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Synthesis and characterization of tungsten carbide fine powders

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Abstract

Fine tungsten carbide (WC) powder was prepared by solid state reaction between tungsten powder (W) and activated carbon cloth as a new carbon (C) source. The effect of temperature and time of heat treatment as well as the effect of C/W ratio on WC phase formation was studied. The results obtained by X-ray powder diffraction (XRPD) show that obtained powder is single WC. Microstructure and morphology was determinate by means of scanning electron microscopy (SEM). Brunauer–Emmett–Teller (BET) method was used for examining specific surface area and texture of obtained powders. It was found that WC powder was successfully synthesized in excess carbon after eight-hour heat treatment at relatively low temperature (1000 °C).

Keywords: WC powder; X-ray diffraction; Scanning electron microscopy; BET method

1. Introduction

Tungsten carbide belongs to the group of interstitial carbides which possess properties characteristic for both ceramics and metals. These materials have high melting point, very high hardness, low friction coefficients, low reactivity, high oxidation resistance, and good thermal and electrical conductivity [1]. This unique combination of properties makes WC appropriate for various applications such as manufacturing of cutting tools and wear-resistant parts, often in form of WC-Co hard materials. Possibility to use WC in electrocatalysis has been intensively studied since 1970s when Levy and Boudart discovered that WC possesses catalytic properties similar to those of platinum group metals [2]. WC has been used as the Pt electrocatalyst support for processes such as methanol oxidation [3–5], oxygen reduction [6,7] and nitrophenol oxidation [8,9]. Since high specific surface is essential for its effective use as catalyst support there is a permanent effort to synthesize high specific surface WC powder at temperature as low as possible in order to minimize production cost [6]. Although there is a number of different methods for WC powder synthesis almost all of them are actually based on direct carburization of tungsten or carbothermal reduction of tungsten oxide to tungsten and subsequent carburization of tungsten. It is well known that that WC can be obtained by simple heating of mixture of W powder and carbon black at temperature 1400–1600 °C. However, there are studies which have shown that the use of different sources of W and carbon can provide intimate mixing of W and C and allow formation of fine WC powder at temperatures significantly lower than 1400 °C. Elementary tungsten, tungsten trioxide (WO_3) [6,8–10] and different tungsten salts [11] have been used as tungsten source whereas carbon powders [3–8,10,12], ethylene (C_2H_4) [8], methane (CH_4) [13] and glucose [10,11] have been used as a carbon source. During thermal treatment, the tungsten salts normally transform into some form of tungsten oxide which undergoes carbothermal reduction to tungsten which finally transforms to WC by carburization. Different methods for the synthesis of WC powder such as direct carburization of tungsten powder [15], carbothermal reduction – carburization [10], mechanical milling and mechanochemical synthesis [3], gas–solid reaction [13], sol–gel procedure [7] and polymeric precursor routes using metal

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alkoxides [6,10–12,14] have been developed. In general, the main goal of ongoing research is to synthesize fine and pure WC powder at relatively low temperature using low cost procedure. The solid state reactions, which normally involve reaction between WO_3 and carbon, are conducted at relatively high temperature ranging from 1200 to 1300 °C. The synthesis temperature can be significantly lowered using techniques such as hydrothermal method or gas–solid reaction in which tungsten salts were used as a source of tungsten. Although the synthesis temperature was lowered to 900 °C, the obtained WC powders were fairly coarse, with particle size of about 1 μm [11,12].

This paper describes a method for synthesis of pure, fine WC powder at temperature as low as 1000 °C. The method consists of simple thermal treatment of a mixture of tungsten powder and viscose rayon cloth. According to the author's knowledge, viscose rayon cloth was used as a carbon source for the first time. The effects of the carbon/tungsten ratio, temperature and duration of heat treatment on properties of the obtained powders were studied.

2. Experimental

2.1. Preparation of tungsten carbide nanopowders

For this study, viscose rayon cloth (Viskoza factory, Loznica, Serbia) was used as a carbon precursor. The cloth was impregnated with a mixture of NH_4Cl and $ZnCl_2$ aqueous solutions. It was found that the addition of NH_4Cl and $ZnCl_2$ can increase the yield of reaction of carbonization [16] which was conducted at 1000 °C in a nitrogen flow. The carbonization process was followed by activation in a CO_2 flow at 850 °C for 1 h. Surface characteristics of activated carbon cloth (ACC) was reported in work by Sekulić et al. [16]. Activated carbon cloth was milled in vibrating mill for 15 min.

Commercial tungsten powder (Koch-Light Laboratories, LTD, purity 99.9%) of average grain size of 1 μm according to manufacturer specification and milled ACC as a carbon precursor were mixed in vibrating mill for 15 min. The carbon/tungsten (C/W) molar ratio was varied in the range of 1–4. The prepared mixtures with different C/W molar ratio were thermally treated at temperature ranging from 700 to 1000 °C with an increment of 100 °C. The heating rate was 1 °C/min. The mixtures were placed in a middle of tube in order to provide uniform heating. The heat treatment was conducted in argon flow for 2, 4 and 8 h. After the treatment, the furnace was cooled to the room temperature.

The carbonization and activation of viscose rayon cloth, as well as the W/C powders mixtures heat treatment were done in horizontal tube furnace (Protherm Furnaces, model PTF 16/38/250, Turkey) under a controlled nitrogen (carbonization), carbon dioxide (activation) or argon (powder mixtures treatment) flow. The employed gaseous contained less than 5 ppm O_2 and H_2O. In all experiments, a gas flow of 0.5 1 per min was used. The gaseous flow was maintained during cooling till room temperature.

2.2. Powder characterization

Adsorption and desorption of N_2 were measured on milled ACC, as well on the obtained powders, at −196 °C using the gravimetric McBain method. Specific surface area, S_{BET}, pore size distribution, mesopore including external surface area, S_{meso}, and micropore volume, V_{mic}, for the samples were calculated from the isotherms. Pore size distribution was estimated by applying BJH method [17] to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the high resolution α_s plot method [18–20]. Micropore surface, S_{mic}, was calculated by subtracting S_{meso} from S_{BET}.

SEM imaging of cloth before milling was done by Philips XL-30 DX4i scaninng electron microsope. The morphology of the milled ACC was studied by field emission scanning electron microscopy (FESEM) TESCAN Mira3 XMU at 20 kV. The morphology and microstructure of the obtained powders were examined using Tescan VEGA TS 5130 MM microscope.

Powders obtained by thermal treatment were characterized by X-ray diffraction (XRD) using Siemens D500 X-ray diffractometer with Cu Kα radiation and Ni filter. The scanning of samples was done at a speed 1°/s in a range of diffraction angle 2θ 5–120°, with the angular resolution of 0.02° for all XRD tests. Williamson–Hall analysis was used to evaluate the crystalline sizes and lattice strain. This analysis is a simplified integral breadth method where both size-induced and strain-induced broadening are deconvoluted by considering the peak width as a function of 2θ [21].

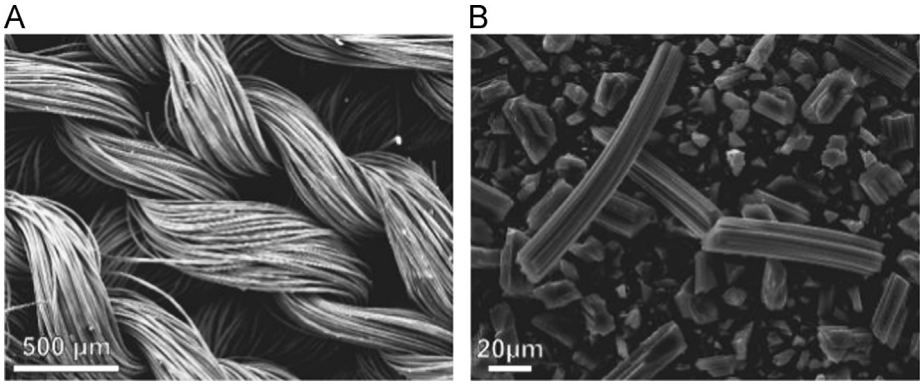

Fig. 1. FE SEM images of ACC (A) before and (B) after milling.