Synthesis of Titanium Carbide by the Combustion of TiO_2-2Mg-C and $3TiO_2$-4Al-3C Systems in a Tubular Furnace

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ABSTRACT: *The combustion process of TiO_2- 2Mg- C and $3TiO_2$-4Al-3C systems in a tubular furnace was investigated. TiC has been synthesized by the magnesiothermic reaction from a mixture of compacted powders of TiO_2, Mg and charcoal as starting materials in the presence and absence of NaCl. The effects of temperature, pressure, and the stoichiometry ratio in the reaction yield have been studied. The results show that the synthesis of titanium carbide in the presence of sodium chloride has a better yield than other methods. Titanium carbide was also synthesized by aluminothermy reaction from a mixture of compacted powders of aluminum, titanium dioxide and charcoal. The reaction processes are modified to achieve a high yield of TiC. The final products were characterized by XRD and SEM.*

KEY WORDS: *Titanium carbide, Magnesiothermic, SEM, Tubular furnace, Aluminothermy, XRD.*

INTRODUCTION

In recent years, much effort has been directed towards the process of development of transition metal powders and based composition (carbides, borides, nitrides, etc) with improved morphology and nanosized particles. Various methods have been explored for their manufacturing such as: melt crystallization, chemical vapor deposition (CVD), laser, carbon reduction, metallic wire explosion, self-propagating high-temperature synthesis (SHS) [1-3].

Titanium carbide (TiC) has been widely used in the fields of wear resistance tools and aerospace materials. Titanium carbide based composites with nickel alloys and iron alloys are currently used in high performance applications where wear and corrosion are the main sources of material failure. Due to its high melting point of 3338 K, the production of bulk materials containing the TiC component has been made possible by TiC powder consolidation only [4,5].

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Although several methods have been employed to produce TiC powder such as carbothermal, self-heated reactive sintering and sol-gel processes [6,7], they have all shown drawn backs such as formation of a coarse sintered structure, a nonstoichiometric composition, TiC_xO_y formation, need for initial titanium powder of high purity, and need for post-milling [8].

The production of high performance materials by combustion synthesis or self-propagating high-temperature synthesis (SHS) is receiving considerable attention since the process offers certain advantages with respect to simplicity and a relatively low energy requirement. One of the potential drawbacks of the SHS process is the possible porous nature of the final products [9-11].

Among the various powder production methods, we have focused our attention on the novel SHS method. The SHS method has some advantages in comparison with other methods, such as low energy consumption for the achievement of high temperatures, high rate of synthesis, simplicity of special equipment and high quality of final products. At the present time, a large number of various binary and complex chemical compositions are already synthesized by the SHS method. Despite of this, the synthesis of nanosized metallic powder and based composition is very poorly investigated [12,13]. For the first time, the self-propagating high-temperature synthesis of titanium carbide powder from the TiO_2- 2Mg- C initial mixture was carried out in ISMAN, Russia [14,15]. Although there are huge number of open-literature investigations on the properties of TiC composites, information on the synthesis of titanium carbide via the magnesiothermic reaction is more than scarce.

Here, we report synthesis of titanium carbide by the combustion of TiO_2-2Mg-C system in a tubular furnace and investigate the effects of temperature, pressure, stoichiometry ratio and NaCl in the synthesis of TiC powder. Also, we synthesize titanium carbide by aluminothermy reaction.

EXPERIMENTAL SECTION

The experiments were carried out in a CARBOLITE STF tubular furnace. All of the chemicals used were of reagent grade. Titanium dioxide, charcoal and magnesium powder were purchased from Merck. Reactant powders were dry-mixed intimately according to the predetermined molar ratios by a DETIN DH26 mixer. The mixed powders were pressed in pellets (20 mm diameter, 5-6 mm thickness) at different pressures. The pellets were put in a graphite boat. The graphite boat was inserted in an aluminosilicate crucible with carbon bed. This set was put in the tubular furnace. The crystal structure of the burned down samples were analyzed by X-ray diffractometer (ADVANCE D8 AXS BRUKER). Standard sample of TiC (02-1179 (D)) was used for characterization of the products. Scanning electron microscopy (SEM) observations were performed with a Philips XL30 scanning electron microscope.

RESULTS AND DISCUSSION

Synthesis of TiC by the magnesiothermic reaction

Titanium carbide was synthesized in a tubular furnace under an argon atmosphere. The different molar ratios of raw materials, titanium dioxide, charcoal and magnesium were milled in a stainless steel container containing stainless steel balls for 3 h. Ethanol was used as milling solution. The powder mixture was dried under vacuum at 60 ^{o}C. The sample was cold isostatically and pressed in pellets (20 mm diameter, 5-6 mm thickness) at different pressures. Then the pellets were put in a graphite boat. The graphite boat was inserted in an aluminosilicate crucible with carbon bed. This set was put in a tubular furnace and sintered under an argon atmosphere for 1 h. The crude product (titanium carbide, unreacted raw materials and by-products) which formed was purified by acidic leaching. The final product TiC was characterized by X-ray diffraction technique (Fig. 1).

Effect of pressur

The effect of pressure on the TiO_2- 2Mg- C pellets was examined. The initial mixtures of titanium dioxide, magnesium and charcoal were pressed at pressures of 127.3, 381.9, 763.8 and 1145.7 MPa. As it is shown in Fig. 2, when the pressure increased from 127.3 to 763.8 MPa, the amount of titanium carbide in the final products was increased. When the pressure increased to 1145.7 MPa, the amount of TiC was dramatically decreased. These results show that there is considerable variation in the TiC yield with respect to the pressure and the pellet pressed at 763.8 MPa gave the highest TiC product (Fig. 2).

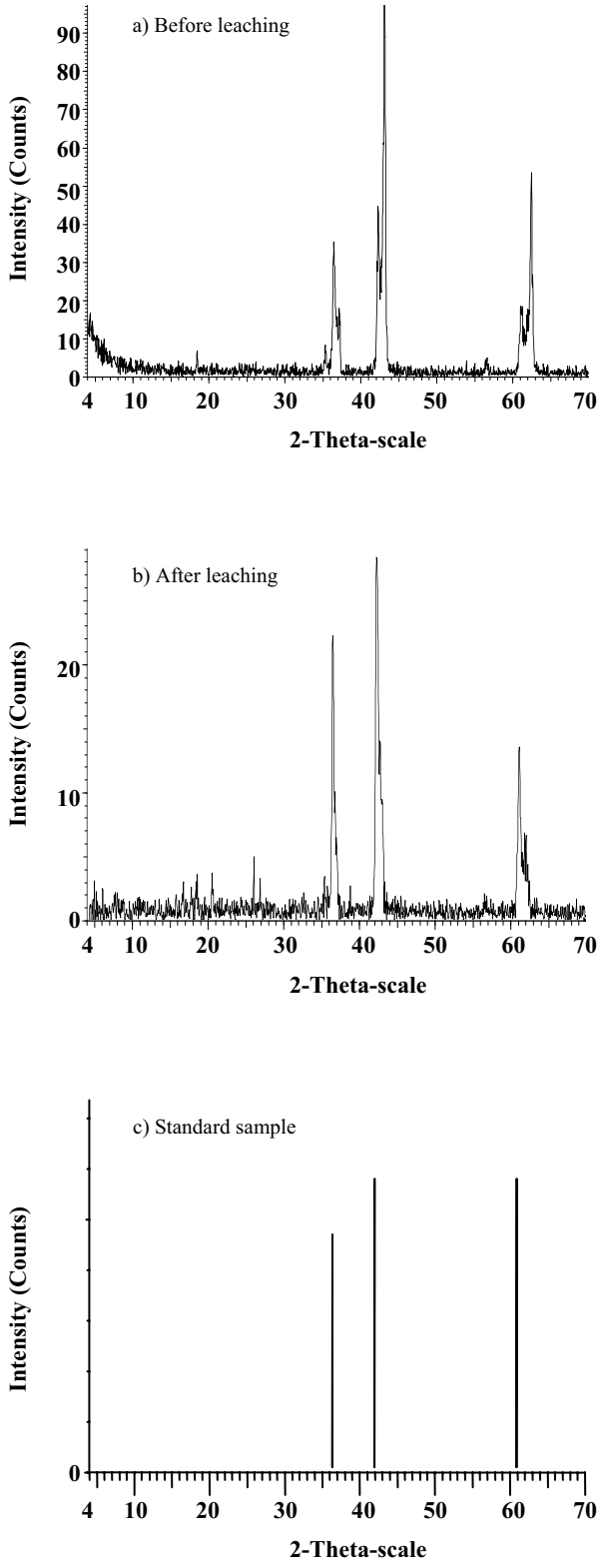

Fig. 1: XRD patterns of TiC a) before leaching, b) after leaching, c) Standard sample (02-1179 (D)).

Effect of temperature

TiC powders were prepared in a tubular furnace under an argon atmosphere with a range of operation temperature from 1250 to 1400 ^{o}C. The reaction yield of these experiments for the production of TiC was investigated. A plot of the intensity of titanium carbide peak (XRD) and operation temperature is shown in Fig. 3. According to the obtained results, a direct relationship between operation temperature and the reaction yield exists.

Effect of stoichiometry ratio

TiC powders were prepared with a range of Mg/TiO_2 molar ratios varying from 2 to 4 in the optimum operating temperature and pressure (1400 ^{o}C and 763.8 MPa) and the reaction yield was investigated. The final products which prepared in different molar ratios, were characterized by XRD. The relationship between the intensity of titanium carbide peak (XRD) and stoichiometry ratio is shown in Fig. 4. The maximum amount of TiC powder is obtained in the stoichiometry ratio of Mg/TiO_2= 2. The molar ratio of Mg/TiO_2= 4 has the lowest reaction yield due to the formation of magnesium carbide (MgC_2) in the reaction mixture. The formation of MgC_2 reduces the amount of free carbon in reaction mixture. Therefore, titanium carbide can not be produced as major phase.

Acidic leaching of reaction mixture

Acidic leaching operation was used for removal of the byproducts (MgO, TiO_2- Mg_2TiO_4) and unreacted Mg from the desired product TiC. Several inorganic acids such as HCl, HCl + HNO_3, H_3PO_4 and H_2SO_4 were tested to determine the optimal leaching conditions. The results showed that there is not an important different between these inorganic acids. Due to the high boiling point and low price of H_2SO_4, this acid was used for the following leaching operations. Fig. 5 shows the XRD pattern of TiC before and after the acidic leaching operation by H_2SO_4.

Synthesis of TiC by the aluminothermy reaction

In this method, titanium carbide was synthesized by the aluminothermy reaction from a mixture of compact powders of titanium dioxide (62.5 wt. %), charcoal (9.375 wt. %) and aluminum (28.125 wt. %). The raw materials were milled and pressed in pellets (20 mm diameter, 5-6 mm thickness) at 763.8 MPa. Then the pellets were put in a graphite boat. The graphite boat was inserted in an

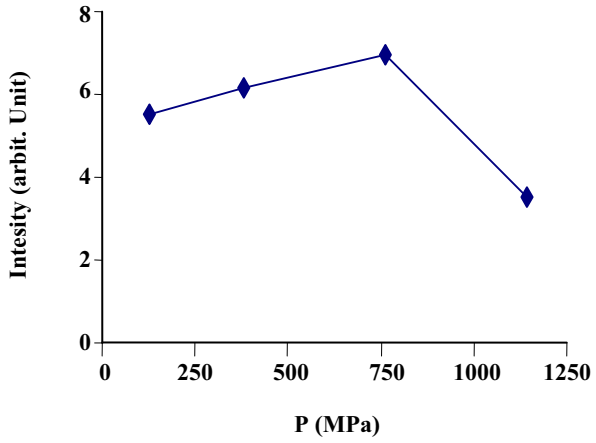

Fig. 2: The effect of pressure on the synthesis of titanium carbide.

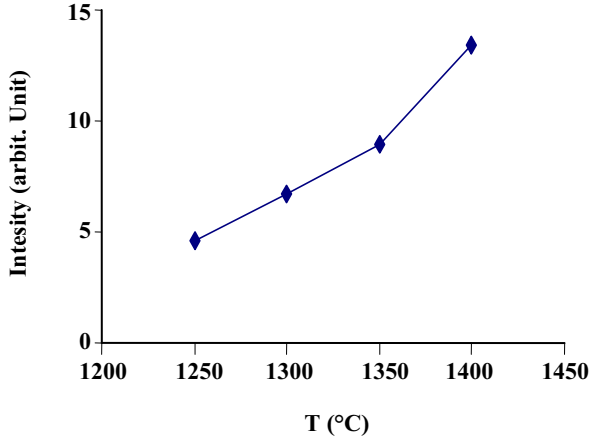

Fig. 3: The effect of temperature on the synthesis of titanium carbide in a tubular furnace.

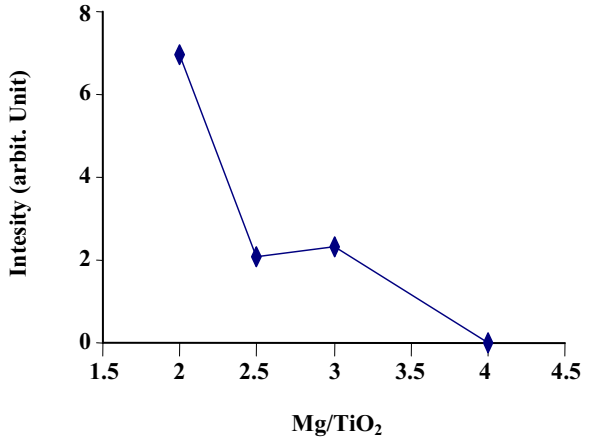

Fig. 4: The effect of stoichiometry ratio on the synthesis of titanium carbide.

aluminosilicate crucible with carbon bed. This set was put in a tubular furnace and sintered under an Ar atmosphere for 1 h. Titanium carbide and some by- product (Al_2O_3) were obtained. To reduce the by-product and unreacted Al, alkaline leaching operation (NaOH solution) was used. Finally, titanium carbide was characterized by XRD.

Effect of temperature

TiC powders were prepared by aluminothermy reaction in a tubular furnace under an argon atmosphere with a range of operation temperature from 1300 to 1400 ^{o}C. The reaction yield of these experiments for the production of TiC was investigated. A plot of the intensity of titanium carbide peak (XRD) and operation temperature is shown in Fig. 6. According to the obtained results, a direct relationship between operation temperature and the reaction yield exists.

Synthesis of TiC by the magnesiothermic reaction in the presence of NaCl as an additive

In this method, titanium carbide was synthesized by the magesiothermic reaction in the presence of sodium chloride as an additive. The raw materials were titanium dioxide, magnesium, charcoal and sodium chloride. These materials were milled and pressed in pellets (20 mm diameter, 5-6 mm thickness) at 763.8 MPa. These pellets were put in a graphite boat in a tubular furnace at 1400 °C for 1 h. Titanium carbide and some by-products were obtained.

To reduce the by-products and unreacted Mg, acidic leaching operation (H_2SO_4) was used. The final product TiC was characterized by X-ray diffraction. Synthesis of titanium carbide in the presence of sodium chloride shows a larger reaction yield than previous methods. The reaction between TiO_2 and Mg is assisted by the melted NaCl (melting point of NaCl = 801 ^{o}C). The XRD pattern of TiC in the presence of 0.25 mol of NaCl is shown in Fig. 7.

Scanning electron microscopy (SEM)

Characterization of TiC was carried out also using scanning electron microscopy (SEM). All the electron micrographs were obtained from powder specimens of TiC. A representative micrograph of TiC is shown in Fig. 8. The resulting microstructures consist of TiC phase. SEM micrographs show that no voids are present in the microstructures of TiC samples and this indicates that the TiC samples are fully dense.

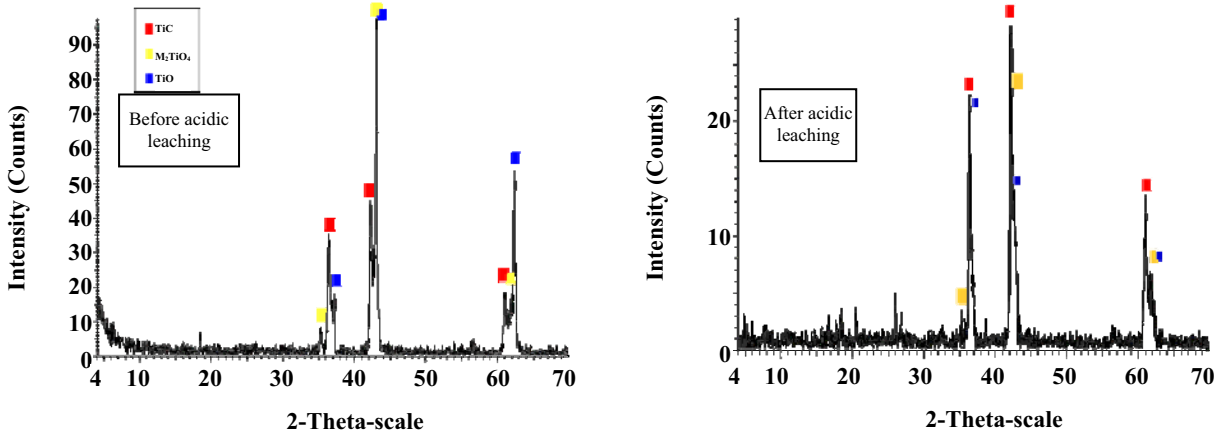

Fig. 5: XRD patterns of TiC before and after acidic leaching.

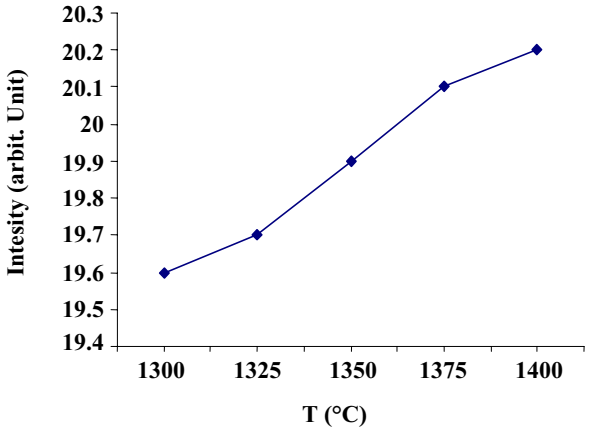

Fig. 6: The effect of temperature on the synthesis of TiC by the aluminothermy reaction.

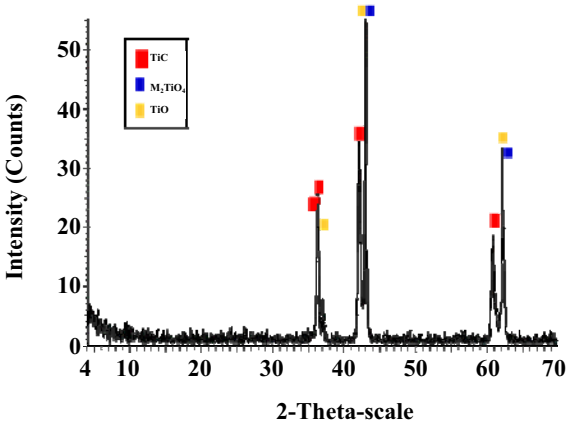

Fig. 7: XRD pattern of TiC in the presence of NaCl (0.25 mol) after acidic leaching.

CONCLUSIONS

The combustion process of the TiO_2/Mg/C and TiO_2/Al/C systems for synthesis of TiC was investigated. The effects of temperature, pressure and stoichiometry ratio on the synthesis of titanium carbide powders have been studied.

In magnesiothermic method, TiC was prepared in good yield according to the following reactions in a tubular furnace under an argon atmosphere:

$$Mg_{(s)} \rightarrow Mg_{(l)} \quad (1)$$

$$TiO_{2\,(s)} + 2Mg_{(l)} \rightarrow Ti_{(s)} + 2MgO_{(s)} \quad (2)$$

$$Ti_{(s)} + C_{(s)} \rightarrow TiC_{(s)} \quad (3)$$

The overall reaction is:

$$TiO_{2\,(s)} + 2Mg_{(s)} + C_{(s)} \rightarrow TiC_{(s)} + 2MgO_{(s)}$$

The method is modified to achieve very high yields (> 80 %).

In aluminothermy method, TiC powder was prepared in good yield according to the following reactions in a tubular furnace under an argon atmosphere:

$$Al_{(s)} \rightarrow Al_{(l)} \quad (4)$$

$$3TiO_{2\,(s)} + 4Al_{(l)} \rightarrow 3Ti_{(s)} + 2Al_2O_{3(s)} \quad (5)$$

$$Ti_{(s)} + C_{(s)} \rightarrow TiC_{(s)} \quad (6)$$

The overall reaction is:

$$3TiO_{2\,(s)} + 4Al_{(s)} + 3C_{(s)} \rightarrow 3\,TiC_{(s)} + 2Al_2O_{3(s)} \quad (7)$$

Titanium carbide was also synthesized by magnesiometheric reaction in the presence of sodium chloride as an additive. NaCl melts at 801 °C and prepares a suitable medium for efficient reaction between TiO_2 and Mg.

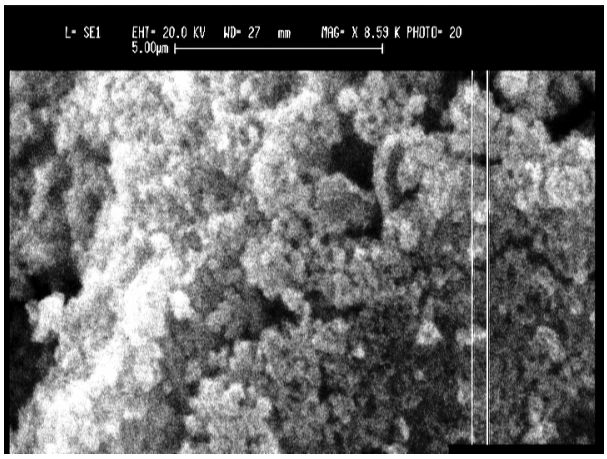

Fig. 8: SEM micrograph showing the TiC phase.

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