EFFECTS OF PROCESS CONTROL AGENT ADDITION IN PROCESSING OF NANO-CRYSTALLINE TiB_2 VIA SHS METHOD

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Nano-crystalline titanium diboride (TiB_2) was prepared by self-propagating high-temperature synthesis through putting a hot filament on top of the compact mixture of TiO_2 , H_3BO_3 and Mg with a stoichiometric ratio. Effects of the addition of various chloride salts e.g. NaClO_4 and NH_4Cl as process control agents on phase evolution and chemical analysis and the morphology of the products were investigated by XRD and SEM techniques, respectively. Analysis of the X-ray diffraction patterns confirmed the formation of TiB_2 together with some intermediate phases such as $\text{Mg}_3\text{B}_2\text{O}_6$ and Mg_2TiO_4 in as synthesized powder. MgO phase was detected as a major phase in the XRD patterns. Nano-crystalline TiB_2 became the major phase in some of the leached samples by HCl. The results also showed that the powder particle characteristics were influenced by the addition of the chloride salts.

Keywords: Titanium diboride (TiB_2), SHS, $\text{Mg}_3\text{B}_2\text{O}_6$, nano-crystalline, PCA.

1. Introduction

Titanium diboride (TiB_2) is a refractory ceramic which has excellent properties such as high melting point, high hardness, and good thermal and electrical conductivity, high wear resistance and considerable chemical stability. It is widely used as cutting tool

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composites, wear resistance parts, metal melting crucibles, electrode materials and cathodes for electro-chemical processing of aluminum (Hall-Heroult process).¹⁻⁴

TiB₂ can be synthesized by different methods such as carbothermic/borothermic reduction of mixed oxides of titanium oxide with boron carbide, solid state reduction of TiCl₄, Mg and MgB₂, ball milling and self-propagating high-temperature synthesis (SHS) followed by acid leaching technique.⁴⁻⁸ The SHS method is a form of controlled combustion synthesis which is a simple method for preparation of advanced ceramics and composites. It is based on systems able to react exothermally when ignited and to sustain them to form a combustion wave. The temperature of the combustion can be very high (as 5000 K) and the rate of wave propagation can be very rapid (as 25 cm/s), hence this process offers the opportunity to investigate reactions in conditions of extreme thermal gradients (as 105 K/cm).⁹ It has several advantages including low processing time and temperature, very low environmental impact, simple operation and generation of fine microstructures due to high cooling rates and finally, low costs and energy consumption.^{10, 11}

For controlling microstructure and homogeneity, different type and amount of SHS diluents can be added to the powder mixture. Khanara et al.¹⁰ and Chaichana et al.⁷ have reported the addition of NaCl for synthesis of nano-crystalline TiB₂ powders.

In this study, synthesis of nano-crystalline TiB₂ via SHS route has been investigated. The effects of addition of different kinds of diluents e.g. NaCl, KCl, NH₄Cl and NaClO₄-H₂O were also studied.

2. Experimental Procedure

TiO₂ (99%), H₃BO₃ (99%) and Mg (98.5%) powders were used to synthesize TiB₂. Stoichiometric amounts of reactants were mixed together according to Eq. (1). A mole of NaCl, KCl and NH₄Cl, and 0.02 mole of NaClO₄-H₂O (sodium perchlorate) were used separately to investigate the effects of process control agent (PCA) addition on the synthesis.

For conducting SHS reaction, a hot filament was placed on top of the compact mixture of TiO₂, H₃BO₃ and Mg with a stoichiometric ratio. All products were ground and washed by distilled water and air dried. Then the MgO was leached using 18% HCl solution under magnetic stirring for 20 min at 40°C and air dried.

The phase analysis of the samples was investigated by XRD using a philips PW-3710 diffractometer with Cu-K_α radiation. The average crystallite size of TiB₂ powders was calculated according to the Scherrer equation (Eq. (2)):^{12, 13}

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

Where D is the average crystallite size in nm, λ is the radiation wavelength (0.154056 nm for Cu-K α). $\beta(2\theta)$ is the breadth (commonly the full-widths at half maximum) of the pure diffraction profile and θ is the position of the analyzed peak maximum. The morphology of the particles was analyzed by scanning electron microscope (SEM) (CamScan MV2300).

3. Results and Discussion

Fig. 1-a shows the XRD pattern of the sample processed via SHS route without using any PCA. Analysis of the XRD pattern indicates coexistence of TiB₂, MgO, Mg₂TiO₄, and Mg₃B₂O₆ phases. In contrary to the results reported by Demircan et. al.¹⁴, traces of reactant powders were not detected. The intermediate Mg₂TiO₄ and Mg₃B₂O₆ phases were found may be due to the incomplete reaction of Mg, TiO₂ and Mg, H₃BO₃ respectively.⁷ Although, leaching was performed with 18% HCl in 40 °C for 20 min, but still there are undesirable phases indicating that MgO was not completely leached and so TiB₂ is observed as minor phase. Khanra et al.¹¹ reported complete elimination of MgO from the synthesized powder by boiling in dilute HCl.

Fig. 1-b shows the XRD pattern of the sample processed via SHS route using 0.02 mole NaClO₄-H₂O as a PCA. Because NaClO₄-H₂O acts as a promoter and increase the velocity of reaction, it was added less than other PCAs. Addition of NaClO₄-H₂O resulted in only slight diminishing of the MgO phase. Fig. 1-c indicates the XRD pattern of the sample synthesized in presence of 1 mole NaCl addition as a PCA. The peak intensities of Mg₂TiO₄ and Mg₃B₂O₆ phases were decreased to some extent. It seems that NaCl can enhance the reaction time of SHS and complete the reaction between reactants and formation of Ti and B elements. Diminution of Mg₂TiO₄ and Mg₃B₂O₆ phases resulted in increasing the magnitude of TiB₂ phase as a final product. Fig 1-d shows the XRD pattern of the sample prepared with addition of 1 mole NH₄Cl. The results indicate approximately elimination of Mg₂TiO₄ phase but the minimum amount of TiB₂ phase was obtained. The melting and boiling point of NH₄Cl is 338 and 520°C respectively, though only in this range it can operate as a diluent and cannot control the process. It seems that the addition of NH₄Cl encourages the formation of Mg₃B₂O₆ phase. Finally, Fig. 1-e shows the XRD pattern of the sample with addition of 1 mole KCl as a PCA. Analysis of the XRD pattern indicated TiB₂ as a major phase. The large difference between melting and boiling points of KCl (770 and 1420°C, respectively) may be responsible for increasing the magnitude of the TiB₂ phase. Addition of KCl can increase the time of reaction and decrease the velocity of wave propagating.

Fig 1. XRD patterns of the samples processed via SHS route (a) without PCA and with different PCAs (b) 0.02 mole NaClO₄-H₂O, (c) 1 mole NaCl, (d) 1 mole NH₄Cl, and (e) 1 mole KCl.

Table 1 shows the mean crystallite size of TiB₂ in the samples synthesized without and with PCA addition. As it is observed, the smallest mean crystallite size belongs to the sample produced in the presence of NaCl. The mean crystallite size of TiB₂ was reported to be 23 nm for the sample processed with addition of 1 mole NaCl.¹¹ It seems that NaCl was melted during SHS process at 801°C and further nucleation occurred in a molten zone which prevents grain and particle growth. Using NaClO₄-H₂O resulted in crystallite coarsening probably due to the exothermic nature of NaClO₄-H₂O which increases the heat of reaction.

Table 1. Mean crystallite sizes of the TiB₂ particles in samples with PCAs and without PCA, calculated by Scherrer formula

PCA	Amount (mol)	Mean crystallite size (nm)
-	-	36
NaClO ₄ -H ₂ O	0.02	43
NaCl	1	30
NH ₄ Cl	1	36
KCl	1	36

SEM micrograph of the sample processed via SHS route without using any PCA exhibits large irregular shape particles with mean particle size of 2 micron together with ultra-fine spherical particles with mean particle size of almost 200 nm (Fig. 2-a). Uniform nano-size particles of TiB_2 with mean particle size of 110 nm could be observed in the SEM micrograph of the sample prepared in the presence with of 0.02 mole $\text{NaClO}_4\text{-H}_2\text{O}$ in Fig. 2-b. It seems the MgO acts as cement, binding the hexagonal TiB_2 particles together to form a large agglomerates.¹⁵ So MgO and other intermediate phases could not leached completely. In the above sample, intensively exothermic nature of the reaction decreases the time of wave propagation, and as a result the particles have not opportunity to grow.

Fig 2. SEM micrographs of the samples processed via SHS route (a) without PCA and with different PCAs (b) 0.02 mole $\text{NaClO}_4\text{-H}_2\text{O}$, (c) 1 mole NaCl , (d) 1 mole NH_4Cl , and (e) 1 mole KCl .

Fig. 1-c indicates SEM micrograph of the sample synthesized with addition of 1 mole NaCl. Ultra-fine particles of TiB_2 were dispersed non-uniformly between some large particles; mean particle size is about 230 nm. As mentioned by Chaichana et al.⁷ the melted NaCl that remain in the system during the SHS reaction may play an important role by coating on the nucleated TiB_2 particles that could reduce their growth and finally decrease the particle sizes. Fig 1-d shows the SEM micrograph of the sample processed with addition of 1 mole NH_4Cl . Approximately uniform structure with agglomerated particles was observed. Amounts of TiB_2 phase is less than other samples and mean particle size of products is about 180 nm. Fig. 1-e shows the SEM micrograph of the sample with addition of 1 mole KCl as a diluent. Agglomerated hexagonal TiB_2 phase in presence of irregular shape substrate was observed. The mean particle size is about 200 nm.

4. Conclusions

The SHS process was carried out with a high exothermic reaction and there was not sufficient opportunity to complete phase transformation to TiB_2 . The mean crystallite and particle size of the sample without any PCA was 36 and 300 nm, respectively. It was determined that addition of PCA is an effective factor in synthesis of TiB_2 in SHS method.

The results show that in the presence of 1 mole NaCl, the mean crystallite size of TiB_2 particles was reduced to 30 nm, while addition of 0.02 mole $\text{NaClO}_4\text{-H}_2\text{O}$ increases the mean crystallite size to 43 nm. Addition of other PCAs affects the mean crystallite size. PCA addition can control the velocity of propagating wave during SHS. $\text{NaClO}_4\text{-H}_2\text{O}$ increases the velocity and other PCAs decrease the velocity of the reaction. Reduced velocity resulted in increased SHS time and helps the formation of TiB_2 phase. Although addition of $\text{NaClO}_4\text{-H}_2\text{O}$ resulted in higher mean crystallite size, but the smaller particle size was achieved (about 110 nm).

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References

1. C. Subramanian, T. S. R. Ch. Murthy, and A. K. Suri, *Int. J. Refract. Metals & Hard Mater.* **25**, 345 (2007).
2. A. Mukhopadhyay, G. B. Raju, B. Basu, and A. K. Suri, *J. Eur. Ceram. Soc.* **29**, 505 (2009).
3. R. Ricceri and P. Matteazzi, *Mater. Sci & Eng.* **A379**, 341 (2004).
4. E. Bilgi, H. E. Camurlu, B. Akgun, Y. Topkaya, and N. Sevinc, *Mater. Res. Bull.* **43**, 873 (2008).
5. T. Saito, T. Fukuda, H. Maeda, K. Kusakabe, and S. Morooka, *J. Mater. Sci.* **32**, 3933 (1997).
6. S. H. Kang and D. J. Kim, *J. Eur. Ceram. Soc.* **27**, 715 (2007).

7. N. Chaichana, N. Memongkol, J. Wannasin, and S. Niyomwas, *CMU. J. Nat. Sci. Special Issue on Nanotech.* **7**, 51 (2008).
8. J. Y. Lok, K. V. Logan, and J. J. Payyapilly, *J. Am. Ceram. Soc.* **92**, 26 (2009).
9. P. Mossino, *Ceram. Int.* **30**, 311 (2004).
10. A. K. Khanra, L. C. Pathak, and M. M. Godkhindi, *J. Mat. Proc. Tech.* **202**, 386 (2008).
11. A. K. Khanra, L. C. Pathak, S. K. Mishra, and M. M. Godkhindi, *J. Mat. Let.* **58**, 733 (2004).
12. B. D. Cullity, S.R. Stock, *Elements of X-ray Diffraction*, Third Ed., (Prentice Hall, Upper Saddle River, NJ, 2001).
13. R. A. Varin, J. Bystrzycki, and A. Calka, *Intermetallics*, **7**, 785 (1999).
14. U. Demircan, B. Derin and O. Yucel, *Mater. Res. Bull.* **42**, 312 (2007).
15. J. Y. Lok, MSc Thesis, Virginia Polytechnic Institute and State University, Virginia, 2006.