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Synthesis of Titanium Carbide Nano Particles by the Mechano Chemical Process

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Abstract Titanium carbides are widely used for cutting tools and grinding wheels, because of their superior physical properties such as high melting temperature, high hardness, high wear resistance, good thermal conductivity and excellent thermal shock resistance. The common synthesizing method for the titanium carbide powders is carbo-thermal reduction from the mixtures of titanium oxide (TiO_2) and carbon black. The purpose of the present research is to fabricate nano TiC powders using titanium salt and titanium hydride by the mechanochemical process (MCP). The initial elements used in this experiment are liquid $TiCl_4$ (99.9%), TiH_2 (99.9%) and active carbon (<32 μm, 99.9%). Mg powders were added to the $TiCl_4$ solution in order to induce the reaction with Cl-. The weight ratios of the carbon and Mg powders were theoretically calculated. The TiC and $MgCl_2$ powders were milled in the planetary milling jar for 10 hours. The 40 nm TiC powders were fabricated by wet milling for 4 hours from the $TiCl_4$+C+Mg solution, and 300 nm TiC particles were obtained by using titanium hydride.

Keywords : Mechano chemical process (MCP), TiC, TiH_2, $TiCl_4$, Nano particles

1. Introduction

Generally, the hard phase of ceramic combines with a metal-based matrix to form cermet. Most of the cermets have high melting point, high hardness, oxidation and corrosion resistance, good thermal stability and thermal shock resistance. The TiC has many applications to mechanical, chemical and electronic devices from among metal carbide [1-5], because it has a high melting point including high hardness, and wear resistance, good thermal conductivity and excellent thermal shock resistance. Currently, the most useful material for cutting tools is tungsten carbide however the titanium carbide comes into the spotlight as effective substitute materials for its higher hardness, superior chemical stability at high temperature and lower density than WC. [6-12].

A number of processes were reported for synthesizing TiC powders, because the mechanical properties of cermet depend on the characteristic of their law material and sintering process. [13-15]. For examples, carbo-thermal method, carburization method, self propagate high temperature synthesis, sol-gel process and gas reaction methods are often used. But each method has some problems of a variety of particle characteristics, particle distribution, morphology, state of agglomeration, chemical purity, and stoichiometry [16, 17].

The most conventional methods to fabricate commercial TiC powders are carbo-thermal reduction from the mixture of titanium oxide (TiO_2) and carbon black.

The related equation of this reaction is as follows : [18]

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g)$$

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$\Delta G = -114.94$ KJ/mol(at 1200K)

It is possible to reduce the cost for using TiO2 powders as a raw material. However, the carbo-thermal reduction process needs high temperature of 2000°C and long solid state reaction time about 20 hours by this process because of TiO_2 and carbon being solid state reaction [18]. In addition, the particle size of TiC powders depends on the size of raw TiO_2 powders, and it is difficult to produce submicron powders by carbo-thermal reduction unless using sub-micron size raw powders [19].

Another method is direct synthesizing carburization method of Ti and carbon to form TiC. This process has also some problems to overcome high cost of raw materials and long synthesizing time(about 20 hours). To obtain the submicron TiC is impossible with this procedure, and the homogeneous formation of TiC powders is also very difficult.

The purpose of this research is to fabricate submicron TiC powders using titanium chloride by a new synthesizing mechano-chemical process (MCP). The TiC particle is synthesized as the following chemical reaction [20, 21].

$$TiCl_4 + C + 2Mg \rightarrow TiC + 2MgCl_2$$
$$\triangle G_{298K} = -571.1311 \text{ KJ/mol}$$

This mechano-chemical synthesizing method is useful to fabricate fine composite powders by combining mechanical energy and thermal energy during milling. This research was focused on obtaining submicron size TiC powders, and phase and microstructural changes of produced powders were studied.

In compare with this process, TiC particle was synthesized by titanium hydride and carbon as following solid state reaction [22].

$$TiH_2 + C \rightarrow TiC + H_2, \Delta G = -222.7 \text{ Kjoule/mol}$$

2. Experimental Procedure

The initial elements used in this experiment are liquid $TiCl_4$ (99.9%) and active carbon (<32 μm, 99.9%). Mg powder was added to react with Cl^- in the $TiCl_4$ solution to form $MgCl_2$. The carbon powder and Mg powder weight percents were calculated to form the TiC and $MgCl_2$, and milled in the planetary milling jar (Pulverrisette 6, Fritsh Gmbh Germany) in argon atmosphere for 10 hours with 600 rpm milling speed. WC-Co balls were used as milling media, and the ball to $TiCl_4$ mixture ratio was 30:1.

The synthesized powders were washed with anhydrous ethyl alcohol of 500 ml, and the TiC powders were separated from $MgCl_2$ melt solution. The separated powders were dried on the hot plate at 80°C.

The heat treatment of ball-milled powders for 5hrs was processed to get rid of remained $MgCl_2$ at the temperature of 1200°C. The heating rate of 10°C/min and a flowing stream of argon at 80 ml/min were supplied. The characteristics of titanium carbide have been studied by X-ray diffraction (XRD) and Fe-SEM (field emission scanning electron microscopy). The analysis of alloying element and particle size measurement were obtained with TEM/EDS (energy dispersive x-ray spectroscopy).

The TiH_2 (<20 μm) powder and carbon were milled with mole ratio of 1:1 in the planetary mill to form TiC by solid state reaction in air or argon atmosphere. The grinding media were stainless steel balls with 10 mm in diameter and milling media to powder ratio was 20:1.

3. Results and Disscusion

Fig. 1 shows the X-ray diffraction patterns of wet reaction milled powders with $TiCl_4$, carbon and Mg. The TiC peak was not found at the milled powders until 3 hours. After milling for 4 hours, TiC phase peak was appeared sharply. Even though the milling time increases up to 5 hours, no other titanium compound phase was appeared except Ti oxide peaks. Titanium oxide formation explains that the remained oxide in the steel jar reacted with dissolved Ti from $TiCl_4$.

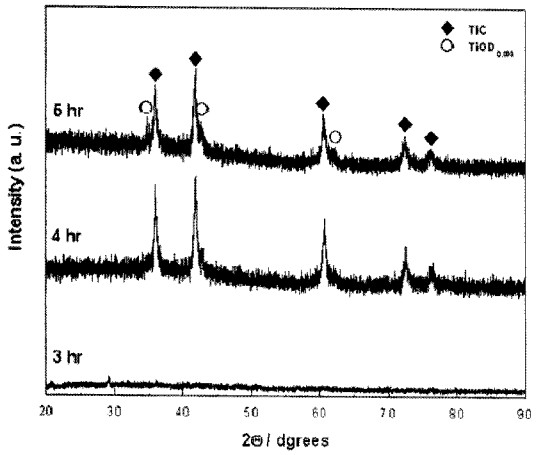


Fig. 1. X-ray diffraction patterns of wet reaction milled powders with $TiCl_4$, carbon and Mg elements for various milling times.

Fig. 2 shows the FESEM morphologies obtained with different magnifications of milled powders fabricated by wet milling for 3 hours. As shown in this figure of FE-SEM morphologies, aggregated nano size particles were obtained after 3 hours milling.

The nano size TiC aggregated particles were obtained after milling time more than 4 hours, and the particle shape was round type. The agglomeration of the TiC particles was caused by the increased surface area of the fine particles and the remaining $MgCl_2$.

Fig. 3 shows the FESEM morphologies obtained with different magnifications of reaction milled powders for 4 hours and 5 hours. As shown in fig. 3, the fine TiC particles were also agglomerated in case of 4 or 5 hours milling. However, the agglomerated particle shape was different from that of 3 hours milled powders. The inner nano size grains were agglomerated to form large agglomerated particles. The SEM morphology of milled composite powders shows the clear surface of agglomerated particles in fig. 3. The particle size was several hundred nanometers. To confirm the composition variation and TiC particle size, TEM image and EDS analysis were carried out. Fig. 4 shows the TEM image of the TiC powders milled for 5 hours. Several kinds of phases were shown in large agglomerated particles and around nano particles in fig. 4. The fine inner particles were considered that the granule TiC, which is surrounded by other particles. The angular TiC surface of each particle in agglomerated parts could be obtained by the mechanical milling effect.

The angular grains of uniform size of 40 nanometer were observed. However, inner fine grains are also agglomerated with several different colored particles. The separated three regions of light gray matrix, mid-gray and dark gray were shown in this picture. In order to confirm the composition of the unknown particles and to get rid of these undesirable particles, heat treatment of the milled particles was required.

Fig. 5 shows the TEM image and EDS analysis results of milled powders for 5 hours, and figure 6 shows the TEM image and EDS results at different regions of heat treated powders. The compositions of these different regions were confirmed by EDS anal-

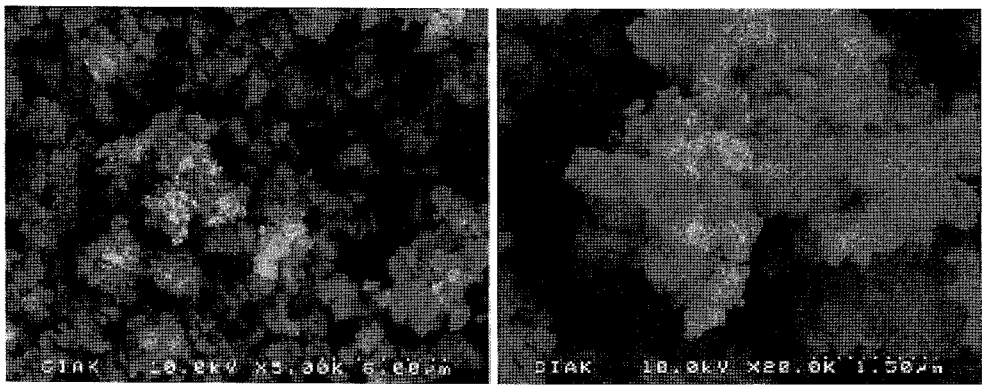


Fig. 2. The FESEM morphologies of milled powders fabricated by wet milling for 3 hours.

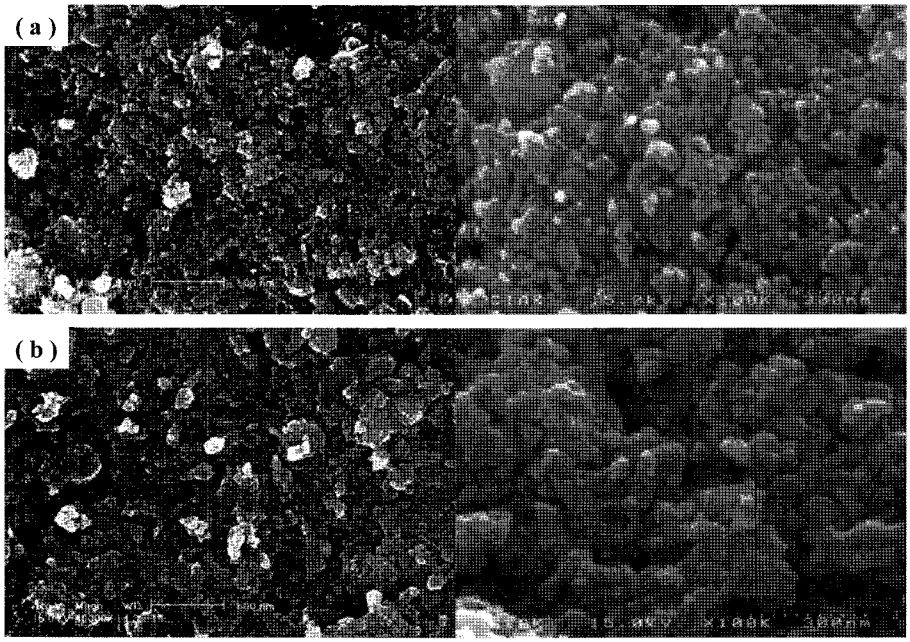


Fig. 3. The FESEM morphologies of TiC powders fabricated by wet milling for (a) 4 hours and (b) 5 hours.

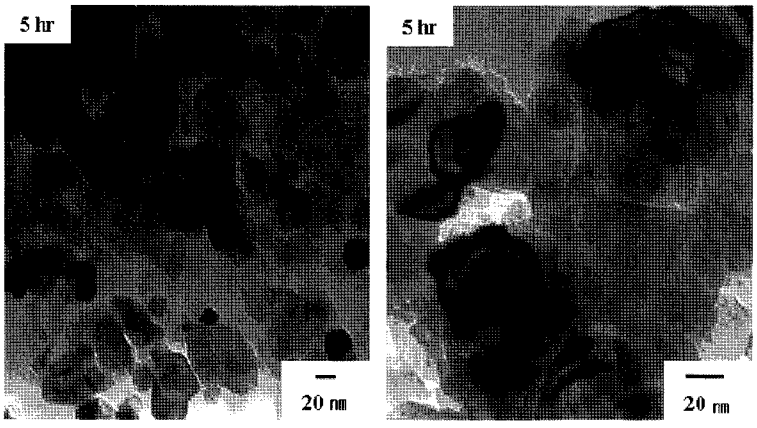
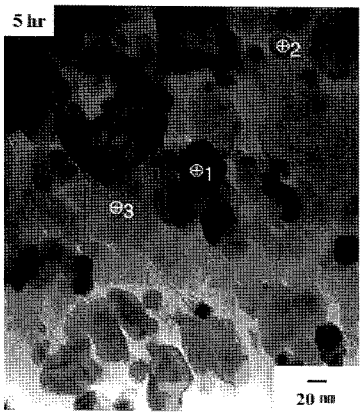


Fig. 4. TEM image of the milled TiC particles for 5 hours.

ysis as shown in fig. 5. From the result of EDS at milled powders, light gray region (3) is the high Mg concentration region of remained $MgCl_2$ after washing, and it was confirmed that the mid-gray and dark gray region was TiC. The size range of the synthesized TiC particle was 20~60 nm. As compare with the TEM image of fig. 5, two kinds of black and gray colored phases were observed instead of three regions shown in the milled powders. It means that $MgCl_2$ of light gray matrix region (3) was removed mostly as shown in EDS data of figure 6. It shows that the remained $MgCl_2$ was removed more effectively by heat treatment.

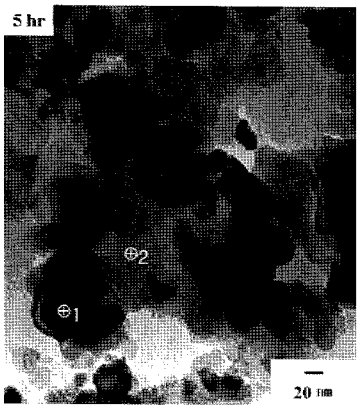
Fig. 7 shows the XRD spectra of the TiH_2-carbon powders milled for various milling times in air atmosphere. As the milling time was increasing, the intensity of initial TiH_2 was decreased, and Ti_2O_3 peak appeared. However, as the milling time reached to 7 hours, titanium oxide peak intensity decreased and TiC peak increased sharply. The titanium oxide



	Mass (%)				Total
	C	*Mg*	Cl	*Ti*	
1	59.72	*2.17*	0.88	*37.23*	100
2	82.48	*3.34*	-	*17.17*	100
3	41.86	*58.14*	-	-	100

Result of EDS

Fig. 5. TEM image and EDS results of the milled TiC and the EDS results.



	Mass (at.%)					Total
	C	O	*Mg*	Cl	*Ti*	
1	71.73	9.99	*0.43*	-0.07	*17.91*	100
2	70.35	13.56	*0.16*	-0.03	*15.96*	100

Result of EDS

Fig. 6. TEM image and EDS results of the heat treated powders at different regions.

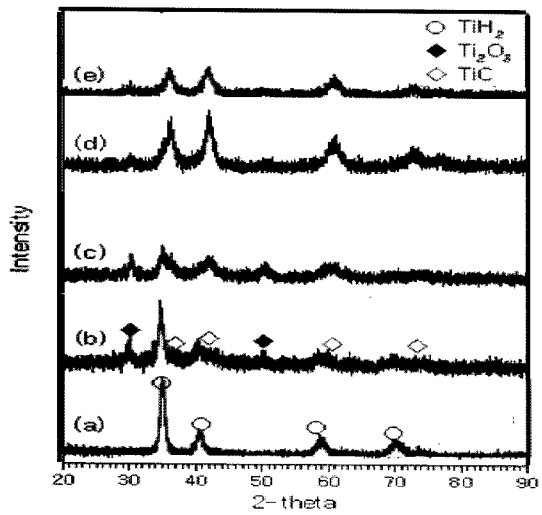


Fig. 7. XRD spectra of the TiH_2-carbon powders milled for (a) 2h, (b) 3h, (c) 5h, (d) 7h and (e) 10h.

was considered to form with remained oxide in the vessel during milling. As the milling time was increasing, oxide phase decreased due to low partial pressure of oxide and oxidation reaction of Ti hydride to form TiC as following reactions.

$$TiH_2 \rightarrow Ti + H_2$$
$$2Ti + 3/2\ O_2 \rightarrow Ti_2O_3$$
$$Ti_2O_3 + 2C \rightarrow 2TiC + 3/2O_2$$
$$H_2 + 1/2O_2 \rightarrow H_2O$$

The measured mean particle size of TiC was 300 nm at the TEM images after 10 hours milling and titanium oxide was co-existed. During milling, Ti particles were oxidized with excess oxygen at the initial stage, TiC phase was obtained from the oxide by carbo-thermal reaction at the

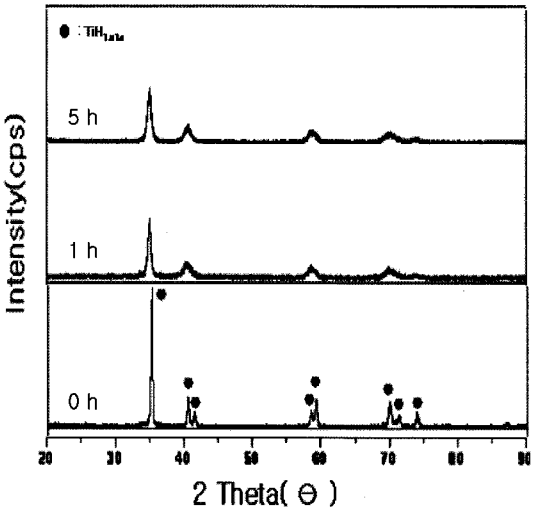


Fig. 8. The change of XRD peaks of mixtures (TiH_2 and carbon black) with milling time.

final milling stage.

Fig. 8 shows the XRD patterns of powders milled 1 and 5 hours in argon atmosphere. TiC phase was not formed in Ar atmosphere even 5 hours milling. In Ar atmosphere, the titanium oxide phase was not formed, but the TiC phase also was not synthesized directly by milling. From these two kinds of results, it could be considered that the oxygen element reacts on the following. $2Ti+3/2O_2 \rightarrow Ti_2O_3$ and $Ti_2O_3+2C \rightarrow 2TiC+3/2O_2$ reaction as a precursor.

4. Summary

1. The TiC powders were fabricated by wet milling for 4 hours from the $TiCl_4$+C+Mg solution.

2. The synthesized TiC particles were agglomerated with 20-60 nm grains.

3. The remained metallic salt $MgCl_2$ was removed effectively by heat treatment at 1200°C.

4. The mean particle size of TiC was 300 nm after 10 hours milling in case of using TiH_2+C solid state reaction.

5. The TiC particles were formed directly by milling in air, but was not synthesized by milling in argon atmosphere.

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