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Formation mechanism of ultra-high temperature nanocomposites by mechanically induced self-sustaining reactions

Bahman Nasiri-Tabrizi 1*, Reza Ebrahimite-Kahrizsangi 1, Wan Jefrey Basirun 2, Touraj Adhami 1

1 Advanced Materials Research Center, Materials Engineering Department, Najafabad Branch, Islamic Azad University, Najafabad, Iran

2 Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author. E-mail: bahman_nasiri@hotmail.com

Postal Address: Materials Engineering Department, Najafabad Branch, Islamic Azad University, Isfahan, Iran.

Abstract

The mechanically induced self-sustaining reactions (MSRs) in TiO2–B2O3–Mg–X (Al, C) quaternary system to synthesize various nanocomposite powders were investigated. Results showed that the phase compositions, structural features and morphological characteristics of the synthesized powders were notably influenced by the type and weight fraction of the reductants. Based on the morphological assessment, the mechanosynthesized nanocomposites had a unique flower-like cluster structure composed of loosely arranged nano-sheets with a side length of about 400 nm and a thickness of about 25 nm.

Keywords

Nanocomposites; MSR; Phase transformation; Flower-like structure; FE–STEM.
1. Introduction

Ultra-high temperature ceramics are a group of advanced materials that are chemically and physically stable at very high temperatures in extreme reactive environments [1]. Among them, titanium diboride (TiB$_2$) and titanium carbide (TiC) have become very important non-oxide ceramic materials as they possess several desirable properties. TiB$_2$ is a representative of refractory compounds with a very high melting point, high hardness, and extraordinary resistance to plastic deformation at high temperatures. In contrast, TiC deforms plastically over the temperature range of 1273–1773 K and it can be precipitation hardened by TiB$_2$ at high temperatures. Therefore, the combination of extreme resistance to plastic deformation, high melting point, precipitation hardening, and high-temperature plasticity suggests that TiB$_2$–TiC composite can be considered as a promising candidate for high temperature applications [2].

To date, self propagating high temperature synthesis (SHS) [3], mechanical alloying (MA) [4], combustion synthesis by direct reaction of elemental reagents [5], arc-plasma method [6], and magnesiothermic, aluminothermic, or carbothermic reduction of metal oxide–boron oxide mixture [7–9] were investigated to fabricate TiB$_2$- and TiC-based composites. Among them, MA process is used to produce any quantity of nanopowder with controlled microstructure because the melting and precisely controlled conditions are not essential and the products have nanostructural characteristics [10–16]. Depending on the processing conditions, the MA method falls into two categories: progressive reaction and MSR mode [2]. In the first type, the reaction may extend to a very small volume during each collision. This effect may lead to a gradual transformation. In the second approach, if the reaction enthalpy is sufficiently high, a self-propagating combustion reaction can be initiated after a certain time. In the MSR mode, the
 occurrence of the combustion reaction causes a rapid increase in temperature of the milling media, which provides the necessary conditions for a quick transformation. Although the various types of transition metal borides such as TiB$_2$ [4,7,17], ZrB$_2$ [18], HfB$_2$ [19], NbB$_2$ [20], MoB$_2$, Mo$_2$B$_5$ [21], and VB$_2$ [22] have been synthesized by MA method, the preparation of TiB$_2$- and TiC-based nanocomposites is still a much-discussed question.

According to our recent findings [23,24], the mechanochemical behavior of TiO$_2$–B$_2$O$_3$–Mg ternary system is strongly influenced by the reductant content and subsequent leaching process. In the present study, the formation mechanism of ultra-high temperature nanocomposites in TiO$_2$–B$_2$O$_3$–Mg–X (Al, C) quaternary system by MSRs was examined. FE–STEM technique for the first time was employed for high-resolution analysis of the microstructural features in this system.

2. Materials and methods

Boron oxide (B$_2$O$_3$, 99.95%), titanium dioxide (TiO$_2$, 99%), magnesium (Mg, > 97%), graphite (C, 99.5%), and aluminum (Al, 99.7%) (all from Merck without purification) were used as the raw materials. Details of the powder components and reductant content are summarized in Table 1. The MA process was carried out in a high-energy planetary ball mill using hardened chromium steel vials (vol. 125 ml) and balls (20 mm in diameter) under a high-purity argon atmosphere (99.99% purity). The weight ratio of ball-to-powder (BPR), total powder mass, and rotational speed were 15:1, 7 g and 600 rpm, respectively. X-ray powder diffraction (XRD, Philips X–ray diffractometer) using a Cu–K$_\alpha$ radiation over a 2$\theta$ angular range between 10° and 90° was employed to evaluate the phase purity and the crystallographic structural properties of the nanocomposites.
The crystallite size ($D$) and lattice strain ($\eta$) of the samples were calculated using the XRD data [10].

\[
B \cos \theta = \frac{0.9 \lambda}{D} + \eta \sin \theta \quad \text{(I)}
\]

where $\lambda$, $D$, $\eta$ and $\theta$ are the wavelength of the X–ray used (0.154056 nm), crystallite size, internal micro-strain and the Bragg angle (°), respectively. Note that $B$ in the above equation is the peak width (in radians) after subtracting the peak width due to instrumental broadening from the experimentally recorded profile. Therefore, when $B \cos \theta$ was plotted against $\sin \theta$, straight lines were obtained for the samples with the slope as $\eta$ and the intercept as $0.9 \lambda/D$.

The values of adiabatic temperature ($T_{\text{ad}}$) would be calculated using the following equation [25]:

\[
Q = (-\Delta H_{298}^\circ) = \int_{298}^{T_{\text{ad}}} \sum C_p (\text{Products})dT \quad \text{(II)}
\]

where $C_p$, $\Delta H_{298}^\circ$, and $Q$ are specific heat capacity, standard enthalpy changes of formation at 298 K, and heat of reaction, respectively.

The morphological features of the specimens were examined by a FESEM (CARL ZEISS-AURIGA 60) and FE–STEM (Hitachi S-4700). Energy Dispersive X-ray Spectrometry (EDS) and elemental mapping analysis attached to the SEM (Vega©Tescan, Brno, Czech Republic) were also utilized for semi-quantitative examination of the samples.

3. Results and discussion

Thermodynamic assessment. The reaction mechanism of the formation of the nanocomposites by MSR is shown in Fig. 1. Generally, the mechanism of the phase formation during the mechanosynthesis is not well understood. However, using some usual thermodynamic data can
help to know the basic information about reactions and to estimate their behavior during the process [26]. Here, the thermodynamic calculations were carried out based on three assumptions: (a) milling container vessel was sealed and isolated, (b) the activity of raw materials was equaled to 1 in accordance with their specifications (solid ingredients), (c) the reactions occurred in the standard condition (in the absence of gaseous components).

According to Fig. 1, it is obvious that the formation of TiB$_2$- and TiC-based nanocomposites by MSR in the above mentioned system was noticeably influenced by the type and weight fraction of the reductants. It seems that in the absence of Al and C (S1), mechanosynthesis includes two stages: first, reduction of B$_2$O$_3$ and TiO$_2$ with Mg, which causes the formation of Ti and B and second, the reaction of elemental Ti and B, which leads to the formation of TiB$_2$ (reactions (1) to (4)). In the presence of 10 wt% C (S2), TiO$_2$ and B$_2$O$_3$ are initially reduced to Ti and B by Mg, respectively. In the second step, the remaining B$_2$O$_3$ reacts with MgO, which causes the formation of Mg$_3$B$_2$O$_6$. Besides, TiC and TiB$_2$ can be formed due to the reaction of elemental Ti with C and B, respectively (reactions (5) to (10)). Considering the faster diffusion of carbon relative to boron, it is most likely that TiC is formed prior to TiB$_2$ during the milling process [27]. With increasing C content to 20 wt% (S3), TiB$_2$ disappears completely and the desired products would be TiC and Mg$_3$B$_2$O$_6$. In this case, the elemental Ti produced by magnesiothermic reaction reacts with C and consequently TiB$_2$ would be completely replaced with TiC (reactions (11) to (15)). On the other hand, in the presence of 30 wt% Al (S4), TiO$_2$ and B$_2$O$_3$ are reduced initially to Ti and B by aluminothermic and magnesiothermic reactions, respectively. In this step, the remaining TiO$_2$ is reduced by Mg. Subsequently, the reactions of elemental Ti and B as well as MgO with Al$_2$O$_3$ cause the formation of TiB$_2$ and MgAl$_2$O$_4$,
respectively (reactions (16) to (21)). With increasing Al content to 60 wt% (S5), similar to the previous sample (S4), TiB$_2$ and MgAl$_2$O$_4$ are the desired products (reactions (22) to (27)). These transformations are mainly related to the change in the standard Gibbs free energy, $\Delta G^\circ_{298}$, and the standard enthalpy of formation, $\Delta H^\circ_{298}$. According to $\Delta G^\circ_{298}$ values, the thermodynamic basis for the occurrence of all the reactions at room temperature is provided owing to the negative standard Gibbs free energy of reactions. Moreover, negative standard enthalpy of formation at 298 K indicates that all the reactions are exothermic.

Phase transitions and structural features. Fig. 2 shows the XRD patterns of the mechanosynthesized nanopowders. In the absence of Al and C (S1), the synthesized powder was composed of TiB$_2$ and MgO. In addition, several additional peaks corresponding to Mg$_2$TiO$_4$ were observed. The formation of Mg$_2$TiO$_4$ as an intermediate phase may be caused by the reaction between un-reacted TiO$_2$ and MgO [5]. It has also been reported that the appearance of Mg$_2$TiO$_4$ may be due to the higher temperature of reaction (> 2000 °C), which favors the decomposition of MgO to Mg. Consequently, the reaction between Mg and un-reacted TiO$_2$ may lead to the formation of Mg$_2$TiO$_4$ [28]. In the presence of 10 wt% C (S2), TiB$_2$, TiC, MgO, and Mg$_3$B$_2$O$_6$ were detected as a result of the mechanical activation. In the case of S3 (20 wt% C), TiB$_2$ was completely removed and the phase components were TiC, Mg$_3$B$_2$O$_6$, and MgO. On the other hand, with the addition of 30 wt% Al (S4), mechanochemical reaction led to the formation of MgFe$_{0.6}$Al$_{1.4}$O$_4$ spinel phase and TiB$_2$. When the Al content increased to 60 wt% (S5), similar to the previous sample (S4), TiB$_2$–MgFe$_{0.6}$Al$_{1.4}$O$_4$ composite was dominant. The manifestation of MgFe$_{0.6}$Al$_{1.4}$O$_4$ may be because of excessive wearing of the steel vials and balls. However, the phase fraction of TiB$_2$ and MgFe$_{0.6}$Al$_{1.4}$O$_4$ rose to 48 and 37 %, respectively, when the Al
content increased to 60 wt%. These findings are in good agreement with the thermodynamic assessment.

In general, a reaction can be a self-sustained combustion, when the adiabatic temperature of the reaction is higher than 1800 K [25]. From Fig. 3a, $T_{ad}$ values were 3282, 3162, 3012, 3235, and 3183 K in the case of S1, S2, S3, S4, and S5, respectively. According to the obtained data, the mode of the reaction in all the samples was MSR. As shown in Fig. 3b, combustion reaction time (CRT) increased from 34 to 62 min, when C value reached 20 wt%. An enhancement in CRT by decreasing the magnesium content (increasing the graphite and aluminium value) is probably related to a reduction of the exothermicity of the reactions. The crystallite size of the composite components is shown in Fig. 3c. Based on the obtained data, a substantial fluctuation was identified in the structural features of the milled powders, where the crystallite size and lattice strain of the composite components ranged from 20±1 to 77±4 nm and from 0.0006±0.00003 to 0.0054±0.0027, respectively.

**Morphological characteristics.** As shown in Fig. 4, the mechano-synthesized powders have a high tendency to agglomerate. However, when Al content reached 60 wt% a unique flower-like structure was formed. From FE–STEM images, it is obvious that the flower-like clusters were composed of loosely arranged nano-sheets with a side length of about 400 nm and a thickness of about 25 nm. It can also be seen that some nano-sheets become slightly curved, which may result from internal stress or other factors [29]. EDS spectrum showed that the main components of the product in terms of element were oxygen, boron, magnesium, and titanium. Boron could not be detected in EDS spectrum due to the strong absorption of the boron Kα line during the analysis. In addition, Fe contamination resulting from the excessive wearing of the steel vials and balls
was not detected due to the low relative Fe weight fraction in the milled specimen. In accordance with elemental mapping analysis, the nanocomposite powder showed an appropriate distribution of elements which confirmed the formation of a homogenous microstructure.

4. Conclusions

TiB$_2$- and TiC-based nanocomposites were successfully synthesized by MSRs in the TiO$_2$–B$_2$O$_3$–Mg–X (Al, C) quaternary system. The mechanochemical reactions in the above mentioned system included two stages: first, reduction of B$_2$O$_3$ and TiO$_2$ with Mg and Al, which caused the formation of Ti and B; and second, the reaction of elemental Ti with C and B, which led to the formation of TiC and TiB$_2$, respectively. According to the obtained data, the mode of the reaction in all the samples was MSR. Based on the FE–SEM and FE–STEM observations, a unique flower-like cluster structure with a side length of about 400 nm and a thickness of about 25 nm was formed in the presence of 60 wt% Al after 40 min of milling. The proposed synthesis strategy provides a facile pathway to obtain various nanocomposite powders that appeared to be potentially suitable for high temperature applications.

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References


Table 1 Details of powder components and reducing agents content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Powder components</th>
<th>Reducing agents content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>TiO$_2$–B$_2$O$_3$–Mg</td>
<td>100 wt% Mg</td>
</tr>
<tr>
<td>S2</td>
<td>TiO$_2$–B$_2$O$_3$–Mg–C</td>
<td>90 wt% Mg–10 wt% C</td>
</tr>
<tr>
<td>S3</td>
<td>TiO$_2$–B$_2$O$_3$–Mg–C</td>
<td>80 wt% Mg–20 wt% C</td>
</tr>
<tr>
<td>S4</td>
<td>TiO$_2$–B$_2$O$_3$–Mg–Al</td>
<td>70 wt% Mg–30 wt% Al</td>
</tr>
<tr>
<td>S5</td>
<td>TiO$_2$–B$_2$O$_3$–Mg–Al</td>
<td>40 wt% Mg–60 wt% Al</td>
</tr>
</tbody>
</table>
Fig. 1 Reaction mechanism of the formation of the nanocomposites by MSRs in TiO$_2$–B$_2$O$_3$–Mg–X (Al, C) quaternary system.
Fig. 2 XRD patterns of the mechanosynthesized nanopowders.
Fig. 3 (a) $T_{ad}$, (b) CRT, and (c) the crystallite size of the specimens as a function of reductant content.
Fig. 4 (a) FE–SEM (b,c) FE–STEM micrographs as well as (d) EDS analysis and elemental mapping images of S5.