

Formation mechanism of $\text{ZrB}_2\text{-Al}_2\text{O}_3$ nanocomposite powder by mechanically induced self-sustaining reaction

M. Jalaly · M. Sh. Bafghi · M. Tamizifar ·
F. J. Gotor

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Abstract $\text{ZrB}_2\text{-Al}_2\text{O}_3$ nanocomposite powder was produced by aluminothermic reduction in $\text{Al/ZrO}_2/\text{B}_2\text{O}_3$ system. In this research, high energy ball milling was used to produce the necessary conditions to induce a mechanically induced self-sustaining reaction. The ignition time of the composite formation was found to be about 13 min. The synthesis mechanism in this system was investigated by examining the corresponding sub-reactions as well as changing the stoichiometry of reactants. Thermal behavior of the system was also studied.

Introduction

ZrB_2 is a well-known material belonging to the Ultra-high temperature ceramics class [1]. The distinctive features of this class of materials make them good selections for use in various applications such as hypersonic flights, atmospheric re-entry vehicles, and rocket propulsion systems. Zirconium diboride has attracted much attention because of its superior oxidation resistance, which is a consequence of the stability of ZrO_2 formed on these materials at high temperatures in oxidizing atmospheres [2].

Ceramic matrix composites consisting of high temperature borides and some other industrial ceramic materials have been of interest in recent years. Alumina is one of the most

commonly used ceramics in various applications such as grinding media, cutting tools, crucibles, tube furnaces, and liners, owing to its several intrinsic characteristics like high hardness, high melting point, good chemical inertness, high wear resistance, and low cost. Nevertheless, some mechanical properties of alumina are not good enough for several applications. The mechanical strength of these materials can significantly improve by the addition of strong compounds like zirconium diboride [3]. $\text{TiB}_2\text{-Al}_2\text{O}_3$ composite that was prepared by mixing alumina and diboride powders, showed excellent mechanical properties [4]. The most important applications of ZrB_2 are in the high-temperature fields, where it is used as a refractory material; hence, the effect of alumina on the oxidation rate of ZrB_2 ceramic should be essentially investigated. Few reports exist on the high temperature oxidation resistance of $\text{ZrB}_2\text{-Al}_2\text{O}_3$ composites. Recently, Li et al. [5] examined the oxidation kinetics of $\text{Al}_2\text{O}_3/\text{ZrB}_2/\text{ZrO}_2$ composite prepared by mixing and hot-pressing.

Self-propagating high temperature synthesis (SHS) has recently been used extensively for the preparation of refractory materials such as carbides, silicides, nitrides, and various composite materials. This kind of synthesis is characterized by its significant negative enthalpy and high adiabatic temperature (T_{ad}) of above 1800 K [6]. Literature survey shows a great attention to the metallothermic reduction of ZrO_2 and B_2O_3 in preparation of ZrB_2 because of its cheaper raw material as well as the high exothermic nature of the involving self-sustaining reactions compared to the other synthesis routes [7–12]. Magnesium has been frequently used to reduce zirconium and boron oxides [7–11] due to good feasibility of MgO leaching, although aluminum has also been employed in a few cases [3, 12] for inducing the reduction reaction in this system. Using Al as reducing agent has also the advantage of in situ making of $\text{ZrB}_2\text{-Al}_2\text{O}_3$ which is a valuable composite.

M. Jalaly (✉) · M. Sh. Bafghi · M. Tamizifar
School of Metallurgy and Materials Engineering,
Iran University of Science & Technology (IUST), Narmak,
16846-13114 Tehran, Iran
e-mail: maisam_jalaly@iust.ac.ir

F. J. Gotor
Instituto de Ciencia de Materiales de Sevilla (CSIC-US),
Americo Vespucio 49, 41092 Sevilla, Spain

When a self-sustaining reaction is induced by the high-energy ball milling of reactants after a critical milling period, called the ignition time, such a mechanochemical process is referred to as mechanically induced self-sustaining reaction (MSR) [6]. MSR and SHS are different methods, although there are common features between both processes. In contrast to the conventional SHS procedure, MSR process has the favorable side benefit of mixing of the reactants as well as the subsequent homogenization of the products together with intensive particle size reduction of both reactants and products, all just in one single step.

All research works that were performed on the ZrB₂ synthesis by use of Al as reducing agent were carried out by thermally combusive SHS methods, rather than MSR reactions [3, 11]. Furthermore, reaction mechanism has not also been clearly explained. The aim of the present work, therefore, was to investigate the mechanosynthesis of ZrB₂–Al₂O₃ powder by aluminothermic reduction using ZrO₂ and B₂O₃ as starting materials and by means of MSR, which has not been reported so far. The mechanistic explanation of ZrB₂ formation in this system was also another target, which has been accomplished through the investigation of sub-reactions, as well as the study of the influence of the reactants stoichiometry.

Experimental

The raw materials, monoclinic ZrO₂ (99 %, Aldrich, USA), B₂O₃ (98 %, Fluka, Germany), and Al (99 %, Aldrich, USA) powders, were used to produce zirconium diboride–alumina composite powder. Elemental zirconium (99 %, Alfa Aesar, Germany) and boron (97 %, amorphous, Aldrich, USA) were also used for studying a sub-reaction. The starting materials were subjected to the high energy ball milling in a modified planetary ball mill (Pulverisette7, Fritsch, Germany). The rotational speed and ball-to-powder mass ratio were 600 rpm and 30:1, respectively. The milling vial and balls (15 mm) were made of hardened chromium steel. All milling experiments were conducted under 5 bar of high-purity argon gas. The vial was purged with argon gas several times, and the desired pressure was adjusted before the start of the milling. The connection of the vial to the gas cylinder during the milling experiments was maintained by a rotating union and a flexible polyamide tube. The pressure change versus time was monitored by a SMC solenoid valve (model EVT307-5DO-01F-Q, SMC Co., Tokyo, Japan) to record the ignition time. A sharp peak due to the pressure rise appears when the MSR reaction occurs. The position of this peak represents the ignition time. The system used in this work has already been shown elsewhere [13].

Thermal behavior of the as-blended mixture was studied by differential scanning calorimetry (DSC) in a TA

Instrument Q600 analyzer using a constant heating rate of 20 °C/min from room temperature to 1400 °C. The DSC measurement was done under a flowing helium atmosphere. Furthermore, isothermal annealing of mixtures was carried out at different temperatures for 30 min under a flowing argon atmosphere at a pressure of 1 bar in a horizontal tubular furnace (IGM1360 model no. RTH-180-50-1H, AGNI, Germany).

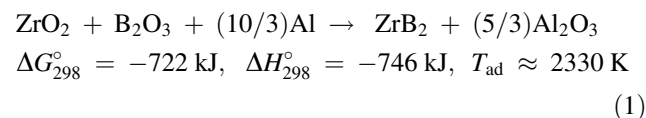
Structural features of the samples were investigated using X-ray diffraction (XRD) analysis by means of a PANalytical X'Pert diffractometer (45 kV, 40 mA) with Cu K α radiation ($\lambda = 0.15406$ nm) XRD analyzer. The crystallite size of sample was estimated by broadening analysis of XRD peaks using Williamson–Hall formula [14].

Scanning electron microscopy (SEM) images were obtained by a Hitachi S-4800 SEM-Field Emission Gun microscope. Transmission electron microscopy (TEM) images were taken using a 200 kV Philips CM200 microscope equipped with a SuperTwin objective lens and a tungsten filament (point resolution $\phi = 0.25$ nm). Powdered samples were dispersed in ethanol, and droplets of the suspension were deposited onto a holey carbon film.

Results and discussion

Mechanosynthesis

The initial purpose of the present work was to synthesize zirconium diboride–alumina composite. In order to achieve this goal, the following reaction was considered:



Stoichiometric amounts of starting materials (Table 1) were milled under aforementioned conditions. The change of internal pressure of the vial versus milling time is shown in Fig. 1. The large pressure rise observed at ~ 13 min milling demonstrates the occurrence of a highly exothermic MSR reaction.

Figure 2 shows the XRD patterns of Al, ZrO₂, and B₂O₃ powder mixture as-received and after different milling times. The XRD pattern of as-blended mixture included only the sharp peaks of Al (ICCD PDF #03-0932), ZrO₂ (ICCD PDF #13-0307), and B₂O₃ (ICCD PDF #06-0297) compounds, which were converted to ZrB₂ (ICCD PDF #34-0423) and Al₂O₃ (ICCD PDF #11-0661) after 13 min milling (just after ignition). Small amounts of Al and ZrO₂ were still remained, which is a typical behavior of mechanosynthesis reactions, especially in the MSR situations [12], due to the entrapment of some powders in the

Table 1 The weight (g) of components involved in the Reaction 5 for the different y values

y	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
B ₂ O ₃	–	0.127	0.238	0.335	0.420	0.495	0.563	0.624	0.679	0.729	0.774
ZrO ₂	2.435	2.260	2.108	1.975	1.858	1.754	1.661	1.578	1.502	1.434	1.371
Al	0.712	0.759	0.801	0.837	0.869	0.897	0.922	0.945	0.965	0.984	1.001

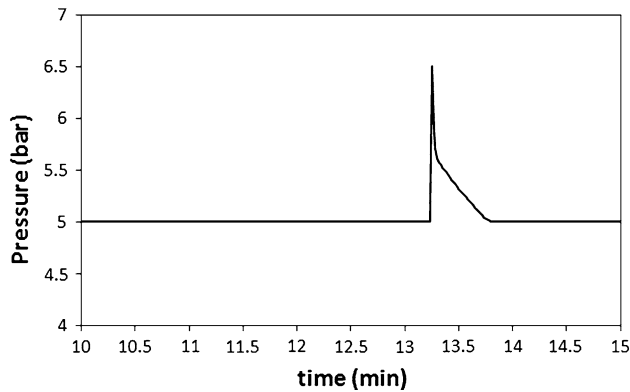


Fig. 1 Pressure inside the vial versus milling time for Al/ZrO₂/B₂O₃ system

dead zones of milling vial. As Fig. 2 shows, a tetragonal ZrO₂ phase (nominated as T-ZrO₂) was detected among the remaining materials in the sample that was milled for 13 min (the ignition point). In fact, zirconium dioxide transformed from its monoclinic crystal structure at room temperature to a tetragonal form, due to the significant temperature rise resulted from the highly exothermic MSR reaction. Because the cooling rate after ignition is very high, there are traces of transformed zirconia remained in the tetragonal state at room temperature. As shown in Fig. 2, a very slight amount of elemental Zr was detected in the XRD pattern for the sample milled for 13 min, most likely due to the incomplete reaction of reduced zirconium with boron. Elemental boron, which may remain due to the incomplete reaction with zirconium, could not be detected, most likely due to its very little quantity and/or its amorphization because of rapid cooling after ignition.

By increasing the milling time, powders trapped in the dead zones can be gradually subjected to the ball impacts and locally reacted. Figure 2 shows the XRD patterns of samples milled for 1 and 2 h. A slight amount of zirconium dioxide was observed after 1 h milling, but it was entirely disappeared after 2 h milling. The crystallite size of ZrB₂ after 2 h ball milling was calculated to be ~83 nm.

The electron micrographs of a sample milled for 2 h are shown in Fig. 3. As these micrographs shows, the product powder contains agglomerates which are composed of particles of sub-micrometric and nanometric sizes with a combination of semi-spherical and platelet morphology. The TEM micrograph in Fig. 3b shows dark polyhedron ZrB₂ particles surrounded by bright alumina nanoparticles.

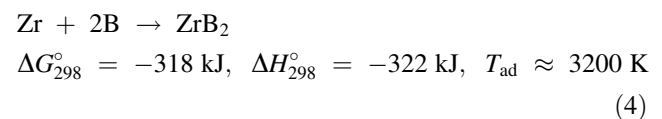
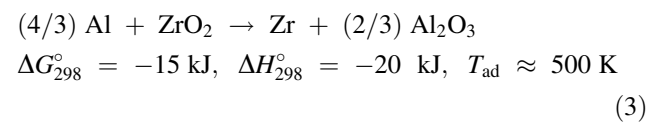
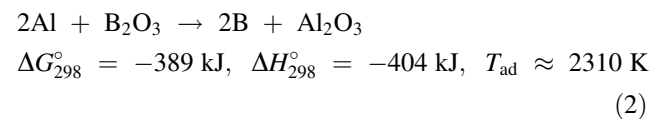
A bigger, single crystal of hexagonal ZrB₂ along with alumina nanoparticles is indicated in a larger magnification in Fig. 3c.

Reaction mechanism

During milling

The mechanistic study of the formation of ZrB₂-Al₂O₃ composite during milling in the present work can be divided into two sections. The overall reaction (Reaction 1) was initially investigated by the study of involved sub-reactions. At the second step, the effect of boron oxide amount on the nature of the reaction was studied.

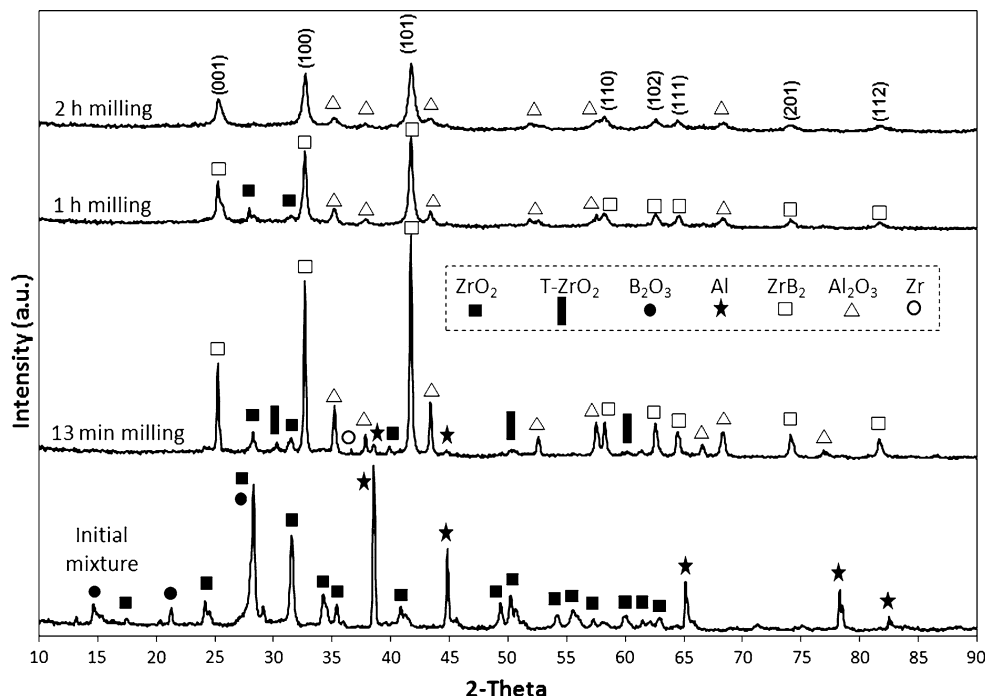
To form zirconium diboride, zirconium, and boron elements must be obtained through the reduction of their corresponding oxides. The sub-reactions involved in this system can be written as follows:



In the above reactions, aluminum reduces boron oxide and zirconium oxide to yield elemental boron and zirconium. ZrB₂ can be subsequently formed by the reaction between these two elements. According to the adiabatic temperatures (*T*_{ad}) and enthalpy values of the above reactions, Reactions 2 and 4 meet the required conditions to satisfy Merzhanov’s criterion [12] to proceed in a self-sustaining manner. However, the reduction of ZrO₂ by Al (Reaction 3) does not satisfy these conditions, and it is hence anticipated to gradually proceed as an ordinary reaction.

When Al, B₂O₃, and ZrO₂ are all present in one system, Al reduces boron oxide in a self-sustaining manner to yield elemental boron together with the release of a great deal of heat; this heat increases the system temperature inside the milling vial to such a level which can trigger the reaction between Al and zirconia to form elemental Zr.

Fig. 2 X-ray diffraction patterns of as-blended and milled samples of Al/ZrO₂/B₂O₃ system



Consequently, ZrB₂ can be synthesized by the reaction between these two elements. The highly exothermic reaction of the reduced B and Zr (Reaction 4) can exert an additional amount of heat to the system, thus causing the further ZrO₂ reduction to proceed more easily. All these three reactions occur simultaneously; thus, only one peak is observed in the pressure–time graph of overall reaction (Reaction 1). This postulation can be confirmed by the existence of a trace amount of residual zirconium as the XRD pattern just after ignition shows (Fig. 2). Although elemental boron was not detected in the XRD pattern, it may be present in consequence of incomplete reaction of ZrB₂ formation and remaining elemental zirconium. Boron can be possibly interpreted to have been present in an amorphous form, if this possible mechanism is factual.

In order to examine the proposed mechanism, these sub-reactions were separately studied. Stoichiometric amounts of Al/B₂O₃, Al/ZrO₂, and Zr/B were mixed according to the Reactions 2–4 and milled under the same conditions. For Reaction 2, the ignition time was found to be about 25 min (Fig. 4), which is a little longer than the ignition time of Reaction 1, due to lower exothermicity of Reaction 2. Reaction 1 includes Al/B₂O₃ ignition along with Zr/B ignition, which can cause the system to be more rigorous than Reaction 1 (only Al/B₂O₃ ignition). Therefore, the ignition time is shorter in the overall system. The XRD patterns of initial materials along with that of sample milled up to the ignition point (25 min) are shown in Fig. 5. It can be seen that the ignited sample contains aluminum oxide, which is an indication of the feasibility of the reduction of boron oxide by Al. Small amounts of the

starting materials were also observed, perhaps due to their entrapment in the dead zones of the vial, as mentioned earlier. However, elemental boron was not detected in the XRD pattern, most likely due to its amorphization as a result of the high temperature rise during the MSR reaction and high cooling rate after ignition. The formation of amorphous boron as a result of metallothermic reduction of boron oxide has already been described in the literature [15, 16].

For Reaction 3, no pressure rise was observed during the milling process as expected from the thermodynamic data. Figure 6 shows the XRD pattern of the un-milled sample together with that of the sample milled up to 4 h in this system. Peak broadening is the only observation, with no sign of the occurrence of any reaction during this long milling time. This confirms that Al cannot reduce zirconia under the conditions applied in the present work even with such a long time period. High energy ball milling at long times can introduce lattice defects into the crystal and induce internal strains. By increasing the milling time, crystalline natures of the initial materials are gradually changing to the amorphous form.

For Reaction 4, the ignition time was around 17 min as shown in Fig. 4. It is evident from the relevant XRD patterns in Fig. 7 that ZrB₂ was completely synthesized after the ignition time of 17 min. Elemental boron used in this section was amorphous, as mentioned in “Experimental” section. Thus, only zirconium is observed in the XRD pattern of initial materials. Consequently, individual study of these sub-systems confirms the validity of the proposed mechanism.

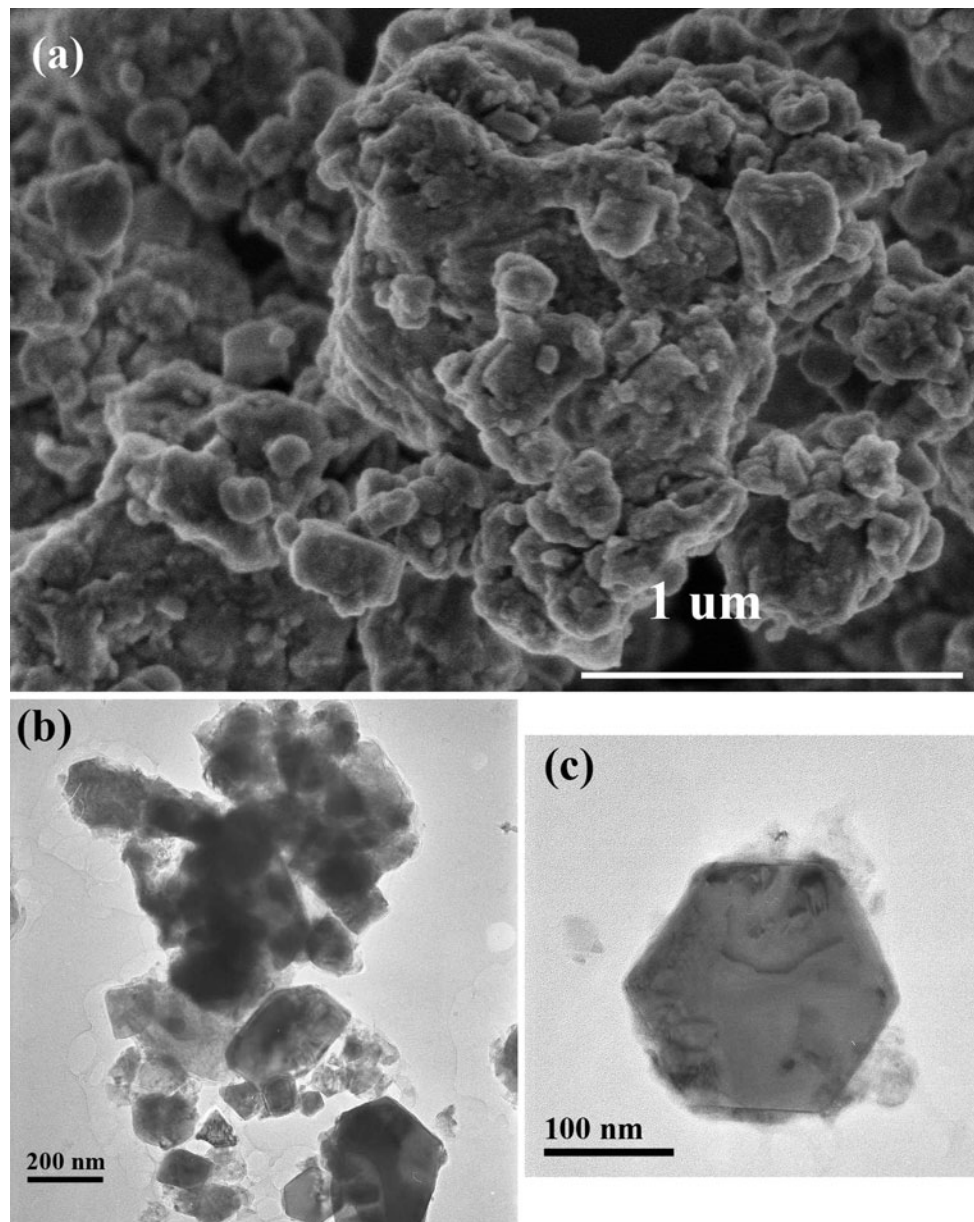
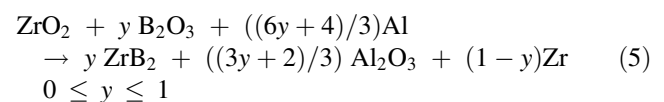


Fig. 3 Electron micrographs of Al/ZrO₂/B₂O₃ system after 2 h milling, **a** SEM and **b** TEM images

As mentioned already, the overall Reaction 1, which is a self-sustaining reaction, is a combination of two self-sustaining reactions (Reactions 2, 4) and one non-self-sustaining reaction (Reaction 3). According to the previously proposed mechanism, B and Zr elements must be obtained at first to form ZrB₂. But, the self-sustaining reduction reaction of boron oxide is not basically the same as non-self-sustaining reduction reaction of zirconium oxide. Therefore, it would be interesting to understand how the latter non-self-sustaining reaction converts to a self-sustaining one. To examine this phenomenon, the following general reaction was developed:



where the amount of B₂O₃ is considered as a variable. The amounts of initial materials used in above reaction were listed in the Table 1 for the different values of *y*. Once B₂O₃ is added to the binary ZrO₂–Al system (Reaction 3), it can be reduced to boron by aluminum. The significant heat generated by this reaction promotes the reduction of zirconia to zirconium. Afterward, the total amount of boron and a stoichiometric portion of reduced zirconium react to

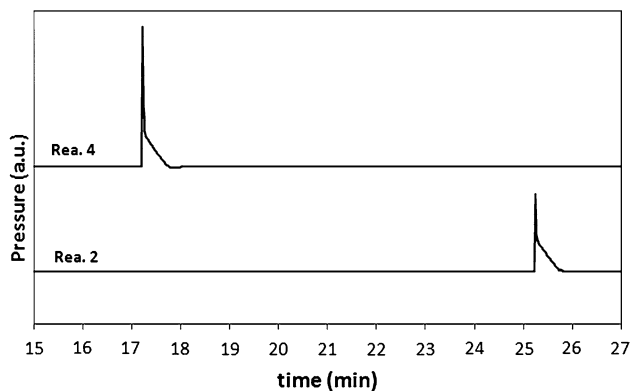


Fig. 4 Pressure inside the vial versus milling time for Al/B₂O₃ and Zr/B systems

form ZrB₂, the rest of unreacted zirconium being left in the product. When y is equal to zero, the Reaction 5 converts to Reaction 3, which is a non-self-sustaining reaction. When y is equal to one, the Reaction 5 changes to Reaction 1, which is a self-sustaining reaction. This implies that there is a transition point between these limiting extends where a gradual reaction transforms to a self-sustaining one, depending on the amount of B₂O₃ in the initial mixture. Therefore, the amount of B₂O₃ is expected to play a crucial role in the sense of the system thermodynamics.

If the adiabatic temperature (T_{ad}) is considered as a measure of the self-sustaining tendency, this transition can be illustrated by plotting T_{ad} of Reaction 5 versus the y values. Figure 8 shows the thermodynamic calculations for T_{ad} and room temperature enthalpy of Reaction 5 as a function of y values ranging from 0 to 1. It is clear that

when y increases, the enthalpy of the reaction becomes more negative, causing more suitable thermodynamic conditions for the reaction to take place. Since a given reaction requires T_{ad} to be at least 1800 K to proceed in a self-sustaining manner (known as the Merzhanov's criterion) [12], it can be seen from Fig. 8 that such a condition is satisfied with y values higher than 0.4. In other words, in the case of compositions with $0 \leq y < 0.4$, the amount of boron oxide is not sufficient to release a great deal of heat by aluminothermic reduction, which is necessary for changing the whole system state to a self-sustaining situation. Therefore, the reaction in these compositions is expected to be unable to take place at room temperature and would require more rigorous situation such as high temperatures or very long-term milling, so that overall reaction can proceed in a gradual way. For compositions with $y \geq 0.4$, the amount of B₂O₃ is sufficient to be reduced in a self-sustaining mode by Al and to simultaneously motivate the reduction of ZrO₂ to Zr.

In order to verify the above thermodynamic prediction, various initial compositions with different y values between 0 and 1 with intervals of 0.1 were examined by high energy ball milling to induce MSR reactions. As can be seen from XRD results in Fig. 9, compositions with $y \geq 0.8$ were observed to behave in a self-sustaining manner and expected products of Reaction 5 have been completely formed after the ignition point of 13 min (results corresponding to $y = 1$ was shown in Fig. 2). But, no ignition occurred in the compositions of $y < 0.8$ even after a long milling time. As an example, the XRD pattern of $y = 0.7$ composition after 2 h milling is shown in Fig. 9. It can be seen that the

Fig. 5 X-ray diffraction patterns of initial and milled samples of Al/B₂O₃ system

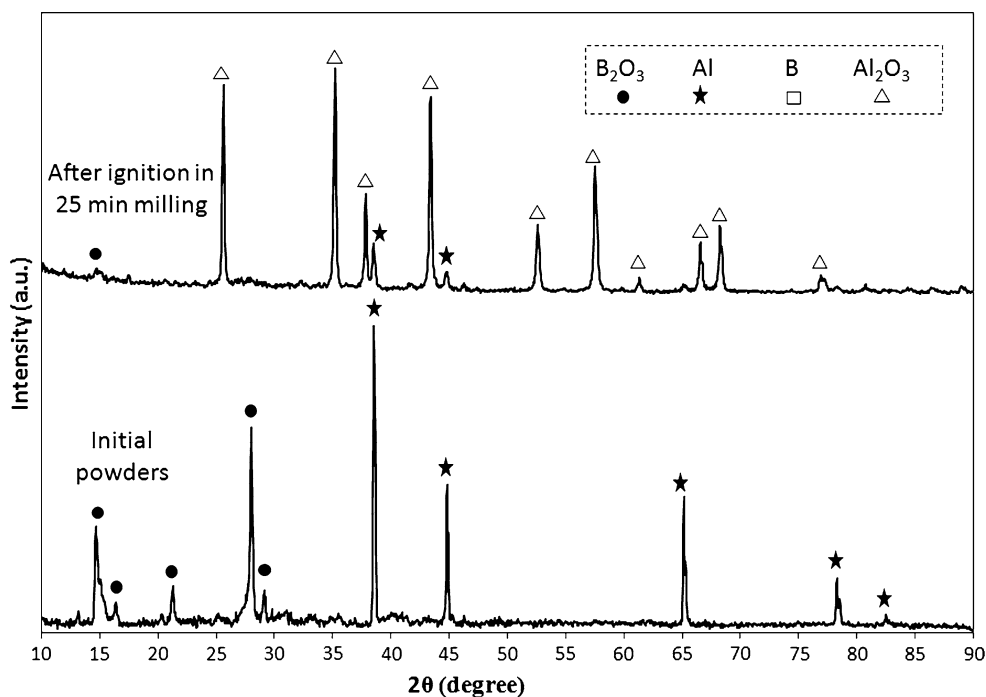


Fig. 6 X-ray diffraction patterns of initial and milled samples of Al/ZrO₂ system

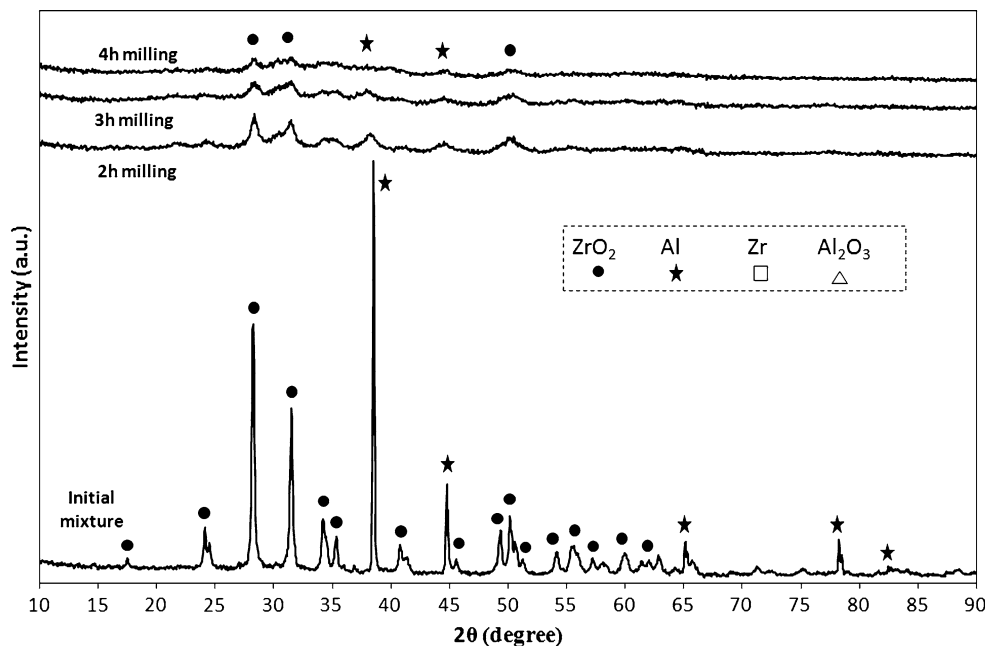
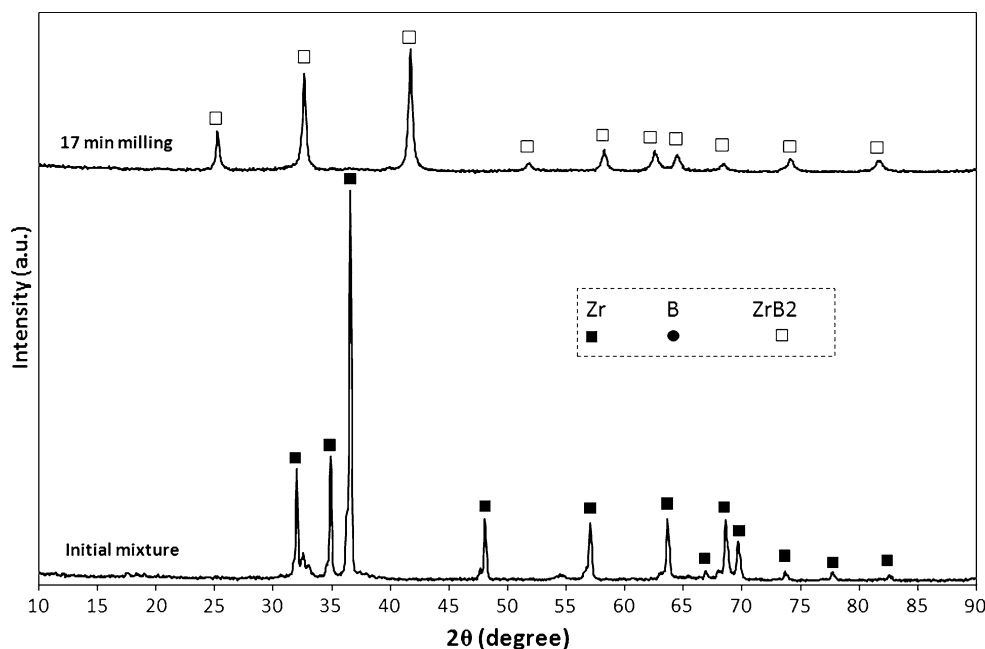


Fig. 7 X-ray diffraction patterns of initial and milled samples of Zr/B system. Boron cannot be observed among initial mixture due to its amorphous state



transition theory of gradual behavior to the self-sustaining mode in this system seems to be valid, although there is a quantitative distinction between thermodynamically calculated and experimentally observed criteria. Ultimately, it can be confidently concluded that in the case of y values less than 0.4, Reaction 5 will never proceed in a self-sustaining mode. For the compositions with $0.4 \leq y < 0.8$, there is no thermodynamic barrier for emerging a self-sustaining reaction, but the experimental conditions applied in the present work have not been severe enough to stimulate the reacting materials to be reduced in a self-sustaining manner.

The main cause of the difference between the thermodynamic calculations and experimental outcome is expected to be the heat loss from the system through heat exchange with the milling vial body, connections, inert gas flow, etc., and consequently insufficiency of energy, including the reaction enthalpy and milling momentum, to induce a very fast self-sustaining reaction. The overall reaction in this range is expected to become self-sustaining if more severe milling conditions are applied. For instance, the self-sustaining reaction occurred for composition of $y = 0.7$ at 1 h milling when the rotational speed of milling

Fig. 8 Calculated adiabatic temperature and room temperature enthalpy of Reaction 5 series versus B_2O_3 molar amount

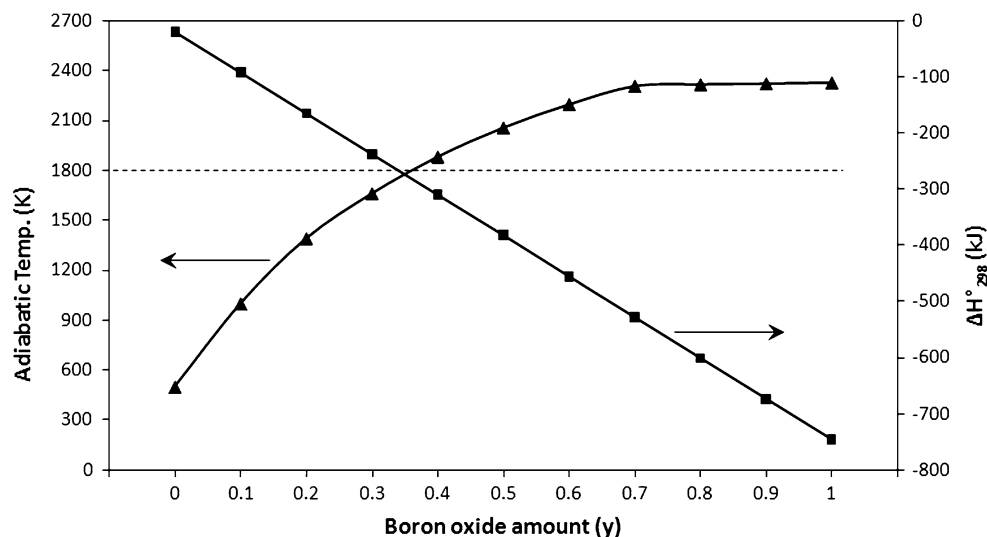
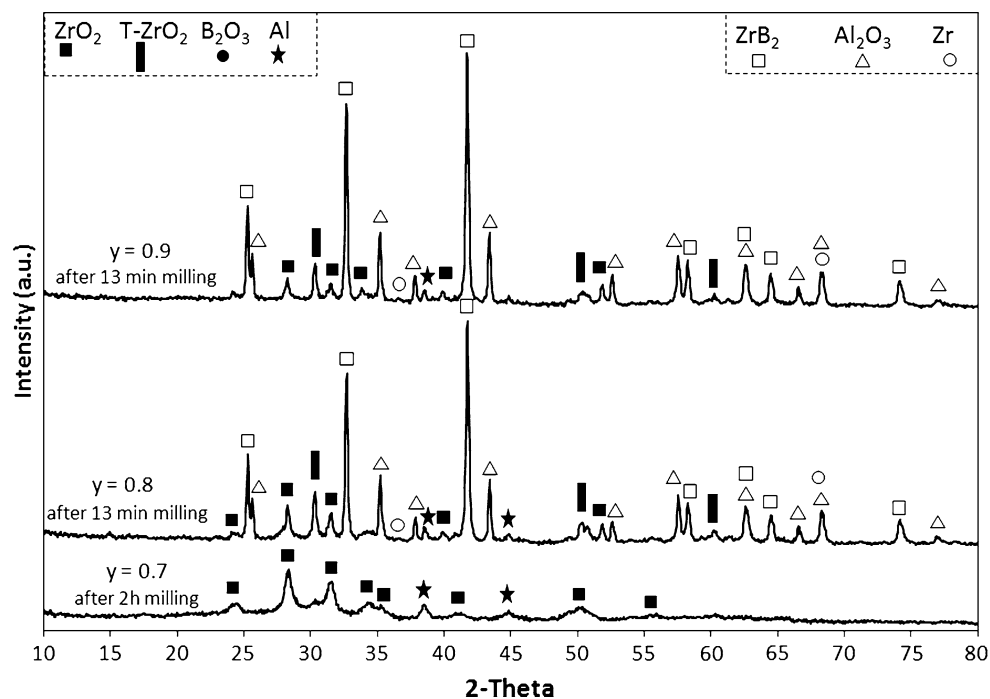


Fig. 9 X-ray diffraction patterns of the different compositions ($y = 0.7$ – 0.9 in Reaction 5) after milling



was increased to 750 rpm. In the case of compositions with $y \geq 0.8$, both thermodynamic and current experimental conditions confirm that this situation is adequate to have a self-sustaining reaction.

Thermal behavior

In order to provide more evidences regarding the proposed reaction mechanism, thermal behavior of as-blended Al/ ZrO_2/B_2O_3 powder mixtures was studied by differential scanning calorimetry (DSC). The DSC curve, shown in Fig. 10, includes one endothermic peak at 660 °C and two major exothermic peaks at around 1000 and 1250 °C. To

clarify the phenomena related to the peaks appeared in DSC graph, some heat treatments at temperatures before and after each DSC peak were performed on the homogenous powder mixtures. To prevent the formation of a stable propagating reaction front, which may cause the occurrence of the overall self-sustaining reaction, loose powder mixtures (un-consolidated) were used and the experiments were accomplished with a slow heating rate (10 °C/min). Figures 11 and 12 show the XRD patterns of products after heating of initial mixture at different temperatures. From the XRD pattern corresponding to the annealed sample at 700 °C in Fig. 11, it is clear that the endothermic phenomenon in DSC is related to Al melting.

The first exotherm starts at about 950 °C extending to about 1050 °C. The XRD patterns taken before (950 °C) and after (1050 °C) the first exotherm are shown in Fig. 11. It can be seen at 950 °C that the small peaks related to the products such as ZrB_2 , Al_2O_3 , and Al_3Zr have appeared together with the sharp peaks of initial reactants. With rising the heating temperature to 1050 °C, the peaks of ZrB_2 , Al_2O_3 , and Al_3Zr have been sensibly intensified and a slight amount of Al_2Zr phase has appeared, although the major phases are still initial ZrO_2 and Al. It can be concluded that the first exotherm observed at about 1000 °C is attributed to the reduction of boron oxide by the corresponding stoichiometric portion of Al with the side product of alumina. A little amount of zirconia has also been reduced due to the high temperature resulted from the heat generated by the reaction between Al/ B_2O_3 , together with subsequent formation of small amounts of ZrB_2 through the reaction between reduced Zr and B elements. An Al-rich zirconium aluminide (Al_3Zr) begins to form around the first exotherm whose amount increases with increasing temperature. Formation of this phase is due to the presence of slight amounts of reduced Zr along with great amounts of Al which can react at high temperatures. At higher temperatures, another less Al-rich zirconium aluminide (Al_2Zr) also finds the chance to be formed. These intermediate compounds are formed in a gradual diffusional mode which is evident from the broad appearance of the DSC graph around the two exotherms. Therefore, no characteristic exotherm can be cited for their formation.

In order to clarify the nature of the second exotherm observed at 1250 °C, heating experiments were performed before (1150 °C) and after (1300 °C) the exotherm. XRD results are shown in Fig. 12. At 1150 °C, accompanied with a considerable increase of all product compounds (ZrB_2 , Al_2O_3 , and Al_3Zr) compared to 1050 °C, a large amount of zirconia and aluminum have still remained unreacted. With increasing temperature to 1300 °C, the major phase was found to be ZrB_2 , even though a small amount of remained ZrO_2 is still observed in XRD pattern. It can be concluded that the second exotherm in DSC pattern relates to the reduction of zirconia by aluminum. Comparison of the results corresponding to the heating at 1300 °C with those of 1150 °C reveals that Al_3Zr phase amount has decreased and Al_2Zr formation has correspondingly grown. This suggests that zirconium aluminide has begun to be converted to lower Al containing aluminides at higher temperatures. In order to reduce the remained ZrO_2 and to decompose zirconium aluminides, heating experiments were carried out at 1400 and 1500 °C. As seen in Fig. 12, a little amount of zirconia is still remained at 1400 °C, whereas the products were free of zirconia at 1500 °C. As to the zirconium aluminides, Al_3Zr was disappeared at 1500 °C while Al_2Zr has been slightly remained among the products.

These all experiments described above, exhibited the preliminary reduction of boron oxide being followed by the reduction of the zirconium oxide at higher temperatures. This general trend is consistent with the mechanism

Fig. 10 DSC curve of as-blended mixture in Al/ ZrO_2 / B_2O_3 system

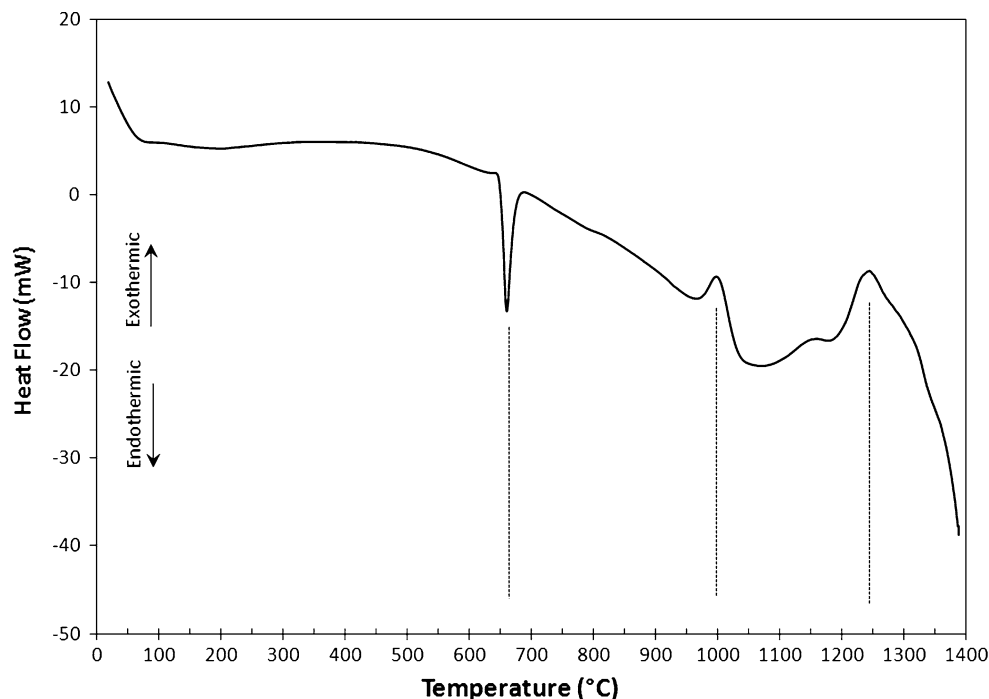


Fig. 11 X-ray diffraction patterns of the blended powders in Al/ZrO₂/B₂O₃ system after heating at 700, 950, and 1050 °C (30 min dwelling at maximum temperature and then cooling to room temperature)

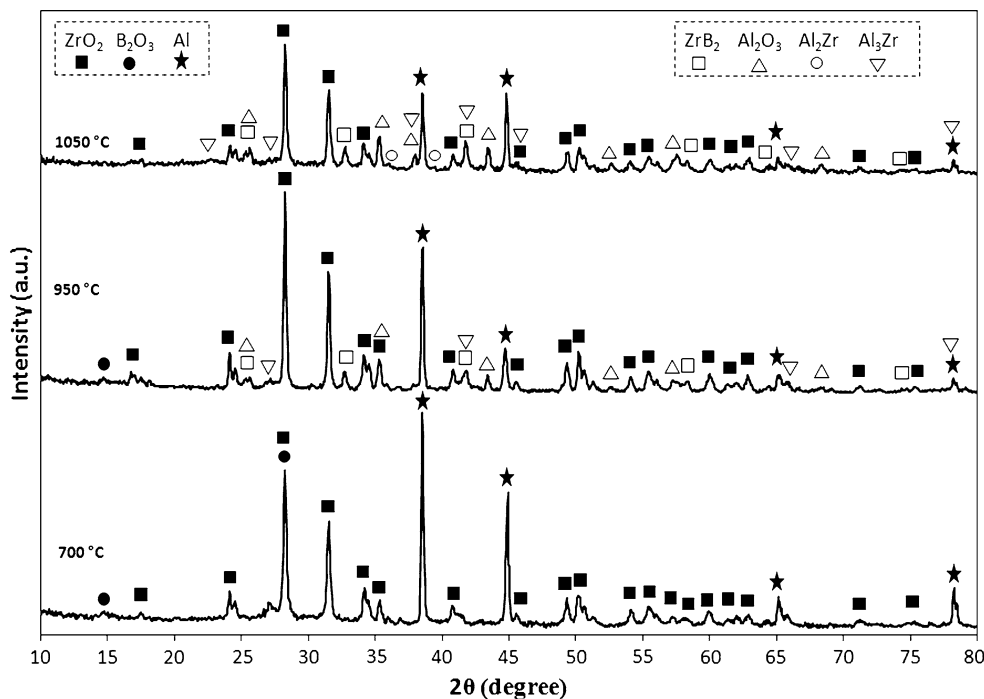
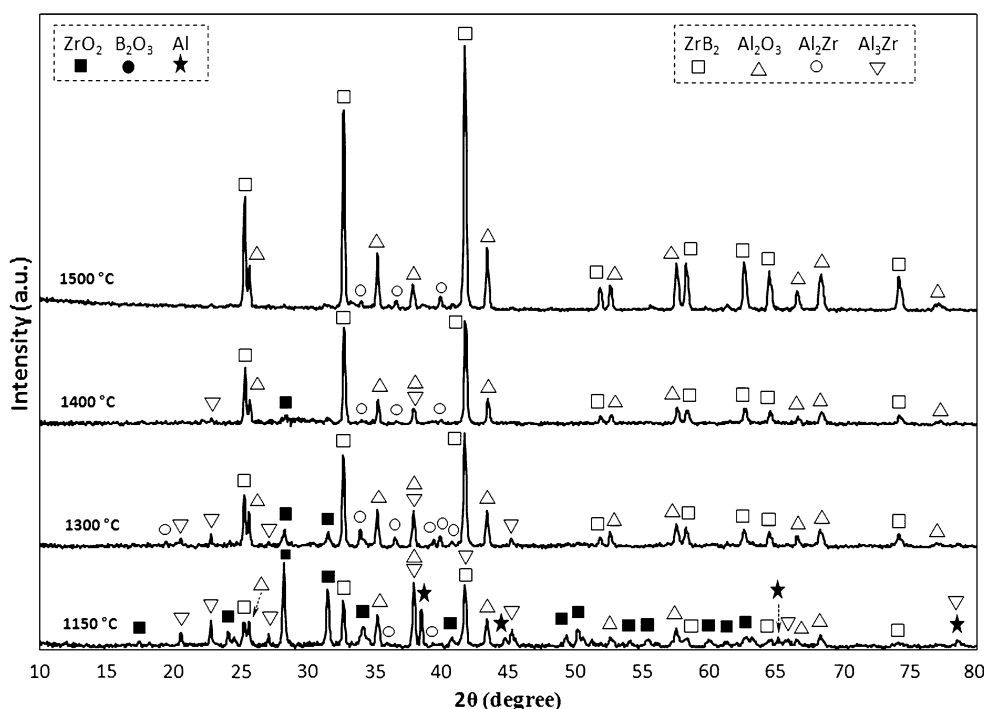


Fig. 12 X-ray diffraction patterns of the blended powders in Al/ZrO₂/B₂O₃ system after heating at 1150, 1300, 1400, and 1500 °C (30 min dwelling at maximum temperature and then cooling to room temperature)



proposed during mechanochemical (milling) synthesis with an exception that intermediate zirconium aluminides were observed in thermal treatment while they were not detected in the milling route. This difference is most likely due to the enough time at high temperatures in the thermal treatments, which can make the conditions suitable for Zr and Al to form zirconium aluminides.

Conclusion

High energy ball milling technique was successfully applied for mechanochemical synthesis of ZrB₂-Al₂O₃ nanocomposite by means of the aluminothermic reduction. Synthesis in Al/B₂O₃/ZrO₂ system found to possess a self-sustaining nature having an ignition time of 13 min.

Examination of the sub-reactions revealed that boron oxide is easily reduced by Al, while Al cannot reduce ZrO_2 to Zr in a self-sustaining manner. It was concluded that the great deal of heat generated through the reduction of boron oxide by Al together with the large amount of heat released by the reaction between the reduced B and Zr, is capable of activating the reduction of ZrO_2 . This mechanism was found to be in good agreement with the general trend observed during thermal treatment of the system with an exception of formation of intermediate zirconium aluminides in the latter case. The amount of boron oxide was recognized to be a critical parameter which can alter the magnitude of reaction heat and consequently cause the system to undergo a transition from a gradual state to a self-sustaining one.

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