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Preparation and sintering of WC–Co composite powders for coarse grained WC–8Co hardmetals

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ABSTRACT

Due to high chemical and geometrical irregularities of WC grain and high uncertainty of WC grain growth, it is hard to prepare coarse grained WC–Co hardmetals with high performance through sintering of WC–Co ball milling powder. A new method for preparing of WC–8Co composite powder is put forward, which merges the preparation of Co powder with the mixing of WC–Co. The compositions, phases, and shapes of WC–8Co composite powder were investigated by chemical element analysis, X-ray diffractometry (XRD), and scanning electron microscopy (SEM), respectively. The phase and shape of raw WC powder do not change during the preparation of WC–8Co composite powder. Microstructures and mechanical properties of WC–8Co hardmetals prepared by sintering of the composite powders were compared with those of WC–8Co hardmetals prepared by sintering of the ball milling powders. The results show that the new coarse grained WC–8Co hardmetals have a better performance than conventional WC–8Co hardmetals for their better uniformity of WC grains. The comparison of microstructures and mechanic properties of sintered alloys also confirms that VC further inhibits the growth of WC grain and improves the performance of WC–8Co hardmetals.

Introduction

WC–Co hardmetals, consist of hard phase WC and ductile phase Co, are prepared by liquid phase sintering [1,2]. Through adjusting the mass fraction and grain size of WC, WC–Co hardmetals can be widely used in mining, machining, drilling, wear-resistance parts, etc. [3–5]. Coarse grained WC–Co hardmetals with 5–10 wt.%Co play an important role in mining and construction due to the perfect combination of wear resistance, thermal fatigue and shock resistance [5,6].

WC–Co hardmetals are usually obtained through the following procedures: ball milling mixtures of WC and Co powder in ethanol or gasoline; drying and granulating, pressing, debinding and sintering. During ball milling, the size of WC particles becomes small and the distribution of WC grain becomes tight through de-agglomeration and crush, while the composition of mixtures becomes homogeneous. It is well known that the initial particle size of WC powder is essential for the preparation of WC–Co hardmetals. Generally, the size of WC grain in WC–Co hardmetals becomes coarser when the initial particle size of WC powder becomes larger [7].

If a conventional process was employed to prepare the coarse grained WC–Co hardmetals, coarse sized WC powder is an indispensable raw material. However, as for the preparation of WC powder, the bigger the particle size of WC powder, the broader the distribution of WC particles, the higher the carburization temperature of tungsten powder.

It seems extravagant that the initial coarse sized WC powder eventually becomes the medium sized WC powder after ball milling. Several researches have been used to directly prepare the WC–Co composite powders through direct carbon reduction [8], chemical reduction with hydrazine hydrate [9], hydrothermal hydrogen reduction [10] and polyol reduction [11] for improving the performances of WC–Co hardmetals. Although the procedure of ball milling is avoided, these methods have some shortages: the direct carbon reaction is not suitable for medium/coarse sized WC–Co composite powder for the powder agglomeration in high temperature; the other methods are not economical and environmental for complicated processes and noxious pollutant. Regarding the above methods, except for direct carbon reduction, WC–Co composite powder was obtained by the reduction of cobalt salt or cobalt oxides, meanwhile WC powder was added directly into cobalt salt or cobalt oxide solutions. For example, 0.66 μm WC powder was added into Co_3O_4 suspension, and then WC–Co composite powder was prepared by the reduction of Co_3O_4 [10]. In other words, the composition, size and shape of WC powder hardly change during the preparation of WC–Co composite powder. Therefore, medium sized WC powder may be used to prepare coarse grained WC–Co hardmetals if an appropriate WC–Co composite powder could be obtained.

Co powder used for hardmetals is prepared by the reduction of cobalt oxalate (CoC_2O_4) or cobalt oxide (Co_2O_3 or Co_3O_4) with hydrogen under 500–600 °C. The former just omits one step of the calcinations of cobalt oxalate compared to the latter [12]. The deposition of cobalt

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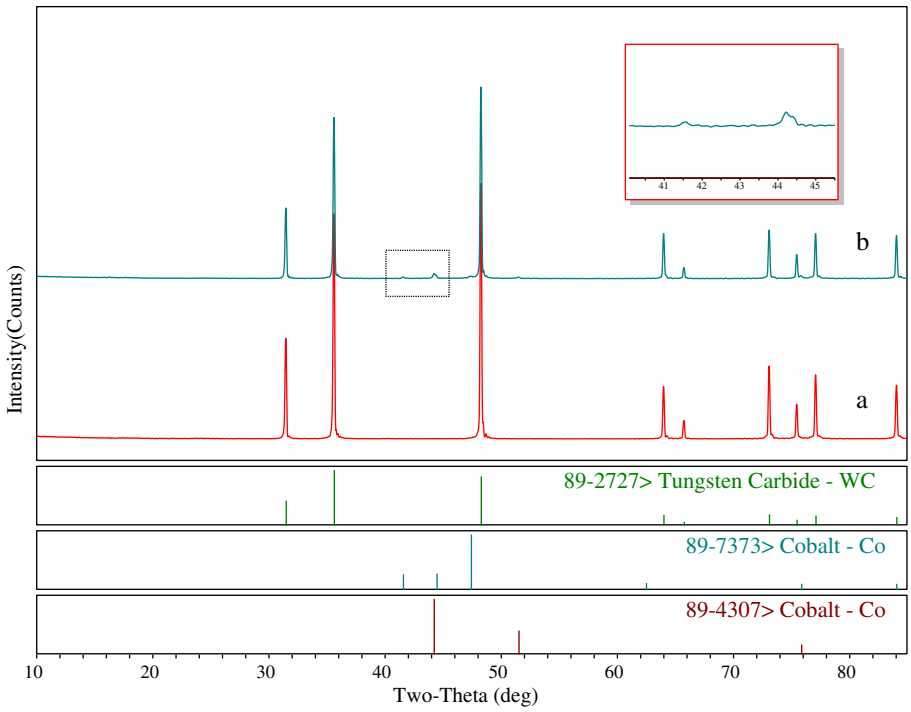

Fig. 1. X-ray diffraction patterns of raw WC powder (a) and WC–Co composite powder (b).

oxalate can be obtained by the reaction of cobalt chloride ($CoCl_2$) with ammonium oxalate ($(NH_4)_2C_2O_4$) in an aqueous solution [13], which is one of the most popular methods of the preparation of cobalt oxalate. Because the melting temperature of WC–Co decreases with the decrease of particle size, the particle size of Co powder should be fine to cause the early spread and flow of Co binder phase [14,15]. As for the preparation of Co powder, the fine Co powder can be obtained through hydrogen reduction at appropriate temperature for the linearity relationship between particle size and temperature.

Eduardo Soares et al. [16] have illustrated that it is more homogeneous and stable for the mixtures of WC–Co powder after ball milling in water than in ethanol, thus WC–Co hardmetals derived from water-processed powder have better mechanic properties than those derived from ethanol-processed powder. In this case, it is feasible that the dispersion of WC powder is conducted in an aqueous solution.

Therefore, it deserves to be explored whether medium sized WC–Co composite powder could be obtained simultaneously during the preparation of Co powder. If so, medium sized WC powder could be directly used to prepare the coarse grain WC–Co hardmetals and ball milling could be avoided. Additionally, cubic carbides (VC, Cr_2C_3, TaC, NbC, TiC) were often added to improve the homogeneity of microstructures and the performances of hardmetals for their inhibiting effects on the grain growth [17].

In the present work, WC–8Co composite powder for preparing coarse grained hardmetals was obtained through direct hydrogen reduction of the mixtures WC–CoC_2O_4. VC, which acts as the most effective inhibitor for the growth of WC grain, was added during the preparation of the WC–8Co composite powder. The microstructures and mechanical properties of coarse grain WC–8Co hardmetals undoped/doped VC were investigated as well.

Table 1
Composition, apparent density and Fsss size of powders.

Powders	C (%)	O (%)	Co (%)	Apparent density (g/cm^3)	Fsss (μm)
WC powder (medium)	6.13	0.03	–	4.12	4.09
WC powder (coarse)	6.14	0.04	–	7.40	20.2
WC–8Co composite powder	5.63	0.26	7.93	2.83	2.84
WC–8Co ball milling powder	5.66	0.53	8.02	3.25	2.82

Experimental procedure

Preparation of WC–Co powders

Cobalt chloride ($CoCl_2$) aqueous solution with a concentration of 0.34 mol/L was obtained by 32.30 g $CoCl_2 \cdot 6H_2O$ dissolved in 400 mL deionized water. (92 − x)g WC (total carbon: 6.13 wt.%) with Fsss 4.09 μm was added into a $CoCl_2$ solution under stirring at 50 °C. Where, x is 0 or 0.5 g VC powder with Fsss 1.5 μm. Subsequently, a 400 mL ammonium oxalate ($(NH_4)_2C_2O_4$) solution with the concentration of 0.357 mol/L, which acted as precipitation agent, was added into the WC–$CoCl_2$ suspension. That slight oversupply of $(NH_4)_2C_2O_4$ was to promote the precipitations of cobalt oxalate (CoC_2O_4). After 2 h stirring at 50 °C, WC–CoC_2O_4 suspensions were filtrated, washed and dried at 120 °C for 2 h in air. Subsequently, WC–CoC_2O_4 powder was reduced at 500 °C for 3 h in H_2 to obtain WC–8Co composite powder.

Coarse sized WC (total carbon: 6.14 wt.%, Fsss 20.2 μm) and Co (Fsss 1.0 μm) were ball milled in a stainless steel jar (36 h, ethyl alcohol, weight ratio of ball to powder is 3.5:1) and dried in the vacuum oven at 100 °C for 2 h. Finally, WC–8Co ball milling powder was obtained through an 80-mesh sieve.

Sintering of WC–Co hardmetals

The above WC–Co powders were mixed with 1.6 wt.% paraffin, granulated and compressed into a rectangular plate under a uniaxial pressure of 250 MPa. Sintering was performed in a sinter-HIP furnace at 1450 °C for 100 min in Ar atmosphere with a 5 MPa pressure.

Material characterizations

The phases of WC powder and WC–8Co composite powder were identified by X-ray diffractometer (D/max 2550, Rigaku). The shapes of the WC–8Co powders were observed by a scanning electron