Journal of Alloys and Compounds 502 (2010) 491–494

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

SHS/PHIP of ceramic composites using ilmenite concentrate

M. Kholghy[a], S. Kharatyan[b], H. Edris[c,*]

[a] Yerevan State University and Isfahan University of Technology, Dept. of Materials Eng, Iran
[b] Yerevan State University, Yerevan, A. Manukyan str. 1, AM-0025, Armenia
[c] Isfahan University of Technology, Dept. of Materials Eng. Isfahan, 8415683111, Iran

ARTICLE INFO

Article history:
Received 21 November 2009
Received in revised form 24 April 2010
Accepted 28 April 2010
Available online 5 May 2010

Keywords:
Combustion synthesis
Tough ceramic
TiB_2
TiC
SHS/PHIP

ABSTRACT

Self-propagating high-temperature synthesis (SHS) process in the mixture of ilmenite, boron carbide and aluminum combined with a pseudo hot isostatic pressing (PHIP) is used in this research to produce a compact multi-ceramic composite $Al_2O_3/TiB_2/TiC$ with Fe as a binder. Several tests were performed to identify the optimum partial weight percent of the ilmenite, boron carbide and aluminum to produce a suitable amount of each components of the product. On the other hand, a number of tests were performed to measure the delay time, optimum compaction time and optimum compaction force to produce a compact high toughness samples. The results of phase analysis using XRD tests and microstructure using SEM and EDS show that the product is a multi-ceramic composite of the $Al_2O_3/TiB_2/TiC$ with Fe as a binder. It was shown that there are no primary reactants in the product. In this work, the combustion characteristics (combustion wave propagation velocity and temperature) of the process, as well as density and hardness of the combustion product were measured. The fracture toughness of the product was measured using Vickers indenter and Brazilian test. This shows that the samples have a high toughness in comparison to conventional ceramics.

1. Introduction

A composite ceramic containing TiC, TiB_2 and Al_2O_3 is expected to have special properties including high wear resistance, a good strength and toughness, high melting point, high thermal shock resistance and low density. Considering these properties, this ceramic can be used as a cutting tool, a drawing die, ceramic ball bearing and light-weight military ceramic, and also as a wear resistance part [1,2]. Producing ceramics like Al_2O_3, TiB_2 and TiC using hot isostatic pressing (HIP) technique and/or conventional sintering or hot pressing is costly because of the facility intensive and time intensive nature of these processes [3]. It should be mentioned that the application of the combination of these materials is limited to a specific application because of the low fracture toughness (K_{IC}). One of the effective methods to increase fracture toughness is creating a matrix binder from a tough material [4].

Ilmenite concentrate ($FeTiO_3$) has the potential to be used as the main raw material in producing a multi-ceramic composite with high hardness and high fracture toughness as well as a lower cost. It may be assumed that Ti contained in the ilmenite can be converted into TiB_2 and TiC and the oxygen content of the ilmenite can be used to produce Al_2O_3. On the other hand, Fe contained in the ilmenite can be reduced to metallic Fe as a suitable binder that can increase fracture toughness [5].

In this research, ilmenite concentrate (from Kahnoj mine in Iran), B_4C and Al were used as raw materials.

For ilmenite processing and obtaining multi-ceramic composite, we used the self-propagation high-temperature synthesis (SHS) method combined with pseudo hot isostatic pressing (PHIP). SHS means the synthesis of compounds in a wave of chemical reaction that propagates over starting reactive mixture owing to layer by layer heat transfer. It is well known that many inorganic refractory materials can be obtained using the SHS or combustion synthesis (CS) method, which is one of the most economical synthesis methods of materials [6–9]. The self-sustaining character of the process allows avoiding the prolonged high-temperature treatment usually required in conventional preparation methods of materials.

The synthesized products are often porous, but they can be easily densified via the application of a mechanical load just after the end of the reaction while the products are hot. Particularly, SHS was used effectively for synthesizing TiC, TiB_2 and a number of composites on their basis [10–14].

SHS/PHIP methods have advantages of lower energy usage, reduced production time, high purity product, and the usage of a plain process and instruments [1,3].

* Corresponding author. Tel.: +98 311 3915709; fax: +98 311 3912752.
E-mail address: h-edris@cc.iut.ac.ir (H. Edris).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.04.204

Table 1
XRF chemical analysis of ilmenite.

Compound	wt%
Al_2O_3	1.38
MgO	0.37
CaO	2.16
Fe_2O_3	47.64
TiO_2	42.59
SiO_2	5.61
Na_2O	0.02
K_2O	0.04
SO_3	<0.05

The main reaction of the process followed by thermodynamic calculation using ISMAN-THERMO software [15] is as follows:

$$3FeTiO_3 + B_4C + 6Al = 3Al_2O_3 + 2TiB_2 + TiC + 3Fe$$

$$P = 1\text{–}10\,\text{atm} \qquad T_{ad} = 2500\,\text{K}$$

Considering the above reaction and the densities of products, the volume percentage of the products is calculated as: 54.3% Al_2O_3, 21.9% TiB_2, 8.7% TiC and 15.1% Fe.

2. Experimental procedure

In the experiments, we used the following raw materials: (1) ilmenite powder, the chemical composition of ilmenite powder was analyzed using XRF system (containing 81% ilmenite, Table 1) and the particle size was less than 20 μm, which was measured by using sieves. (2) B_4C powder from REACHIM (120824) Russia, with 98% purity and particle size less than 10 μm, (3) Al powder with 98% purity and nearly 20 μm particle size.

Considering the above reaction and the purity of ilmenite, the calculated amount of powders are prepared and dried for 20 h in an oven at 80 ± 5 °C. The dried powder was put in a ball mill of the 200 mm diameter, 150 mm length, ratio of ball to powder of 25 and ball diameter of 5–15 mm with 60 rpm, and was milled for 7 h. This conditions suggested by the Russian Metall Co.[1] which is the producer of SHS/PHIP system. The milled powder was used to make a disc of 60 gm weight, 50 mm in diameter and 14 mm height using a hydraulic press with the pressure of 5 MPa. This amount of pressure achieved through several tests, was found to produce carryable samples without cracks.

The discs are transferred to a SHS/PHIP system as shown in Fig. 1. SHS/PHIP system was designed to eliminate dust and gases produced in the reaction period through the quartz sand around the disc sample. The sand in the compaction period has the role of transferring force as a pseudo isostatic pressure system.

Several samples were produced by changing pressure, delay time and compaction time. The optimum conditions were chosen in order to produce a sample through a complete combustion reaction and without cracks and defects. Finally, the optimum conditions of pressure of 90 MPa, delay time of 15 s and pressing time of 10 s were achieved. Several samples were produced by these optimum conditions to confirm the repeatability of the method.

To decrease internal stresses after SHS, after compaction the samples were transferred to a furnace with 1000 °C temperature and were cooled with the cooling rate of 2 °C/min.

To measure the combustion wave propagation rate a photocell was installed on the other side of the sample in front of the combustion source (Fig. 1). By measuring the distance between the combustion source and photocell and measuring the length of the time between starting combustion and detection of light by the photocell, the rate of combustion wave propagation was calculated. To measure the combustion temperature a thermocouple of W-Re(20)/W-Re(5) was used. This thermocouple was placed in a way that when the sample was pressed the thermocouple was pushed 4 mm deep in the sintered materials and the precise reaction temperature was measured. All of these adjustments were controlled by an automatic PLC system.

Preparing ceramic samples for a single edge notched beam (SENB) test to determine fracture toughness is very complicated, therefore, the Brazilian test was used [16]. The product samples were prepared for the Brazilian test according to Yu et

[1] Moscow Steel and Alloys Institute, Metall.

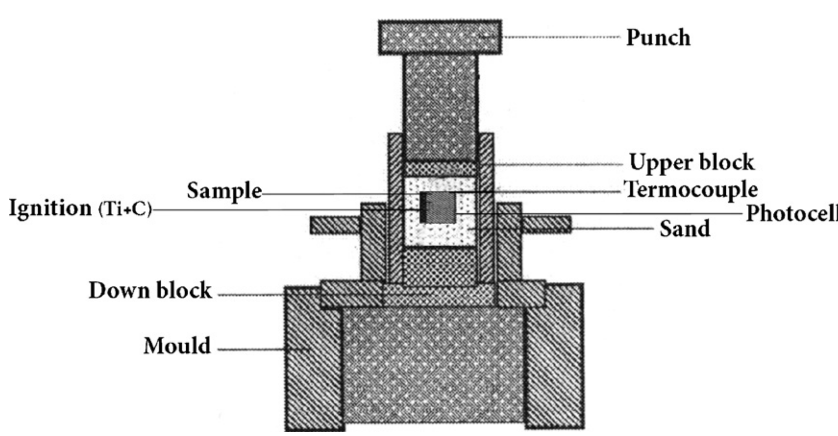

Fig. 1. Schematic of the SHS/PHIP experimental system.

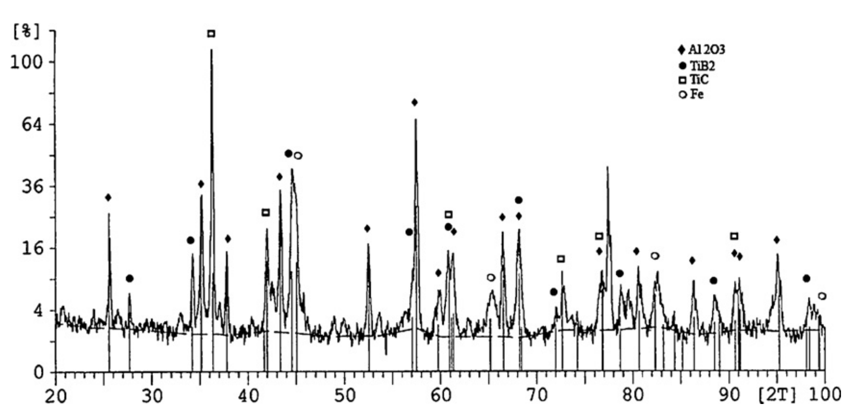

Fig. 2. XRD pattern of the different synthesized products.

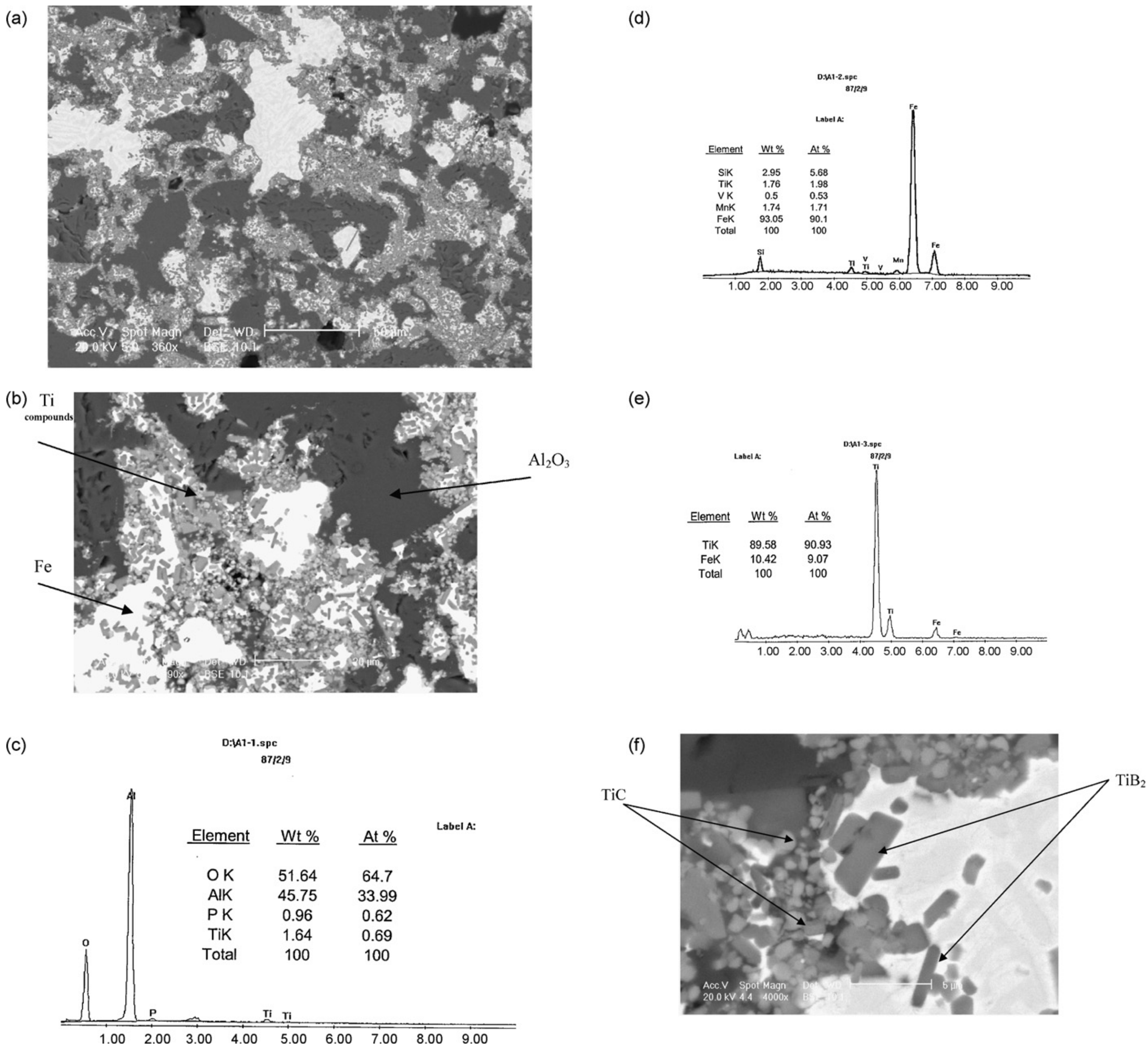

Fig. 3. (a) SEM micrograph of synthesized product, general view. (b) Detailed SEM micrograph of Al_2O_3, Fe and Ti compounds. (c) EDS analysis of Al_2O_3 phase. (d) EDS analysis of Fe area. (e) EDS analysis of Ti compounds. (f) SEM micrograph of the elongated shape phase (TiB_2) and equiaxial/irregular shaped phase (TiC).

al. [17] work in a cylindrical specimen of 20 mm diameter and 8 mm height. The loading speed rate was 500 mm/min.

3. Results and discussion

3.1. Phase constituents of combustion synthesized products

As shown in Fig. 2, which is an X-ray diffraction pattern of the sintered sample, there are clearly three phases of Al_2O_3, TiB_2 and TiC and there is no peak related to the primarily used raw materials. This confirms that the total amount of the primary materials reacted with each other and converted in to the products. The purity of the used ilmenite concentrate was 81%. Therefore, to compensate for the lower amount of ilmenite in the stoichiometric reaction, a certain amount of ilmenite was added. Primary tests that were performed without adding a certain amount of concentrate show Fe_3C instead of Fe in the products. Furthermore, there was no TiC in the products. This may be because of the low amount of Ti in the reactants.

3.2. Microstructure of combustion synthesized composite $Al_2O_3 + TiB_2 + TiC + Fe$

Study of the microstructure of the product was performed, using SEM and EDS installed on SEM. The whole area and distribution of phases are shown in Fig. 3a which confirms the presence of different phases. The results of a more detailed study are shown in Fig. 3b. As can be seen in Fig. 3c–e the dark areas are Al_2O_3, the light areas are Fe and the gray areas are Ti compounds. Fig. 3f shows the presence of Ti compounds including its elongated shape phase and nearly equiaxed phase. By comparing the images to the results presented in references such as [1] and [5], it can be clearly identified that the grey elongated grains are TiB_2 where as grey equiaxed or irregular shaped grains are TiC.

An image analysis using Image Tool [18] computer program was performed on the microstructural images of the samples. The results of the image analysis method in volume percentage show 18% Fe, 44% Al_2O_3 and the remaining 38% included carbide and

Table 2
Summary of tensile strength and fracture toughness results.

Material	Tensile strength (MPa)	K_{IC} (MPa m$^{1/2}$)
Product	20.5	3
Pure alumina	15	2.2
B_4C	23.3	3.5

boride. The reason for the differences between image analysis results and predicted amounts, which were given in Section 1, can be explained by the presence of impurities in ilmenite. According to Table 1, the ilmenite impurities are mostly iron oxide and silica.

3.3. Density, hardness and fracture toughness

The density of the SHS/PHIP product after cutting and grinding was measured based on ASTM CGO7 standard and the density was 3.93 gm/cm^3. The apparent porosity was measured equal to 7.3% and the density of the product was 92.7% of the theoretical density according to ASTM CGO7 standard.

The samples hardness was measured by the Vickers hardness method with different forces of 0.5–60 kg and the average result was 1500 HV.

It should be mentioned that we tried to measure the fracture toughness of the samples using the Vickers indentation fracture toughness test [19], but there was no detectable crack produced using different forces in Vickers test. The average of the Brazilian tests results (tensile strength) for the products was 20.5 MPa. The fracture toughness (K_{IC}) of the samples was calculated to be 3.0 MPa m$^{1/2}$ according to Zhang [20]. To compare the fracture toughness of the samples with similar material the same tests was performed for pure alumina and B_4C (typical armor component). The results are shown in Table 2. It can be concluded that the samples have suitable fracture toughness in comparison to pure alumina and B_4C.

3.4. Combustion characteristics

The average combustion temperature of three measurements was 2000 °C and the average of combustion wave propagation velocity was measured to be equal to 1 cm/s.

4. Conclusion

Combustion process using ilmenite concentrate as a precursor combined with the SHS/PHIP method caused the production of a multi-ceramic composite of Al_2O_3/TiB_2/TiC with Fe binder. The combustion wave propagation velocity was measured to be equal to 1 cm/s and the combustion temperature was 2000 °C.

The very high hardness and high fracture toughness of the samples are outstanding properties of the composite. This composite can be used as high wear resistant tools that need high fracture toughness.

On the other hand, this composite has a low density, which makes it suitable for applications such as light ceramic armors.

References

[1] Z. Xinghong, Z. Chuncheng, Q. Wei, H. Xiaodong, V.L. Kvanin, Compos. Sci. Technol. 62 (2002) 2037–2041.
[2] A. Alizadeh, E. Taheri-Nassaj, N. Ehsani, J. Eur. Ceram. Soc. 24 (2004) 3227–3234.
[3] I. Song, L. Wang, M. Wixom, L.T. Thompson, J. Mater. Sci. 35 (2000) 2611–2617.
[4] S.B. Li, B.S. Zhang, G.W. Wen, J.X. Xie, Mater. Lett. 57 (2003) 1445–1452.
[5] Z. Zou, J. Li, Y. Wu, Key Eng. Mater. 280–283 (II) (2005) 1103–1106.
[6] A.G. Merzhanov, in: Z.A. Munir, J.B. Holt. (Eds.), Combustion and Plasma Synthesis of High-Temperature Materials, VCH Publishing Inc., New York, 1990.
[7] Z.A. Munir, U. Anselmi-Tamburini, Mater. Sci. Rep. 69 (7–8) (1989) 277–365.
[8] Y. Miyamoto, J. Miner. Soc. Japan 18 (6) (1988) 383–391.
[9] H.C. Yi, J.J. Moore, J. Mater. Sci. 25 (1990) 1159–1165.
[10] I.P. Borovinskaya, V.A. Bunin, G.A. Vishnyakova, A.V. Karpov, Int. J. SHS 8 (4) (1999) 441–451.
[11] J.B. Holt, D.D. Kingman, G.M. Bianchini, Mater. Sci. Eng. 7 (1985) 321–327.
[12] H.Y. Wang, Q.C. Jiang, Y.Q. Zhao, F. Zhao, B.X. Ma, Y. Wang, Mater. Sci. Eng. A 372 (1–2) (2004) 109–114.
[13] S.L. Kharatyan, Kh.V. Manukyan, H.H. Nersisyan, H.L. Khachatryan, Int. J. SHS 12 (1) (2003) 9–34.
[14] A.A. Hambartsumyan, H.L. Khachatryan, A.B. Harutyunyan, S.L. Kharatyan, Mater. Res. Bull. 42 (2007) 2082–2089.
[15] ISMAN-THERMO software.
[16] J. Rodriguex, C. Navarro, V. Sanchez-Galvez, J. de Phys. IV 4 (1994) 101–106.
[17] Y. Yu, J. Yin, Z. Zhong, Int. J. Rock Mech. Mining Sci. 43 (2006) 623–627.
[18] UTHSCSA Image Tool, version 3.0, 2002.
[19] C.B. Ponton, R.D. Rawlings, Mater. Sci. Technol. 5 (1989) 865–872.
[20] Z.X. Zhang, Int. J. Rock Mech. Mining Sci. 39 (3) (2002) 401–406.