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ARTICLE

Synthesis and Characterization of WC-6Co Nanocrystalline Composite Powder

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Abstract: WC-6Co nanocrystalline composite powders without excess C and decarburization phases were synthesized via a facile route including spraying conversion, calcination and in situ reduction-carbonization processes. The phase constituents obtained by XRD show that the as-prepared powders after each step of the preparation are amorphous, WO_3 and Co_3O_4 phases, WC and Co phases, respectively. Pure WC-Co composite powders could be obtained by a reduction-carbonization process heat treated at 900 °C for 1 h under a hydrogen atmosphere due to the catalytic effect of Co on the carbonation reaction. The effects of heat treatment temperature on phase constituents of powders were investigated in a range of 700~900 °C. Morphology and microstructure of powders were observed by SEM and HRTEM. The results indicate that the morphology of powder is spherical. The grain size of WC is about 0.36 μm, and the crystalline size of WC is about 56 nm, which indicates that the WC grain is polycrystalline and composed of many crystallites. It is also found that the individual particles of WC are bonded together under the action of Co. Furthermore, a few sintering necks could be observed in the composite powders due to the contacts between WC particles. The stoichiometry of WC-Co composite powders could be adjusted easily. Moreover, the formation process and mechanism of the sphere structure were also discussed in this paper.

Key words: WC-6Co composite powder; phase constituents; low-temperature synthesis; polycrystal

WC-Co cemented carbides have been widely applied in cutting tools, wear-resistant parts, dies and micro-drills due to their excellent mechanical properties such as high hardness, wear resistant and toughness [1-3]. With the reduction of WC grain size in the WC-Co cemented carbides to a range of micrometer or nanometer scale, the hardness and toughness increase significantly[4,5], and the preparation of ultrafine or nanoscale grain and homogeneous WC-Co composite powders is a key factor [6,7].

Conventionally, WC-Co composite powders are obtained through the following procedures [4]: Firstly, decomposing ammonium paratungstate and cobalt oxalate into the metal oxides. Secondly, reducing tungsten oxides and cobalt oxides into the pure metals by hydrogen or carbon. Thirdly, carbonizing W to form the WC powders at 1400~1600 °C. Finally, ball milling mixtures of WC and Co powders with ethanol or acetone. The impurity is hard to avoid during the processes mentioned above, and the distribution of W, Co and C elements are inhomogeneous. Moreover, a significant abnormal growth of WC grain occurs inevitably during the fairly high carbonization temperature treatment.

Due to the disadvantages of the conventional method, a large amount of methods have been developed to prepare WC-Co composite powders with ultrafine or nanoscale WC grains[2,4,8-10], such as mechanical ball milling and mechano-chemical synthesis, carbothermal reduction-carburization, solgel procedure, spray conversion with fluidized bed reaction, and chemical vapor phase reaction synthesis. The high distortion of the WC fabricated by mechanical ball milling method inevitably led to the abnormal grain growth

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in the subsequent sintering process [11]. Furthermore, the impurity is hard to avoid in the mechanical ball milling method. H. Lin et al. [12] obtained nanosized WC-Co powders with an average grain size of 80 nm using a spray-drying method. S. Lee et al. [13] determined that quasi-nano-sized WC core-Co shell structure composites were successfully fabricated by the wet chemical reduction method. However, most of these methods were achieved in a laboratory scale, and it is difficult to implement them in industrial applications.

Recently, a rapid facile process for industrial application which is a three-step route including spray conversion, calcination and in situ reduction-carbonization processes has been proposed in literature [6]. The proposed route has advantages of low temperature carbonization (900 °C) in addition to the advantages of controllable phase constitution of composite powders and homogenous distribution of W, C and Co elements. To take full advantage of the potential of the proposed method, the current paper investigated the characteristics of the powders including phase constituent, morphology, microstructure, crystalline size and grain size. The formation process and mechanism of the sphere structure were discussed as well.

1 Experiment

1.1 Preparation of composite powders

The proposed route includes a simple three-step route involving spray conversion, proper calcination under a nitrogen atmosphere and in situ reduction-carbonization processes under a hydrogen atmosphere to form WC-Co composite powders. Ammonium metatungstate (AMT, W content≥73 wt%), cobalt acetate ($C_4H_6O_4{\cdot}Co{\cdot}4H_2O$) and glucose ($C_6H_{12}O_6$) were used as the raw materials, which were of analytical grade and used without further purification. The raw materials were dissolved in distilled water in a special ratio according to the composition of WC-6Co(wt%). The solution of AMT, cobalt acetate and glucose allowed uniform mixing at the molecular level, and the uniformity could be sustained in the following processes. The temperatures of intake air and exhaust air were about 240 °C, and 100 °C to 120 °C, respectively. The centrifugal speed was 12000 r/min. The spray dried powders were then decomposed during subsequently calcination process at 550 °C for 20 min under a nitrogen atmosphere in a tubular furnace. The heating rate of the calcination was 5 °C/min. The calcined powders were directly reduced and carbonized to WC-Co composite powders at 900 °C for 1 h under a hydrogen atmosphere. The heating rate of the heat treatment was 5 °C/min.

1.2 Characterization

The formed phases of powders and crystalline size of WC were detected by X-ray diffraction (Brand: PANalytical, Model: Empyrean) with Cu Kα (λ=0.154 06 nm) at a scanning step size of 0.026° in the scan range of 20°~80°. The morphology of powders, microstructure of powders and distribution of elements were observed by the scanning electron microscopy with an EDS attachment (Brand: FEI, Model: MLA650F) and high resolution transmission electron microscopy (Brand: FEI, Model: Tecnai G2 F30). N_2 adsorption-desorption isotherm was obtained by a Micromeritics ASAP 2020 analyzer at 77 K.

2 Results and Discussion

2.1 Phase constituents

The phase constituents of as-prepared powders are shown in Fig. 1. The phase of the powder after spray conversion is nearly amorphous for the broad characterizing diffraction peaks. The diffraction peaks of the powders calcined at 550 °C for 20 min agree well with WO_3 and Co_3O_4 (PDF cards No. 83-0947 and 72-0479). It could be claimed that the amorphous powders have been transformed into WO_3 and Co_3O_4 after calcination process. It is difficult to precisely identify C which may be owing to that C was amorphous or the small atomic scattering factor of C atoms. Moreover, the diffraction peaks of powders heat treated at 900 °C for 1 h match well with the WC and Co phases (PDF cards No. 65-8828 and 15-0806). It could be concluded that WO_3 and Co_3O_4 powders have been transformed into WC and Co powders, respectively.

The transformation from amorphous powder to WO_3 and Co_3O_4 powders during calcination process is attributed to the following comprehensive chemical reactions[14,15]:

$$(NH_4)_6{\cdot}(H_2W_{12}O_{40}){\cdot}XH_2O \rightarrow 12WO_3+(X+4)H_2O\uparrow+6NH_3\uparrow \quad (1)$$

$$3Co(CH_3COO)_2{\cdot}4H_2O \rightarrow Co_3O_4+3(CH_3)_2+4CO\uparrow+2CO_2+12H_2O\uparrow \quad (2)$$

Fig. 2 shows the effects of in situ reduction-carbonization temperature on the phase constituents of powders. The in situ reduction-carbonization temperatures were set to 700, 800, 850 and 900 °C.

The W-Co binary phase diagram indicates that an intermediate compound Co_3W is present in the W-Co system. The formation of the Co_3W is due to the reaction of W and Co [16]. In our experiments, we find that the intermediate compound Co_3W was detectable in addition to the main W and Co_6W_6C phases when the temperature is 700 °C. As shown in Fig. 2, the WC phase appears in addition to the Co_6W_6C, CCo_2W_4 and W phases when the temperature is 800 °C. In the W-Co-C ternary equilibrium phase diagram, $M_{12}C$, which is sometimes formularized as $CCo_2{+}xW_{4-x}$, is the common shorthand for M_6C and Co_6W_6C, has a wide composition range spreading between CCo_2W_4 and Co_3W_3C [16]. In our experiments, it is found that $M_{12}C$ phase appears in the powders when the temperatures are set to 700, 800 and 850 °C. The results of phase constituents in our experiments match with the

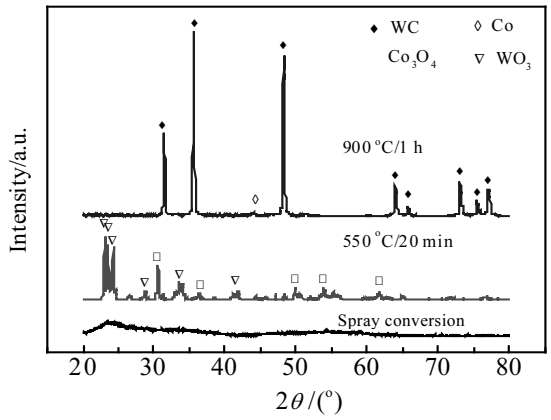

Fig. 1 XRD patterns of powders after spray conversion, calcination and reduction-carbonization processes

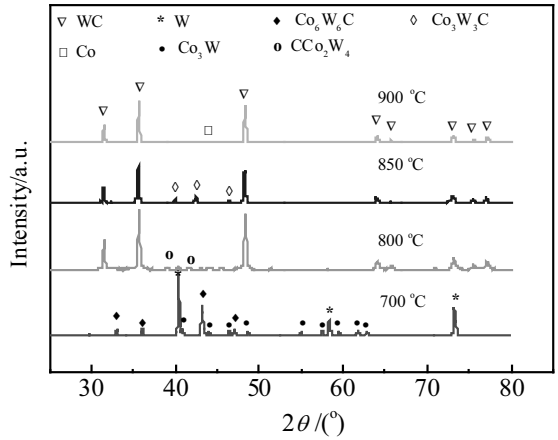

Fig. 2 XRD patterns of powders heat treated at different temperatures

W-Co-C ternary equilibrium phase diagram quite well. The absence of W_2C in this experiment in the heat treatment stage is related to the different starting materials. From the results mentioned above, it can be inferred that the phase constituents of powders heat treated at different temperatures are highly complex.

For the WO_3/Co_3O_4/Amorphous carbon mixed powders, Co_3O_4 is reduced into pure Co around 400 °C, which makes the WO_3/Co_3O_4/Amorphous carbon mixed powders into WO_3/Co/Amorphous carbon mixed powders[16]. Some effects of Co on the formation of WC were reported in the previous studies [16-18]. Firstly, the reaction sequence becomes much more complicated with the addition of Co. Secondly, it is found that the catalytic behavior of Co would be helpful for the formation of WC. Thirdly, the carbon decomposed from glucose is more active than carbon black. Therefore, the WC formation rates of WO_3/Co/Amorphous carbon mixed powders is higher than that of WO_3/Carbon black or WO_3/Co/Carbon black mixed powders. Moreover, Co is one of the best catalysts for the decomposition of carbon monoxide[17], which can provide more active carbon to reduce oxides and carburize W to WC. In a word, the presence of Co promotes the formation of WC at a lower carbonization temperature.

According to PDF card No. 65-8828, the maximum intensity of WC peaks is (100) plane (2θ=35.678°) and the relative intensity ratios between the major peaks are 0.44 for $I_{(001)}/I_{(100)}$ and 0.83 for $I_{(101)}/I_{(100)}$. The calculated values of relative intensity ratios of as-prepared powders are 0.49 and 0.82, which were closed to the theoretical values. It indicates that WC has been crystallized integrally[19]. Furthermore, the WC crystalline size was measured by XRD using the Scherrer method. The peak position and full-width at half-maximum (FWHM) were calculated from all the diffracting peaks and the average of all the peaks. The crystalline size of WC is calculated to be about 56 nm.

2.2 Morphology and microstructure

Fig. 3 shows that the structure of as-prepared powders in each stage is spherical. The mean diameters of powders are about 70 μm for spraying conversion, 60 μm for calcination and 30 μm for reduction-carbonization process. This spherical structure feature is maintained in the following processes. The surface is smooth after spray conversion stage (Fig. 3a), but it become rough after calcination stage and even rougher after reduction-carbonization stage (Fig. 3b and 3c). Moreover, small pores appear on the surface (Fig. 3c). The reduction of the powder diameter in each stage is probably due to the diffusion and removal of gases in the products and volume decreasing in the transformation processes from AMT+$C_4H_6O_4$·Co·4H_2O +$C_6H_{12}O_6$ to WO_3+ Co_3O_4+ amorphous carbon mixed powders, and then to WC-Co composite powders. The increasing roughness of the surface probably results from the evaporation of water and the diffusion of CO, CO_2, and other gases[6].

Some of the WC-Co composite powders have hollow spherical structure and are porous (Fig. 3d). During the spray conversion process, the solution is dispersed from the rotating nozzle and drops down along the spiral trajectory. According to the results mentioned above, the formation process of the hollow spherical structure could be explained as follows. With a temperature gradient from the interface (high) towards the interior (low) of the droplet, the water on the surface of droplet evaporates more quickly than that inside the droplet, which causes a concentration of AMT, $C_4H_6O_4$·Co·4H_2O and C element at the surface of droplet. With the evaporating of water, the solute on the surface crystallizes to form the shell of the sphere structure. The thickness of shell increases with further evaporation of the water diffused from the inner to the surface of the droplet. And finally the precursor powders with hollow spherical structure are obtained.

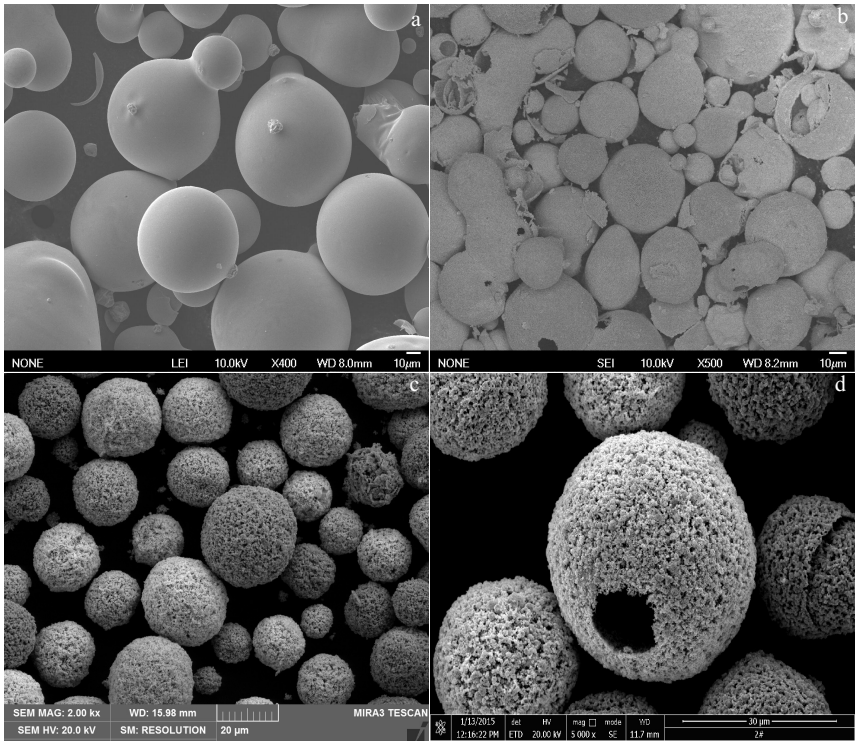

Fig. 3 SEM images of powders prepared after spray conversion (a), calcination (b), and reduction-carbonization processes (c, d)

The formation mechanism of the hollow structure could be attributed to the Ostwald ripening phenomena which consists of recrystallization and growth[20,21]. Spherical structure is formed and some nanoparticles grow on the surface due to the evaporation of the water. Subsequently, the inner nanoparticles are formed and accompanied by the growth of surface nanoparticles at the expense of inner ones via Ostwald ripening. With further increasing the reaction time, the inner nanoparticles further dissolve and transfer out, and then the final hollow structure is formed.

Fig.4a shows the detailed microstructure of WC-Co composite powder. The individual particles of WC are wrapped in cobalt, and the individual particles ware bonded together into a long and thin strip. In order to observe the details of the WC particles, the H_3PO_4 and H_2O_2 solution is used to dissolve Co from the WC-Co composite powders. It can be seen in Fig. 4b that the WC particles are irregular polygon. In addition, a few sintering necks (the mutual bonding between the two WC particles) are observed between the WC particles indicated by the arrow marked in Fig. 4b-4c. There is a certain contact condition between WC and WC particles. Sintering necks would be formed in solid phase sintering among the particles. Moreover, even at low temperature, the nanocrystalline WC has an extremely high surface area and rapid mass transport. These two factors mentioned above can lead to the occurrence of the mutual bond between WC particles.

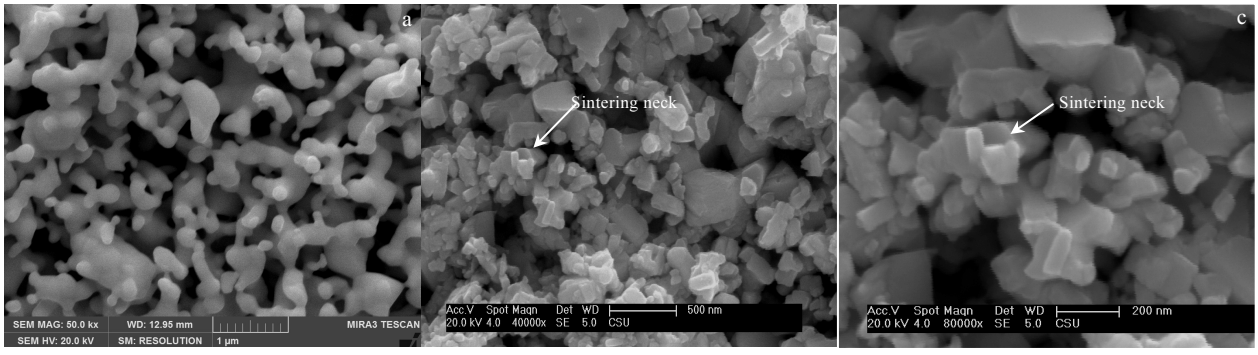

Fig. 4 SEM images of WC-6wt% Co composite powder (a) and WC powder (b, c)

The average grain size of WC is about 0.36 μm obtained from these SEM images. It is significantly noted that the mean grain size is about 6 times lager than the crystalline size in this paper, which indicates that WC grain is polycrystalline and composed of many crystallites[22].

Aside from refining the basic composition of WC-Co cemented carbide, all components in the composite need to be uniformly distributed in order to achieve the expected improvements in mechanical properties. A homogeneous distribution of W, C and Co elements is obtained in our products as shown in Fig. 5.

The N_2 adsorption-desorption isotherm of WC-Co composite powders, as shown in Fig. 6, has no jump in the whole P/P_0 range from 0.0 to 1.0 and is convex downward. The isotherms for WC-Co composite powders are of the type Ⅲ classification, which indicates that the as-prepared products are representative of the nonporous materials. This is not associated with the results of porous surface observed in Fig. 3c and 3d. It could be explained as follows. During the reduction-carbonization process, the process of gases diffusion from the inside of spheres forms small pores, while at the later stage of the reduction-carbonization process, the amount of gas is reduced. Meanwhile, the densification process via particle rearrangement is mainly driven by the spreading of the Co binder. The spreading seems to occur by viscous flow of a low viscosity layer formed near the contact between Co and WC [23].

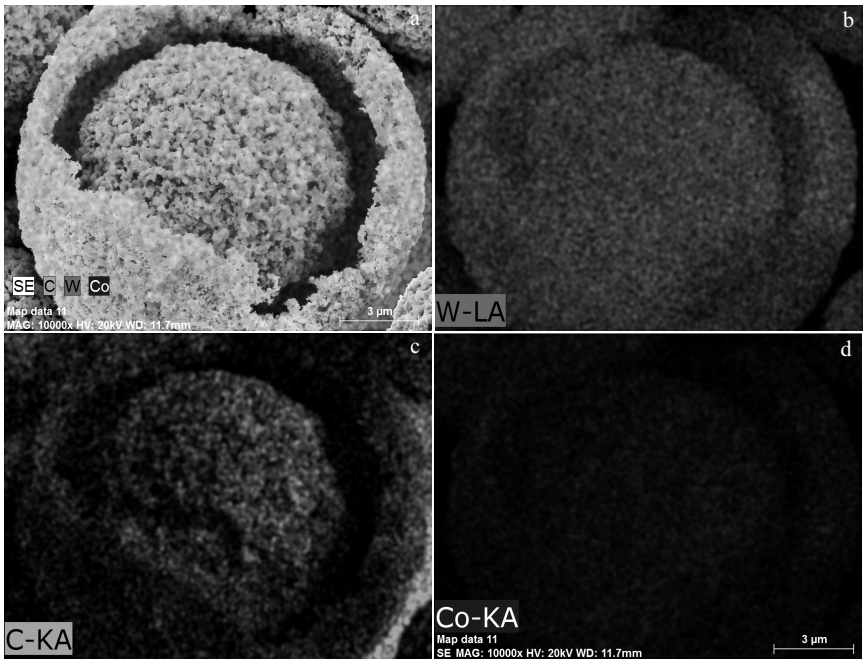

Fig. 5 SEM image (a) and mapping of element distribution of WC-6 wt%Co composite powder: (b) W, (c) C, and (d) Co

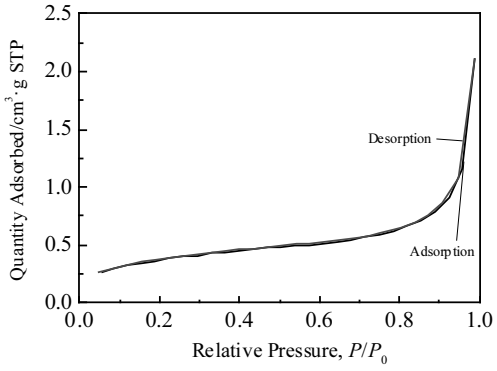

Fig. 6 N_2 adsorption-desorption isotherm of WC-6wt%Co composite powder

Nanostructure of WC-Co composite powder is shown in Fig.7. From the HRTEM image in Fig.7a, the clear lattice fringes are observed which indicates high crystallinity of WC, and the interplanar distance is 0.26 nm which is indexed with the (100) plane of WC grain according to PDF card. In addition, the stacking faults are observed in Fig. 7a. The corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 7b. Since no mechanical milling is conducted, there are sharp awn lines between the diffraction spots indicating the presence of stacking faults which appear at the stage of WC formation when the carbon atoms diffuse into W during in situ reduction-carbonization process [24,25].

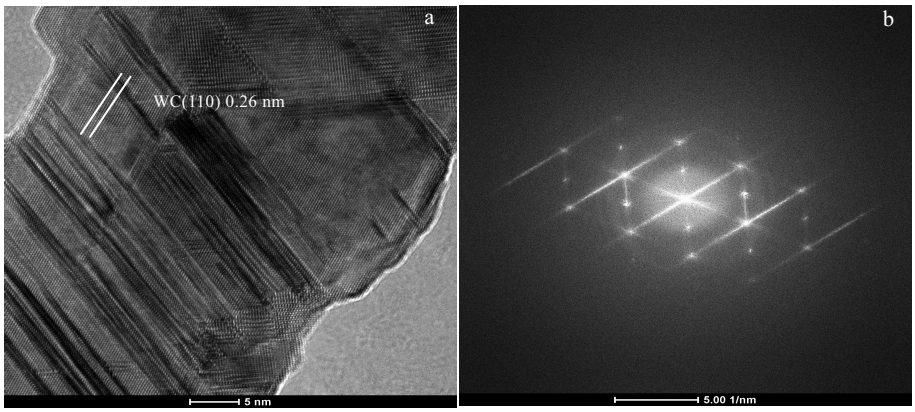

Fig. 7 TEM image of WC-6 wt%Co (a) and corresponding SAED pattern (b)

3 Conclusions

1) WC-6Co nanocrystalline composite powders without excess C and decarburization phases are successfully fabricated by spraying conversion, calcination and in situ reduction-carbonization processes. The heat-treatment temperature is 900 °C due to the catalytic effect of cobalt on the carbonation reaction, which is lower than the conventional carbonation temperature (1300 °C)

2) The grain size of WC is about 0.36 μm, and the crystalline size of WC is about 56 nm, which indicates that the WC grain is polycrystalline and composed of many crystallites.

3) The individual particles of WC are bonded together under the action of Co. Furthermore, a few sintering necks could be observed in the composite powders due to the contacts between WC particles.

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纳米晶 WC-6Co 复合粉合成及特性研究

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摘　要：使用喷雾转化、煅烧和原位还原碳化技术制备了纳米晶WC-6Co复合粉末。通过XRD研究相组成发现，经过喷雾转化处理后粉末为无定形相、经煅烧后的粉末为WO_3与Co_3O_4相、经还原碳化工艺后的物相是WC与Co相；由于Co对碳化过程的催化作用，将煅烧后的粉末置于氢气气氛中加热至900 ℃还原碳化1 h，即可将粉末碳化完全，制备出WC与Co相共存的纯净复合粉。研究了还原碳化温度（700~900 ℃）对粉末相组成的影响，并通过SEM和HRTEM观察粉末形貌与微观组织。结果表明：制备的粉末具有球形结构，WC晶粒约0.36 μm，亚晶尺寸约为56 nm，说明WC晶粒是多晶体。同时发现粉末中的WC单颗粒被Co相互粘结在一起，且在WC与WC颗粒的接触部位发现存在烧结颈。还讨论了复合粉球形结构的形成过程和机理。

关键词：WC-6Co 复合粉；相组成；低温合成；多晶体

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