Synthesis of Nano-Crystalline TiC Powder from Active Impure Ti Chips via Self Propagating High-Temperature Synthesis and the Effect of Al on the Synthesis Temperature

Mansour Razavi* and Mohammad Reza Rahimipour

Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

Abstract

In this research, the possibility of production of TiC powder from inexpensive raw materials via simple methods has been investigated. Impure Ti chips, carbon black and Al powder were activated by a high-energy ball mill. Then they were synthesized by the method of self propagating high-temperature synthesis (SHS) at various temperatures. XRD study indicated that TiC within 1000°C to 1300°C temperature range has been synthesized where the temperature in a sample containing Al was less than 1000°C. From the broadening of the diffraction lines in the XRD patterns, it was concluded that the TiC crystallites were nano-sized and the lattice parameter had deviated slightly from the standard size. The existence of Al increased the lattice parameter of TiC and the strain in the process.

Introduction

Titanium carbide (TiC) with the cubic structure of NaCl has desirable properties as reinforcing phase in composites [1]. Lattice parameter of this material is 0.4327±0.0001 nanometers [2]. In comparison to other carbides such as tungsten carbide (WC), TiC has 33% higher hardness than WC, less weight and higher temperature stability [3]. TiC can be used as a reinforcing phase in composites or can be used alone. In case of using TiC, other materials such as SiC, TiN, NbC, TiC, TiB_2, WC and C to reach the required toughness along with the needed hardness, should be added (because toughness of TiC is low) [4-6]. In the industry, SiC, Al_2O_3 and TiC respectively are highly used as reinforcing phases for produce composites currently [7].

One of the synthesis methods of TiC is self-propagating high-temperature synthesis (SHS). Merzhanov first developed this method in 60's [8]. In this process the temperature was increased to a certain degree and then reaction starts and the necessary heat for continuation of the reaction will be obtained from the heat reaction [9].

High purity of products, easily method and inexpensive equipments, saving time and energy, possibility of producing unstable phases in one step, reducing the separation between matrix and reinforcing phases, reaching to near-net shape and high mechanical properties of materials, are the advantages of SHS method [9-12].

For performance a self-propagating reaction, the following conditions should be satisfied [8,11]:

1. Reaction should be exothermic ($\Delta H_{reaction} < -167$ kJ/g·mol).
2. The heat loss rate should be less than the rate of produced heat.

In this research, the feasibility of producing TiC from cheaper materials by SHS method and the effects of Al on the synthesis temperature and grain size has been studied.

Experimental

The titanium used in this research was commercial pure. The X-ray Fluorescence Spectrometry (XRF),

*corresponding authors. E-mail: m-razavi@merc.ac.ir

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used to analyze the Ti, revealed that it contained impurities with the composition of 0.32 wt.% Al, 0.37 wt.% Si and 0.41 wt.% V. To produce titanium its profile was used. The titanium crushed chips were ball milled for 5 hours to achieve the particle size <50 mesh. Carbon black was used as carbon source. Carbon black size is < 250 mesh. Also 99.9% purity aluminum powder with <250 mesh size was used.

The materials were mixed according to stoichiometric ratio along with 10 wt.% Al in a full energized planetary ball mill for 5 hours. Three similar balls with the diameter of 20 mm were used. In order to protect the materials from oxidation, the argon gas was charged with the purity of 99.99% and pressure of 2.5 atm. Subsequently, disc specimens with 20 mm diameter and 5mm thickness were produced in a steel die using 1000 kg load.

Because the high temperature rate plays a major role in the SHS method, the muffle furnace temperature was increased and then tables were put in at once. Furthermore in order to control inner furnace atmosphere and prevent oxygen from mixing with the material, these were buried under 5 cm of active coke. The samples were kept in the furnace for 10 minutes with various temperatures. After cooling down the specimens in the furnace, they turned to powder and were prepared for further examinations.

In order to identify the produced phases and compounds, the XRD analysis was performed with Cu K_α (λ = 1.54 Å) radiation with the voltage and current of 30 kV and 25 mA respectively. The crystallite size and strain were evaluated through Williamson-Hall method [13] and the lattice parameter was also obtained by Nelson-Riley method [14] with following equations:

$$b\cos\theta = \frac{0.9\lambda}{d} + 2\eta\sin\theta \quad \text{Williamson-Hall } eq.$$

$$F(\theta) = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \quad \text{Nelson-Riley } eq.$$

Where b is full width of peak at half intensity (rad), θ is position of peak in the pattern (rad), λ the wavelength of X-ray (nm), η microstrain in the powder and $F(\theta)$ is the Nelson-Riley function.

Results and Discussion

Ti-C Binary System

XRD pattern of sample containing Ti and C which has been exposed to 1300°C temperature by SHS methods, is presented in Fig. 1a. The acquired dominant phases at 1300°C were TiO_2 and TiC. Although the materials had been buried under coke but titanium oxide peaks still was found in the compound, which is the outcome of existence of oxygen in the mentioned system. In Figure 1b XRD pattern of sample, which were synthesized at 1000°C, is shown. In this temperature, TiC was not synthesized and the identified phases were limited to Ti and TiO_2. Therefore TiC was synthesized at 1000°C to 1300°C in this system (Ti-C).

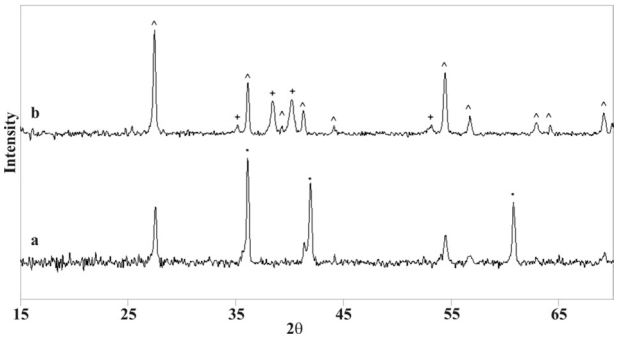

Fig. 1. XRD patterns of samples that were synthesized by the SHS method in Ti-C system (a) 1300°C (b) 1000°C TiC (*), Ti (+), TiO_2(^).

The synthesis mechanism of TiC from Ti and C elements starts by diffusion of C into Ti forming TiC layer. The diffusion coefficient of C in TiC is three times higher than diffusion coefficient of Ti in TiC. As the reaction temperature increases, Ti start to melt and TiC layers are dissolved in it, then C penetrate into open porosities and cover the layer. There after, C diffusion in the TiC dissolution layer for reaching Ti to form TiC nucleus which growth. Obviously, carbon morphology effects on final carbide structures, speed and mechanism of reaction [11,15].

The grain size of TiC produced by SHS technique at 1300°C temperature was calculated according to the Williamson-Hall equation as Fig. 2 illustrates. The result of this calculation is presented in Table 1. In Table 1, η and d are strain and grain size respectively. According to this calculation the crystal size of TiC is in nanometer order (about 50 nm).

The lattice parameter of TiC can be calculated in accordance with Nelson-Riley equation. In Figure 3 the variations of the lattice parameter are plotted based on $F(\theta)$. By extrapolation of the curve in Fig. 3 and determination of the best fitted curve intersect at $x = 0$ abscissa, the lattice parameter of TiC can be

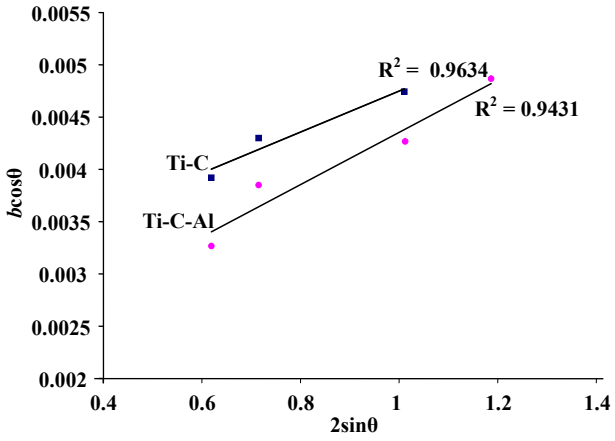

Fig. 2. Calculations of strain and crystal size by Williamson-Hall method in Ti-C and Ti-C-Al systems at 1300°C temperature.

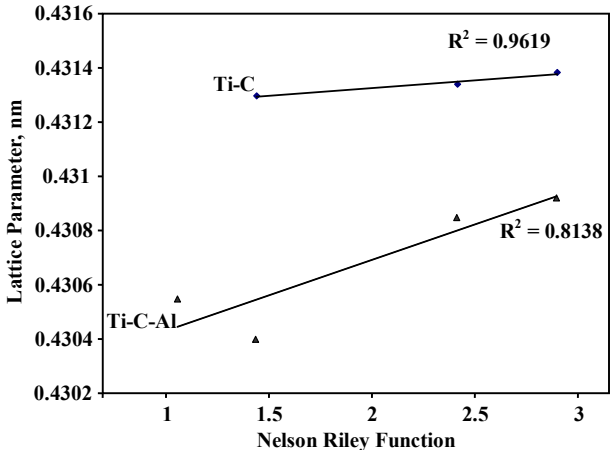

Fig. 3. Determination of TiC lattice parameter in Ti-C and Ti-C-Al systems using Nelson-Riley method at 1300°C temperature.

Table 1
The mean size of the particles and the strain caused by SHS in accordance to Williamson-Hall equation in Ti-C and Ti-C-Al systems 1300°C temperature

System	$b\cos\theta = 2a\sin\theta + b$		d_{TiC}, nm	η_{TiC}, %	R^2
	a	b			
Ti-C	0.0020	0.0028	49.52	0.20	0.9634
Ti-C-Al	0.0025	0.0019	72.97	0.25	0.9431

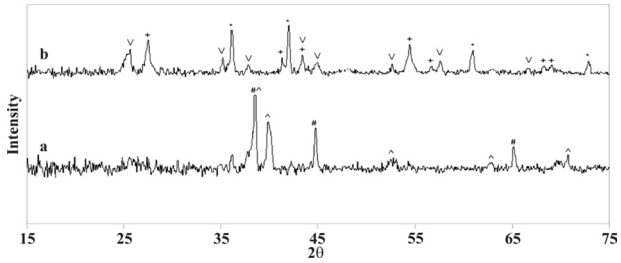

Fig. 4. XRD patterns for samples synthesized by the SHS method in Ti-C-Al system 1000°C (b) 1300°C Al (#), Ti (^), TiO_2 (+), Al_2O_3 (ᵛ), TiC(*).

determined. The lattice parameter was estimated to be 0.4312 nm, which is far from ideal. The deviation from the standard of lattice parameter of TiC synthesis is 0.0015 nm. It is believed that this deviation was caused by high rate temperature in SHS method. Of course the nonexistence of calibration in the instruments and not considering the exact stoichiometric ratio of the produced TiC, also effect the deviation [2,16].

Ti-C-Al Ternary System

XRD pattern obtained in the sample containing Ti, C and Al produced at 1300°C by SHS method is shown in Fig. 4b. It can be observed a considerable amount of Al_2O_3 and TiO_2 produced with TiC at 1300°C. Figure 4a shows the XRD pattern for the same sample at 1000°C. The dominant phases at this temperature were Al, Ti, their oxides and also very weak TiC peaks.

From Figure 4, the temperature of synthesizing for TiC via SHS method from Ti, C and Al should be less than 1000°C. Because the oxidation of aluminum is very exothermic reaction; therefore, as it was expected the existence of Al decreases the production temperature of TiC. The synthesis mechanism of TiC from Ti, C and Al elements was explained regarding the following steps [17]:

1. On initial heating, the aluminum melts and spreads over the titanium particles. At this stage, $TiAl_x$ compounds form at the interface between the aluminum melt and the titanium particles. Thus: $2Ti + 2C + xAl = TiAl_x + Ti + 2C + Q_1$
2. As the temperature further increases, the dissolved titanium in aluminum covers carbon particles and titanium diffuses into the carbon which lead to formation TiC.
   Thus: $TiAl_x + Ti + 2C = TiAl_x + TiC + C + Q_2$
3. When the temperature increases more, $TiAl_x$ compound gradually diminishes and Ti dissolves in the mixture.
   Thus: $TiAl_x + TiC + C = TiC + Ti + xAl + C - Q_3$
4. When the temperature reaches the melting point Ti, the molten Al and Ti enters into carbon po-

rosity and TiC dissolve in this molten mixture. Therefore, TiC is produced and starts growing. Thus: $TiC + Ti + xAl + C = 2TiC + xAl + Q_4$

However, very little oxygen in the mixture could create Al_2O_3 and as a result the speed of the reaction increases. Without oxygen the reaction has the following from [18]: $2Ti + 2C + xAl = 2TiC + xAl + Q$ ($Q = Q_1 + Q_2 - Q_3 + Q_4$).

The grain size of synthesized TiC at 1300°C was calculated from Williamson-Hall method as Fig. 2 illustrates. A summary of the results for the particle size is presented in Table 1. Due to existence of Al and an excess amount of heat, the crystal size were found to be larger than the TiC synthesized from Ti-C system (about 73 nm but still nanosized).

In Figure 3 the Nelson-Riley function curve for determining synthesized TiC lattice parameter is shown. According to the mentioned figure, lattice parameter is found to be 0.4302 nm which has a 0.0025 nm deviation from the standard of lattice parameter of TiC. This value is more than the lattice parameter of Ti-C system. Since the generated heat of Al_2O_3 is very high, the rate of heat in this process is relatively higher, it causes more defects and that affects the lattice parameter. Also the existence of strain in the each system can be caused by milling and SHS process may be the cause for the lattice parameter deviation (Table 1).

Conclusions

- It was shown that it is possible to produce nano TiC crystals from impure Ti chips, carbon black and Al by mechanical activation and SHS methods.
- The synthesizing temperature of TiC in Ti-C system was found to be 1000°C to 1300°C, which temperature in a sample containing 10 wt.% of Al was decreased under 1000°C.
- TiC crystal sizes in both procedures were in the range of nanometer. This value for Ti-C system was found to be 50 nm and for Ti-C-Al was 73 nm.
- Lattice parameter in both systems deviated from the standard value. It was shown that the deviation was higher in sample containing Al, which is suggested to be caused by defects and strain. In addition, non-stoichiometric ratio and non-calibrated apparatus could be the other two reasons for such deviation.

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