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International Journal of Refractory Metals & Hard Materials 26 (2008) 242–250
International Journal of REFRACTORY METALS & HARD MATERIALS
www.elsevier.com/locate/IJRMHM

Ultrafine hardmetals prepared by WC–10 wt.%Co composite powder

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Received 13 February 2007; accepted 11 April 2007

Abstract

Ultrafine tungsten carbide–cobalt (WC–10 wt.%Co) composite powder was synthesized via spray-drying and direct reduction and carburization process in vacuum, which includes precursor preparation by spray-drying of a suspension of ammonium metatungstate (AMT) and cobalt carbonate ($CoCO_3$), calcination to evaporate volatile components, formation of tungsten–cobalt mixed oxide powder ($CoWO_4/WO_3$), ball-milling with carbon black, and subsequent direct reduction and carburization reaction in vacuum. The synthesis temperature of WC–10 wt.%Co composite powder without η or graphite phases is lower than 1000 °C. The calculated particle size by BET test is 0.29 μm. Coarse WC powder (FSSS: 0.9 μm) and Co powder (FSSS: 1.0 μm) (WC:Co = 9:1 in mass) were added into the obtained WC–10 wt.%Co composite powder with addition of 30 wt.%, 50 wt.% and 70 wt.%, respectively. Results show that the hardmetal fabricated from 70 wt.% (WC–10 wt.%Co composite powder) + 30 wt.% (90 wt.%WC + 10 wt.%Co coarse powder) mixed powders exhibits a fine microstructure as well as optimum mechanical properties.
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Keywords: WC–Co; Spray-drying; Direct reduction and carburization; Composite powder

1. Introduction

Ultrafine and nanosized WC–Co composite powder has attracted substantial interest in recent decades [1–3]. The high strength and high hardness of hardmetals fabricated from those powders are primarily attributable to the uniform distribution of tungsten and cobalt, as well as the small grain size effect of WC [4]. Therefore, a variety of methods for producing WC–Co composite powder have been explored, such as carbothermic reaction in hydrogen atmosphere [5], vapor phase reaction process [6], spray-drying continuous fluidized reduction/carburization [1,2,7], and high energy ball milling [3,8]. However, it is seemed that the environment-contamination and highly cost are hardly avoidable with such processes in industrialization. Properties of the cobalt sources conventionally employed are listed in Table 1. During the decomposing of soluble cobalt salts, production equipment would be eroded and the air would be polluted by the released gases such as NO_x, SO_x, Cl_2, etc. Additionally, in some gas–solid reaction processes, although carbonaceous gas (such as CO/CO_2, CH_4, C_2H_2, etc.) are applied for their favorable fluidity and high carbon activity, accurate control industrially may not be easily achieved regardless of the fine obtained powders.

It is generally considered that discontinuous grain growth is difficult to control during liquid-phase sintering of ultrafine or nanosize WC–Co powders because of their high-surface energy [9]. Hence grain growth inhibitors (such as VC, Cr_3C_2, NbC, TaC, Mo_2C, etc.) are added [10,11]. Meanwhile, various rapid sintering methods are adopted to prohibit the grain growth, such as spark plasma sintering [12,13], and microwave sintering [14]. However, these new sintering processes are nowadays only restricted to laboratory and may be described as impractical in production on large scale.

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doi:10.1016/j.ijrmhm.2007.04.004

Table 1
Properties of different cobalt sources

Cobalt sources	Solubility	Thermal-decomposition	Equivalent price	Environmental characteristic
$Co(NO_3)_2 \cdot 6\,H_2O$	Perfect	Perfect	High	Bad
$CoCl_2 \cdot 6H_2O$	Good	Bad	Medium	Bad
$CoSO_4 \cdot 7H_2O$	Good	Bad	Medium	Bad
$CoCO_3$	Bad	Perfect	Low	Good

In this work, combining advantages of both a new experimental method and the manufacture practice, ultrafine tungsten carbide–cobalt (WC–10 wt.%Co) composite powder was synthesized via spray-drying and direct reduction and carburization process in vacuum [15–17]. Three different hardmetal grades were prepared by adding coarse WC powder (FSSS: 0.9 μm) and Co powder (FSSS: 1.0 μm) (WC:Co = 9:1 in mass), in amounts corresponding to 30 wt.%, 50 wt.% and 70 wt.%, into the obtained WC–10 wt.%Co composite powder. Microstructure and mechanical properties of hardmetals fabricated by the above-mentioned powders were studied.

2. Experimental

2.1. Starting materials

Commercial AMT ($(NH_4)_6(H_2W_{12}O_{40}) \cdot 4H_2O$) powder (99.9 wt.%), $CoCO_3$ powder (99.98 wt.%), carbon black (99.9 wt.%), WC powder (FSSS: 0.9 μm), VC powder (FSSS: 0.6 μm), Cr_3C_2 powder (FSSS: 0.6 μm) and Co powder (FSSS: 1.0 μm) were used in this work.

2.2. Experimental procedures

AMT and $CoCO_3$ were mixed in distilled water stoichiometrically for the final composition of WC–10 wt.%Co. The suspension was agitated and fed into the nozzle rotating at 20,000 rpm with a solution feeding rate of 25 ml per minute and spray-dried in a hot air at 250 °C. Then the spray-dried powder was calcinated in air at different temperatures from 500 to 700 °C for 2 h to remove the volatile components. The obtained $CoWO_4/WO_3$ mixed oxide powder, calcined at 700 °C, was added with carbon black stoichiometrically according to reactions shown as formula (1) and (2), homogenized for 48 h in a tilting ball mill in an absolute ethylic alcohol

$$WO_3 + 4C = WC + 3CO\uparrow \quad (1)$$

$$CoWO_4 + 5C = Co + WC + 4CO\uparrow \quad (2)$$

After drying and sieving, the powders were fired in a vacuum furnace in a graphite crucible of $240 \times 260 \times 40$ mm in size. After measuring the contents of total carbon, free carbon, cobalt, oxygen and the value of BET, the WC–10 wt.%Co composite powder was blended in hexane with 0.4 wt.% VC, 0.4 wt.% Cr_3C_2 and 2 wt.% paraffin by planetary ball milling for 12 h (ball-to-powder weight ratios = 8:1) under a rotation speed of 180 rpm. Three

Table 2
Composition and labels of the hardmetals

Hardmetals type	WC–10wt.%Co/ wt.%	WC/ wt.%	Co/ wt.%	VC/ wt.%	Cr_3C_2/ wt.%
YG0	100	0	0	0.4	0.4
YG3	70	27	3	0.4	0.4
YG5	50	45	5	0.4	0.4
YG7	30	63	7	0.4	0.4

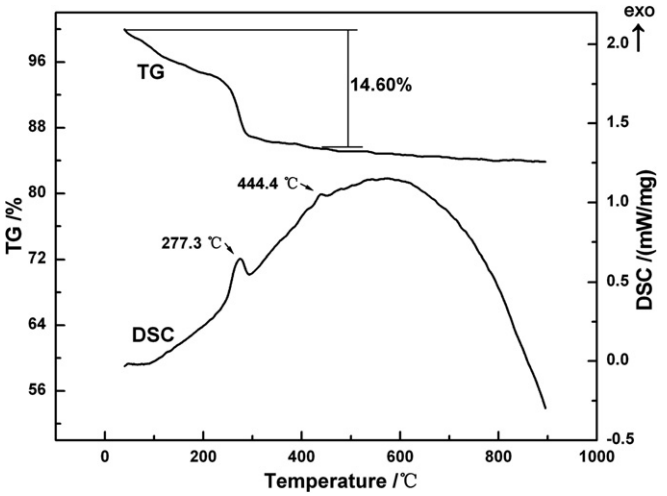

Fig. 1. TG/DSC curves of the spray-dried powder from room temperature to 1000 °C by a heating rate of 5 °C/min in air.

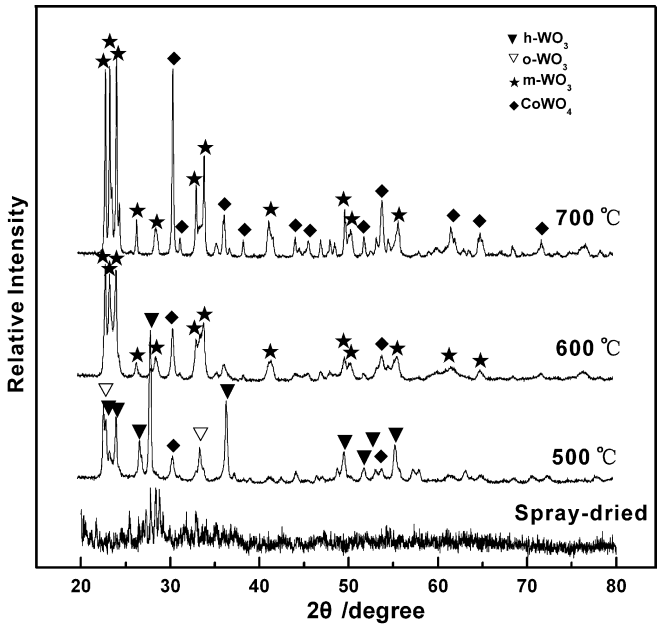

Fig. 2. XRD patterns of the spray-dried powder and samples calcined at various temperatures.

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