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In situ synthesis of WC–Co nanocomposite powder via core–shell structure formation

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ABSTRACT

Cemented carbide WC–Co nanocomposite powders were synthesized through in situ reduction and carbonization of a core/shell precursor in vacuum. Samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The results revealed that WC–Co composite powders can be obtained at 950 °C for 1 h and the particle size is in the range from 30 to 50 nm with good dispersion. The formation mechanism of the WC–Co composite by in situ reduction and carbonization reactions was proposed. The preparation process could be divided into three steps: first, the reagents were dissolved and mixed to an aqueous solution; second step is to synthesize a carbon encapsulated core/shell nanostructure precursor using hydrothermal route, and finally, in situ reduction and carbonization of the precursor to the desired nanocomposite powders in vacuum.

1. Introduction

With inimitable properties, such as excellent wear resistance, high hardness and toughness, WC–Co has been widely used in military, aerospace, automotive, electronics, mining and machining [1–3]. Furthermore, the hardness and the strength of cemented carbides increase remarkably when the grain size is reduced to a range of nanometer, as well as the toughness improves greatly [4–7]. In the previous twenty years, research and preparation of nanocrystalline WC–Co cemented carbides has become one of the hot issues in the field of high-performance hard materials [8,9].

The conventional methods involve production of WC and Co separately, and forming the cement powder by mixing the two constituents [10]. The results have shown that the conventional methods are difficult to prepare nanostructured alloys. A crucial step in the preparation of nano grade cemented carbides is to directly obtain homogeneous nanocrystalline cemented carbide powder of WC–Co. Nowadays, many methods have been developed to synthesize WC–Co nanocomposite powders, such as mechanical alloying [11], co-precipitation [12], spray conversion process [13,14], and high energy ball milling [15,16]. Most of the methods mentioned above involve many disadvantages [17–19], such as the complicated processing procedures, the use of some special equipment, uncontrollable reaction gas atmosphere, and high carbonization temperature. To obtain high-performance hard materials, it is necessary to develop an inexpensive and facile method which uses simply process, user-friendly reagents and easy-operating equipments to synthesize pure phase configuration and uniformity of different components.

To directly prepare nanocrystalline powder of WC–Co, an essential step in the process is to prepare a precursor mixing two or more compounds [5]. Core/shell structured nanoparticles are constructed of cores and shells of different chemical compositions, which are now attracting more and more interest to be investigated [20,21]. Presently, core/shell structured nanoparticles with a carbon shell have stimulated great interest [22]. A series of works have been done on the synthesis of metal@C, oxides@C or compound@C [23–25]. Particularly, the carbonaceous sheath is penetrable for small molecules such as NH_3, CO or CO_2, which is in favor of the reaction carried out smoothly. So this idea can be used to synthesize core/shell nanoparticles in which the core is a compound of tungsten and cobalt, and the shell is carbon. Then it can be converted to uniform nanostructured WC–Co powders by in situ reduction and carburization without expensive reductive gas and complex equipment. However, up until now, this method has not been developed as the post synthesis methods, while relative reports are rare.

In this work, we will show a facile method to prepare nanometer WC–Co composite powders. Here, the hydrothermal method was adopted to prepare the carbon-shelled core–shell precursor to which the elemental W, Co and C are tightly mixed

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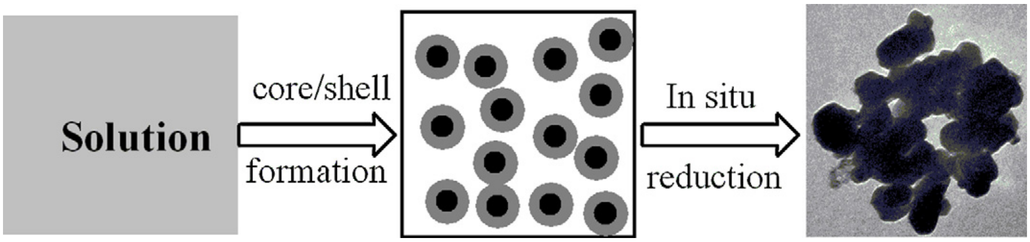

Fig. 1. The schematic illustration of preparation mechanism of WC–Co nanocomposite powders.

together. The WC–Co nanocomposite powders were obtained through in situ reduction–carbonization of the precursor at lower temperature and shorter time in vacuum. The formation mechanism of the WC–Co composite powders was explored.

2. Experimental details

Commercial ammonium metatungstate [AMT, $((NH_4)_6(H_2W_{12}O_{40})\cdot 4H_2O)$], cobalt chloride ($CoCl_2\cdot 6H_2O$) and soluble starch $(C_6H_{10}O_5)_n$ (molecular weight 342.29) were used as the source of W, Co and C, respectively. All of the reagents used were of analytical grade, which were purchased from Chengdu Kelong Chemical plant. In order to form a final product of WC–10 wt%Co, $CoCl_2\cdot 6H_2O$ (0.4 g) and $(C_6H_{10}O_5)_n$ (0.69 g) were together dissolved in 40 ml deionized water to form a transparent purple solution. AMT (1.17 g) was dissolved in 20 ml deionized water under vigorous stirring at 50 °C. After being completely dissolved, the solution was mixed with the above mentioned solution and added into a 100 ml capacity Teflon-lined autoclave. The autoclave was sealed into a stainless steel tank and maintained at 200 °C for 8 h without shaking or stirring. When the autoclave had been naturally cooled to room temperature, the products were taken out and diluted by adding 100 ml deionized water to form suspension. The puce precursor powders were obtained by spray-drying the suspension with hot air at 250 °C with a solution feeding rate of 25 ml min^{-1}. Finally, the target products were obtained by heating the precursor powders in a vacuum furnace at 950 °C for 1 h, with the temperature rate increase of 10 K min^{-1}.

Phase identification was performed by an X-ray diffractometer (XD-3, Purkinje, Beijing) using Cu Kα radiation (λ = 0.15406 nm) at a scanning rate of 0.02°/s in the 2θ range of 30–88°. The transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were operated at a FEI Tecnai-G2F20 using an accelerating voltage of 200 kV.

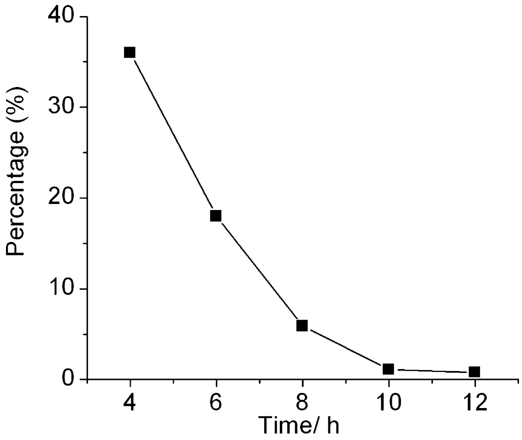

Fig. 2. The function of the amount of residual mental ions versus hydrothermal time.

3. Results and discussion

Convenient strategy of WC–Co nanocomposite is schematically shown in Fig. 1. The whole progress involved three primary steps. The first step is to prepare and mix aqueous solutions of the precursor compounds. The second step is to prepare the nanostructured core/shell precursor using hydrothermal and spray drying. The last step is in situ reduction and carbonization to obtain the desired nanocrystalline powder.

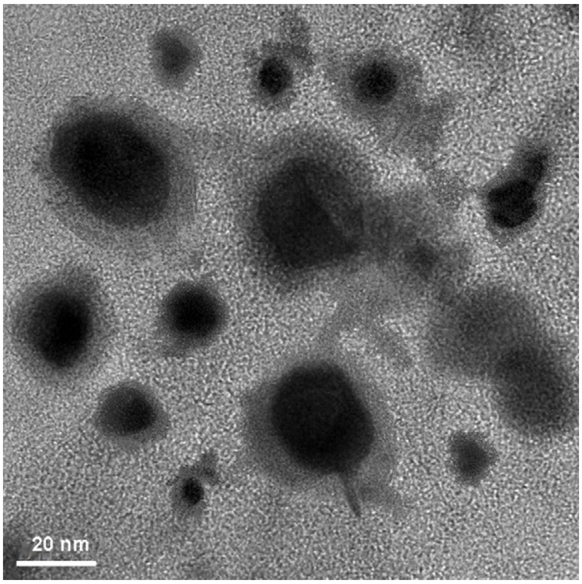

Fig. 3. HRTEM images of the as-prepared precursor.

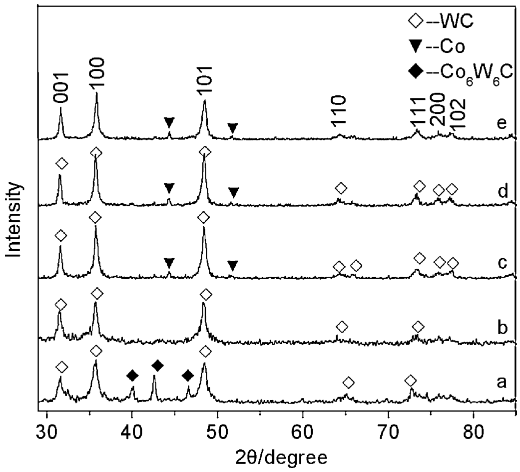

Fig. 4. XRD patterns of the samples prepared at: (a) 850 °C, 1 h; (b) 900 °C, 1 h; (c) 950 °C, 1 h; (d) 1000 °C, 1 h; (e) 1000 °C, 4 h.