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The Study of the Synthesis of Nanosized Refractory Carbides by Carbothermal Reduction of Precursor Gels and their Characteristics

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In the present study, four refractory carbides – TiC, NbC, TaC and SiC – have been produced by carbothermal reduction of a precursor prepared by sol-gel and coat-mix (SiC) process. Binary hydrogels, in which the oxide gel and a pyrolysable organic compound are combined, were prepared as precursors for synthesis of corresponding carbides. The phase structure, crystallite size, morphology and specific surface area of the synthesized powders are investigated by XRD, SEM and BET respectively. Spark plasma sintering (SPS) method (up to 1850 °C, heating rate of 100 °C/min and dwelling time of 5 min.) was used for investigation of compacting of these carbides.
Keywords: transition metal carbide, SiC, nanosized powders, synthesis, SPS sintering, properties.

1. 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.

It has been proved that in many cases properties of nanostructured materials differ from those for materials produced from conventional coarse-grained polycrystals with the same composition [4]. One of the ways to get materials with fine-grained structure is application of nanoparticles as a raw component in the compacting process [5].

Recently different methods of synthesis were used for production of nanopowders – hydrolysis, hydrothermal synthesis, pyrolysis, co-precipitation method, sol-gel method, high energy milling, microwave synthesis, plasma synthesis etc. [6 – 9]. Our research is focused on the investigation of chemical processing routes to obtain nanosized powders of carbides with a narrow particle size distribution.

In the present study, four refractory carbides – TiC, NbC, TaC and SiC – have been produced by carbothermal reduction of a precursor prepared by sol-gel process.

2. EXPERIMENTAL

Binary hydrogels, in which the oxide gel and a pyrolysable organic compound are combined, were prepared as precursors for synthesis of corresponding carbides.

As shown in [10], the best results in the fabrication of TiC nanoparticles are obtained, when Ti isopropoxide, sucrose and acetic acid (Ti : C = 1 : 3.7) as raw materials were used. Sucrose was dissolved in warm acetic acid (T ~ 80 °C) and cooled to the room temperature. Ti isopropoxide was slowly added and stirred approximately for 3 h. The excess of acetic acid was evaporated at 80 °C. Then it is possible to obtain TiC nanoparticles with a specific surface area of 50 – 100 m^2/g (the heat treatment of 1350 – 1400 °C) with a relatively small content of oxygen and free carbon.

For NbC (TaC) fabrication Nb (Ta) hydroxide was precipitated from a solution of $NbCl_5$ ($TaCl_5$) (0.01 mol) in dilute HCl using ammonia. The hydroxide was washed, then suspended in water (at 0 °C for Nb and at room temperature for Ta) and treated with H_2O_2. After 1 h Nb (Ta) peroxo acid had formed. Excess of H_2O_2 and water was removed by heating at 80 °C and then sucrose solution (Nb (Ta) : C = 1 : 7.0) was added.

All the gels were dried at 100 °C – 110 °C, grinded and sieved through sieve, then heated in Ar flow with the heating rate of (300 – 350) °C/h until 1400 °C and treated for 1 h.

The precursor for SiC synthesis (Si particles covered by the layer of C) was prepared by the coat-mix processing. Si particles were mechanically mixed with phenolic or epoxy resin in a definite proportion and then thermally treated in Ar flow. At 1500 °C liquid Si reacts with C forming SiC.

Chemical composition of the nanopowder (Ti, Ta, Nb, Si, C_{total}, O) was determined by chemical analysis. Phase composition and crystallite size (the crystallite sizes were calculated from XRD using Scherrer formula) of the synthesized powders was performed via X-ray diffractometry (XRD) (Advance D8, Bruker AXS).

BET argon adsorption/desorption method was used for determination the specific surface area of nanopowders. Morphology and particle size of powder particles and microstructures of ceramic materials were investigated by the scanning electron microscope (SEM) Hitachi, S4800. Density of sintered samples was determined by the Archimedes method.

Samples of carbide ceramics were made by the methods of spark plasma sintering (SPS). Compacting by

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the SPS method was performed by the Toshiba equipment (Dr. SINTER, SPS-825.CE): at 1700 or 1850 °C, heating rate of 100 °C/min and dwelling time of 5 min, cooling with furnace. The pressing pressure was of 30 MPa. Sintering was made in vacuum.

3. RESULTS AND DISCUSSION

Characteristics of produced powders (the heat treatment at 1400 °C, for SiC – 1500 °C) are given in Table 1. All products have a small content of oxygen and to reduce it the proportion C/Me must be increased, but this increases the content of free carbon. If the conditions of synthesis are optimal (molar ratio of gel-derived C to Me, heating rate and temperature and heat-treating time) XRD analysis of the produced products shows the presence of intensive carbide lines and only traces of oxide phases (Fig. 1). In the case of tantalum carbide also the traces of Ta_2O_5 have been found.

The results show that at an appropriate molar ratio of resin-derived C to Si high purity SiC can be produced. The colour of the powder is light grey, indicating that the free carbon content is low.

For all transition metal carbides the crystallite size of the carbide phase lies in the range of 45 – 65 nm, only for silicon carbide this is of 12 – 15 nm. The specific surface of carbides treated at 1400 °C (for SiC – at 1500 °C) is of 25 – 35 m^2/g, but for TiC SSA reaches 65 – 70 m^2/g. The average particle size for all carbides is in the range of 40 – 60 nm.

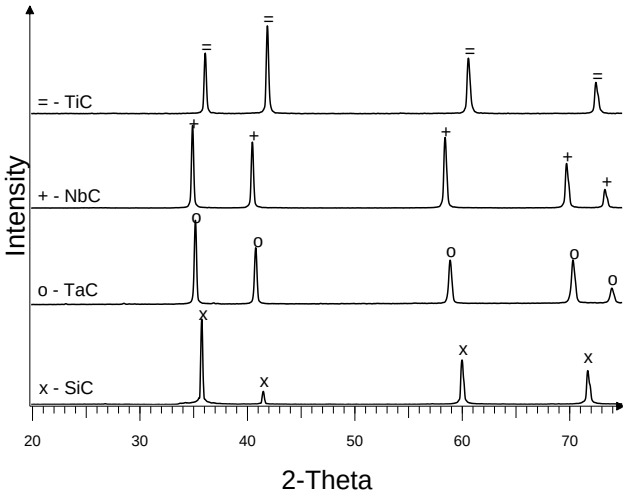


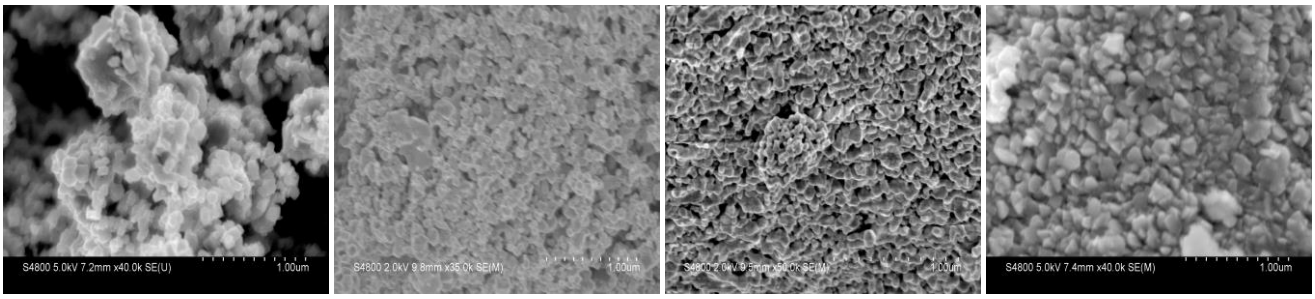
Fig. 1. XRD analysis of the produced products

In Fig. 2 there are the pictures of electron microscopy of these powders. For all transition metal (Ti, Nb, Ta) carbides the particle size is of approximately 50 – 150 nm, but for SiC the particle size is in the range of 100 – 200 nm.

Characteristics of ceramic samples produced by the SPS sintering are given in Table 2. Intense shrinkage of material begins at 1080 – 1120 °C, finishing at 1700 °C (for TiC and TaC ceramics) (Fig. 3) and at 1400 – 1850 °C (for NbC ceramics). The sample density does not reach 100 %, probably due to the presence of free carbon in samples.

Table 1. Properties of synthesized carbide nanopowders

Compound	SSA, m^2/g	d_{50}*, nm	Chemical composition, wt.%					Phase composition	Crystallite size, nm
			Me	O	N	C_{total}	C_{free}		
TiC	65-70	50	76.6	1.7	0.1	21.5	1.6	TiC	45 – 50
NbC	30-35	60	86.7	1.0	0	11.8	0.8	NbC	60 – 65
TaC	25-28	40	91.7	0.6	0	6.7	0.7	TaC	40 – 45
SiC	25-30	70	68.2	1.8	0	29.4	0.8	β-SiC	12 – 15
* – calculated from SSA									



a b c d

Fig. 2. Micrographs of nanopowders, obtained by chemical synthesis: a – TiC; b – NbC; c – TaC; d – SiC

Table 2. Properties of SPS sintered carbide ceramics

Compound	T_{begin}, °C	T_{end}, °C	Grain size, μm	Density, g/cm^3	Open porosity, %	Phase composition	Crystallite size, nm
TiC	1120	1700	0.2 – 0.6	4.0	5.3	TiC	60 – 70
NbC	1380	1850	0.6 – 1.0	6.6	8.6	NbC	60 – 80
TaC	1080	1700	0.4 – 0.8	14.1	0.4	TaC	50 – 60

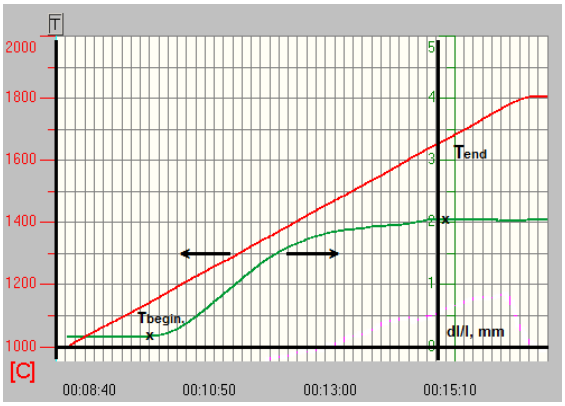


Fig. 3. Fragment of the shrinkage curve of titanium carbide in the range from 1000 °C to 1800 °C at the SPS process

The grain size of the ceramics is comparatively small (Fig. 4): for TiC ceramics the grain size is of 0.2 – 0.6 μm, when the crystallite size is of 60 – 70 nm, for NbC – 0.6 – 1.0 μm and for TaC approximately 0.4 – 0.8 μm, when the crystallite size is of 60 – 80 and 50 – 60 nm, respectively.

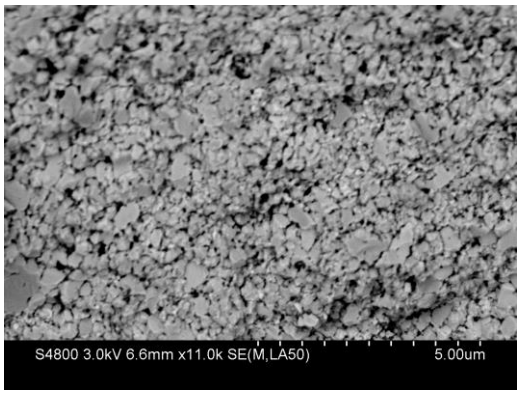


Fig. 4. Microstructure of the sample of TiC compacted at 1700 °C by SPS

A significant decrease of admixtures has been observed in ceramic material during sintering. For example, during sintering interaction between titanium oxycarbide and free carbon occur; therefore, ceramics consists of purer TiC (Fig. 5).

The obtained results are in good correspondence with the research of other authors, where nanopowders of Ti, Nb, Ta carbides are produced by different methods. Nanopowders with the particle size in the range of 20 – 100 nm were produced using reactions both in a solid, liquid or gas phase at low temperatures (550 °C) in autoclave [11 – 13], both in liquid and solid phase reactions at temperatures up to 1350 °C [14 – 17]. In spite of the relatively high temperature of synthesis, comparatively pure Ti, Nb and Ta carbides of the cubic phase as well as SiC nanopowders also could be obtained by the descripted method.

It was found during investigations, that rapid consolidation of binderless nanostructured carbide by spark plasma sintering (SPS) or similar to this method pulsed current activated sintering (PCAS) [18] results in a material with relatively fine-grained structure.

Sintering temperature of produced nanosized carbides (1700 – 1850 °C) is significantly lower than sintering temperature of submicron carbides [19, 20].

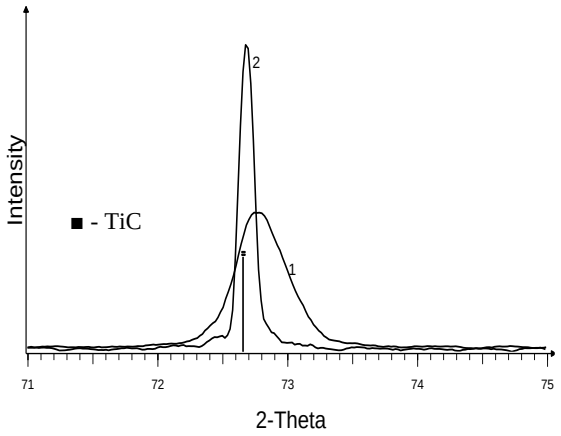


Fig. 5. Fragment of the phase composition of TiC nanopowder (1) and sample of TiC compacted at 1700 °C by SPS (2)

4. CONCLUSIONS

Nanosized transition metal (Ti, Nb, Ta) and silicon carbides were prepared. Ti isopropoxide, sucrose and acetic acid were used for sintering of TiC. For production of NbC and TaC the corresponding hydroxides are obtained from a solution of $NbCl_5$ ($TaCl_5$) (0.01 mol.) in dilute HCl using ammonia, and carburized by sucrose. All carbides are produced by thermal treatment of the gel at 1400 °C. SiC is obtained by the coat-mix processing from Si particles and phenolic or epoxy resin at 1500 °C.

Synthesized one phase products are quite pure and contain small amount of oxygen and free carbon admixtures and the average particle size is of 40 – 70 nm. Also the crystallite size of Ti, Ta and Nb carbides are in the same range that would be the evidence that the produced particles are monocrystalline.

Sintering of carbide nanopowders by the SPS method results in a relatively dense material with the fine-grained structure (grain size up to 1 μm). In comparison with the submicron carbide powders, the sintering temperature (1700 – 1850 °C) of produced nanosized carbides is noticeably lower.

They can be successfully utilized both for production of compact nanostructured materials, both as components for production of different kinds of composite materials.

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