Powder Technology 217 (2012) 482–485

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Phase and microstructure evolution during the synthesis of WC nanopowders via thermal processing of the precursor

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ARTICLE INFO

Article history:
Received 3 April 2011
Received in revised form 25 August 2011
Accepted 3 November 2011
Available online 10 November 2011

Keywords:
WC nanopowders
Powder synthesis
Precursor
Phase evolution

ABSTRACT

Tungsten carbide (WC) nanopowders with granular particle of ~20–80 nm were prepared by a new precursor method at only 1000 °C. The process has two steps in which the amorphous WO_3–C mixtures were first produced from salt solution containing tungsten and carbon elements by air drying and subsequent calcining at 400 °C for 1 h, and secondly treated at temperatures in the range of 500–1300 °C for 1–2 h. Reaction path of the WO_3–C system was discussed by X-ray diffraction (XRD) and thermogravimetry–differential scanning calorimetry (TG–DSC), and microstructure of reaction products was studied by scanning electron microscopy (SEM) and transmission electron microscope (TEM), respectively. The results show that the phase evolution of WO_3 follows mainly $WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W \rightarrow WC$ and the incomplete carburization reaction occurs at low carburization temperature and short carburization time. In addition, the increase of carburization temperature contributes to the grain growth of WC powders which is relatively slow at 1000–1200 °C and enhanced significantly at 1200–1300 °C.

1. Introduction

WC–Co composites are a group of sintered materials with outstanding mechanical properties, such as high hardness and excellent wear resistance [1–4]. Though Ti(C, N)-based cermet is a potential replacement for WC in the cutting tool field, tungsten monocarbide presently is the most important one among all hard materials [5]. Recently, the growing consumption for printed circuit board (PCB) microdrills has promoted the fabrication of submicrometer and ultrafine WC-based hardmetals [6]. Previous studies [7–9] also had shown that the reduction of WC grain size improved significantly the mechanical properties of WC-based hardmetals. Therefore, the preparation of WC nanopowders is critical.

The traditional industrial method for the synthesis of micrometer size powders is by carbonizing W with C at 1400–1600 °C in a flowing hydrogen atmosphere [10]. The coarse grain of WC powders results from long time carbonization at high temperature. Other techniques for the synthesis of WC nanopowders have recently been reported such as mechanical alloying [11], plasma-assisted chemical vapor synthesis [12], mechanochemical synthesis [13], combustion synthesis [14], but these methods are too cumbersome, time consuming and expensive for industrial production.

More recently, Swift et al. [15] in their initial work have demonstrated the lowering of synthesis temperature of WC powders by using the "carbon-coated WO_3" technology which is facile and low-cost. The synthesizing temperature is as low as 1100 °C, but the particle size of WC powders is sub-micrometer. In this study, a new precursor method was designed to synthesize nanometer WC powders at only 1000 °C. Ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40} \cdot XH_2O$) and glucose ($C_6H_{12}O_6$) were purposely used as tungsten source and carbon source, respectively. The goal of this work was to investigate the phase and microstructure evolution of reaction products during powder synthesis, and to provide fundamental basis for the production of high-quality WC nanopowders.

2. Experimental

The starting powders used in this study were ammonium metatungstate (Zigong Cemented Carbide Corp., Ltd., China), glucose (Beijing Jingqiu Chemistry Corp. Ltd., China) and the purity is more than 99%. At first, the starting powders were dissolved into hot distilled water. After air drying the precursor solution at 30 °C for 36 h, the well-proportioned precursor mixture was obtained, and then calcined in silica tube furnace (model XD-1200NT, China) with flowing argon atmosphere at 400 °C for 1 h to form the complex oxide–carbon mixture.

All carbothermal reduction–carburization (CRC) experiments were carried out with 100 g of the oxide–carbon mixture in a vacuum carbon tube furnace (model HZA2000-140, China). The furnace was evacuated to 3.8×10^{-2} Pa using a rotary vacuum pump and then heated to the destination temperature at a rate of 7–10 °C/min. After reaching the destination temperature, the samples were isothermally treated for 1–2 h.

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doi:10.1016/j.powtec.2011.11.005

The phase evolution of reaction products was investigated by XRD (DX-2000, China) using Cu Kα radiation with a step size of 0.04°/s. The average crystallite size of the synthesized powder was estimated from the Scherrer equation [16]. Microstructural examinations of samples were observed by SEM (JSM-5900LV, Japan) and TEM (JEM-100CX, Japan). In addition, TG–DSC (NETZSCH STA 409 PC/PG, Germany) was performed under a constant Ar gas flow of 20 ml/min with a heating rate of 10 °C/min.

3. Results and discussion

3.1. Phase evolution at lower temperatures

Fig. 1 shows the XRD patterns of eight sets of samples as a function of synthesis temperature from 400 to 900 °C. According to Ref. [17], ammonium metatungstate can transform into WO_3 during calcining at 400 °C, lastly accompanied by the decomposition of all the crystalline H_2O, NH_3 and condensed H_2O. It is known that the reduction of WO_3 into its lower oxides such as $WO_{2.9}$, $WO_{2.83}$, $WO_{2.72}$ and WO_2 is feasible during carbothermal reduction. According to stepwise reduction theory of oxides [10], the reduction temperature of $WO_3 \rightarrow WO_{2.9}$ is the lowest among all reduction reactions of WO_3. However, the thermodynamical reduction temperature of $WO_{2.9}$ is about 415 °C, as shown in Eq. (1).

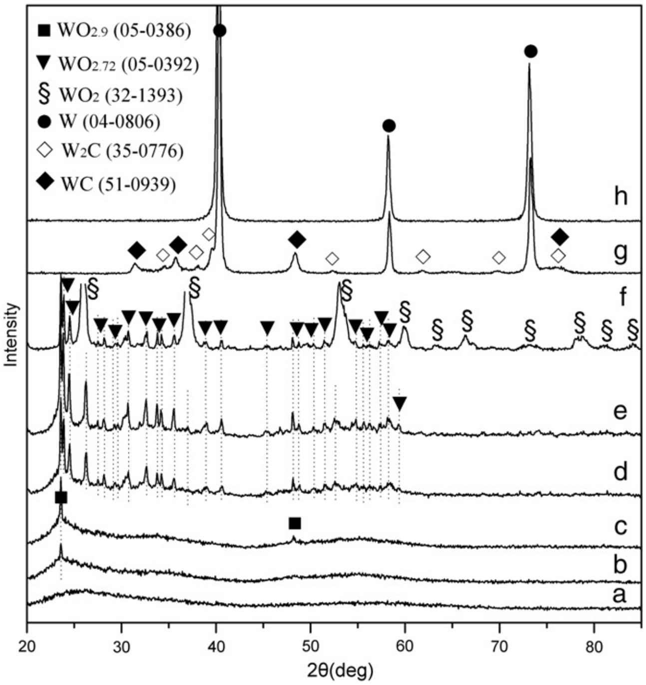

Fig. 1. XRD patterns of calcined products at 400 °C for 1 h (a) and reaction products at different CRC temperatures for 2 h: (b) 500 °C, (c) 600 °C, (d) 700 °C, (e) 750 °C, (f) 800 °C, (g) 850 °C and (h) 900 °C.

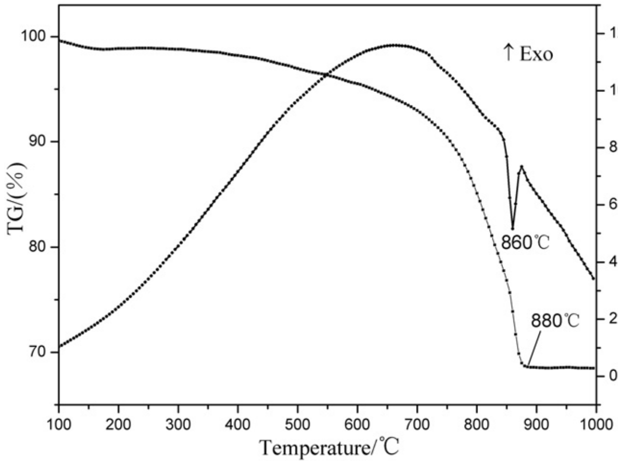

Fig. 2. TG–DSC curves of tungsten oxide–carbon mixtures measured in Ar atmosphere.

$$10WO_3(s) + C(s) = 10WO_{2.9}(s) + CO(g) \qquad (1)$$
$$\Delta G_T = 109720\text{–}159.401\ \ T(J/mol)$$

Obviously, this reaction can not thermodynamically occur during calcining the precursor mixture at 400 °C for 1 h. Therefore, the calcined products at 400 °C (in Fig. 1a) are just oxide (WO_3)–carbon mixtures. Note that the thermodynamic data of individual reactants, used for the calculation of standard free energy of Reactions (1)–(4), were taken from the handbooks [18].

The peak broadening of WO_3 has been clearly observed in Fig. 1a. The peak broadening of WO_3 is closely related to its fine crystallinity, which can be testified by the fact that crystalline size of WO_3 calculated by Scherrer equation is estimated to be only ~1.9 nm in Fig. 1a. It indicates that the WO_3–C mixtures are of amorphous structure. In other words, C and W elements in the oxide–carbon mixture have been mixed homogeneously at molecular level.

From Fig. 1b and c, we have observed the appearance of $WO_{2.9}$ (JCPDS 05-0386) phase. It implies that the reduction of $WO_3 \rightarrow WO_{2.9}$

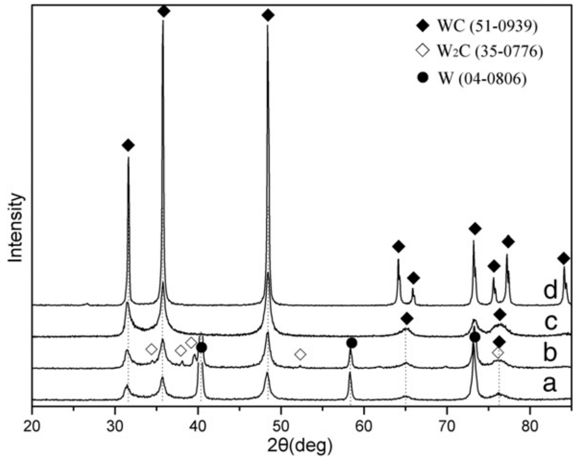

Fig. 3. XRD patterns of reaction products at higher temperatures: (a) 950 °C for 2 h, (b) 1000 °C for 1 h, (c) 1000 °C for 2 h and (d) 1300 °C for 2 h.

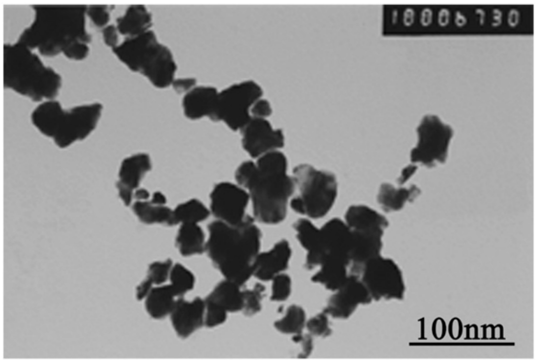

Fig. 4. TEM image of WC powders obtained at 1000 °C for 2 h.