The role of boron oxide and carbon amounts in the mechanosynthesis of ZrB$_2$–SiC–ZrC nanocomposite via a self-sustaining reaction in the zircon/magnesium/boron oxide/graphite system

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Abstract

Herein, ZrSiO$_4$/B$_2$O$_3$/Mg/C system was used to synthesize a ZrB$_2$-based composite by means of a high energy ball milling process. A mechanically induced self-sustaining reaction was achieved in this system. A nanocomposite powder of ZrB$_2$–SiC–ZrC was prepared with an ignition time of approximately 6 minutes of milling. The role of the stoichiometric amounts of B$_2$O$_3$ and carbon was investigated to clarify the governing mechanism for the formation of the product.

Keywords: Nanocomposites; Mechanosynthesis; Self-sustaining;

1. Introduction

Zirconium diboride (ZrB$_2$) has an excellent combination of physical and chemical properties, such as high melting temperature, high hardness, low electrical resistivity, chemical inertness, and high thermal stability that make them extremely interesting for

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high-temperature applications [1]. A new emerging family of materials able to withstand ultra-high temperatures is under development based on these refractory compounds [2]. These materials, called ultra-high temperature ceramics (UHTCs), can potentially be used at temperatures above 1800°C because of their outstanding thermal and chemical stability, strength at high temperatures, and oxidation resistance [3-5].

UHTCs are currently composed of HfB_2 and ZrB_2 as single or binary compounds, and as composites with other refractory ceramics. SiC is one of the most widely used materials for making applicable composites with ZrB_2, because the addition of SiC improves the oxidation resistance, densification behavior, and thermal shock of ZrB_2–SiC composites [6-10]. In these composites, a complex oxide scale constituted of a refractory oxide skeleton and amorphous glass components form after high-temperature oxidation, reducing oxygen permeability, and providing improved high-temperature resistance [11]. ZrC is also an appropriate ceramic compound which has been used to add to ZrB_2 as a sintering aid or reinforcement for making a useful composite [12]. Ternary composites of ZrB_2–SiC–ZrC have also been of interest recently by a number of researchers through various methods and reactions [13-16].

Zircon ($ZrSiO_4$), as a single source for both zirconium and silicon, may be employed for the synthesis of ZrB_2–SiC-based composites, which has not been used widely so far. Only few works have reported the use of $ZrSiO_4$ as a feedstock for preparation of zirconium compounds-based composites. For example, ZrN–Si_3N_4 [17] and ZrC–SiC [18] composites have been prepared from zircon by carbothermic reduction processes. Fe-ZrC [19] and W-ZrC [20] composites have also been obtained

by aluminothermic reduction of Fe_2O_3 and $ZrSiO_4$ and reactive sintering of WC and $ZrSiO_4$, respectively.

The authors have previously reported a preparation of the ternary composite of ZrB_2–SiC–ZrC in a novel approach [21]. This composite was synthesized by a mechanically induced self-sustaining reaction (MSR) of magnesiothermic reduction with an ignition after 6 min of milling. The primary mechanism of composite formation was discussed in our previous work [21]. In order to complete our study of the mechanism, the goal of the present work was to investigate the effect of boron oxide and carbon amounts on the reaction progression, and presence or absence of self-sustaining reaction, which can be considered as a novel approach for studying this system.

2. Experimental

$ZrSiO_4$ (98%, Alfa-Aesar, USA), B_2O_3 (98%, Fluka, USA), graphite (99%, Fluka, USA) and Mg (99%, Riedel-deHaen, Germany) powders were used as initial materials to synthesize the target products. High-energy ball milling was performed in a modified planetary ball mill (Pulverisette7, Fritsch, Germany) with a ball-to-powder mass ratio of 30:1. Three grams of powder together with seven tempered steel balls (15 mm) were placed in a tempered steel vial (67 Rc) for each milling experiment. The volume of the vial was 50 ml. All milling experiments were conducted under 5 bars of high-purity argon gas. The vial was purged with argon gas several times, and the desired pressure was applied before milling. The vial had a continuous connection to the gas cylinder during the milling experiments by a rotating union (Deublin, Germany) and a flexible polyamide tube. A spinning speed of 600 rpm for both the rotation of the supporting

disk and the superimposed rotation in the direction opposite to the vial was always used. The gas pressure was continuously monitored during the milling process by a pressure transducer (AKS, Danfoss, Denmark) to record the ignition time. A sharp peak due to the pressure rise appears when an MSR reaction occurs. The position of this peak shows the ignition time. The system used in this work has already been illustrated elsewhere [22]. Magnesium oxide by-product was removed by leaching the as-milled powder in a 1M-HCl solution at 80 °C for 1 h.

X-ray powder diffraction (XRD) patterns of samples were acquired with a PANalitycal X'Pert diffractometer (45 kV, 40 mA) with Cu Kα radiation (λ=0.15406 nm). Data were collected in the range of 10–90° (2θ) in step-scan mode with a step of 0.03 and a counting time of 1 s/step. The overall carbon contents in the samples were determined by the elemental analysis of C made by a LECO elemental analyzer (mod. CHNS-932).

3. Results and Discussion

3.1. Mechanosynthesis

The zirconium diboride-based composite can be synthesized by mechanochemistry route in a $ZrSiO_4$, B_2O_3, Mg and C mixture by means of the following magnesiothermic reaction equation:

$$ZrSiO_4 + B_2O_3 + 7Mg + C \rightarrow ZrB_2 + SiC + 7MgO \qquad (1)$$
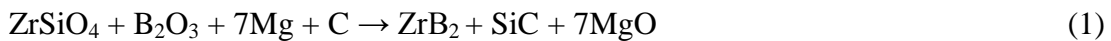
$\Delta G°_{298} = -1270$ kJ, $\Delta H°_{298} = -1300$ kJ, $T_{ad} \approx 2750$ K

The details of the mechanosynthesis process, together with the primary mechanism of this reaction, were reported in our previous work [21]. This system was observed to ignite after 6 min of milling with a great pressure rise at ignition moment.

The XRD patterns of the synthesized product after the ignition point at 6 min showed that the product included ZrB_2, MgO, SiC and ZrC. In order for the small amounts of the remaining initial materials to be consumed completely, the milling process was continued up to 3 hours, resulting in ZrB_2 as the major product with nanometric grain size of approximately 60 nm. MgO was completely removed by a leaching method discussed above, leaving the ternary nanocomposite of ZrB_2–SiC–ZrC. The presence of ZrC among products of reaction *(1)* was attributed to a high chemical affinity between zirconium and carbon.

The governing mechanism for reaction *(1)* was explained [21] to be composed of different sub-reactions. The triggering step was realized to be the self-sustaining reduction of boron oxide by magnesium, yielding elemental boron and magnesia together with a significant amount of heat. The temperature of the system increases greatly as a result of this heat that can cause the reduction of zircon by Mg to form Zr and Si. Afterwards, ZrB_2, ZrC and SiC compounds form concurrently as a result of reaction between Zr, Si, B and C.

3.2. The role of boron oxide amount

In order to clarify the crucial role of boron oxide in triggering the current system and to prove our previously proposed mechanism in greater detail, the boron oxide amount was changed in the present work to control the released heat and follow the phenomena. As pointed above, zircon and boron oxide must be reduced to their corresponding elements to form the target compounds. These sub-reactions are as follows:
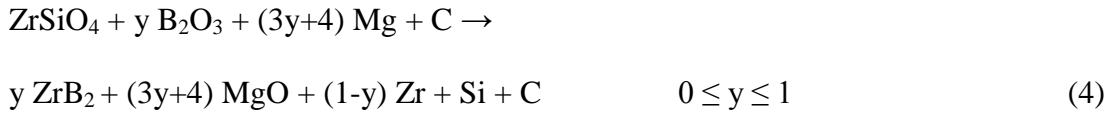
$$3Mg + B_2O_3 \rightarrow 2B + 3MgO \tag{2}$$

$\Delta G°_{298} = -515$ kJ, $\Delta H°_{298} = -532$ kJ, $T_{ad} \approx 2630$ K

$$4Mg + ZrSiO_4 + C \rightarrow Zr + Si + C + 4MgO \qquad\qquad (3)$$

$$\Delta G^\circ_{298} = -363 \text{ kJ}, \ \Delta H^\circ_{298} = -377 \text{ kJ}, \ T_{ad} \approx 1575 \text{ K}$$

The adiabatic temperatures of the above reactions indicate that reaction *(2)* can progress in a self-sustaining manner, while reaction *(3)* does not satisfy the Merzhanov criterion, and hence is expected to be an ordinary reaction. These expectations were demonstrated experimentally to be valid before [21].

It would be interesting now to understand how boron oxide can induce ignition when it is added to the non-self sustaining reaction *(3)*. To examine this phenomenon, the following general reaction was developed:

$$ZrSiO_4 + y \ B_2O_3 + (3y+4) \ Mg + C \rightarrow$$

$$y \ ZrB_2 + (3y+4) \ MgO + (1-y) \ Zr + Si + C \qquad\qquad 0 \le y \le 1 \qquad (4)$$

Due to the high affinity of Zr and Si to react with C, especially during high-temperature ignition, ZrC and SiC should be formed in a subsequent step, instead of elemental Zr, Si and C. Here, the amount of B_2O_3 is considered to be variable. When y is equal to zero, reaction *(4)* reverts to reaction *(3)*, which is a gradual reaction (non-self-sustaining). When y is equal to one, reaction *(4)* is similar to reaction *(1)*, which is self-sustaining. A transition point between these two limits must exit when the boron oxide is increasingly incorporated to the $ZrSiO_4$–Mg–C system, in which the nature of the reaction changes from a non-self-sustaining reaction to a self-sustaining one. For compositions in which the reaction occurs, once B_2O_3 is added to the ternary $ZrSiO_4$–Mg–C system (reaction *3*), it is reduced to B by Mg in a self-sustaining manner, and the heat generated causes the $ZrSiO_4$ to be reduced to Zr and Si. Subsequently, the total amount of boron reacts with the stoichiometric portion of the reduced Zr to form ZrB_2. The remaining Zr should react with carbon present in the system because of the higher

reactability of Zr to C, rather than to Si [21]. The rest of carbon and the stoichiometric portion of Si can form SiC, with the remainder of the Si staying in an elemental form.

Therefore, the amount of B_2O_3 is expected to be a critical thermodynamic and kinetic parameter. Because the T_{ad} is considered to be a measure of self-heating capacity of mixtures that determines the onset of the MSR process, this transition may be illustrated by plotting the T_{ad} of reaction *(4)* versus y values. Figure 1 shows the thermodynamic calculations for T_{ad} and $\Delta H°_{298}$ in reaction *(4)* at various compositions of y = 0–1 at intervals of 0.1. When y increases, the enthalpy of the reaction becomes more negative, making the thermodynamic conditions more suitable for the reaction to take place. It can be seen from Fig. 1 that for y ≥ 0.2, T_{ad} is greater than 1800 K, and the reaction can theoretically behave in a self-sustaining mode. In other words, for compositions in the range of 0 ≤ y < 0.2, the amount of B_2O_3 is insufficient to release enough heat through a self-sustaining magnesiothermic reduction to permit the whole system to be self-sustaining. Therefore, reactions at these compositions are not expected to be able to occur easily at room temperature and require more rigorous situation such as high temperatures or very long-term milling to permit the overall reaction to gradually proceed. For compositions of y ≥ 0.3, the amount of B_2O_3 seems to be adequate to be reduced in a self-sustaining reaction by Mg and to simultaneously cause the $ZrSiO_4$ to be reduced to Zr and Si for the formation of the boride and carbide phases.

In order to verify this prediction, typical compositions of different y values between 0 and 1 with intervals of 0.1 were examined by high energy ball milling. The XRD results in Fig. 2 show that only the y = 1 and 0.9 compositions behaved in a self-sustaining manner, and showed the expected products after ignition times. No ignition

occurred for compositions of y ≤ 0.8 during the long-term milling experiments, although the Merzhanov criterion for emerging a self-sustaining reaction in the range of $0.2 \leq y \leq 0.8$ is satisfied. Consequently, the theory of transition from gradual behavior to the self-sustaining behavior for this system appears to be valid, although there is a quantitative difference between the theoretically calculated and experimentally determined criteria.

This inconsistency is not unusual because the known rule regarding an adiabatic temperature of at least 1800 K was empirically determined for SHS processes [23]. Although the same criterion may be applicable for MSR processes, many exceptions exist, and it has been found that not all SHS reactions can be initiated by high energy ball milling [24]. There are significant differences between the SHS and MSR synthesis routes. For example, SHS is commonly performed using a consolidated, compact powder with limited heat loss to the environment, whereas the powder used for MSR is in close contact with the milling media, which leads to a greater heat loss. For the synthesis of some refractory materials, the MSR effect was observed only when the T_{ad} was well above 1800 K [25].
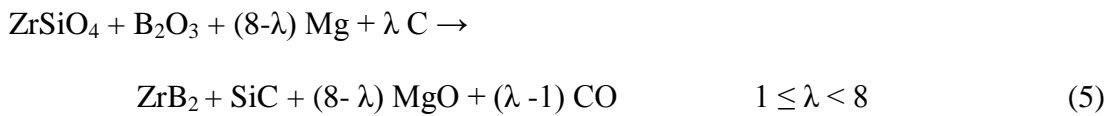
Observations show that both gradual and self-sustaining kinetics are possible for the same reactant mixture, depending on the milling conditions, and the transition between these regimes appears to be related to the milling intensity [26]. The experimental conditions used in this work were probably not severe enough to sufficiently activate the reacting materials to undergo a self-sustaining reduction in the range of $0.2 \leq y \leq 0.8$. These compositions may be self-sustaining under more severe milling conditions. As the rotational speed is considered one of the most important parameters in determining the energy transferred to a powder charge in a planetary mill, the milling experiments were performed again with an increased rotational speed of 750

rpm for those values of y where no reaction occurred at a speed of 600 rpm ($y \leq 0.8$).

Figure 2 shows that self-sustaining reaction for a composition of $y = 0.8$ occurred after

5 min. For the compositions of $y \leq 0.7$, the mixtures did not ignite again during long-

term milling experiments, despite the increased rotational speed. As an example, the

XRD pattern for a composition of $y = 0.7$ after 2 h of milling at 750 rpm is shown in

Fig. 2. These results confirm the aforementioned theory regarding the relation of

severity of experimental conditions for the provision of enough energy for activating the

reactants.

3.3. The role of carbon amount

In this section, the important question is whether carbon only plays a role as a

carbide-forming element or can also act as a reducing agent. In order to determine the

role of carbon, the following reaction was developed:

$$ZrSiO_4 + B_2O_3 + (8-\lambda) \, Mg + \lambda \, C \rightarrow$$

$$ZrB_2 + SiC + (8-\lambda) \, MgO + (\lambda -1) \, CO \qquad 1 \leq \lambda < 8 \qquad (5)$$

where Mg is increasingly substituted by C. For $\lambda = 1$, carbon is not a reducing agent and

reaction *(5)* transforms into reaction *(1)*, and for $\lambda = 8$, all magnesium is substituted by

carbon that should act as the sole reducing agent in the system. If carbon has a reducing

role, the formation of CO is required to be present among the products. The standard

free energy of reaction *(5)* versus temperature is shown in Fig. 3 for some typical

compositions. It is clear that the Gibbs free energy value of the reaction at low

temperatures becomes more positive with increasing λ value. For reactions with $\lambda \geq 4$,

$\Delta G°$ is above zero, indicating that the reaction is thermodynamically unfavorable. It can

be observed that the addition of carbon to the system results in more positive enthalpy

values and conditions for happening the reaction become more difficult. Figure 4 shows

the adiabatic temperature and room temperature enthalpy values of the reaction *(5)* versus λ for values lower than 4. Based on the Merzhanov criterion, Fig. 4 shows that the compositions with λ ≤ 2.1 should behave in a self-sustaining manner and the compositions with 2.2 ≤ λ < 4 should not exhibit self-sustaining ignition. For compositions with λ ≥ 3.7, the enthalpy values are positive; hence there is no data point for T_{ad} for these compositions in Fig. 4.

Milling experiments were carried out at different compositions to study the role of carbon in the ignition. Contrary to the predictions mentioned above, the self-sustaining reactions were observed to occur until the composition of λ = 3.8. Fig. 5 shows the XRD patterns of three samples with T_{ad} > 1800 K (λ = 1.5, 2 and 2.1) and Fig. 6 shows the XRD patterns of six typical compositions with T_{ad} < 1800 K (λ = 2.2, 2.5, 3, 3.5, 3.8, 3.9). Figure 7 illustrates the ignition time values for all these compositions. As can be seen, the ignition time increases with carbon content due to the decreasing exothermicity of the reaction. Remaining free carbon is observed to be present in XRD patterns of all compositions (except in λ = 1.5) in Figs. 5 and 6. By increasing the amount of carbon in the system (λ), the peak intensities of ZrB_2 and ZrC (products) decreased and those of remaining zircon increased, especially from λ = 3.5. Figure 6 shows the appearance of ZrO_2 phase after ignition in all samples with T_{ad} < 1800 K. It is evident that the amount of this phase increases with λ value. The weight percent amount of carbon among the starting mixture of reactants in reaction *(5)* was calculated. Also, carbon weight percent was measured by elemental analysis after ignitions for samples of λ = 1, 1.5, 2, 2.1, 2.2, 2.5, 3, 3.5, 3.8 and after 3 hours of milling for sample of λ = 3.9 (without ignition). Both these calculated and measured series of values are shown in Fig. 7. These two curves fit well as seen in this figure.The comparison between carbon

amount calculations among starting materials and carbon amount quantifications among products in these samples indicates that there is no carbon loss in the samples after ignition suggesting that CO gas is not formed in this system. It implies that a portion of all initial carbon converted to carbide compounds (SiC and ZrC) and the rest of the carbon remains as free carbon among products.

These all above evidences demonstrate that the reaction *(5)* is not a real reaction and carbon does not participate in this system as a reducing agent. In other words, magnesium is the only reducing agent in the system and despite a self-sustaining reaction is observed, the heat released does not induce the carbothermic reduction of the remaining zircon. Consequently, when the carbon amount is increased in the initial mixture more than the stoichiometric amount of reaction *(1)*, i.e $\lambda = 1$, it acts only as an inert material within the mixture. Due to the lubricant nature of the graphite, increasing the carbon amount lessens the effectiveness of the ball impacts and hence, the ignition is delayed to the longer times. Excessive carbon amounts also decrease the real adiabatic temperature of reaction *(1)*. When the initial carbon amount increases further, the amount of magnesium is not enough to reduce completely zircon to zirconium, and it appears as a remaining phase among the products. The presence of intermediate phases such as zirconium oxide and magnesium silicate is an evidence for partial dissociation of zircon into its constituent binary oxides. Ultimately, when the carbon amount in the sample is too high ($\lambda = 3.9$), the ignition was not observed even after 3 hours of high energy ball milling.

4. Conclusion

Mechanosynthesis of ZrB_2–SiC–ZrC nanocomposite was performed using a magnesiothermic reduction. The synthesis in the $Mg/B_2O_3/ZrSiO_4/C$ system was found

to be self-sustaining with an ignition time of 6 min of milling under the experimental conditions used. Examination of the effect of boron oxide on the reaction progress revealed that B_2O_3 amount is an important processing parameter, which can alter the nature of the reaction. By studying the role of carbon in the reaction progression, it was concluded that carbon does not participate in the reaction as a reducing agent. It seems that carbon acts only as a carbide-forming agent.

Acknowledgements

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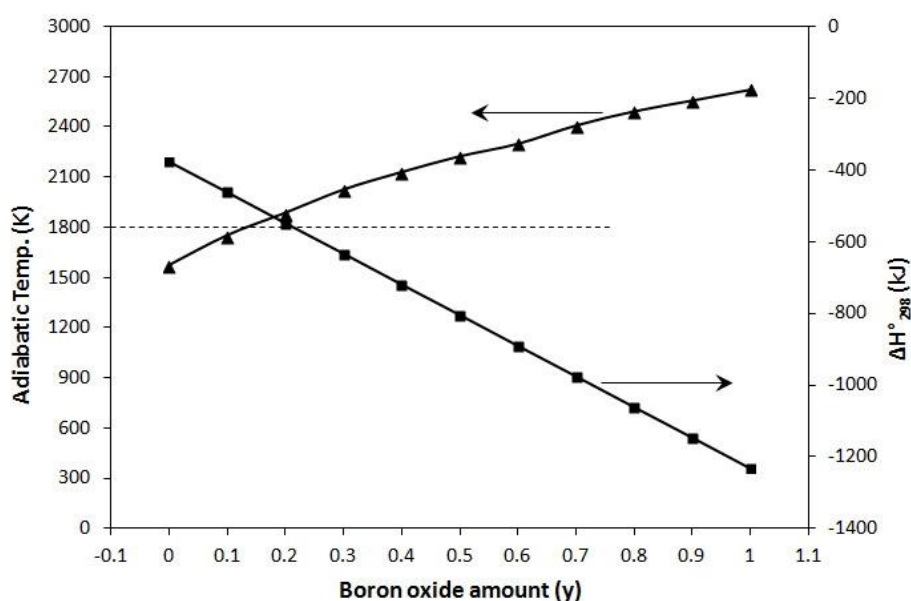
Fig. 1. Calculated adiabatic temperature and room temperature enthalpy of reaction *4* versus the molar amount of B_2O_3 (y).
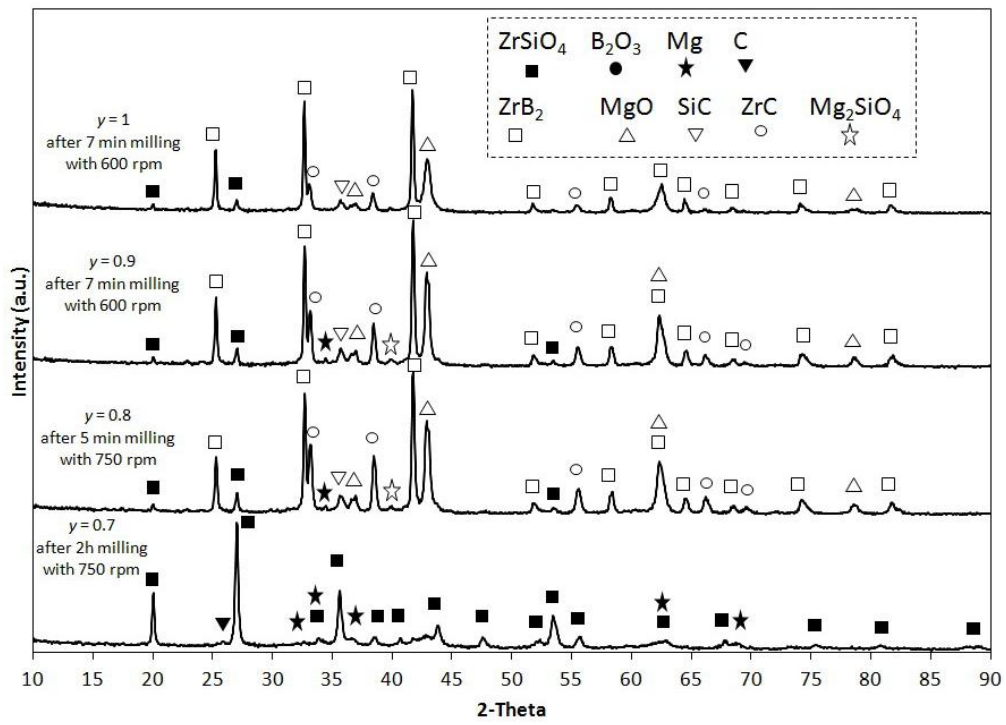
Fig. 2. X-ray diffraction patterns of compositions for y = 1, 0.9, 0.8 and 0.7 in reaction *4* at
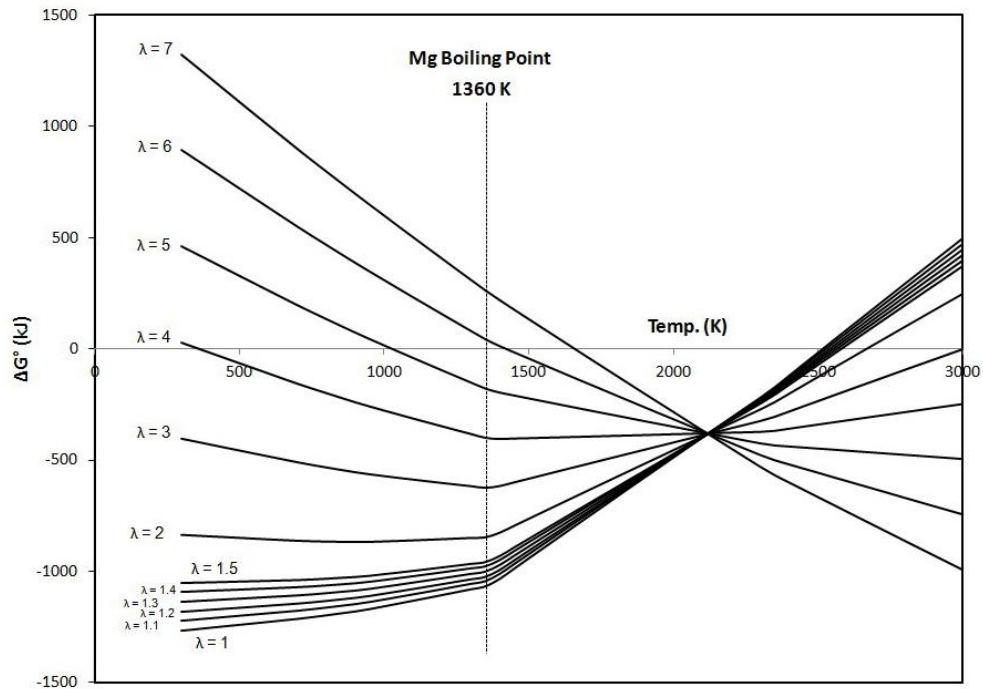
milling speeds of 600 and 750 rpm.

Fig. 3. Standard Gibbs free energy changes of the reaction *5* versus temperature for different λ
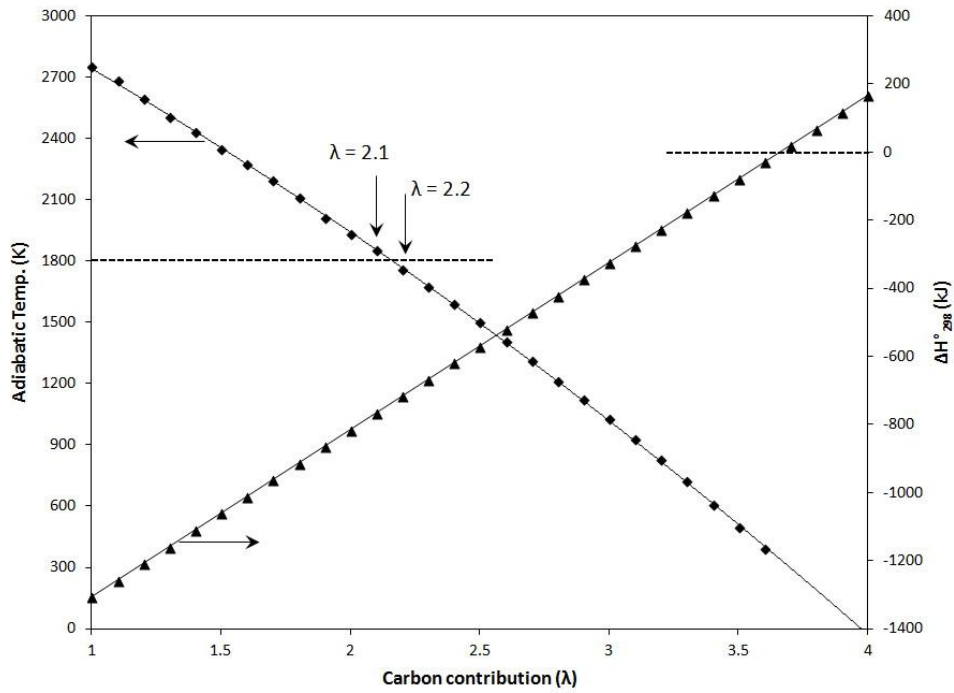
values.

Fig. 4. Calculated adiabatic temperature and room temperature enthalpy of reaction *5*
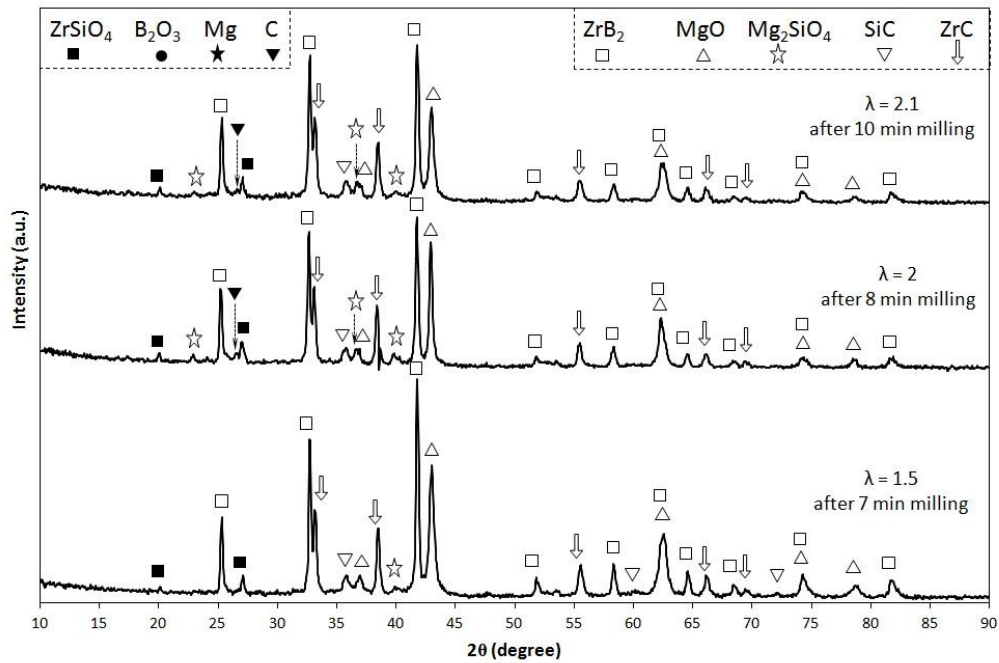
versus the molar amount of carbon (λ).

Fig. 5. X-ray diffraction patterns of compositions for λ = 1.5, 2 and 2.1 in reaction *5*
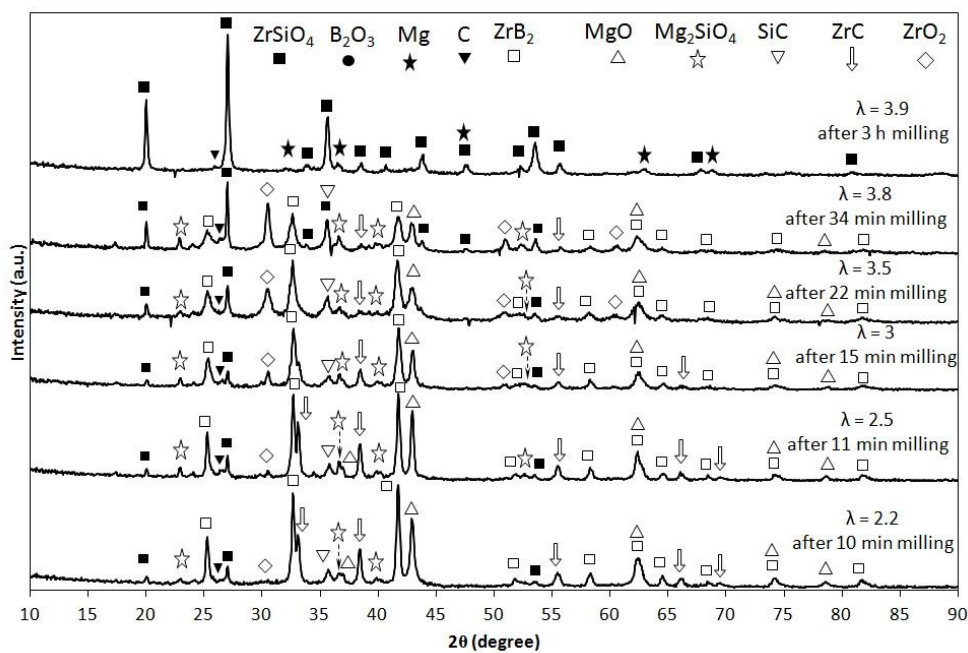
immediately after ignition times.

Fig. 6. X-ray diffraction patterns of compositions of reaction *5* for λ = 2.2, 2.5, 3, 3.5 and 3.8

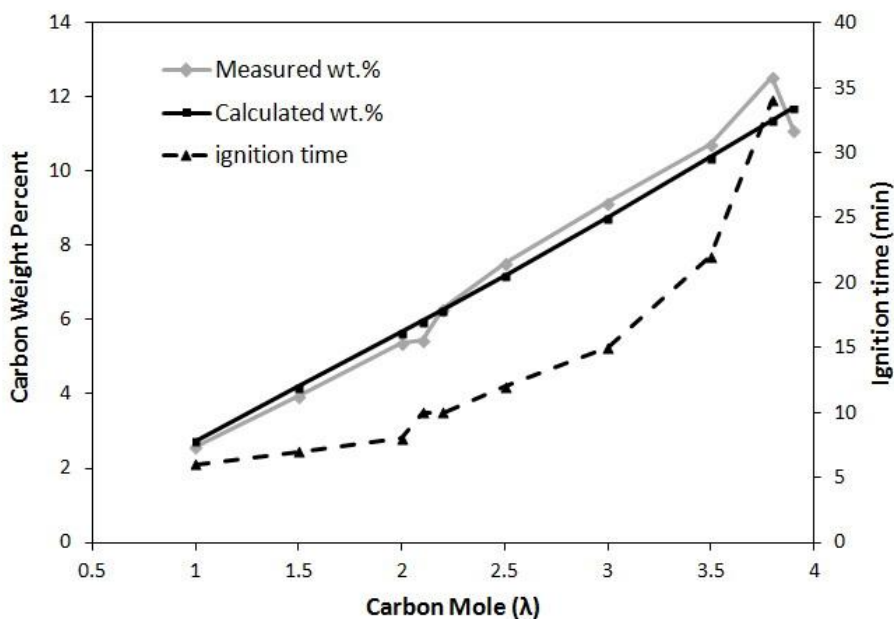with different ignition times and λ = 3.9 after 3 hours of milling without ignition.

Fig. 7. Calculated weight percent of carbon among initial materials, measured weight

percent of carbon among products and ignition times of reaction *5* versus the molar

amount of carbon (λ).