity to react with the remained B_2O_3 to form $Mg_3(BO_3)_2$, according to reaction (9). The XRD pattern of the sample milled for 3h (Fig. 7) indicated that the magnesium borate peaks diminished by increasing the milling time.

4. Conclusions

An attempt has been made here to investigate the reaction mechanism during the synthesis of the ZrB_2-SiC-ZrC composite by mechanochemical technique. Thermodynamics evaluations and experimental results indicated that the Mg content, within a range of 5-7mol, played a key role in the mechanochemical behavior of the $Mg/ZrSiO_4/B_2O_3/C$ system. The results of this research work can be summarized as follows:

1. Thermodynamic calculations showed that T_{ad} increased with the increase in the Mg content. When the Mg value was in the range of 5.72-7mol, the adiabatic temperature of the system was over 1800 K, which met the empirical criterion for occurring in the MSR mode.
2. Based on the DTA analysis, the first exothermic reaction occurred after melting of the Mg powder attributed to the initiation of B_2O_3 reduction by Mg (magnesiothermic reaction). Subsequently, the magnesiothermic reduction of $ZrSiO_4$ and the formation of the ZrB_2, ZrC and SiC phases took place. By increasing the milling time to 45min, an exothermic reaction occurred before magnesium melting, indicating that all the exothermic reactions happened simultaneously. In addition, the quantity of $Mg_3(BO_3)_2$ significantly decreases with an increase in the milling time.
3. According to the amounts of Mg in the $Mg/ZrSiO_4/B_2O_3/C$ mixtures, reactions can be divided into the following three groups resulting in different behaviors:

- With the Mg content in the range of 5-11/2 mol, gradual magnesiothermic reduction and formation of $Mg_3(BO_3)_2$ as a by-product and no carbothermal reaction.
- With the Mg content in the range of 11/2-6 mol, the magnesiothermic reduction occurred in MSR mode and activated the carbothermal reaction which continued gradually to 3h.

The mixture powder with 6-7mol Mg, MSR mode reaction and the occurrence of carbothermic reduction, simultaneously.

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