Songklanakarin J. Sci. Technol.
30 (2), 239-242, Mar. - Apr. 2008

Songklanakarin Journal of Science and Technology
http://www.sjst.psu.ac.th

Original Article

Production of titanium carbide from ilmenite

Kanokon Nuilek[1], Napisporn Memongkol[2], and Sutham Niyomwas[3]*

[1]*Department of Mining and Materials Engineering,*

[2]*Department of Industrial Engineering,*

[3]*Department of Mechanical Engineering, Faculty of Engineering,*
Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.

Received 28 September 2007; Accepted 8 May 2008

Abstract

The production of titanium carbide (TiC) powders from ilmenite ore ($FeTiO_3$) powder by means of carbothermal reduction synthesis coupled with hydrochloric acid (HCl) leaching process was investigated. A mixture of $FeTiO_3$ and carbon powders was reacted at 1500°C for 1 hr under flowing argon gas. Subsequently, synthesized product of Fe-TiC powders were leached by 10% HCl solutions for 24 hrs to get final product of TiC powders. The powders were characterized using X-ray diffraction, scanning electron and transmission electron microscopy. The product particles were agglomerated in the stage after the leaching process, and the size of this agglomerate was 12.8 μm with a crystallite size of 28.8 nm..

Keywords: titanium carbide, ilmenite, carbothermal reduction synthesis, leaching, Gibbs energy

1. Introduction

Ilmenite, with the chemical formula $FeTiO_3$, is an economically important and interesting mineral. It is an opaque mineral, black to brownish-red, with a metallic or submetallic luster, and belongs to the Hematite-Ilmenite-Magnetite Group in the Oxide and Hydroxide Class. Ilmenite is currently mined in Australia, Brazil, Russia, Canada, Sri Lanka, Norway, China, South Africa, Thailand, India, Malaysia, Sierra Leone, and the United States. In Thailand, it was found in tin ore (cassiterite) deposits in Chiangrai, Chiangmai, Lamphun, Kanchanaburi, Ratchaburi, Suphun Buri, Phuket, Phanga, and Ranong. Ilmenite is the chief source of titanium dioxide, TiO_2, which is used in paint pigments, welding-rod coating, and in the manufacture of the metal titanium (Wattanachit, 2004).

Titanium carbide (TiC) attracted great interest for many structural applications due to its extremely high melting temperature, high hardness, high chemical resistance, and good electrical conductivity. Therefore, titanium carbide can be used in cutting tools, grinding wheels, wear-resistant coatings, high-temperature heat exchangers, magnetic recording heads, turbine engine seals, and bulletproof vests, etc. In addition, a promising field of application comprises plasma and flame spraying processes in air, where titanium carbide-based powders show higher-phase stability than tungsten carbide-based powders (Ling and Dutta, 2001).

TiC can be synthesized by direct reaction between Ti and carbon under vacuum at high temperature of 1900°C - 2900°C (LaSalvia *et al*., 1995). This method is expensive because of the high cost of elemental Ti and energy intensive process. TiC is commercially produced by the carbothermal reduction of TiO_2 using carbon black through the following reaction (Swift and Koc, 1999; Das *et al*., 2002; Woo *et al*., 2007):

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g) \quad (1)$$

As ilmenite is a chief source of TiO_2, it would be more

*Corresponding author.
Email address: sutham.n@psu.ac.th

economical to use ilmenite as a precursor for TiC production. However, the involved leaching process of leaching out FeO from $FeTiO_3$ appears to be more difficult than that of leaching out Fe from TiC (Sarker *et al*., 2006). Many research groups have proved that Fe-TiC can be synthesized in-situ by carbothermal reduction of ilmenite (Welham, 1996; Das *et al*.,2002; Niyomwas, 2005; Niyomwas, 2006; Nuilek *et al*., 2006).

In the present study, the production of TiC powders from $FeTiO_3$ powder by carbothermal reduction synthesis coupled with leaching process was investigated. 4

2. Experimental

2.1 Raw materials and experimental setup

Ilmenite powder (mean particle size of 145.6 μm) and activated carbon powder (Ajax Finechem) were used as precursors. Scanning electron microscope (SEM) micrographs of these precursors are presented in Figure 1.

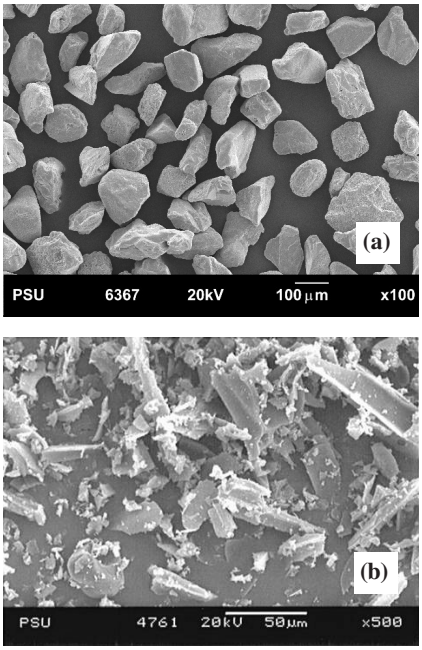

Figure 1. SEM micrographs of precursors: (a) ilmenite (b) activated carbon.

The experimental setup is shown in the Figure 2. A tube furnace (Carbolite, CTF 18/75/600) with maximum working temperature of 1800°C was used in the experiments. The *in-situ* reaction was performed in an alumina crucible, located in a furnace tube, with one end connected to an Ar gas supply system, and another end partially open. Before heating, the furnace tube was evacuated and flushed with pure Ar gas for 2-3 times to remove O_2 and moisture. Then, the pure Ar gas introduced at a constant flow rate (3 Lpm) to the furnace throughout the experimental process to maintain an inert atmosphere. An opening in the end cover of the

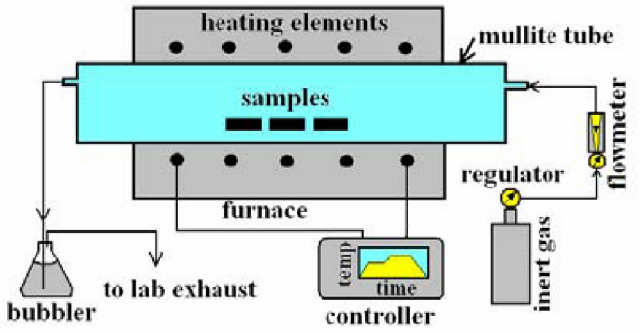

Figure 2. The schematic of experimental setup.

furnace serves as the exit for the gas. However, the gas in the outside environment cannot enter the system due to the small pressure difference maintained by the flowing Ar gas.

2.2 Experimental procedure

A mixture of raw materials was prepared in accordance with the stoichiometry ratio (ilmenite to carbon mole ratio = 1/4). Each mixture was milled with a planetary mill for 2 hr at 250 rpm. After milling, the samples were heated at 10°C/min to 1500°C in alumina crucible under flowing argon gas (3 Lpm) gas. After soaking at the final temperature for 1 hr, the furnace was turned off, allowing the products to cool down in the furnace. Leaching was performed at room temperature for 24 hrs in 10% HCl solutions. The powders as the resulted products were analyzed by X-ray diffraction (XRD, PHILIPS with Cu Kα radiation), SEM (JSM-5800 LV, JEOL) and transmission electron microscope (TEM, JEM-2010,JEOL).

3. Results and Discussion

3.1 Thermodynamic analysis

The overall chemical reaction can be expressed as:

$$FeTiO_3(s) + 4C(s) = Fe(s) + TiC(s) + 3CO(g) \qquad (2)$$

The equilibrium compositions of the $FeTiO_3$-C system at different temperatures were calculated using Gibbs energy minimization method and the results are shown in Figure 3. It can be seen that it is thermodynamically feasible to fabricate an iron matrix composite reinforced with TiC using the carbothermal reduction process. With increasing temperature, ilmenite dissociates to FeO and TiO_2. FeO is reduced to Fe by carbon and remains as an iron phase throughout the temperature increase to 2000°C. (Niyomwas, 2005; Niyomwas, 2006; Nuilek *et al*., 2006). On the Differential Thermal Analysis (DTA) graph in Figure 4, two endothermic peaks were observed (maxima at 1091.73°C and 1258.1°C, respectively). The first and the second endothermic peaks are thought to arise from carbothermic reactions mentioned

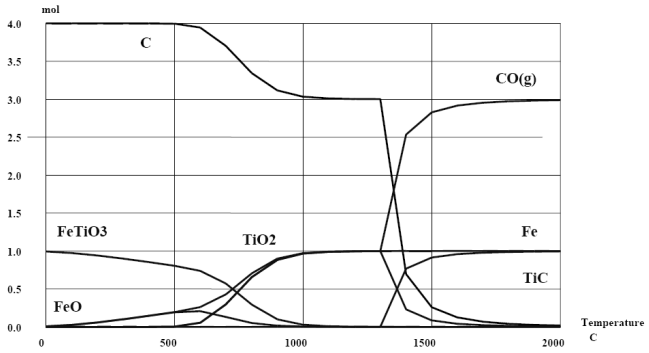

Figure 3. Gibbs energy minimization plots of $FeTiO_3$-C system in an argon atmosphere.

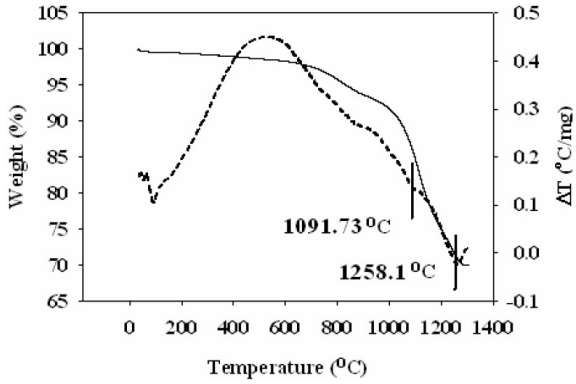

Figure 4. Thermogravimetric Analysis (solid line) and Differential thermal analysis (dashed line) thermogram for the $FeTiO_3$-C system.

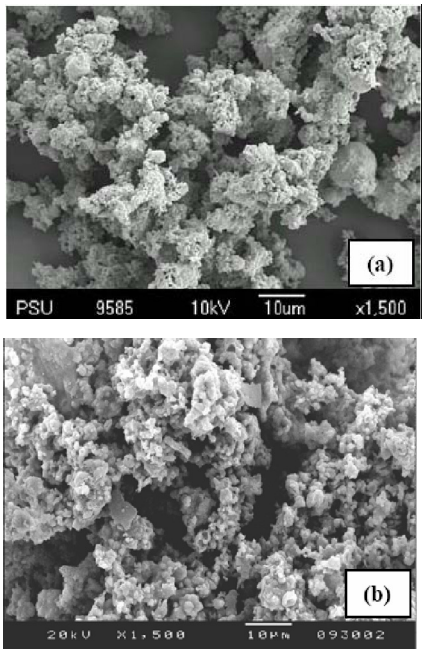

Figure 5. SEM images of (a) Fe-TiC and (b) TiC.

earlier (Niyomwas, 2006; Jing and Yisan, 2007), which were confirmed by a weight decrease in the Thermogravimetric Analysis (TGA) graph shown in Figure 4.

3.2 Characterization of synthesized products

The morphology of the products obtained from SEM micrographs in Figure 5 shows good inter-particle cohesion within agglomerated particles of both Fe-TiC (before leaching) and TiC (after leaching) as identified by XRD patterns presented in Figure 6. Figure 7 shows the steps of the fabrication process for TiC powder, where the agglomeration caused by the high reaction temperature can be further processed to a smaller size.

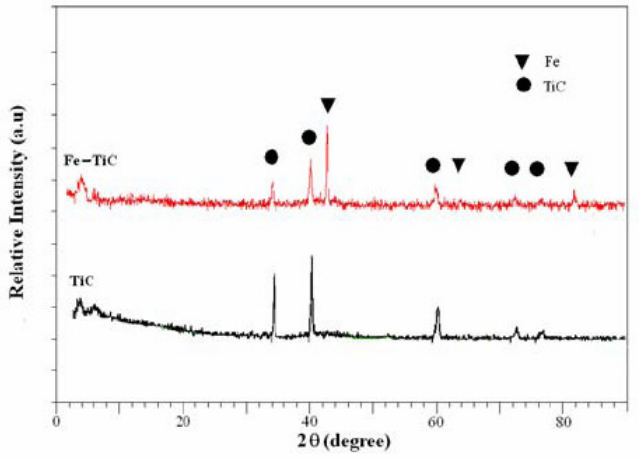

Figure 6. XRD patterns of Fe-TiC composite (as synthesized) and TiC ceramics (as leached).

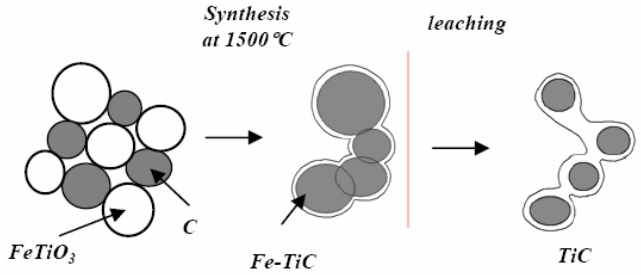

Figure7. Steps of the fabrication process.

The particle size of TiC was then analyzed by laser particle size analysis (LPSA, Coulter LS230), showed a mean particle size of 12.8 µm. The crystallite size of resulted product was 28.8 nm, which was calculated from the full-width at the half-maximum of the (200)-peak of the TiC, according to the Scherrer Equation (Cullity, 1978). The product particles show agglomeration of small crystals to forms bigger balls, which are then inter-connected with other ball to form the irregular shape of the product particles. This suggestion was confirmed by TEM analysis, with an image shown in Figure 8.

4. Conclusions

TiC powders were produced from leaching out Fe

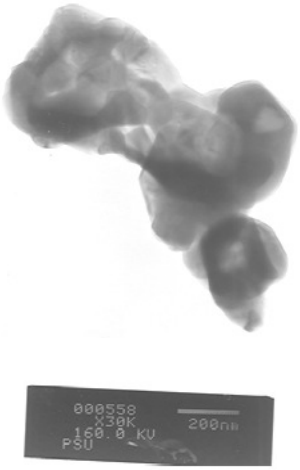

Figure 8. TEM image of the TiC product powders.

from Fe-TiC that was *in-situ* synthesized by a carbothermal reduction process from ilmenite at 1500°C. The resulted product of TiC shows good inter-particle cohesion within agglomerated particles. The mean particle size of the TiC powder was 12.8 μm with a crystallite size of 28.8 nm.

Acknowledgements

The authors are pleased to acknowledge the financial support for this research by the Prince of Songkla University Research Fund.

References

Cullity, BD. 1978. Elements of X-ray diffraction, 2nd ed. Addison-Wesley, Reading, MA, U.S.A., pp. 100-102.

Das, K., Bandyopadhyay,T.K. and Das, S. 2002. A review on the various synthesis routes of TiC reinforced ferrous-based composites. Journal of Materials Science. 37, 3881- 3892.

Jing, W and Yisan, W. 2007. In-situ production of Fe-TiC composite. Materials letters. In Press.

LaSalvia, J.C., Kim, J.C., Lipsett, D.K. and Meyers, M.A. 1995. Combustion synthesis in the Ti-C-Ni-Mo system Part 1 Micro-mechanism. Metallurgical and Materials Transaction A. 26, 3001-3009.

Ling, Y., and Dutta, S.P. 2001. Application trend in advanced ceramic technology. Technovation. 21, 61-65.

Niyomwas, S. 2005. Synthesis of Fe-TiC composite by carbothermic reduction of Ilmenite. Proceeding of PSU-UNS International Conference on Engineering & Environment 2005, Novisad, Serbia-Montenegro, May 18-20, 2005, No. T11- 22, 1-4. 10

Niyomwas, S. 2006. Effect of temperature and precursors on preparation of Fe-TiC composite from ilmenite. EPD Congress 2006, The 2006 Annual Meeting of The Minerals, Metals and Materials Society (TMS), San Antonio, TX, USA, Mar. 12-16, 2006, 857-864.

Nuilek, K., Memongkol, N., and Niyomwas, S. 2006. The effect of TiO_2 on synthesizing Fe-TiC composites. Proceeding of 4th Thailand Material Science and Technology Conference, Bangkok, March 2006, CP12, 320-322.

Sarker, M.K., Rashid, A.K.M.B. and Kurny, A.S.W. 2006. Kinetics of leaching of oxidized and reduced ilmenite in dilute hydrochloric acid solutions. International Journal of Mineral Processing. 80, 223-228.

Swift, G.A., Koc, R. 1999. Formation studies of TiC from carbon coated TiO_2. Journal of Materials Science. 34, 3083-3093.

Wattanachit, W. 2004. Upgrading ilmenite ore by hydro-chloric acid leaching. Master of Science Thesis in Inorganic Chemistry. Prince of Songkla University, Hat Yai, Thailand, pp.1-2.

Welham, N.J. 1996. A parametric study of the mechanically activated carbothermic reduction of ilmenite. Minerals Engineering. 9, 1189-2000. 11

Woo, Y.C., Kang, H.J and Kim, D.J. 2007. Formation of TiC particle during carbothermal reduction of TiO_2. Journal of the European Ceramic Society. 27, 719-722.