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Acceleration effect of cobalt on carburization of tungsten at low temperature

Wangbin Zhan [a], Haibin Wang [a], Shuhua Liang [b], Xuemei Liu [a], Xiaoyan Song [a, *]

[a] College of Materials Science and Engineering, Key Laboratory of Advanced Functional Materials, Education Ministry of China, Beijing University of Technology, Beijing, 100124, China
[b] School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China

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ABSTRACT

The acceleration effect of cobalt on carburization of tungsten at low temperatures was studied by a series of experiments of W, C and Co reactions and theoretical evaluations. Due to Co addition, the formation temperature of WC was greatly reduced (e.g. a decrease from 1300 °C to 850 °C by addition of 1.0 wt% Co). Below the formation temperature of the ternary phase, the converted fraction of W carburization increases with increased Co. Modeling of reaction kinetics revealed that the process of W carburization is dominated by carbon diffusion, and the reaction rate constant is increased much with the increase of Co. The mechanism was proposed that Co acts as the medium for rapid diffusion of C atoms and promotes W carburization by accelerating reaction diffusion kinetics. The present findings will facilitate to develop methods for synthesis of WC-Co composite powders at low temperatures.

1. Introduction

WC-Co cemented carbides are widely used in industries as significant tool materials due to the excellent combination of hardness, wear resistance and fracture strength [1–3]. The conventional method for preparing WC-Co powder is mixing Co with WC particles which are synthesized by W carburization reaction at high temperatures (generally above 1300 °C [4]) As a reason, the submicron or nanoscale WC particles are difficult to obtain due to rapid coarsening at high carburization temperatures. Many methods have been developed to prepare fine WC powders by reducing reaction temperature or shortening holding time, such as spray conversion process [5], co-precipitation [6,7], serial chemical reactions [8], and in-situ reduction and carburization [9–11]. Concerning these methods, Co is involved in the intermediate reaction products. However, the role of Co in the process of WC formation reaction has not been deeply understood yet. Kim et al. [12] prepared the precursor powder and used H_2 as the reduction atmosphere and CO as the carburization atmosphere, and found that the time for reduction and carburization was shortened with increasing Co content. Zhang et al. [13] proposed that Co played a role as catalyst during the reduction process of ammonium paratungstate. Systematic studies are thus needed to describe quantitatively the effect of Co on the behavior of W carburization reaction and the mechanisms.

In this paper, we performed a series of simple experiments using W, C and Co powders as raw materials, in order to study the effect of Co addition on the solid-state W carburization reaction and deduce the mechanism for the reaction kinetics. Understanding the law of controlling the Co-assisted W carburization reaction, means that a method of preparing WC-Co composite powder at low temperatures can be developed.

2. Experimental

The tungsten (99.95% purity), cobalt (99.5% purity) and carbon black (99.8% purity) powders were used as the raw materials, and their morphologies are shown in Fig. 1. The powders were mixed with different Co additions in a range of 0-20 wt%. The powder materials were mixed by ball-milling with a rotation speed of 200 rpm for 20 h and a ball-to-powder weight ratio of 3:1, and pure ethanol was used as a liquid medium. Both the vial and milling balls were made of cemented tungsten carbides. The as-milled powder mixture was put in a tube furnace filled with gas of Ar and 5% H_2. To investigate the reaction process of tungsten carburization, the samples of powder mixtures with a different Co contents were heated with a rate of 6.6 °C/min to the specified temperature and held for 3 h, then cooled to 400 °C with a rate of 6.6 °C/min. Below

* Corresponding author.
E-mail address: xysong@bjut.edu.cn (X. Song).

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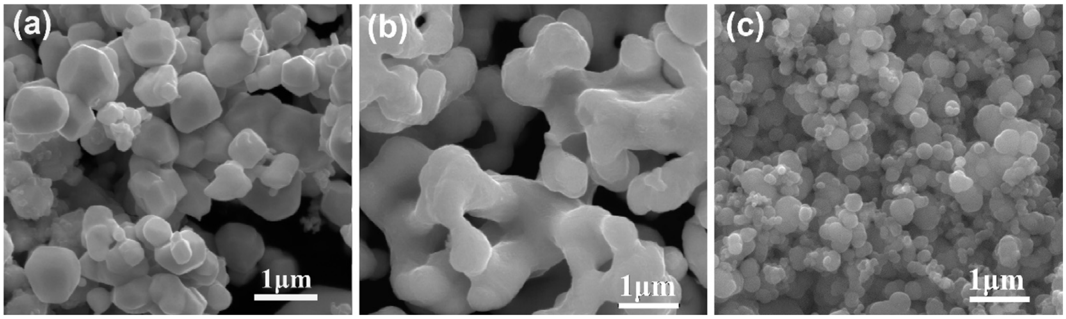

Fig. 1. Morphology of raw powder materials: (a) tungsten, (b) cobalt, (c) carbon black.

400 °C, the samples had natural cooling to room temperature. Isothermal heat-treatment was also performed at 800 °C for different holding times.

The phase constitution of powder samples was examined by the X-ray diffraction (XRD, Ultima IV) with CuK_α radiation. The morphology of the powder particles were observed by the scanning electron microscopy (SEM, Nova NanoSEM 200) using the mode of secondary electron image.

3. Results and discussion

3.1. Effect of cobalt at different temperatures

The effect of Co addition on the reaction of tungsten carburization was firstly investigated for different temperatures with a constant holding time of 3 h. Fig. 2 shows the comparison of the reaction products of tungsten carburization with and without 20 wt% Co addition. As the XRD results shown in Fig. 2(a), for no Co addition in the raw powders, the W powder almost had no carburization at temperatures below 850 °C. Above this temperature, W starts carburization and W_2C is firstly formed as the reaction product. With further increasing temperature to 1000 °C, diffraction peaks of WC appeared in the XRD pattern, indicating the formation of WC by carburization depends strongly on the temperature, and a critical temperature is required. At 1300 °C, pure WC was obtained for the raw powders with no Co addition.

In contrast, as shown in Fig. 2(b), where 20 wt% Co was added in the raw powders to examine its effect on W carburization, both the W_2C and WC formation temperatures obviously decreased as compared with those without Co addition (Fig. 2(a)). It indicates that Co addition facilitates W carburization and also phase transformation of $W_2C \rightarrow WC$ at lower temperatures. WC was obtained with a little W_2C at 850 °C. With further increasing temperature to 900 °C, the ternary phase of Co_6W_6C (generally denoted as η phase, in forms of Co_3W_3C and Co_6W_6C [14,15]) appeared in the reaction products, along with WC and W_2C. With the temperature increased to 950 °C, the number of W_2C peaks decreased, and at 1000 °C W_2C disappeared, leading to WC as the main phase and Co_6W_6C and Co coexisting in the reaction products.

As seen in Fig. 2, at temperatures below 900 °C, the phases in the products of W carburization are W, W_2C and WC in the cases with and without Co addition, respectively. The contents of the three phases can be evaluated by the adiabatic method, as given in Equation (1) [16,17],

$$X_j = \left(\frac{K_i^j}{I_j} \sum_{j=1}^{n} \frac{I_j}{K_i^j} \right)^{-1} \quad (1)$$

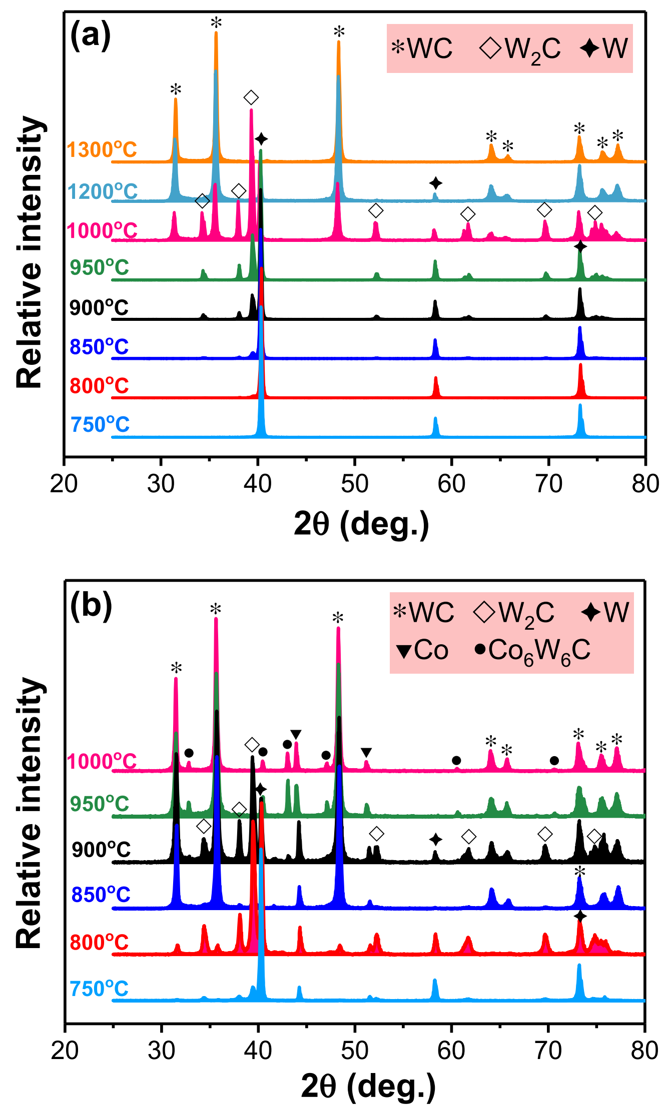

Fig. 2. XRD patterns of the reaction products of tungsten carburization at a series of temperatures with different cobalt contents in the raw powders: (a) 0 wt%, (b) 20 wt%.

$$K_i^j = \frac{K_j}{K_i} \quad (2)$$

where j denotes one phase in the material, X_j represents the weight fraction of the component j phase, i is representative for the phase selected to work as an internal standard, and I_j denotes the