

Investigation of Phase Evolution of TiC-TiB₂ Nanostructure Fabricated by MASHS

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In current research, nanostructure of titanium diboride/titanium carbide was fabricated by combustion synthesis of mechanically milled reactant powders. The stoichiometric mixture of Ti and B₄C as starting materials milled for 1, 3, 6 and 9 h. Milled powders pressed to form pellets. Green compacts were placed in a tube furnace preheated to 1100 °C in inert atmosphere (Ar). The samples were investigated by XRD and SEM analysis after different milling times and synthesis process. TiC and TiB₂ were not formed during milling process. Analysis of the synthesized samples showed TiC was the first formed phase followed by TiB₂, while other phases were not detected in the samples that were pre-milled for 6 and 9 h. Increasing of milling time helped significantly to improve distribution of TiB₂ in the products. The crystallite size of TiB₂ and TiC in the composite based on powder milled for 9 h was calculated to be 46.2 nm and 34.6 nm respectively.

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1. INTRODUCTION

The development of ceramic-matrix composites (CMCs) is increased in recent years because they can effectively combine the advantageous properties of individual components enhance the intrinsically low fracture resistance of monolithic ceramics [1,2]. When TiB₂ is combined with Al₂O₃, this composite has a better oxidation resistance and exhibits superior mechanical strength than the individual compounds [3].

Novel Si₃N₄-TiN-SiC composites were developed to facilitate the electrical discharge machining of the Si₃N₄-based ceramics [4,5]. TiC-TiB₂ composite has been shown to possess higher fracture toughness and better wear resistance than those of TiB₂ and TiC single-phases [1,6]. This composite has represented promising materials for use in forming dies and cutting tools and also has exhibited good behavior as high-temperature structural components in heat exchangers and engines [1]. Furthermore, in comparison to conventional cermets based on WC and TiC, cermets based on TiC-TiB₂ composites exhibit a higher hardness and chemical stability at high temperatures [7].

Consolidation of these materials into usable, dense and high-strength pieces is difficult because of the extremely high melting temperatures of TiB₂ and TiC, their high degree of covalent bonding and low self-diffusion coefficient of the constituent elements. The processing of these ultra-refractory composites into components with full density through traditional routes requires extremely high temperatures [8,9].

Dense TiC/TiB₂ ceramics have been fabricated by reactive hot pressing [12] and transient plastic phase processing [9,10], but they are costly for the time-intensive and facility-intensive nature of these processes. Many other methods, such as reactive sintering [11], spark plasma synthesis [12], and self-propagating high-temperature synthesis (SHS) -also termed combustion synthesis (CS) [13,14] have been developed for synthesis of such TiC-TiB₂ ceramic composites. When compared with conventional methods, combustion synthesis or self-propagating high-temperature synthesis (SHS), is a relatively novel and simple route for the synthesis of a variety of advanced materials, including borides, nitrides, aluminides, silicides, intermetallics, etc. [15-18].

The SHS process take advantage of the self sustaining merit from highly exothermic reactions and hence has the potential of time saving, low energy

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requirement, and yielding of high purity products [15-18].

It also represents an in situ processing technique for the preparation of composite materials with interpenetrating phase microstructures and improved properties [3,19]. Preparation of the TiC-TiB₂ composites has been investigated by using the SHS reaction [20-23]. Experimentally, a self-sustaining SHS reaction can be started either by igniting the sample at one end (combustion wave) or by uniformly heating the sample to the ignition temperature (thermal explosion, TE).

It has been demonstrated that, regardless of which SHS mode is utilized, the products of the reaction are identical and the maximum reaction temperatures are nearly the same [24].

Although TE is a much less-studied SHS process, it could be the controllable mode and more amenable for external pressure application than the combustion wave mode [25]. Kanetake and Kobashi [26] produced porous titanium matrix composites containing TiC and TiB₂ through combustion reaction of Ti with B₄C under different blending ratio of Ti/B₄C. On the other hand ball milling (BM) is a solid-state powder process involving welding and fracturing of powder particles in a high-energy ball mill [27]. BM has been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloys and components [27]. In addition, it has been found that BM may increase powder reactivity [28, 29]. Recently, with the aim of synthesizing dense nanostructured TiC/TiB₂ composites, the mechanical activation of elemental (Ti, C and B) reactants followed by the field-activated pressure-assisted synthesis (FAPAS) has been proposed [30].

In the present investigation, we suggest a new synthesis route for fabrication of TiC-TiB₂ ceramic composites based on the in situ formation of both phases. Reactants consisted of Ti and B₄C, that firstly were mechanically activated by high energy planetary mill and then synthesized by thermal explosion to achieve a composite microstructure.

1. 1. Theoretical Background TiC-TiB₂ composite can be synthesized by optimal chemical molar ratio between titanium and B₄C equal Ti:B₄C=3:1 through following reaction:



The reaction formation enthalpy, ΔH and Gibbs free energy, ΔG of reaction (1), have been calculated using the thermodynamic data from the Ref [31]. The ΔH and ΔG of the above reaction is equal to 680 (kJ/mol) and 668 (kJ/mol) respectively. It is also negative, which indicated that reaction is exothermic.

In the SHS process the maximum possible temperature during the exothermic reaction is attained

under the adiabatic condition without heat loss. The theoretical limit, designated as the adiabatic temperature T_{ad} , can be calculated from heat capacities and enthalpies of formation and transformation [32]. It has been empirically suggested that combustion reactions will not become self sustaining unless $T_{ad} \geq 1800$ K [33]. The adiabatic temperature of SHS reaction at room temperature was theoretically calculated using the thermodynamic data from the Ref. [31]. T_{ad} is calculated following equation:

$$-\Delta H_{f,T_0}^{\circ} = \int_{T_0}^{T_{ad}} \Delta Cp \, dT \quad (2)$$

According to Equation (2), the calculated T_{ad} for reaction (1) equals to 3230 K [34].

2. MATERIALS AND METHOD

In the present work, titanium (98% , 45 μm , Merck), B₄C (95% , 100 μm , Merck) powders were used as starting materials. The amount of the constituents in the mixtures were calculated according to stoichiometric ratio Ti: B₄C = 3: 1. The reactant powders were mixed and mechanical activation was performed in a Retsch PM 100 planetary ball mill unit. The milling process was conducted at 250 rpm, for 1, 3, 6 and 9 h using stainless steel balls and jars having an internal volume equal to about 150 cm³ and a ball-to-powder mass ratio equal to 15:1.

In order to minimize oxidation, all powder handling and loading were performed inside a glove box filled with argon. Then, the jars were sealed and transferred to the mill. The milled powder was then pressed in a steel die under a pressure equal to 250 MPa into pellets of 10 mm in diameter and 4-6 mm in height rendering a green density ranging between 55-65% TD. The pellets were put on an alumina boat and were placed into the tube furnace (resistance heating).

The furnace was preheated to 1100 °C. The experimentally observed ignition temperature (T_{ig}) of thermal explosion of the 3Ti+B₄C blend is almost 950 °C [11, 35, 36].

In work of Klinger et al. [25], each sample was placed between the preheated (700-1100 °C) rams. One can see that there is a critical furnace temperature, T_f , at which ignition of the TE of B₄C-Ti blend takes place, and that this temperature also depends on the type of starting powders used [25]. Flow of Argon was initiated from one end of the furnace, while ensuring a positive pressure of the gas at the other end. The set-up used in the present research was similar to that described in the work of Advani et al. [37].

The Argon gas was required to avoid nitridation and oxidation of the samples which was seen to occur at higher furnace temperatures. The samples were placed

in the hot zone of the furnace until they were synthesized.

After the synthesis process, the samples were firstly allowed to cool and then removed from the furnace. Phase identification and crystallite size determination of both milled powders and synthesized products were made by using XRD analysis (mod.PW1830, Philips Analytical B.V, the Netherland) with Cu K α radiation and Ni filter. The analysis of green powders and synthesized samples was performed in diffraction angle (2θ) range 0-80 $^\circ$ with scan step and scan time of 0.01 $^\circ$ and 10s, respectively.

Crystallite size was determined by means of Scherrer method. The microstructure of products was examined by scanning electron microscopy (SEM) (mod.XL30, Philips, the Netherland).

3. RESULTS AND DISCUSSION

Products had a fragile sponge-like structure and they could easily be ground in an agate mortar and pestle. In the powder form, they were subjected to XRD analysis. XRD patterns of mechanically milled Ti-B₄C mixtures are shown in Figure 1. The reflections observed in 14-21 $^\circ$ (2θ) range are due to the presence of some crystalline boron as an admixture in the boron carbide powder. These patterns shows neither the titanium diboride nor titanium carbide phase formed during the milling process. This result can be justified by considering the possibility of combustion during the milling which is examined by the ignition temperature of the mixture. The same criterion was used for the self-propagating high-temperature synthesis [38].

According to Takacs and Mc Henry, the ball temperature in a SPEX or planetary mill does not exceed 100 $^\circ\text{C}$ provided that no exothermic reaction takes place during milling [39]. If a reaction cannot occur in the SHS mode without pre-heating, it is also unlikely to initiate combustion in the mixture of reactants during milling [40]. Figure 2 shows the X-ray diffraction patterns of the samples with 1, 3, 6, 9 h milling times and also synthesized.

Almost in samples pattern with lower t_{BM} (milling time) such as 1, 3 h, there is little amount of TiC or TiB₂, and they are contained a few peaks of TiC, TiB₂ and transient compounds. It indicated that full conversion of the reactants into products had not occurred according to the chemical reaction (1). In the samples with higher than 3h milling time, conversion was completed and transient phases could not exist.

SEM images of the milled powders show that with increasing milling time, the agglomerates grew in size from 25 to 35 μm to 45-55 μm after 6 and 9 milling time respectively (Figure 3(a) and (b)).

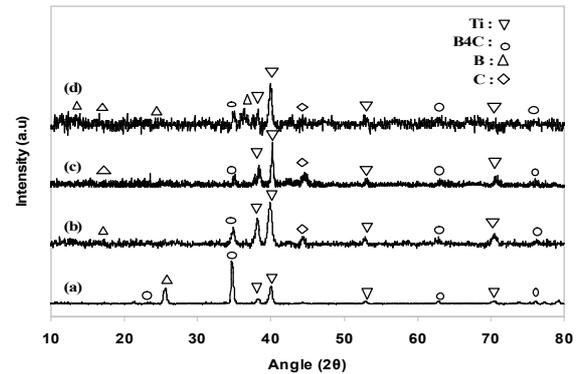


Figure 1. XRD patterns of the mixtures mechanically milled for: (a) 1 h, (b) 3 h, (c) 6 h, (d) 9 h

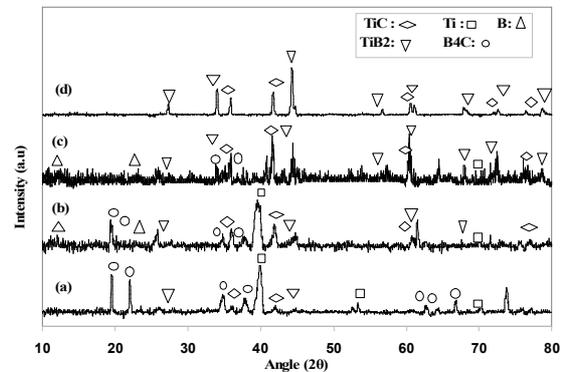


Figure 2. XRD patterns of the samples with, (a) 1 h, (b) 3 h, (c) 6 h, (d) 9 h and synthesized in 1100 $^\circ\text{C}$

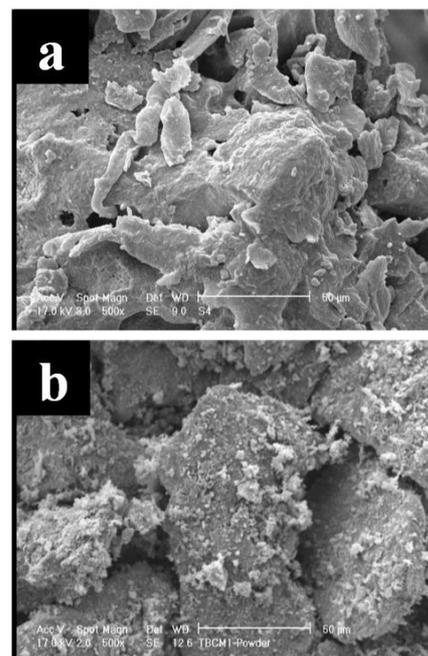


Figure 3. Microstructure of powder mixtures mechanically milled for: (a) 6 h and (b) 9 h.

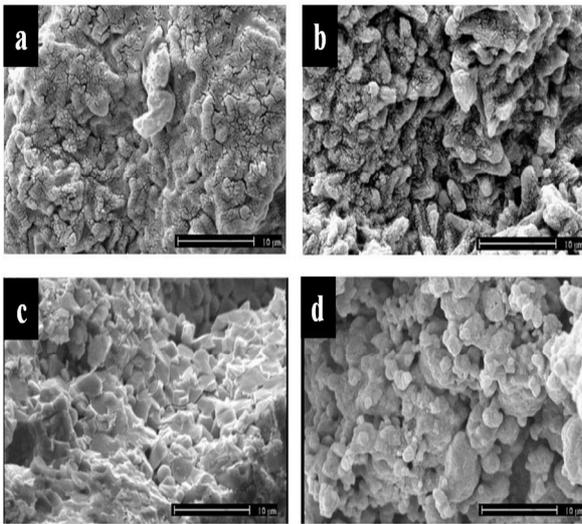


Figure 4. The scanning electron micrographs of products with 1, 3, 6 and 9 h co-milled powders.

Figure 4 shows the scanning electron micrographs of products with 1, 3, 6 and 9 h co-milled powders. The fine grains were bound to each other and were difficult to break. This could be due to coarsening of grains during SHS reaction propagation, which could have increased the hardness of these lumps. In (Figure 4b) the distribution of the TiC and TiB₂ is not uniform. The elongated grains are TiB₂, whereas the irregular or equiaxed grains are TiC.

The porosity existing in the microstructure is because some gas remained in the compacts during the reaction. During exothermic reactions, very high temperatures (>2150°C) were achieved within a fraction of a minute. Since the combustion temperature was much higher than the boiling point of transient compounds, evaporation of impurities was expected.

Almost all TiB₂ grains have clubbed structure because TiB₂ grains have enough space to grow amply between the TiC grains. The clubbed structure of TiB₂ is very useful to improve the fracture toughness of TiC-TiB₂ composites. The Scherrer method was used for calculation of average crystallite sizes (D). Scherrer formula (ignoring the defect or strain contribution)

$$D = \frac{0.9\lambda}{\beta_c(2\theta)\cos\theta} \quad (3)$$

where $\beta_c(2\theta)$ is the corrected broadening of the diffraction line measured at half of the maximum intensity for the peak that appeared at the Bragg angle 2θ and λ is the corresponding wavelength of the X-ray radiation. The crystallite sizes of TiB₂ and TiC in the composite formed from powders milled for 9 h and subsequent combustion synthesized matter were 46.2 nm and 34.6 nm, respectively.

4. CONCLUSIONS

The present study showed that the combination of high energy mechanical milling and self-propagating high-temperature combustion synthesis is a promising route for preparation of fine-grained and nanocrystalline composites in the TiC-TiB₂ system. Neither TiC nor TiB₂ was formed during milling, and other phases were not detected in the product which was mechanically activated for 9 h. TiC was the first phase to form, following by TiB₂. Increasing of the milling time t_{BM} helped significantly improve the distribution of TiB₂ in the synthesized composites. The crystallite sizes of TiB₂ and TiC in the composite based on milled powder for 9 h milling time and subsequent combustion synthesized product were 46.2 nm and 34.6 nm, respectively.

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در تحقیق حاضر، نانوساختار تیتانیوم دی بوراید - کاربید تیتانیوم از طریق سنتز احتراقی پودرهای واکنشی که آسیاب مکانیکی شده بودند، تولید شد. مخلوط استوکیومتریک شامل Ti و B₄C به عنوان مواد واکنشی به مدت ۱، ۳، ۶ و ۹ ساعت، آسیاب شد. مخلوطهای پودری آسیاب شده به شکل قرصهایی پرس شده و سپس درون یک کوره تیوبی با اتمسفر داخلی آرگون که تا دمای ۱۱۰۰ °C پیش گرم شده بود قرار گرفتند. نمونه‌ها بعد از زمانهای مختلف عملیات آسیاب و پس از فرآیند سنتز احتراقی، از طریق آنالیز XRD و SEM مطالعه شدند. این بررسی‌ها نشان داد که فازهای TiC و TiB₂ در طول فرآیند آسیاب تشکیل نشده‌اند. آنالیز نمونه‌های سنتزی نشان داد که در ابتدا فاز TiC در نمونه‌ها تشکیل می‌شود و در ادامه آن فاز TiB₂ به وجود می‌آید. در عین حال در نمونه‌هایی که به مدت ۶ و ۹ ساعت، پیش آسیاب شده بودند، هیچ‌گونه اثری از فازهایی غیر از TiC و TiB₂ مشاهده نشد. نتایج همچنین نشان داد که افزایش زمان آسیاب در توزیع بهینه فاز TiB₂ در محصول نهایی، تأثیر قابل ملاحظه‌ای دارد. اندازه بلورک فازهای TiC و TiB₂ در کامپوزیتی که از سنتز احتراقی مخلوطی با ۹ ساعت عملیات آسیاب شکل گرفته بود، به ترتیب ۳۴،۶ و ۴۶،۲ نانومتر محاسبه شد.

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