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Synthesis and Characterization of Nanosized Titanium Carbide by Carbothermal Reduction of Precursor Gels

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Investigations have been made on obtaining of nanosized powders of titanium carbide (TiC) by carbothermal reduction of a precursor prepared by sol-gel process. Two methods of precursor gels fabrication of TiC were used: Ti (IV) chloride, ethyleneglycol and citric acid (series A) and Ti (IV) n-propoxide, saccharose and acetic acid (series *B*). The resulting xerogels are calcined under flowing argon at different temperatures ranging from 800 °C to 1400 °C with holding time from 0.5 h to 10 h. TiC nanopowders were obtained with the specific surface area of 30 m^2/g – 200 m^2/g and the size of TiC crystallites of 40 nm – 45 nm. Only the TiC phase has been found by the XRD analysis, but the presence of also some oxygen and free carbon depending on synthesis conditions has been found by chemical analysis. For compacting investigations with spark plasma sintering (SPS) method (1800 °C, heating rate of 100 °C /min and dwelling time of 5 min.) TiC nanopowder (SSA of 88 m^2/g, containing 72.7 wt. % Ti, 6.6 wt. % O, 20.5 wt. % C_{total} and 7.2 wt. % C_{free}) was used. The sintering begins at 1150 °C, but change of density ends at 1650 °C. The density at this temperature reaches only 89 % of the theoretical and does not rise until 1800 °C. This is probably due to the presence of free carbon in investigated sample, retarding sintering. A significant decrease of admixtures has been observed in ceramic material during sintering.

Keywords: titanium carbide, nanosized powders, synthesis, sintering, properties.

INTRODUCTION

The carbides of the transition metals – Ti, Zr, Hf – are important ceramic materials used for high-temperature applications, due to their superior mechanical and electrical properties at elevated temperatures [1 – 3]. These materials exhibit high strength, good chemical, corrosion and oxidation resistance.

Generally the traditional methods of production of transition metals carbides allow getting powders with large micrometer size, which makes difficult the obtaining of the dense compact materials with high performance characteristics. One of the advantages of nanosized carbide powders is a relatively lower temperature of the compaction of materials, compared with submicrometer powders [8]. Recently for such nanopowders productions have been used variety methods of synthesis in solid, liquid or gaseous phases [1 – 8].

Our research is focused on the investigation of chemical processing routes to obtain nanosized powders of refractory carbides with a narrow particle size distribution. In the present study, titanium carbide (TiC) has been obtained by carbothermal reduction of a precursor prepared by sol-gel process.

EXPERIMENTAL

Two methods of precursor gels fabrication for production of TiC were used: Ti (IV) chloride, ethyleneglycol and citric acid were used in the first method (series A) and Ti (IV) n-propoxide, saccharose and acetic acid were used in the second method (series B).

In series A $TiCl_4$, citric acid and ethylene glycol are mixed in proportion 0.05M : 0.12M : 0.8M and stirred at 80 °C. Transparent gel is formed, which is evaporated at 80 °C and dried at 100 °C – 110 °C. The dried gel is heated in Ar flow with the heating rate of (150 – 200) °C/h and the thermal treatment time of 0.5 h.

In series B Ti isopropoxide + saccharose + acetic acid (Ti : C = 1 : 3.7) were used. Saccharose is dissolved in warm acetic acid (T ~ 80 °C) and cooled to the room temperature. Ti isopropoxide is slowly added and stirred approximately for 3 h. The left acetic acid is evaporated at 80 °C. The gel is dried at 100 °C – 110 °C. The dried gel is grinded and sieved through sieve and heated in Ar flow with the heating rate of (300 – 350) °C/h and the thermal treatment time of 1 h – 2 h.

After drying, the resulting xerogels are calcined under flowing argon at different temperatures ranging from 800 °C to 1400 °C with holding time from 0.5 h to 10 h.

Content of Ti, C_{total}, O, phase composition and specific surface area (SSA) was investigated. Morphology of powder particles and ceramic materials were investigated by the scanning electron microscope S4800.

Spark plasma sintering (SPS) was used for compacting investigations of this nanopowder at 1800 °C, heating rate of 100 °C/min and dwelling time of 5 min.

RESULTS AND DISCUSSION

Characteristics of series A samples are given in Table 1, Figs. 1 and 2. After treatment at 800 °C almost amorphous product was obtained (SSA appr. 230 m^2/g), consisting of some products of titanium oxide reduction

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products (lower oxides) and titanium oxycarbide. With the increase of temperature of thermal treatment also the percentage of TiC content rises, but also oxide phases still remain.

Only the sample treated at 1360 °C consists of almost only TiC phase with a small amount of TiO_2 (rutile) admixture (Fig. 1).

The SSA of the sample decreases to 30 m^2/g and the crystallite size grows up to 40 nm – 45 nm (Table 1). Sample consists of regular particles with the size of appr. 100 nm (Fig. 2).

Characteristics of series B samples are given in Table 2 and Figs. 3 and 4. As it follows from Table 2, if Ti isopropoxide is used, then comparatively pure titanium carbide is obtained at temperatures over 1360 °C. The XRD pattern of the product produced at optimal conditions with Ti-isopropoxide as starting material exhibits the intensive TiC line (Fig. 3) and only traces of oxide phases. The main admixture is free carbon (Table 2), and this could be the reason of significantly high (190 – 250 m^2/g) specific surface area of the product. The particle size of the powder obtained at 1400 °C is in the range of 50 nm – 70 nm, close to the size of crystallites (40 nm – 45 nm).

Titanium carbide containing 72.7 wt. % Ti, 6.6 wt. % O, 20.5 wt. % C_{total} and 7.2 wt. % C_{free} and with SSA of 88 m^2/g was used for compacting investigations. As it follows from Fig. 5, sintering begins at 1150 °C, but change of density ends at 1650 °C.

The density at this temperature reaches 89 % of the theoretical and does not rise until 1800 °C. This is probably due to the presence of free carbon in the sample, retarding sintering.

The grain size of material sintered at 1800 °C is 500 nm – 600 nm (Fig. 6), but the crystallite size is 100 nm – 120 nm (the crystallite sizes were calculated from XRD using Scherrer formula).

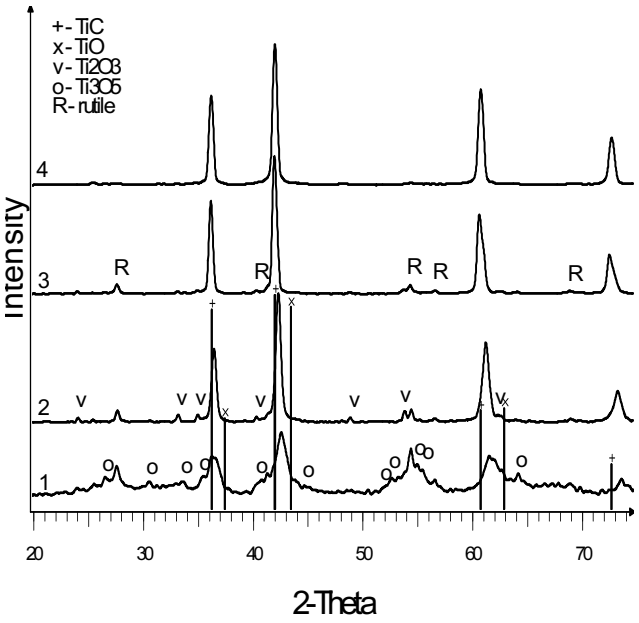
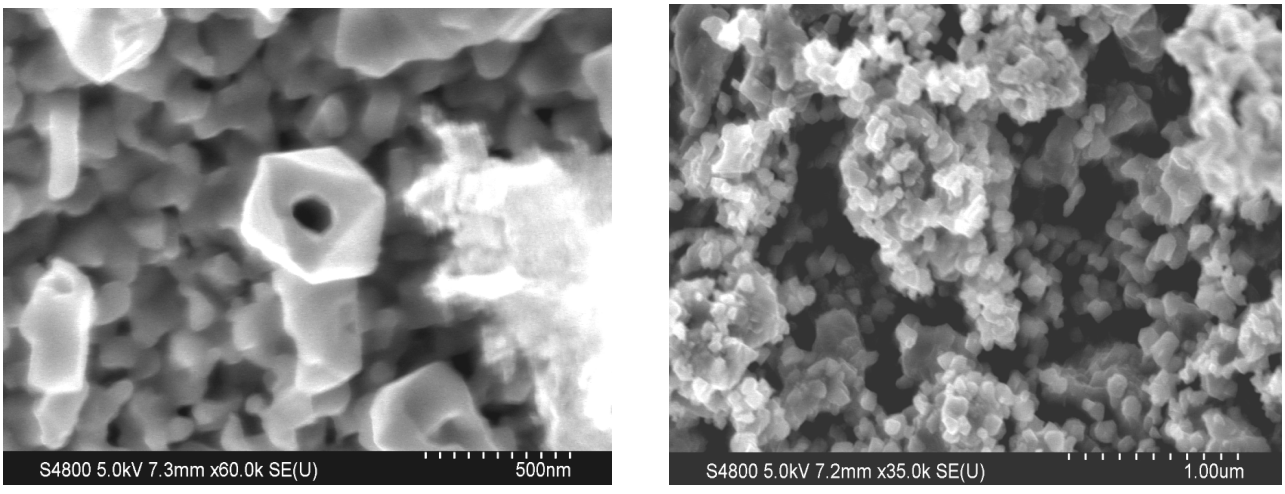


Fig. 1. The dependence of phase composition of A series samples on the temperature of thermal treatment: 800 °C (1); 1000 °C (2); 1200 °C (3) and 1360 °C (4)

Table 1. The results of thermal treatment of the gel (A series)

Temperature, °C	Thermal treatment time, h	SSA, m^2/g	Phase composition	The size of TiC crystallites, nm
800	0.5	230	Ti(C,O), Ti_2O_3, Ti_3O_5, TiO_2 (R+A)	7 (amorphous)
1000	0.5	210	TiC(O), Ti_2O_3, TiO_2 (R+A)	20
1100	0.5	200	TiC(O), Ti_2O_3, TiO_2 (R+A)	20
1200	0.5	160	TiC, TiO_2 (R), Ti_2O_3 traces	30
1260	10	90	TiC, TiO_2 (R), Ti_2O_3 traces	40
1360	1	30	TiC, TiO_2 (R) traces	42



a b

Fig. 2. Micrographs of A series nanopowders obtained at 1260 °C 10 h (a) and 1360 °C 1 h (b)

Table 2. The results of thermal treatment of the gel (B series)

T, °C	Time, h	SSA, m^2/g	Chemical analysis , wt.%					Phase composition	The size of TiC crystallites, nm
			Ti	O	N	C_{total}	C_{free}		
1350	1	240	58.5	7.8	0.04	23.2	13.2	TiC, TiO_2 (A+R) traces	30
1350	2	250	66.5	7.3	0.07	23.5	11.5	TiC, TiO_2 (R) traces	45
1360	1	190	67.0	3.2	0.15	24.7	9.3	TiC	43
1400	1	45	76.6	1.7	0.10	21.0	3.6	TiC	42

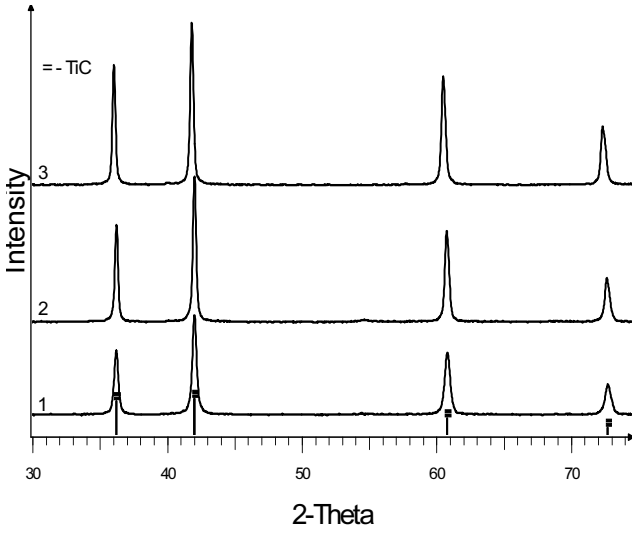


Fig. 3. The dependence of phase composition of B series samples on the temperature of thermal treatment: 1350 °C, 1 h (1); 1350 °C, 2 h (2) and 1400 °C, 1 h (3)

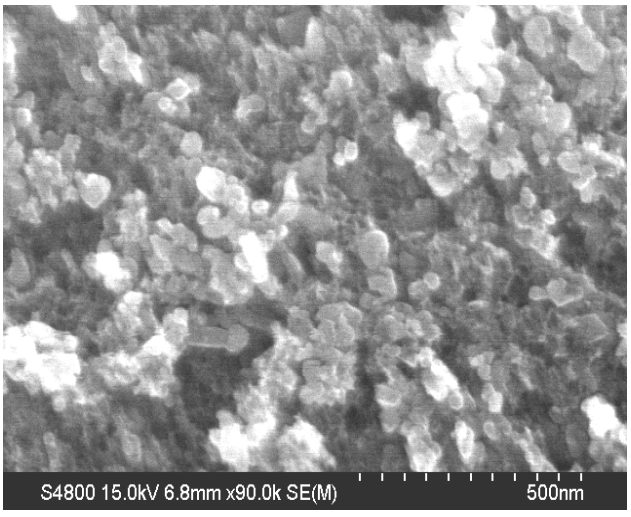


Fig. 4. Micrographs of B series nanopowders obtained at 1400 °C 1 h

A significant decrease of admixtures has been observed in ceramic material during sintering. During sintering interaction between titanium oxycarbide and free carbon occur; therefore ceramics consists of more pure TiC (Fig. 7).

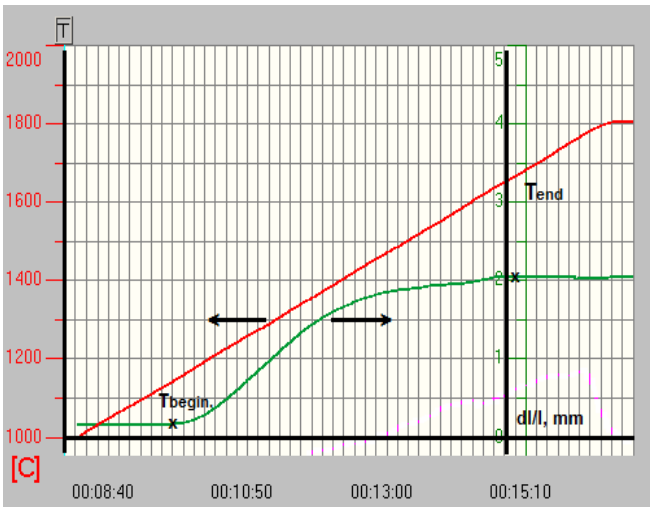


Fig. 5. Fragment of the shrinkage curve of titanium carbide in the range from 1000 °C to 1800 °C at the SPS process

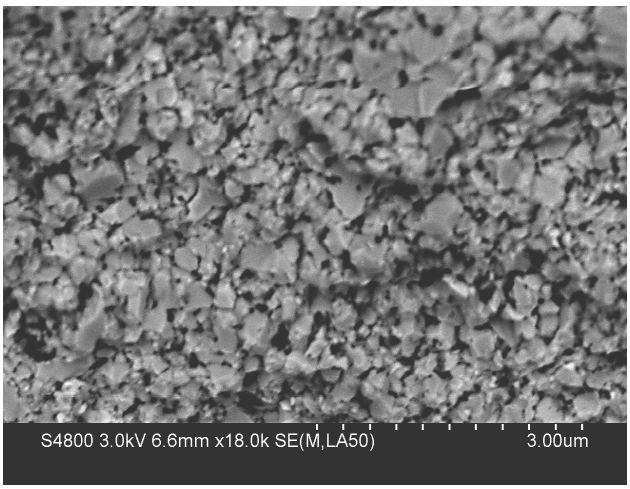


Fig. 6. Microstructure of the sample of TiC compacted at 1800 °C by SPS

CONCLUSIONS

TiC nanopowders with the specific surface area in the range of 30 m^2/g – 200 m^2/g have been produced by two methods of precursor gels fabrication of titanium carbide and the following calcination under flowing argon at different temperatures ranging from 800 °C to 1400 °C.

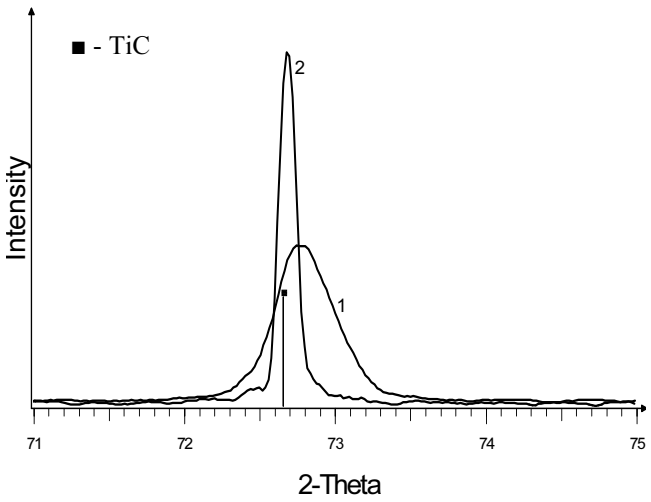


Fig. 7. Fragment of the phase composition of TiC nanopowder (1) and sample of TiC compacted at 1800 °C by SPS (2)

Samples of TiC ceramics have been prepared by the spark plasma sintering (SPS) method with the density of 89% and grain size in the range of 500 nm – 600 nm (crystallite size of 100 nm – 120 nm). Low density of sample can be explained by the presence of free carbon in the sample.

Acknowledgments

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