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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

M. Jalaly [a,*], M.Sh. Bafghi [a], M. Tamizifar [a], F.J. Gotor [b]

[a] School of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran 16846-13114, Iran
[b] Instituto de Ciencia de Materiales de Sevilla (CSIC-US), Americo Vespucio 49, 41092 Sevilla, Spain

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ABSTRACT

Herein, $ZrSiO_4/B_2O_3$/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 min of milling. The role of the stoichiometric amounts of B_2O_3 and carbon was investigated to clarify the governing mechanism for the formation of the product.

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 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

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[*] Corresponding author. Tel.: +98 9127387902; fax: +98 2177240480.
E-mail address: maisam_jalaly@iust.ac.ir (M. Jalaly).

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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 1 M-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:

$$\begin{aligned}&ZrSiO_4 + B_2O_3 + 7Mg + C \rightarrow ZrB_2 + SiC + 7MgO\\&\Delta G^{\circ}_{298} = -1270\ \text{kJ},\quad \Delta H^{\circ}_{298} = -1300\ \text{kJ},\quad T_{ad} \approx 2750\ \text{K}\end{aligned} \tag{1}$$

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 h, 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:

$$\begin{aligned}&3Mg + B_2O_3 \rightarrow 2B + 3MgO\\&\Delta G^{\circ}_{298} = -515\ \text{kJ},\quad \Delta H^{\circ}_{298} = -532\ \text{kJ},\quad T_{ad} \approx 2630\ \text{K}\end{aligned} \tag{2}$$

$$\begin{aligned}&4Mg + ZrSiO_4 + C \rightarrow Zr + Si + C + 4MgO\\&\Delta G^{\circ}_{298} = -363\ \text{kJ},\quad \Delta H^{\circ}_{298} = -377\ \text{kJ},\quad T_{ad} \approx 1575\ \text{K}\end{aligned} \tag{3}$$

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:

$$\begin{aligned}&ZrSiO_4 + yB_2O_3 + (3y+4)Mg + C\\&\rightarrow yZrB_2 + (3y+4)MgO + (1-y)Zr + Si + C \qquad 0 \leqslant y \leqslant 1\end{aligned} \tag{4}$$

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–C, rather than that of Zr-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. Fig. 1 shows the thermodynamic calculations for T_{ad} and ΔH°_{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 $y \geqslant 0.2$, 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 $0 \leqslant y < 0.2$, 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 $y \geqslant 0.3$, 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 $y \leqslant 0.8$ during the long-term milling experiments, although the Merzhanov criterion for