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Synthesis of Titanium Carbide by Means of Pressureless Sintering

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Received: 4 June 2020; Accepted: 14 August 2020; Published: 18 August 2020

Abstract: In this study, titanium carbide was obtained by low-temperature pressureless (at pressure less than 1 MPa) sintering of a mixture of elementary titanium and graphite powders in a hot-pressing plant with a preliminary mechanical treatment of the initial mixture. The sintering was carried out at temperatures of 900 and 1000 °C in argon media. As a result, cubic modification (Fm3m) of titanium carbide was obtained. The content of impurities was about 12–13 wt.%

Keywords: titanium carbide; mechanical activation; synthesis of elements; pressureless sintering

1. Introduction

Currently, the synthesis of high-melting compounds for high technology applications is one of the topical problems of material sciences. Titanium carbide exhibits such properties as high values of hardness, crack and wear resistance, fatigue limit and modulus of elasticity, and heat resistance, and is a promising compound of this type [1]. Titanium carbide is widely used as an abrasive material, a component of hard-alloy tools, cutting tools, and carbidosteels, as well as in the manufacture of dispersed-hardened alloys, metal alloying, and ceramics. A new and prospective application of titanium carbide is the synthesis of MAX phases Ti_2AlC and Ti_3AlC_2. This method is thoroughly described in [2,3].

MAX phases are hexagonal-structure ternary carbides or nitrides with a formula $M_{n+1}AX_n$, where n = 1, 2, 3, and M is an early transition metal; A is an A-group element; and X is carbon or nitrogen [4]. These compounds are divided into classes depending on the MAX phase coefficient n: M_2AX (211); M_3AX_2 (312); M_4AX_3 (413). MAX phase may be used as a precursor for synthesis of MXenes: two dimensional materials prepared by leaching of A element from the structure of the MAX phases. A variety of chemical properties of MXenes allow them to be applied for hardening of composite materials; water purification; gazo-and biosensors; and photo, electro, and chemical catalysis, and as a lubricator [1]. However, the most interesting results of MXenes application were received in the field of energy accumulation. It is known that the use of two-dimensional titanium carbide Ti_3C_2 in Li-and Na-ion batteries leads to the significant increase of their capacity (comparably to a graphene) and stability during 10,000 cycles [5].

There are many methods for obtaining titanium carbide powder but quite often they require high energy consumption due to high temperatures of the process. Among them, some methods can be outlined: carbothermal reduction of titanium dioxide [6], the magnesiothermic method [7], the plasma method [8], the mechanical activation of titanium and carbon powders [9], and synthesis from elements.

Carbothermal reduction of titanium dioxide is the most common method of titanium carbide production due to its simplicity and relative cheapness compared to elemental titanium. The process is carried out in high-temperature furnaces in inert medium and requires high temperatures (~2000 °C) that result in high energy consumption. Moreover, the synthesis of titanium carbide from TiO_2 is low-yielding due to gas generation during the process of titanium dioxide reduction [1,10–12].

The magnesiotermic process is carried out in argon medium at high pressure to suppress magnesium evaporation. A feature of magnesiotermic method is the need for acid treatment of the products to remove magnesium oxide [13,14].

Mechanical activation of a mixture of elements powders is a very promising method of titanium carbide production. Sometimes mechanical activation is accompanied by self-propagating high-temperature synthesis (SHS) process. SHS is an auto-wave process similar to the propagation of the combustion wave. It is widely used for the synthesis of high-melting compounds, including titanium carbide. In this process, the chemical reaction is localized in a combustion zone spontaneously propagating through the active medium. Grinding of the powder mixture is accompanied by an increase in the interface between the components, as well as a large energy release caused by friction of particles and balls. As a result of the mechanical activation of the mixture of titanium and carbon powders, its self-combustion can occur with subsequent formation of titanium carbide [1,9,15–17].

Additionally, SHS can be combined with high-pressure consolidation process for synthesis of titanium carbide [18]. The initial mixture (C/Ti = 0.95) was subjected to pressures to 3 GPa and then ignited by a passing electric current through a carbon heater at 1.5–2 kV·A during 2 s. This method is suitable for obtaining titanium carbide ceramics.

Another way to obtain titanium carbide is via synthesis from elements. The high cost of titanium powder limits the application of this method, but it is highly effective and requires quite low temperatures due to the high exotermicity of the process. Currently, there is a lack of data on the conventional low-temperature solid-state technique of titanium carbide synthesis from elements.

A conventional carbon material for obtaining TiC is carbon black [19]. Due to the technological features of carbon black production, it contains harmful impurities, such as sulfur, which worsen the characteristics of titanium carbide. In article [20], a successful attempt was made to obtain titanium carbide by mechanical activation using activated carbon and natural graphite as a carbon material.

There are no data in the literature concerning the traditional solid-state technique for preparation of TiC from powders of elements. This might be due to difficulties with compacting initial mixtures into dense pellets. On the other hand, the hot-pressing technique allows one to compact the mixture that results in the expansion of the number of interface contacts and thereby accelerates the rate of the chemical reaction. Having studied the various synthesis methods of titanium carbide presented in the literature, we decided to perform a low-temperature synthesis of titanium carbide by pressureless (at pressure less than 1 MPa) sintering of a mixture of elementary titanium and graphite powders in a hot-pressing plant with a preliminary mechanical activation of the initial mixture.

2. Materials and Methods

The mixture of titanium powder (LLC TMK, 99.9 % pure, grain size of 0.1–1 mm) and graphite (Sigma-Aldrich, PCode 101508101, grains size < 20 μm) were mechanically treated in a water-cooled planetary ball mill AGO-2, in argon media at acceleration of 20 g with stainless steel balls for 10 min. The diameters of balls and jar were 5 mm and 50 mm, respectively; the balls mass was 200 g, and the mass of the mixture was 10 g. The obtained mechanically activated mixture was loaded into a die to obtain a green body 10 mm in diameter and 5 mm in thickness. The die was set into a hot-pressing plant TST.017.000.00 PS (developed at the Institute of Automation and Electrometry of the Siberian Branch of the Russian Academy of Sciences), and was pressed at a low pressure below 1 MPa and sintered at 900 °C and 1000 °C (samples TiC-900 and TiC-1000 respectively) during 30 min under an inert argon media. We consider the above procedure as pressureless sintering in a hot press.

The phase composition of the as-sintered samples was investigated by XRD using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with CuKα radiation. The quantitative phase analysis of the sintered materials was carried out using the Rietveld method in TOPAS 4.2 software (Bruker AXS). Electron microscopy studies were carried out on an electron microscope Hitachi S3400N equipped with Oxford Instruments Energy Dispersive Spectroscopy (EDS) analyzer.

3. Results and Discussion

The results of X-ray phase analysis are demonstrated in Figure 1. According to analysis of X-ray diffraction patterns, the initial mixture contained pure titanium and graphite powders without impurities. Several X-ray diffractograms were recorded from different parts of the samples and similar results were obtained. The resulting samples are represented by cubic titanium carbide slightly contaminated by unreacted titanium and carbon. The presence of titanium oxide in the samples can be explained by partial oxidization of the initial mixture with air oxygen.

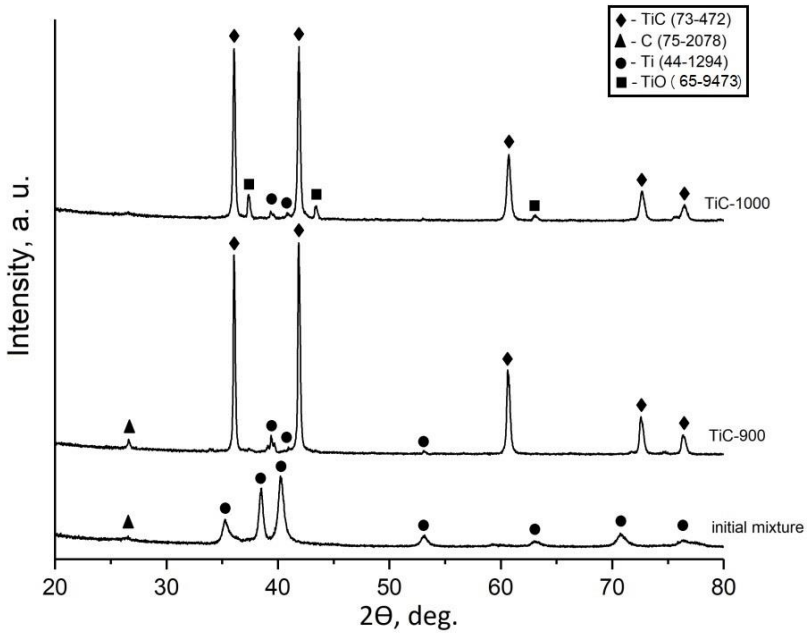

Figure 1. X-ray diffraction patterns of initial mixture and the obtained samples.

Precision analysis of structural parameters of TiC was carried out using a Rietveld method. In parallel, concentrations of other phases were evaluated. Experimental X-ray pattern for the sample TiC-1000 is shown in Figure 2, together with the theoretical one obtained using a full-profile analysis. Quantitative parameters of TiC in the sample are listed in Table 1.

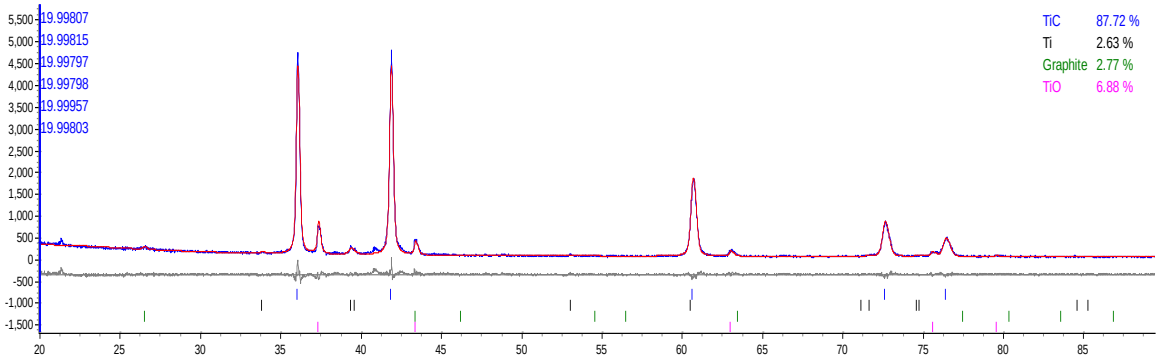

Figure 2. X-ray diffraction patterns of initial mixture and the sample obtained at 1000 °C. Results of calculation of unit cell parameters are presented in Table 1.

Table 1. Concentrations of the components and parameters of TiC estimated from full-profile Rietveld analysis of X-ray diffraction data for TiC-900 and TiC-1000 samples.

Sample	Phase Composition (wt.%)		Unit Cell Parameter of TiC (Å)	The Grains Size (nm)	Strain (%)
TiC-900	TiC	87.0 ± 1.1	4.3221 ± 0.0002	95 ± 3	0.244 ± 0.012
	Ti	7.6 ± 1.2			
	C	5.4 ± 1.0			
TiC-1000	TiC	87.7 ± 0.9	4.3163 ± 0.0002	81 ± 3	0.383 ± 0.014
	Ti	2.6 ± 1.0			
	TiO	6.9 ± 1.1			
	C	2.8 ± 0.8			

Comparison of the samples TiC-900 and TiC-1000 shows that the concentration of TiC increases with the sintering temperatures, whereas the concentration of Ti and C decreases. Unfortunately, sample TiC-1000 contained 6.9 wt.% impurity of TiO. The values of the lattice parameter of TiC (symmetry space group Fm3m with cubic elementary cell) determined for both TiC-900 and TiC-1000 samples are close to the data reported in the reference literature, 4.3274 Å (PDF2 file 32-1383). The lattice parameters of the sample TiC-1000 are slightly less than that for TiC-900 sample. Additionally, there are differences in the grain size and the average strain in the crystal lattice. These changes might be caused by partial oxidation of the sample TiC-1000, resulting in the decrease in the grain size and formation of dislocations stabilized by the impurity oxygen atoms in the crystal lattice of TiC. The titanium oxide TiO and TiC are isostructural, and the lattice parameter of TiO, 4.1705 Å (PDF2 file 65-9473) is smaller than TiC. Therefore the introduction of oxygen into the TiC crystal lattice should lead to the decrease in the lattice parameter in agreement with the experimental observation and with the data reported earlier [21].

The scanning electron microscopy patterns are shown in Figure 3. As seen, the samples, TiC-900 and TiC-1000, have similar morphologies: powders consist of aggregates 20–60 micrometers in size, and the aggregates are formed of nanoparticles with the size estimated from X-ray patterns as 81–95 nm (see Table 1). The following composition of the samples was determined by EDS microanalysis (in atomic percent): 48.5 ± 0.2% Ti, 47.5 ± 0.7% C and 4.0 ± 0.7% other elements for TiC-900 sample and 50.1 ± 0.6% Ti, 45.9 ± 0.2% C and 4.0 ± 0.6% other elements for TiC-1000 sample; other elements are Al, Si, P, and Fe (originated from the sample holder) and traces of oxygen in the TiC-100 sample. Typical EDS spectrum is presented in Figure 4. The EDS data agree fairly well with the phase composition data determined by X-ray analysis.

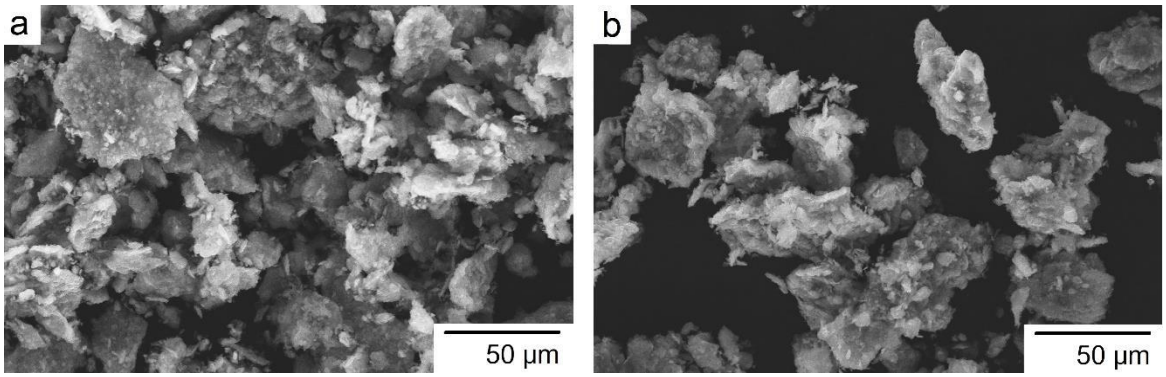

Figure 3. SEM images of the samples: (**a**) TiC-900; (**b**) TiC-1000.

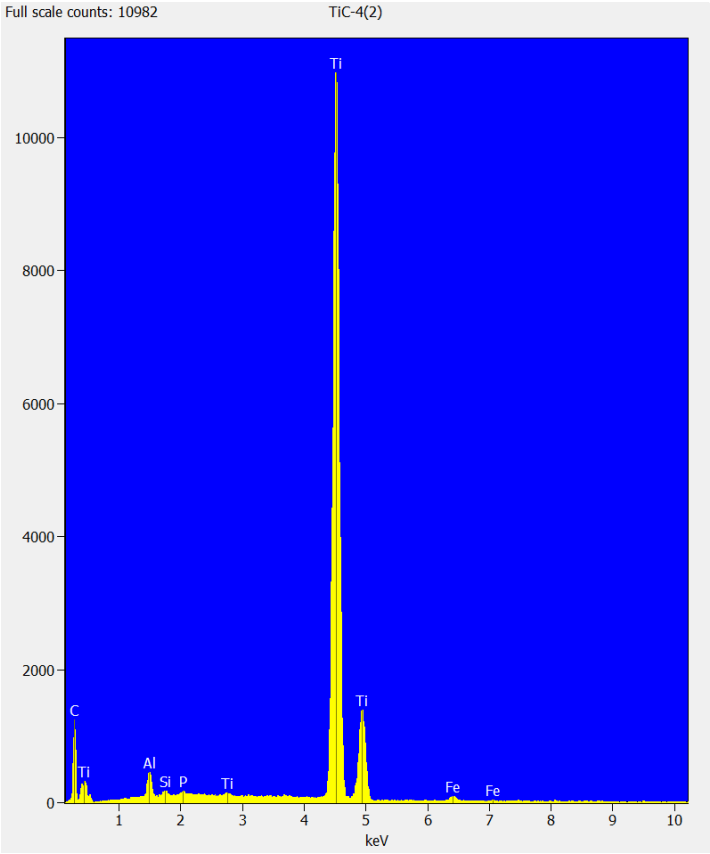

Figure 4. Energy Dispersive Spectroscopy (EDS) spectrum obtained from the surface of the TiC-1000 sample.

4. Conclusions

As a result of experiments of titanium carbide synthesis by pressureless sintering in a hot-pressing plant, a cubic titanium carbide containing a small amount of impurities was obtained. In principle, the impurities of Ti and C may be removed by longer sintering. The presence of impurities of TiO may be avoided by preventing the oxygen traces in the surrounding media. The unit cell parameter was similar to a theoretical one. Thus, a hot pressing technique even at low pressures (in fact, a pressureless sintering) allows one to accelerate the rate of the chemical reaction and obtain TiC at low temperatures. Thus, presureless sintering in a hot press may be regarded as a promising technique for preparation of high-temperature materials.

Author Contributions: Conceptualization, N.U. and T.K.; methodology, T.K.; software, A.U.; validation, N.U., T.K. and A.U.; formal analysis, T.K.; investigation, T.K.; resources, T.K.; data curation, T.K.; writing—original draft preparation, T.K.; writing—review and editing, N.U., T.K.; visualization, T.K.; supervision, N.U.; project administration, N.U. All authors have read and agreed to the published version of the manuscript.

Funding: The work was supported by Ministry of Science and Higher Education of Russia (project no. FSUN-2020-0008).

Acknowledgments: Authors thank B.B. Bokhonov (Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia) for carrying out scanning microscopy studies. The work was carried out within a scope of State task of Ministry of Science and Higher Education of Russia (project no. FSUN-2020-0008).

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

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