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Research article

Effect of Mg Content on Synthesis of TiC Powder from Leucoxene by Self-Propagating High-Temperature Synthesis Method

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Abstract: Titanium carbide (TiC) composite powder was synthesized via the self-propagating high-temperature synthesis (SHS) method using leucoxene as a source of titanium oxide (TiO_2) and magnesium (Mg) as an initiator. The effect of Mg content on synthesized TiC composite powder was characterized in terms of chemical composition and morphology by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Results showed that adding 1.5 moles Mg into the reactant system leached with 0.1 M hydrochloric acid solution was the optimal condition, and TiC was apparent in the XRD analysis at a particle size of less than 150 μm.

Keywords: Compsites, Titanium Carbide, Leucoxene, Self-propagating High-temperature Synthesis,

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1. Introduction

Distinctive features of titanium carbide (TiC) composite materials include high-temperature strength, good thermal and electrical conductivity, uncomplicated formability and good corrosion resistance. Therefore, TiC composites are used in various applications, such as multiple types of engine shaft parts [1-3]. TiC composites can be synthesized by different methods, including mechanical alloying [4], electrochemical production [5], thermal plasma technique [6], active-sintering [7] and carbonization [8-9]. However, these methods require complicated procedures and high amounts of thermal energy during the synthesis process. The self-propagating high-temperature synthesis (SHS) method utilizes the high-exothermic heat released from fuel agents such as magnesium (Mg) [10-12], aluminium (Al) [13-15] and titanium (Ti) [16]. Fuel agents were used to initiating the chemical reaction that then propagated self-sustainable until completion. A literature review [17-18] determined that TiC composites were mainly synthesized using Al as the fuel agent. The SHS products formed as a hard solid that was difficult to use. Hence, Mg was selected

as the fuel agent in this study to form products as a friable powder. The thermodynamic calculations shown as equations (1) and (2) indicate the difference in exothermic heat (ΔH) released when using aluminium or magnesium as the fuel source.

$$1.5TiO_2 + 1.5C + 2Al = 1.5TiC + Al_2O_3, \quad \Delta H = -538.986\ kJ/mol, \quad T_{ad} = 2{,}082\ °C \tag{1}$$

$$TiO_2 + C + 2Mg = TiC + 2MgO, \quad \Delta H = -461.721\ kJ/mol, \quad T_{ad} = 2{,}724\ °C \tag{2}$$

Leucoxene (a tailing from the manufacturing process of ilmenite ore was used as the source of titanium dioxide (TiO_2). This was mixed with carbon (C) as the reactant and magnesium (Mg) was used as the fuel agent. The objective of this study was to present an alternative method with low energy consumption for the synthesis of TiC composite powders.

2. Materials and Experimental Procedures

Leucoxene (Sakorn Minerals Co., Ltd., Thailand) and activated carbon (99%; Ajax-Finechem) were used as the reactants. Magnesium (99%; Riedel-deHaen) was used as an ignitor to start the combustion reaction of the reactant system. For powder preparation, leucoxene was high-energy milled using a planetary ball mill at 250 rpm for 30 minutes (Retsch, Germany) and sieved through a 325-mesh size for powder screening to give a particle size of less than 45 microns. The composition of the leucoxene powder was determined by the X-ray diffraction (XRD) technique. Then, the sieved-leucoxene powder was dry mixed with activated carbon and magnesium powders using zirconia balls in a polyethylene bottle for 3 hours. The reactant ratios are presented in Table 1. Reaction systems 2-4 were increasingly added with 0.5 mole aliquots of Mg. The adiabatic temperature (T_{ad}) of the combustion reaction was calculated based on the enthalpy (ΔH) of the reaction [19-20], using HSC® chemistry computer software. The homogeneously mixed reactant powder was then mechanically compacted into a cylindrical shape in a graphite mold with a diameter of 1 inch.

Table 1. Mole ratios and calculated-adiabatic temperatures of the reactions.

	Reaction system	**T_{ad} (°C)**
1	$TiO_{2(s)} + C_{(s)} + 2Mg_{(s)} \rightarrow TiC_{(s)} + 2MgO_{(s)}$	2,724
2	$TiO_{2(s)} + C_{(s)} + (2+0.5)Mg_{(s)} \rightarrow TiC_{(s)} + (2+0.5)MgO_{(s)}$	2,867
3	$TiO_{2(s)} + C_{(s)} + (2+1.0)Mg_{(s)} \rightarrow TiC_{(s)} + (2+1.0)MgO_{(s)}$	3,222
4	$TiO_{2(s)} + C_{(s)} + (2+1.5)Mg_{(s)} \rightarrow TiC_{(s)} + (2+1.5)MgO_{(s)}$	3,698

The graphite mold was loaded into the SHS reactor (Figure 1). The SHS chamber was evacuated and filled with argon gas (0.5 MPa) to provide an inert environment. The reaction was started at the top of the compacted reactant using high heat from a tungsten filament. Self-sustained combustion was initiated and the wavefront propagated to the bottom of the compact reactant. After cooling, the SHS products were leached to remove by-products or impurities by soaking in the hydrochloric acid solution for 24 hours and then filtered using No. 41 filter paper. The filtered powder products were washed with distilled water and dried in an oven at 120 °C for 12 hours. The chemical composition and microstructure of the final powder products were characterized by XRD (PAN Analytical Empyrean with Cu Kα radiation) and scanning electron microscopy (SEM) (PHILIPS with FEI/FEG Quanta 450).

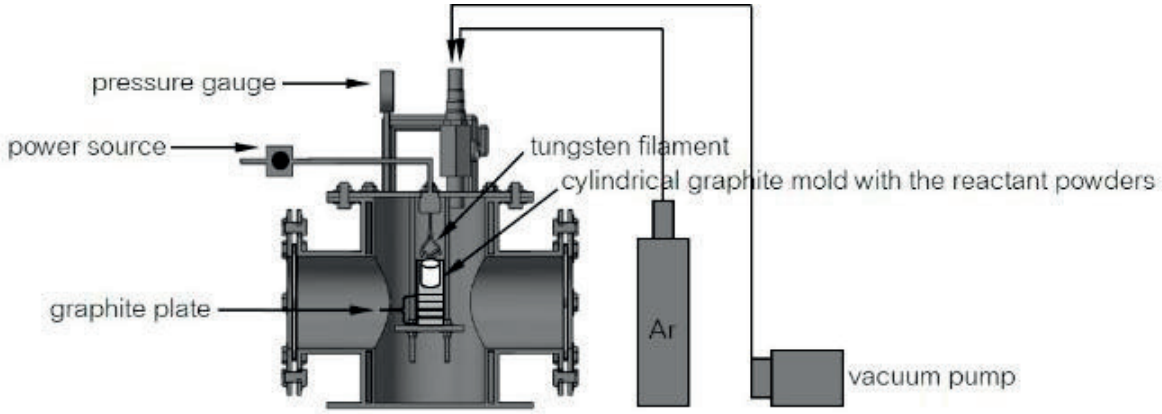

Figure 1. Schematic of the experimental setup in the SHS reactor.

3. Results and Discussion

The calculated adiabatic temperatures (T_{ad}) of reactant systems 1-4 were more than 1,800 ˚C (Table 1), indicating that the designed reaction systems were feasible for synthesizing by the SHS method and enabling self-sustained combustion [11]. Figure 2 shows that the expected SHS products from reaction system No.1 contained titanium carbide (TiC) and magnesium oxide (MgO) phases, which appeared in the left side of T_{ad} dash line.

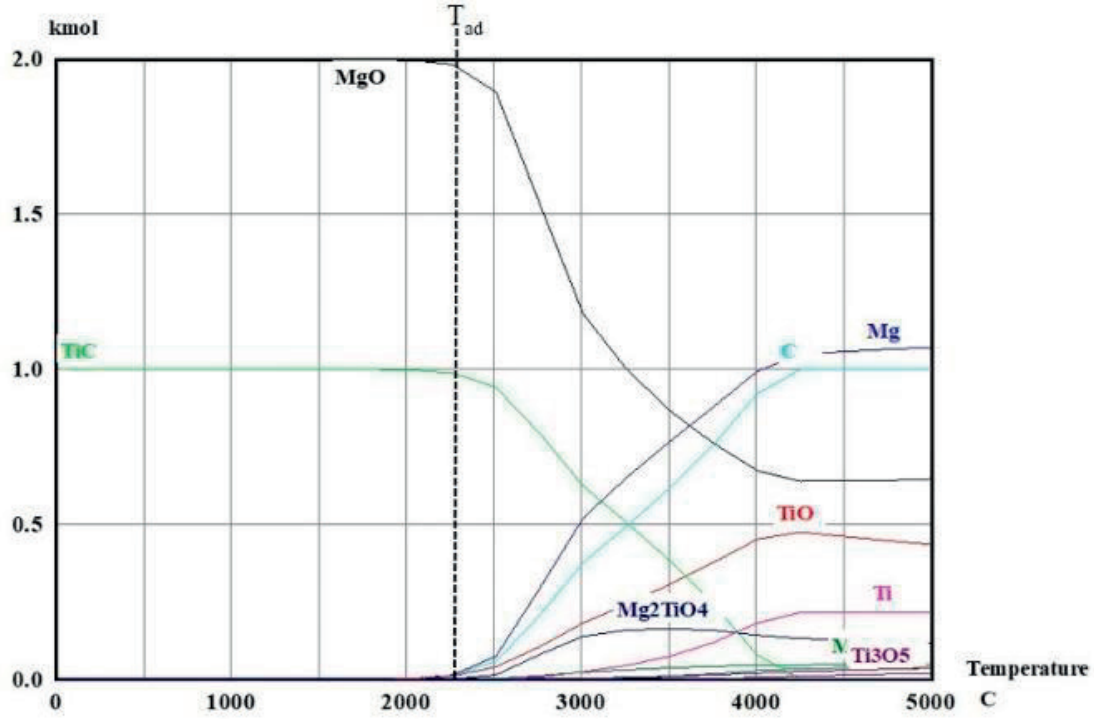

Figure 2. Equilibrium composition plot of reaction system No. 1.

Figure 3(a)-(d) exhibits the SHS products from reaction systems 1-4. Figure 3(a) shows the powder product covered by black particles due to incomplete combustion according to rapid cooling (in a second) of the reaction (see Figure 4). Products from reaction system No. 1. identified by XRD (Figure 5(a)), were MgO (ICDD No. 01-087-0653), residual intermediate phases of Mg_2TiO_4 (ICDD No. 01-072-7010), TiO_2 (ICDD No. 01-089-8302) and TiO_2 (ICDD No. 01-075-2545). White particles covered the surface of the products from reactant systems 2-4 (Figure 4 (b), (c) and (d)). Peaks identified by XRD shown in Figure 5(c) indicated that reaction system No. 3 presented TiC

and intermediate phases. Furthermore, all reaction systems in Figure 3 also indicated completion of the combustion reaction due to an increment of the thermal energy, consistent with the calculated adiabatic temperature.

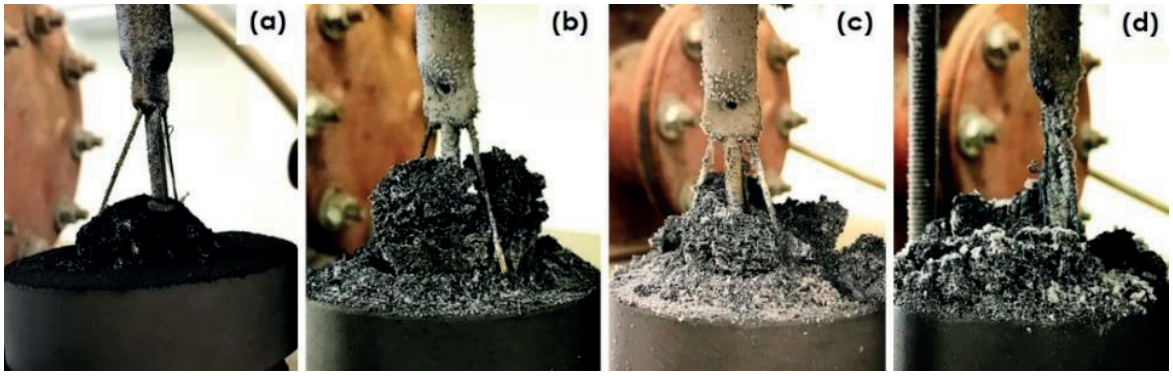

Figure 3. SHS products from reaction systems 1-4.

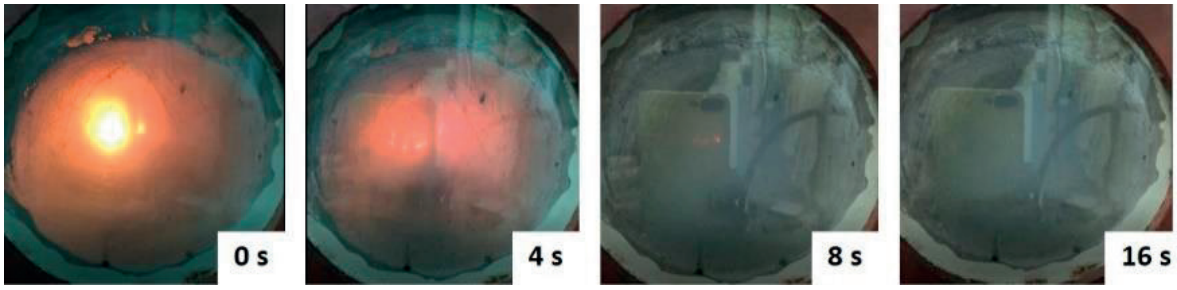

Figure 4. Digital snapshot images representing the SHS phenomena of some samples.

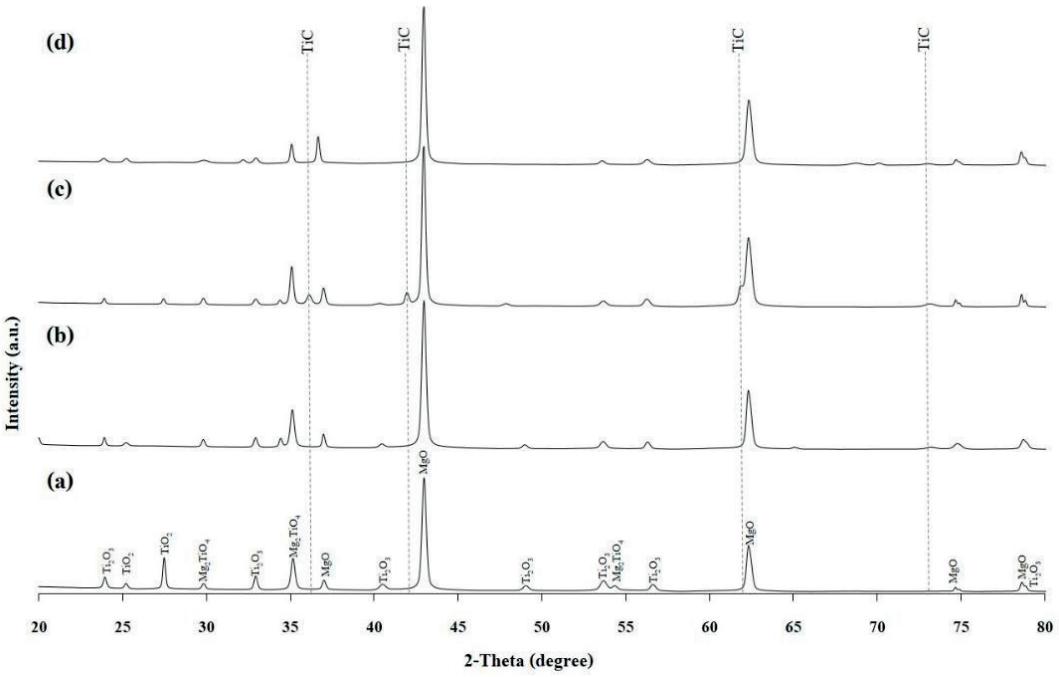

Figure 5. XRD patterns of SHS products with different reaction systems (a) No. 1, (b) No. 2, (c) No. 3 and (d) No. 4.

The SHS product from reaction system No. 3 was then leached by soaking in hydrochloric acid and characterized by the XRD technique (Figure 6). From Figure 6, some intermediate phases of MgO and Mg_2TiO_4 were eliminated. Moreover, the $Mg(OH)_2$ phase appeared in the leached product. This unwanted phase was formed by the reaction between MgO and HCl solution during the leaching process crystallized into solid $Mg(OH)_2$. This result concurred with Sang-Hoon Choi et al. (2019. However, using a higher HCl solution removed the intermediate substances [21-24]. Therefore, future studies should focus on the leaching method, especially the type of acid solution [25-27].

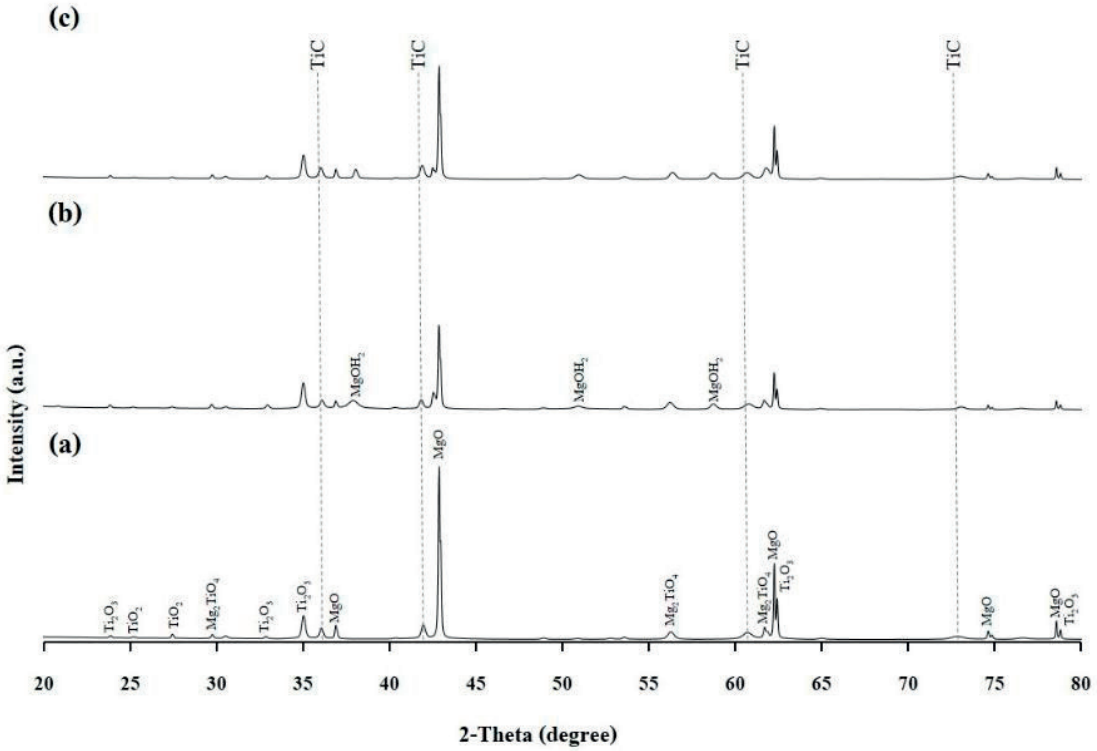

Figure 6. XRD patterns of the product from reaction system No. 3 (a) before leaching, (b) after leaching with 0.1 M HCl solution, and (c) after leaching with 0.5 M HCl solution.

Microstructures of the typical product (before and after leaching) are shown in Figure 7. Before leaching (Figure 7(a)), product particles were crumbled with an irregular shape. Hair-like crystals formed and covered the clumped particles. The hair-like crystals disappeared after leaching (Figure 7(b)) and the particles had an average size of 150 μm. The hair-like crystals were magnesium oxide (MgO) and this compound was eliminated by leaching with hydrochloric acid solution [21-27].

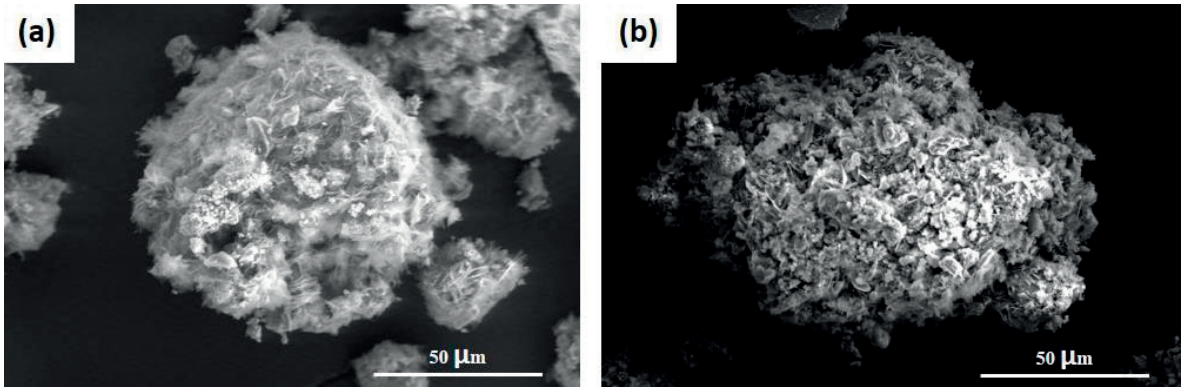

Figure 7. SEM images of the product from reaction system No. 4 (a) before leaching and (b) after leaching with 0.5 M HCl solution.

4. Conclusions

Leucoxene was successfully used instead of commercial titanium oxide (TiO_2) powder to synthesize titanium carbide (TiC) composite by the self-propagating high-temperature synthesis (SHS) method. The TiC phase was presented when 1.0 mole of Mg fuel was added to the reaction system. The SHS reaction produced a powder product with a particle size of less than 150 µm.

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Conflicts of Interest: The authors declare no conflicts of interest.

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