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Phase evolution in the synthesis of WC–Co–Cr_3C_2–VC nanocomposite powders from precursors

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ABSTRACT

WC–Co–Cr_3C_2–VC nanocomposite powders were prepared by a new precursor method, in which the amorphous oxides–C mixtures were first produced from salt solution containing tungsten, cobalt, vanadium, chromium and carbon elements by air drying and subsequent calcining at 350 °C for 1 h, and secondly reduced and carbonized at high temperature. Phase evolution of the reaction products was investigated systemically. The results show that the amorphous oxides–C mixtures contribute to reduction of synthesis temperature. The phase evolution of tungsten oxides follows mainly $WO_3 \rightarrow WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W \rightarrow WC$. During the whole process of powder synthesis, Co element reacts easily with W and C elements to form η phases (such as Co_3W_3C, Co_6W_6C and $Co_3W_9C_4$). Synthesis time can promote the formation of WC phase powders, but the elimination of η phases strongly depends on synthesis temperature. At 1100 °C for 2 h, the pure-phased WC–Co–Cr_3C_2–VC nanocomposite powders with granular particle of ~100–200 nm were obtained. The significant grain growth occurs especially at 1300–1400 °C.

1. Introduction

WC-based cemented carbides have many industrial applications in such fields for cutting metal, drilling, and mining under severe conditions, because of their high performance of hardness, toughness and wear resistance [1]. Owing to its high brittleness, tungsten carbide is typically used in the form of a metal matrix composite with cobalt as the matrix. Previous investigations have shown that the toughness and hardness increase simultaneously with the refining of WC [2]. Thus, the production of nanosized WC–Co powders is critical. Also, the addition of several carbides such as VC and Cr_3C_2 is beneficial to the reduction of WC grain size [3,4]. Morton et al. [5] suggested that a mixture of VC with at least one of the other grain growth inhibitors may be the best way to control the grain growth throughout the entire sintering.

The traditional industrial method for the synthesis of WC micropowders is by carbonizing W with C at about 1400 °C in a flowing hydrogen atmosphere [6,7]. The coarse grain of WC powders results from long-time carbonization at high temperature. Due to the disadvantages of the conventional route, other techniques for the synthesis of WC and WC–Co nanopowders have recently been reported, such as thermal plasma synthesis [8], mechanical alloying [9], mechanochemical synthesis [10], combustion synthesis [11], spray conversion process [12], etc. but these methods are too cumbersome, time consuming and expensive for industrial production.

In the present paper, we propose a new precursor method for rapid synthesizing WC–Co–Cr_3C_2–VC nanocomposite powders at low temperature. Ammonium metatungstate (AMT, $(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), ammonium dichromate($(NH_4)_2Cr_2O_7$), ammonium vanadate ($NH_4VO_3$) and glucose ($C_6H_{12}O_6$) were purposely used as starting materials. The goal of this work was mainly to investigate the phase evolution of reaction products during powder synthesis, and to provide fundamental basis for the production of high-quality WC–Co–Cr_3C_2–VC nanopowders.

2. Experimental procedure

Water-soluble salts of ammonium metatungstate (Zigong Cemented Carbide Corp., Ltd., China), cobalt nitrate (Chengdu Jinshan Chemistry Agent Corp. Ltd., China), ammonium dichromate (Chengdu Jinshan Chemistry Agent Corp. Ltd., China), ammonium vanadate (Chengdu Jinshan Chemistry Agent Corp. Ltd., China) and glucose (Beijing Jingqiu Chemistry Corp. Ltd., China) were mixed in distilled water, in a ratio according to the composition of WC–8Co–0.3Cr_3C_2–0.2VC (in wt.%). The purity of all the starting powders was more than 99%. 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

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(model KTL-1600, China) under flowing Ar gas (99.99% purity) at 350 °C for 1 h to form the complex oxide–carbon mixture. And then, the mixture of 50 g was weighted, and directly reduced and carbonized in the tube furnace under flowing Ar gas. After reaching the carburization temperature, the samples were isothermal treated for 0–4 h.

The phase composition analysis of reaction products was investigated by X-ray diffraction (XRD) (model DX-2000, China) using CuKα radiation with a step size of 0.04°/s. The average crystallite size of the synthesized powder was estimated from the Scherrer equation [13]. The morphology and particle size analysis was also done by the use of SEM (Model S4800, Hitachi, Japan).

3. Results and discussion

Fig. 1 shows the XRD patterns of samples as a function of synthesis temperature from 350 to 900 °C. To facilitate discussion, the effect of vanadium and chromium on phase analysis was not considered due to the addition of a trace quantity of ammonium dichromate and ammonium vanadate. According to Ref. [14], ammonium metatungstate can transform into WO_3 during calcining at 350 °C. In addition, cobalt nitrate can be decomposed into Co_3O_4 or Co_2O_3 at about 300 °C [15]. For the reactants of WO_3, Co_3O_4 (or Co_2O_3) and carbon, $CoWO_4$ can form at low temperature because the ΔG values for the formation reaction of $CoWO_4$ phase are lower than zero [16]. However, the complete reduction temperatures of tungsten and cobalt oxides are more than 350 °C [16,17]. Therefore, the calcined products at 350 °C (in Fig. 1b) are just V/Cr-doped W/Co oxides–carbon mixtures. Fig. 1a shows the diffraction peaks of single-phase WO_3 powders as reference phase whose purity is more than 99%. There are more than two peaks for single-phase WO_3 in Fig. 1a, and yet only an apparent and smooth "peak" is shown in the diffraction patterns of the V/Cr-doped W/Co oxides–carbon mixtures obtained at 350 °C for 1 h (in Fig. 1b). The broadening peak in Fig. 1b locates at about 20–35°, in which there are five strongest peaks of single-phase WO_3 in Fig. 1a, (002) peak in 23.143°, (020) peak in 23.643°, (200) peak in 24.366°, (−202) peak in 33.575° and (202) peak in 34.034°, respectively. These peaks in Fig. 1b are so broad that the pattern appears more like that from an amorphous material than a crystalline material. It indicates that the oxides–carbon mixtures are of amorphous structure. In other words, C, W, Co, V and Cr elements in the oxides–carbon mixtures have been mixed homogeneously at molecular level. Noting that the diffraction peak in Fig. 1c shifts toward high angle compared with that in Fig. 1b. It seems that the reduction reaction of tungsten and cobalt oxides has started at 450 °C, in line with the experimental result of Ref. [16]. From Fig. 1d and e, $WO_{2.9}$ (JCPDS 05-0386) phase appears in the reaction products at 550 °C and 650 °C. At 750 °C, $WO_{2.9}$ phase in the reaction products disappears and two other phases of $WO_{2.72}$ (JCPDS 05-0392) and WO_2 (JCPDS 32-1393) occur in Fig. 1f. Here, $WO_{2.72}$ and WO_2 can be obtained via the Reactions (1) and (2).

$$50/9WO_{2.9}(s) + C\ (s) = 50/9WO_{2.72}(s) + CO\ (g) \quad \Delta G_T = 97729\text{–}156.740\ T\ (J/mol) \tag{1}$$

$$25/18WO_{2.72}(s) + C(s)\ 25/18WO_2(s) + CO(g) \quad \Delta G_T = 148247\text{–}160.921\ T\ (J/mol) \tag{2}$$

From Fig. 1g, it can be observed that the main phases in the reaction productions are WO_2 and W (JCPDS 04-0806), while the rest phase is a small amount of Co_6W_6C (JCPDS 22-0597), so called as η

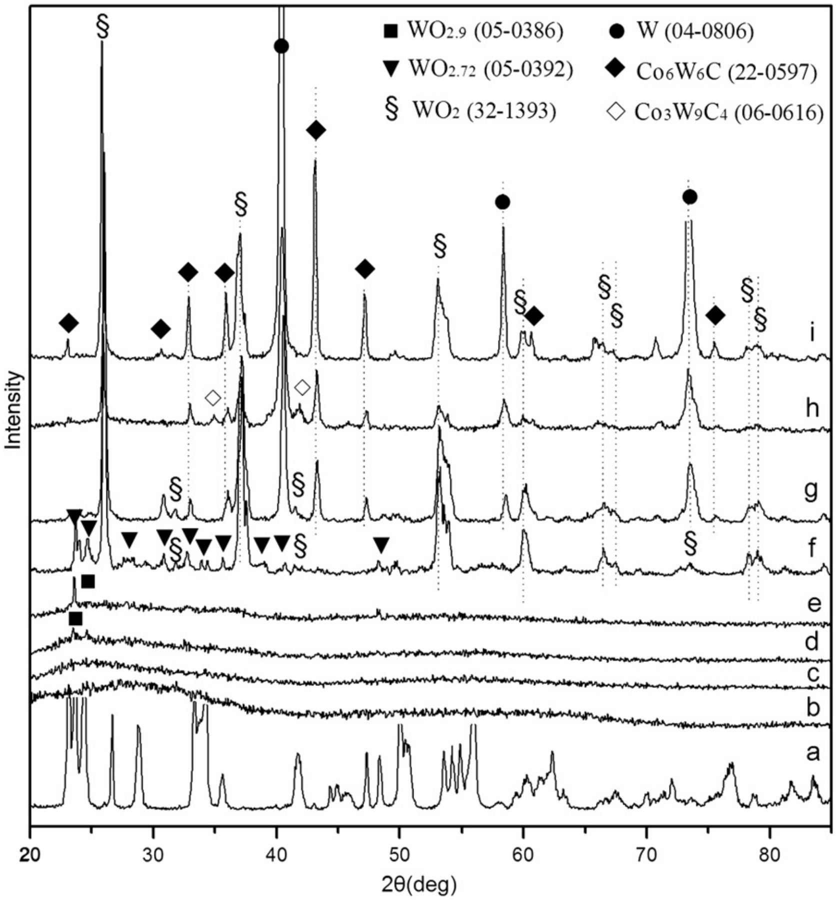

Fig. 1. XRD patterns of WO_3 (reference powder) (a), calcined products at 350 °C for 1 h (b) and reaction products at different CRC temperatures for 2 h: (c) 450 °C, (d) 550 °C, (e) 650 °C, (f) 750 °C, (g) 800 °C, (h) 850 °C and (i) 900 °C.