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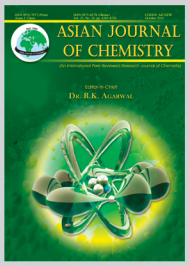

Synthesis of Ultrafine WC-Co Core-shell Composite Powders by Chemical Reduction Method

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The WC-Co core-shell composite powders were prepared by a solution chemical reduction method. The resulting ultrafine composite powders were investigated by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy, respectively. The core-shell microstructure (tungsten carbide coated with cobalt shell) was confirmed by the characterization results. It reveals that the present chemical reduction method is an effective route to synthesize ultrafine WC-Co core-shell composites, which would be benefit to inhibit the discontinuous grain growth and binder pooling during the sintering cemented carbide.

Key Words: Core-shell, WC-Co, Composite.

INTRODUCTION

WC-Co cemented carbides are widely used in many industrial fields including cutting tools, mining tools, saw blade tips, milling cutters, machine tools, cement drills and wear parts, owing to their exceptional high hardness, excellent wear resistance and better toughness than that of other hard materials[1-4]. When the grain size is reduced to a range of submicron meter or nanometer, the hardness and the strength of cemented carbides have a remarkable increasing as anticipated from the well-known empirical Hall-Petch relationship[5] and the toughness and ductility of the materials improve greatly for the increased volume fraction of grain boundaries, thus showing an excellent combined mechanical properties of the hard material[6]. Hence, ultrafine WC-Co composite powder has attracted substantial interest in recent decades[7,8].

It is generally considered that the uniform carbide-microstructures in WC-Co cemented carbide require a homogeneous distribution of the cobalt phase, because the non-uniform Co-particle distribution on a microscopic scale would lead to inhomogeneous densification, discontinuous grain growth and binder pooling during sintering[9,10]. Moreover, due to the inheritance of the properties of alloy organization to the nature of raw material powders by sintering, the raw material will greatly impact the quality of alloy particle size, alloy organization compact and uniformity, thus affecting the strength and toughness of cemented carbide. Therefore, developing new methods to prepare WC-Co composite powders which have advantages of homogeneous distribution of the cobalt phase, relatively stable that abnormal grain growth will not take place during subsequent sintering, high efficiency and economic, pure phase configuration and homogeneous particle size distribution, is quite significant.

A variety of methods have been reported to synthesize WC-Co composite powders in the past, such as spray conversion process[11,12], high energy ball milling[7,13], co-precipitation[14], serial chemical reactions[15], two-step processing[16], *etc*. However, most of the previous methods had not resolved the current issues on how to ensure uniform distribution of Co binder in the hard phase of tungeston carbide (WC) and could not avoid the environmental contamination and high cost in industrialization[17], including the complicated processing procedures, complex control of the gas atmosphere, time-consuming, high carbonization temperature hence leading to particle coarsening and so on. In this work, we attempted to develop a new method, namely the solution chemical reduction method, which has the advantages of generating homogeneous distribution of the cobalt phase and avoiding abnormal grain growth during subsequent sintering, to prepare the core-shell WC-Co composite powders by coating the WC powders with Co. The microstructures of resulting WC-Co core-shell composite powders were also studied.

EXPERIMENTAL

Tungsten carbide (average grain size d_{50} = 0.5 μm) was supplied by the Laboratory of Rare-Earth Nano-Materials of Sichuan. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, CP), hydrazine hydrate ($N_2H_4 \cdot H_2O$, > 80 %), sodium hydroxide

(CP), all analytical grade, were commercially available from Chengdu Changzheng Chemical Reagent Co., Ltd., China. Distilled water was used throughout all of the experiments.

Synthesis of WC-Co core-shell composite powders: Tungsten carbide powders (9.6 g) were put into a certain concentration of NaOH solution (50 mL) in a water bath at 80 ºC under stirring, then aqueous solution of $CoCl_2$ (15 mL) and hydrazine hydrate (20 mL) were added into the tungsten carbide suspension sequentially. The reducibility of the reaction solution remained during the coating process by adding hydrazine hydrate at regular intervals. After stirring for 1 h, the precipitates were filtered and washed three times with distilled water, followed by vacuum drying at 35 ºC for 12 h. The reaction equations are as follows.

$$Co^{2+} + 4OH^- = [Co(OH)_4]^{2-}$$

$$2[Co(OH)_4] + N_2H_4 \cdot H_2O = 2Co\downarrow + N_2\uparrow + 5H_2O + 4OH^-$$

XRD analysis was performed on a diffractometer (X'Pert Pro, Phillips, Holland) using Cu Kα radiation with a scanning rate of 0.04º min^{-1}. The morphology and structure of the as-prepared WC-Co core-shell composite powders were analyzed on a SEM (S-3400N, Hitachi, Japan) operating at 20 kV, TEM (JEOL J EM-100CX) and an EDS (EMAX, Horiba, Japan).

RESULTS AND DISCUSSION

XRD measurements were carried out to determine the composition and phases of the as-prepared WC-Co composite. The result is presented in Fig. 1.

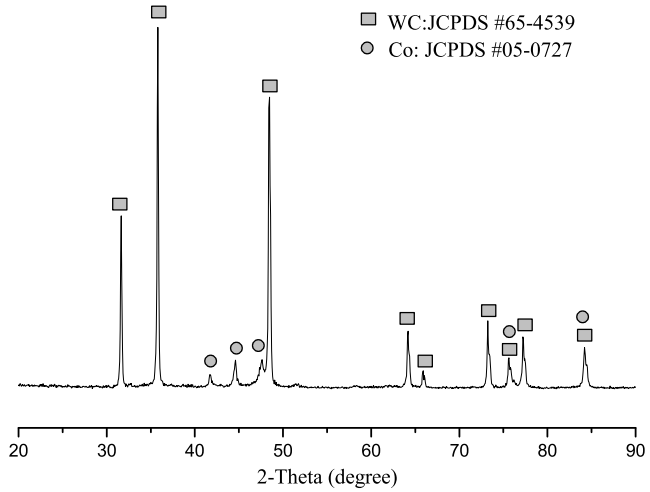

Fig.1. XRD pattern of the prepared WC-Co core-shell composite powders

As shown in Fig. 1, the sharper diffraction peaks appearing at 2θ=31.49º, 35.62º, 48.30º, 64.04º, 65.67º, 73.06º, 75.48º, 77.13º, 84.08º ascribed to that of hexagonal WC were observed. The XRD peaks at 2θ=41.63º, 44.57º, 47.57º, 76.02º, 84.08º well correspond to the reflection of Co (100, 002, 101, 110, 103). The crystallite size (D) of Co was in the range of 34-54 nm estimated by the Scherrer equation ($D = k\lambda/\beta\cos\theta$). These results indicate that WC-Co composite powders were successfully prepared by the solution chemical reduction method.

Morphology and microstructure: The SEM images of the synthesis composite powders are shown in Fig. 2. The SEM image (Fig. 2a) shows that the WC powders have smooth surfaces with an irregular-rounded morphology. The scanning electron microscopy image of the prepared WC-Co composite powders (Fig. 2b) indicates that the powders have rough surfaces with a mean average particle size of about 0.5 μm and the WC powders are almost completely coated by needle-like Co. It clearly exhibits that the needle-like Co coat homogeneously on the surface of tungsten carbide black particles in Fig. 3b, with combining the follow EDS mapping.

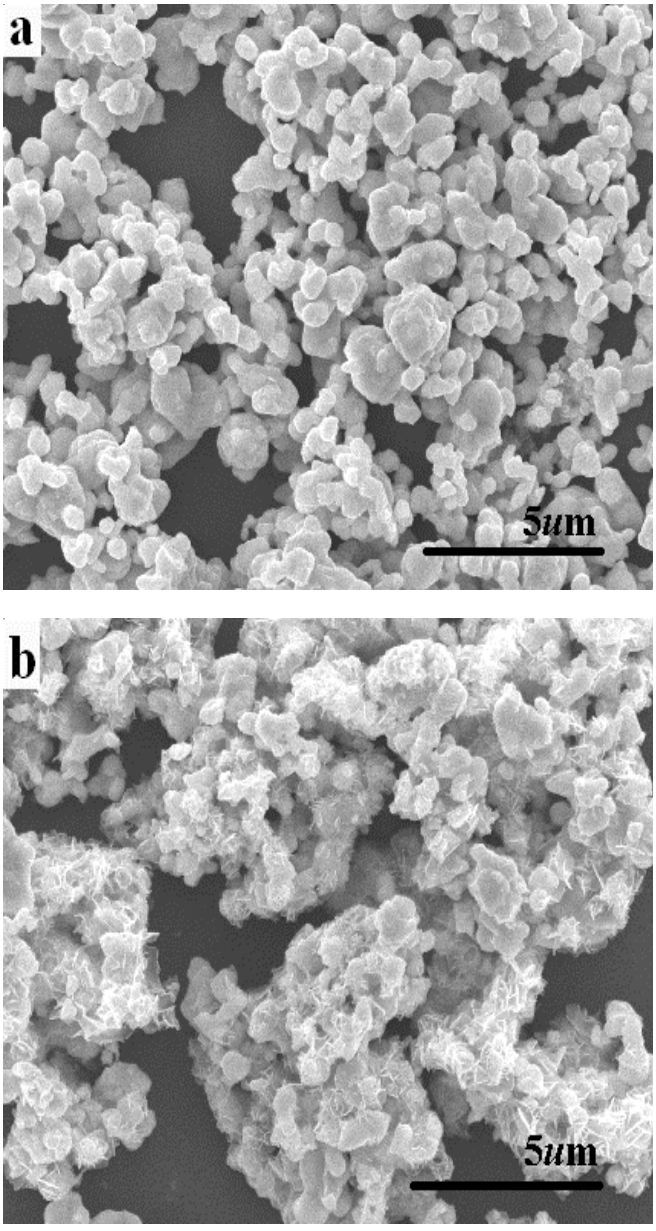

Fig. 2. Scanning electron microscopy images of the WC (a) and prepared WC-Co core-shell composite samples (b)

Energy dispersive spectroscopy analysis: In order to examine the core-shell structure of the produced composite powders, energy dispersive spectroscopy analysis was further performed on the synthesized WC-Co sample. The scope of scanning is showed in Fig. 3a, while the energy dispersive spectroscopy results are shown in Fig. 3b-d. It could be seen from Fig. 3b that the composite powders are composed of W, C and Co,indicating reduction reaction is complete. The distribution of cobalt and tungsten carbide with strong consistency

and no separate aggregation of cobalt are shown clearly in Fig. 3c and Fig. 3d, owing to heterogeneous nucleation. From the energy dispersive spectroscopy result, it can be considered that the surface shell is Co.

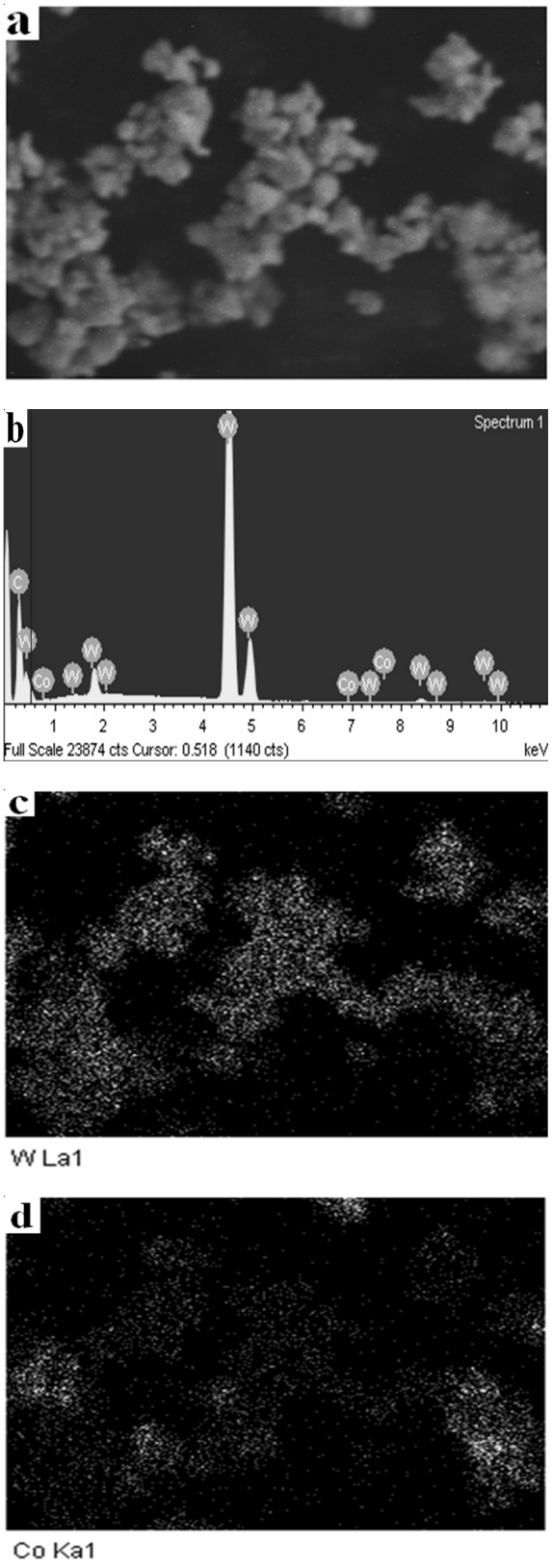

Fig. 3. Energy dispersive spectroscopy (EDS) mapping of the prepared WC-Co core-shell composite samples

Conclusion

WC-Co core-shell composite powders were synthesized by a solution chemical reduction method. The surfaces of WC powders are almost completely coated by needle-like Co. The result suggests that the solution chemical reduction method is an effective route to synthesize ultrafine WC-Co core-shell composites.

ACKNOWLEDGEMENTS

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