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Preparation of nanosized W- and WC-based powders and their processing

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Abstract. Nanosized particles of tungsten and WC_{1-x} or W_2C with the average particle size of 10–14 nm have been prepared by evaporation and reduction of oxide by hydrogen, ammonia, or hydrocarbones in the radio-frequency nitrogen plasma. The consolidation of carbides containing nanoparticles by hot pressing at 1800 °C provides formation of a single WC-phase bulk material with the fine-grained microstructure.

Key words: nanosized materials, W-based powders, nitrogen plasma.

1. INTRODUCTION

During recent years increasing attention has been focused on manufacturing nanostructural W- and WC-based materials, because it will lead to essential improvement of mechanical and physical properties of these materials due to a large fraction of atoms at the grain or intercrystalline boundaries [1,2]. Main problems in fabrication of nanostructural materials involve preparation of high-quality nanosized precursor powders including uniform particulate composites and elimination of the grain growth during sintering. Several preparation routes of nanosized tungsten- or carbide-based powders such as carbothermal reduction and mechanical alloying are known [3]. Among these methods the plasma-chemical synthesis of nanosized W and WC powders by reduction of oxide and halide by methane or hydrogen in hydrogen or argon arc discharge plasma has been studied for many years [4]. However, a pure nanosized WC powder has never been obtained.

The aim of the present work is to prepare nanosized W- and WC-based powders in a nitrogen inductively coupled plasma, because nitrogen as a plasma-

forming gas makes the process more economical and will give an opportunity to produce WC composites with carbonitrides.

2. EXPERIMENTAL

The nanosized powders of W, tungsten carbide, and its particulate composite with Co are prepared by evaporation of coarse commercially available WO_3, CoO powders and their subsequent reduction and condensation into the radio-frequency nitrogen plasma.

The elaborated experimental apparatus consists of a radio-frequency (5.28 MHz) oscillator with maximum plate power 100 kW, water-cooled cylindrical reactor, heat exchanger, gas and powder supply systems, and a filter for collecting the products [5].

The flow rate of the plasma-forming gas is 8.0 m^3/h and the feed rate of the raw powder is 1.2–1.8 kg/h. The raw powder is introduced into the plasma flame through 8 tubes with a diameter of 2 mm by the carrier gas – nitrogen. The reducing gas, hydrogen, ammonia, or hydrocarbons, is injected into the reactor in the vapour region at a distance of 20–30 mm below the introduction plane of oxides. The optimal flow rate of the reducing gas is determined by studying the dependence of chemical compositions of the products on the ratio of reductor and oxygen.

The products are collected in a solution of stearic acid in hexane in order to prevent their oxidation. The chemical and phase compositions are determined by conventional chemical and X-ray powder diffraction analysis. The specific surface area (SSA) of powders is determined by the BET argon adsorption-desorption method. The powders are consolidated by hot pressing at 1600–1800 °C with the holding time one hour. The microstructure of bulk samples is investigated by a scanning electron microscope.

3. RESULTS AND DISCUSSION

According to the results of the studies, the complete reduction of tungsten oxide and the formation of nanosized W particles in the nitrogen high-temperature flow are obtained at multiple excess of hydrogen or ammonia (5–6 times) with respect to oxygen or at stechiometric ratio of carbon and oxygen C/O = 1 (Table 1).

All the prepared powders have high specific surface area and the calculated average particle size is in the range of 10–14 nm, because the low boiling temperature of the oxide ensures good conditions for complete evaporation of the particles and the high melting temperature of tungsten and carbides essentially limits the growth of the formed particles. The increase of the specific surface area with the content of carbon partially indicates presence of some amount of X-ray amorphous carbon. Chemical analysis of samples evidences that the content of nitrogen in the powder is low. It can be explained by the instability of the tungsten nitride at high temperature.

Table 1. Characteristics of the prepared powders

Raw powder	Reducing agents	Content of N, C, wt%		SSA, m^2/g	Diameter, nm	XRD
		N	C			
WO_3	H_2, H/O = 6	<0.3	–	22	14.3	W, β-W (tr)
WO_3	NH_3, H/O = 6	<0.5	–	26	12.0	W, β-W (tr)
WO_3	C_nH_m, C/O = 1	<0.3	0.6	22.7	13.6	W, β-W (tr)
WO_3	C_nH_m, C/O = 1.1	<0.3	0.7	29.1	11.9	W_2C
WO_3	C_nH_m, C/O = 1.4	<0.4	6.2	32.5	10.7	WC_{1-x}, W_2C
WO_3, CoO	C_nH_m, C/O = 1.4	<0.4	6.2	30.8	13.4	WC_{1-x}, Co, W_2C

XRD patterns of the prepared nanosized tungsten particles show only presence of the α-W and traces of the β-W phase. According to the XRD studies, additional heat-treatment of the powders at 800–850 °C leads to phase transition β-W→α-W.

The phase composition of the prepared carbides is more complicated and depends on the ratio C/O. At C/O = 1.1–1.2, the product consists of W_2C, but at C/O = 1.4 the content of carbon in the product reaches 6.2 wt% and it contains WC_{1-x}, W_2C, and obviously some amount of the X-ray amorphous carbon. Further increase of the ratio C/O and therefore increase in the products of the content of carbon up to 7.2 wt% leads to the decrease of intensities of diffraction maxima corresponding to W_2C, but there are no changes in the phases observed (Fig. 1). Additional heat-treatment of the products containing 6.3–7.3 wt% of carbon at 1400–1500 °C in argon provides formation of single WC-phase particles having specific surface area 7–15 m^2/g (Table 2).

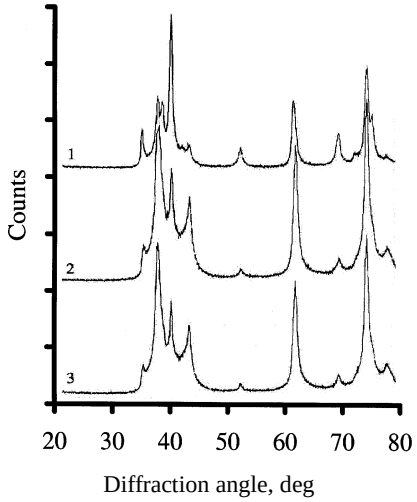

Fig. 1. XRD patterns of tungsten carbide with different carbon content (wt%) in the products: 1 – 6.3; 2 – 6.7; 3 – 7.3.

Table 2. Specific surface area and phase composition of calcinated samples

Sample	Content of C, wt%	Temperature, °C	SSA, m^2/g	XRD
1	7.3	1400	15.0	WC, W_2C (tr)
1	7.3	1500	7.5	WC
2	6.7	1500	7.4	WC
3	6.3	1500	7.1	WC, W_2C (tr)

The heat-treatment studies indicate the possibility to obtain WC bulk materials by sintering or hot-pressing process of nanosized W and tungsten carbide powders at high temperature. Figures 2 and 3 show parameters of the hot-pressing process and densification of W and carbide powders. The densification of the W powder starts at 600 °C and includes several separate stages at 1000–1250, 1600–1650, and 1700–1800 °C. Keeping of samples for an hour has little influence on densification. The consolidation of the tungsten carbide starts at 1200 °C and is very intensive in the temperature range of 1500–1700 °C, reaching maximum density at 1800 °C after 15 min.

XRD patterns of hot pressed at 1800 °C tungsten carbide samples show an essential change of the phase composition. Both samples with starting carbon content of 6.7 and 7.3 wt% contain only the WC phase (Fig. 4). Obviously high temperature and applied pressure as well as the presence of WC_{1-x} promote phase transition and formation of the WC. The microstructure of W and WC bulk specimens exhibits about oval-shaped grains having well defined boundaries, but of strongly different grain size (Figs. 5 and 6). The coarse microstructure of tungsten

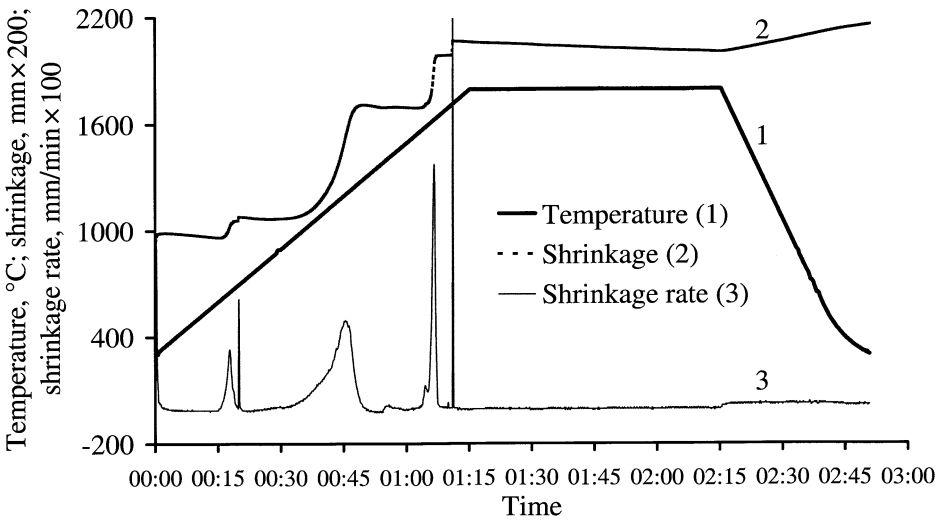

Fig. 2. Parameters of the hot-pressing process of the W-based powder.

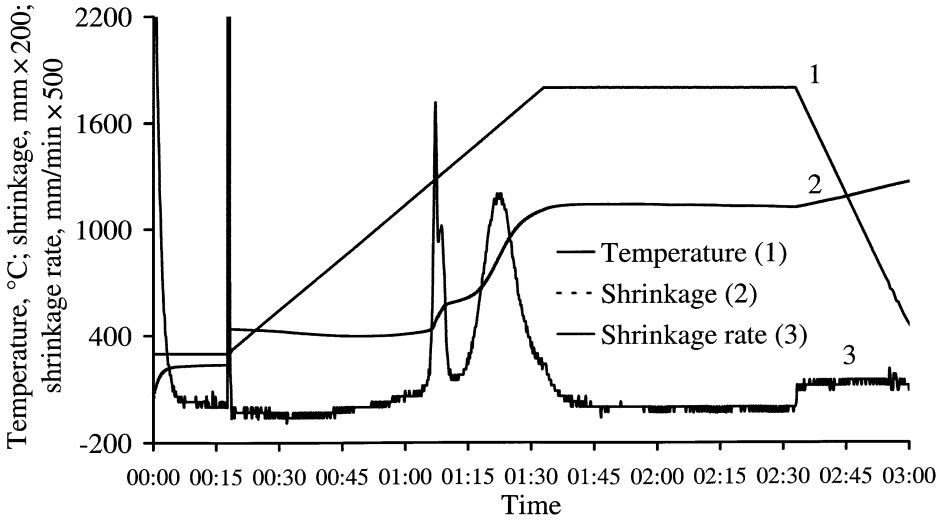

Fig. 3. Parameters of the hot-pressing process of the tungsten carbide powder.

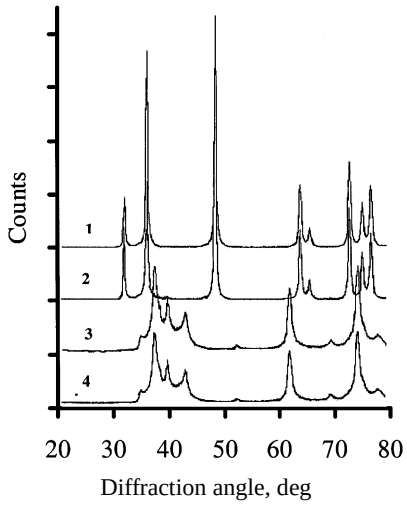

Fig. 4. XRD patterns of nanosized tungsten carbide powders (3, 4) and their hot-pressed (at 1800 °C) samples (1, 2) with carbon content in the products 6.7 wt% (curves 1 and 3) and 7.3 wt% (curves 2 and 4).

specimens with grain size of 5–10 μm demonstrates drastic grain growth during conventional hot pressing. The microstructure of WC bulk specimens is much finer and grain size is in the range of 0.5–1 μm. Further decrease of the W grain size could possibly be reached by minimizing such hot-pressing parameters as temperature and time, as well as by introducing well-known grain growth inhibitors.

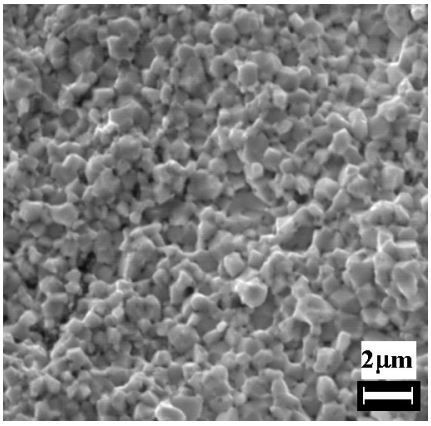

Fig. 5. Microstructure of the tungsten powder, hot-pressed at 1800 °C.

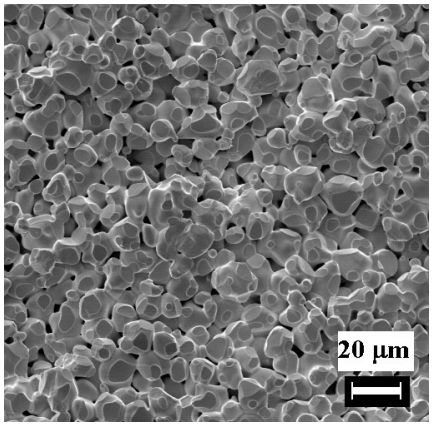

Fig. 6. Microstructure of the hot-pressed tungsten carbide powder.

4. CONCLUSIONS

1. Evaporation and reduction of tungsten oxide in the nitrogen radio-frequency plasma permit preparation of nanosized W particles with small admixture of nitrogen.

2. Evaporation and reduction of tungsten oxide by hydrocarbons at the ratio of C/O = 1.4 in the nitrogen plasma result in obtaining nanosized carbide particles with the average size of 10–12 nm, consisting of WC_{1-x} and W_2C phases.

3. Hot pressing of nanosized tungsten carbide particles at 1800 °C leads to the formation of single WC-phase parts with a fine-grained microstructure.

REFERENCES

1. Srivatsan, T. S., Woods, R., Petraroli, M., and Sudarshan, T. S. An investigation of the influence of powder particle size on microstructure and hardness of bulk samples of tungsten carbide. *Powder Technol.*, 2002, **122**, 54–60.
2. Mu-Jen Yang and German, R. M. Nanophase and superfine cemented carbides processed by powder injection moulding. *Int. J. Refract. Met. Hard Mat.*, 1998, **16**, 107–117.
3. Koc, R. and Kodambaka, S. K. Tungsten carbide (WC) synthesis from novel precursors. *J. Europ. Ceram. Soc*., 2000, **20**, 1959–1969.
4. Ishizaki, K., Egashira, T., Tanaka, K., and Celis, P. B. Direct production of ultra-fine nitrides (Si_3N_4 and AlN) and carbides (SiC, WC and TiC) powders by the arc plasma method. *J. Mater. Sci*., 1989, **24**, 3553–3559.
5. Grabis, J., Steins, I., Rasmane, D., and Heidemane, G. Nanosize YSZ-NiO powder produced by ICP technique. *J. Europ. Ceram. Soc*., 1997, **17**, 1347–1442.

Nanopulbrite valmistamine W ja WC baasil ja nende töötlemine

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Osisega 10–14 nm volfram-, WC_{1-x} ja W_2C nanopulbrite valmistamiseks kasutati oksiidide aurustamist kõrgsageduslämmastikplasmas ja taandamist vesinikus, ammoniaagis või süsivesinikus. Karbiidide nanopulbrite kompakteerimine viidi läbi kuumpressimise teel temperatuuril 1800 °C, mis võimaldas saada peeneteralise ühefaasilise mikrostruktuuriga kompaktse volframkarbiidse materjali.