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Synthesis of ultrafine cubic tungsten carbide in a discharge plasma jet

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ABSTRACT

Hexagonal tungsten carbide (WC) is widely-used for the production of metal-working tools, but there is a great interest to the cubic modification of WC. The possibility of obtaining the ultrafine cubic tungsten carbide in an electrodischarge plasma jet generated by a high-current pulsed coaxial magnetoplasma accelerator is shown in this report. According to X-ray diffraction and high resolution transmission electron microscopy the product predominantly consists of a cubic tungsten carbide phase $WC_{0.86}$ (95% mass). Lattice constant of obtained tungsten carbide is $a = 4.2536$ Å. This constant differs from the lattice constant ($a = 4.2355$ Å) for ICDD card no. 00-020-1316 (cubic WC_{1-x}) nonetheless both of them are in the possible range for cubic tungsten carbide structures. The high cooling rate, realized in the system based on coaxial magnetoplasma accelerator, provides the formation of the cubic WC lattice and the narrow range of particle size distribution (10–40 nm).

Introduction

Tungsten carbide is the basis of tools for metal cutting and rock drilling and the subject of many scientific research groups around the world [1–3]. Using modern technologies it is possible to obtain ceramic nanostructured materials with a density not less than 97% both from the pure tungsten carbide and with cobalt or nickel additives [4]. Also processes of WC ceramic sintering and coating deposition are actively investigated [5–9]. Some reports about a catalytic activity of the tungsten carbide are published [10–12].

There is a special interest to the cubic high-temperature modification of tungsten carbide [1]. Its existence at room temperature is ambiguous but significant achievements in this area have already been reported [1,13–22]. The high-temperature cubic tungsten carbide modification is characterized by the enhanced photo- and electrocatalytic activity [10,11,14] and the larger density of states near the Fermi levels [13]. The value of the superconducting transition temperature is higher than that of hexagonal carbides W_2C and WC [1]. However, the insufficient knowledge about the properties of the cubic tungsten carbide modification, in comparison with the hexagonal ones, limits its industrial application. Some difficulties of obtaining and studying this modification are connected with the narrow range of the temperature stability according to the phase diagram [1] and with the phase transition from cubic to hexagonal modification at temperatures of 700–800 °C [23]. This phase transition prevents the sintering of ceramic samples and negatively impacts on the development of this theme as the way of industrial application.

The cubic modification can be obtained by quenching from the melt [1]. The cooling rate of 10^8–10^{11} K/s is necessary to form the cubic lattice [24]. The plasmadynamic synthesis of crystalline phases in the supersonic tungsten–carbon electrodischarge plasma jet is suitable due to high temperatures and speed of plasma [3,25]. The possibility is known to obtain ultrafine crystalline materials based on titanium, silicon and boron by using the system based on a coaxial magnetoplasma accelerator (CMPA) [26–28]. Such a way the plasmadynamic method is perspective to synthesize the ultrafine cubic tungsten carbide.

Experimental

A sketch map of the system is shown in Fig. 1. It consists of three main elements such as capacitive energy storage, CMPA (1–7) and working chamber. Capacitive energy storage has the following energy parameters: a maximum charging voltage value of 5.0 kV and a maximum charging capacity of 28.8 mF.

Z-axis pinch accelerator (1–5, 7) based on the graphite electrode system and an inductor (6) are formed CMPA in general. The graphite electrode system consists of non-magnetic metal cases (1, 3) and graphite inserts (4, 7). The insulator is positioned between central electrode and metal case and formed the plasma formation zone (2, 5).

The electric signals were registered in real time by a two-channel Tektronix TDS1012 oscilloscope (OSC). Plasma flow process was recorded

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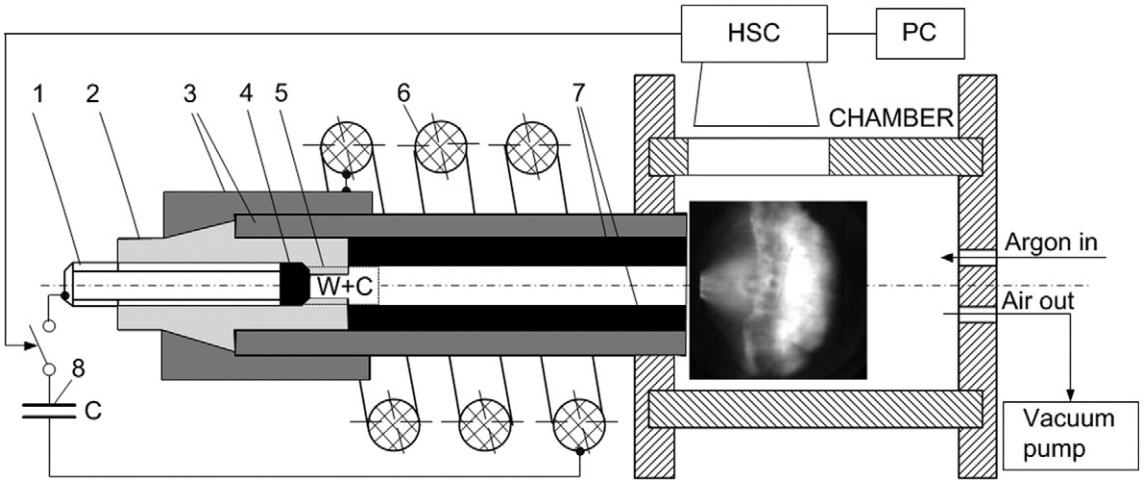

Fig. 1. Schematic diagram of the plasma jet system.

with a Photron FASTCAM SA 1.1 high-speed camera (HSC). The photoregistration system triggering was realized with pushing a button in the camera software PC suit. At certain moment the HSC triggered power keys to supply the energy to the CMPA. A typical plasma development image is shown in Fig. 1. The value of plasma speed was estimated by means of a set of images and was equal to 2.8 km/s. Also the time of plasma glow disappearing was found and therefore the cooling rate was estimated at 10^8 K/s.

In such a way powdered product was synthesized in the supersonic tungsten–carbon plasma jet flowing into the chamber filled up with argon atmosphere at room temperature and atmosphere pressure. The working chamber was preliminarily evacuated before filling up with argon. The value of charging energy was 27 kJ. The precursor in the form of tungsten and carbon black mix (0.5 g W + 0.25 g C) was put into the plasma formation zone. The mix of precursors was prepared using high-energy ball mill (SPEX Sample Prep. Mixer/Mill 8000 M). Tungsten and carbon black were mixed for 5 min in the tungsten carbide vial without using of balls. The tungsten and carbon black powders were purchased in the Chemical department of Tomsk Polytechnic University. The averaged particle sizes for tungsten and carbon black are 4.3 μm and 125 nm, respectively.

Under the influence of high currents solid precursors are converted into the plasma state, heated to the temperature of about 10,000 K [25], accelerated and shot into the chamber space, where the cooling process is initiated. The work cycle of the system was up to 0.3 ms. The chamber was opened and the powdered product (mass of 0.485 g) was collected after an hour.

X-ray diffractometry (*XRD*) was carried out using Shimadzu XRD7000 (CuKα-radiation) diffractometer with the counter monochromator Shimadzu CM-3121. Qualitative X-ray analysis was made using a database PDF2 +. Quantitative analysis was performed using independent references: WC + C and WC + W mixes with [WC]/[C] = 0.11; 0.33; 1; 3; 18.75 and [WC]/[W] = 0.25; 2.33; 9; 19; 27.4 mass ratios were prepared, scanned by the X-ray diffractometer and used for interpretation of the synthesized product diffraction pattern. The size of coherent scattering regions was estimated according to Debye–Scherrer formula. Interplanar distances and full width at half maximum values are defined with PCXRD standard software (ver. 7.00 Rel. 001).

High-resolution transmission electron microscopy (*HRTEM*) was carried out using the JEOL JEM 2100F microscope. The sample was deposited on the amorphous carbon film, preliminarily sprayed onto standard copper net. The particle size distribution histogram was made by measuring the size of several hundred particles in HRTEM pictures. An energy dispersive X-ray spectroscopy (EDS) analysis was carried out using an EDXS microscope attachment with the possibility of the scanning area visualization (STEM-image).

Scanning electron microscopy (*SEM*) was carried out using a JEOL JSM 7500F microscope. The test sample was placed on a special adhesive tape designed for the analysis of powder samples.

Results and discussion

The resulting powder product mass is less than the initial precursor mix mass. It can be explained with the losses of materials on the reactor walls and material losses during the chamber opening and powder collecting. The losses are 35% and this value is typical for our system.

Fig. 2 shows XRD patterns of the synthesized powder, initial tungsten and carbon black, TEM-image of carbon black and SEM-image of tungsten. Precursors consist of a tungsten cubic phase (2θ = 40.238°, 58.227°, 73.164°) and carbon black, which is characterized by the presence of two widened maximums. Six high-intensity maximums (2θ = 36.515°, 42.425°, 61.610°, 73.826°, 77.711°, 92.940°) of the cubic lattice appear in the XRD pattern of the synthesis product. Also the presence of five low-intensity peaks (2θ = 34.300°, 37.940°,

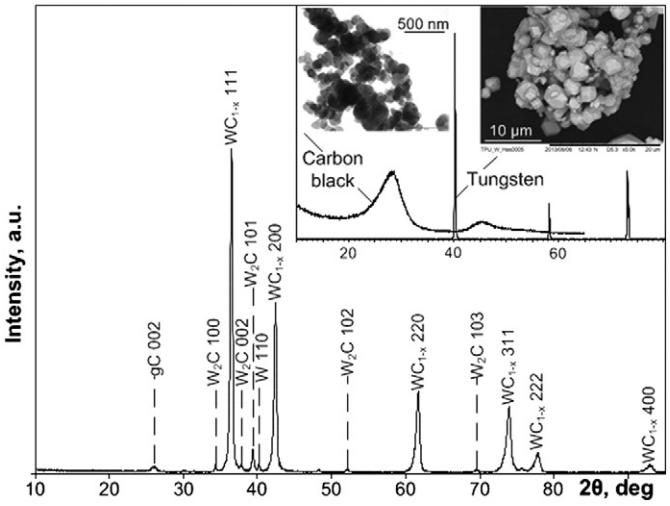

Fig. 2. XRD patterns of the synthesized powder product and precursors; TEM and SEM images of precursors.