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Study on nanometer ε-cobalt powder prepared by precipitation–hydrogen reduction in Co(II)–$(NH_4)_2CO_3$–H_2O system

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ABSTRACT

Nanometer ε-cobalt powder was fabricated by liquid-phase deposition–hydrogen reduction method. Different precipitators were mixed with $CoCl_2$ solution respectively to prepare the precursor of $Co_2(OH)_2CO_3$ precipitation. Then the precipitation was washed, dried and hydrogen-reduced. Nanometer ε-cobalt powder was obtained. The characteristics of the precursor and cobalt powder from different precipitating agent were analyzed and compared. The precipitation mechanism of the Co-based precursor in Co(II)–$(NH_4)_2CO_3$–H_2O system was discussed and summarized for the first time. The results show that the use of $(NH_4)_2CO_3$ as precipitating agent is conducive to preparing fine and uniform precursor and cobalt powder. Processing parameters of hydrogen reduction exert a great influence on particle size of cobalt powder: the lower reduction temperature, the finer the particle size, but the higher the oxygen content of cobalt powder. Close-packed hexagonal ε-Co powder with BET particle size less than 100 nm and oxygen content lower than 0.8 wt.% can be fabricated when reduction process was carried out at 400 °C. Moreover, the nanometer cobalt powders had spherical shape with good dispersibility.

1. Introduction

The effective control of grain growth on the premise of densification during the sintering of ultrafine WC–Co hardmetal is one of the technical difficulties and key points of ultrafine WC–Co cemented carbide fabrication. In recent years, the researches on sintering and WC grain growth control of the ultrafine/nano grained WC–Co cemented carbide are popular, and the most studies focus on two directions including the use of special sintering equipments or grain growth inhibitors [1–3]. Although Co binder phase provides strength and toughness for hardmetals and plays an important role in densification and microstructure evolution of ultrafine WC–Co cemented carbide during sintering, few investigations about Co binder are reported. Studies show that ultrafine WC–Co cemented carbide with uniform microstructure and better properties can be obtained when the BET particle size of spherical cobalt powder was less than 0.5 μm [4]. Ultra-fine spherical ε-cobalt powder is more easily dispersed in the milling process, and not only could shorten the milling time thereby reduce the damage of WC particles, but also conduce to homogeneous distribution of cobalt powder in the WC–Co powder mixture, effectively eliminate the formation of cobalt pool and avoid abnormal growth of WC grains, thereby enable ultrafine WC–Co cemented carbide to high quality [5].

At present, the industrial production method of cobalt powder used in WC–Co hardmetals fabrication is still traditional oxalate precipitation–hydrogen reduction technique. The purity of produced cobalt powder is 99.5 wt.% with dendritic morphology, intermingled coarse particle and average particle size of 1.0–3.0 μm [6,7]. The commercial nanometer Co powder is usually produced by arc process and electron explosion process, which is too expensive to industrial mass production. In the laboratory, ultrafine spherical cobalt powder with an average particle size below 0.5 μm can be obtained by micro-emulsion process, polyatomic alcohol reduction process, high-pressure hydrogen reduction process and complexing chemical reduction process in aqueous solution. However, limited to environmental demands and facility cost, above processes were difficult to further promotion [8–12].

Generally, liquid precipitation–calcination process is applied in the preparation of nanometer Co_3O_4 [13–15]. As we all know, cobalt powder can be obtained by hydrogen reduction of Co_3O_4. Consequently, liquid precipitation–hydrogen reduction is a feasible method for the production of ultrafine/nanometer cobalt powder on the base of Co_3O_4 preparation. However, few reports about liquid precipitation–hydrogen reduction used in the production of cobalt powder can be found. From the point of view of technique, liquid precipitation–hydrogen reduction method is a modification of traditional industrial production process of cobalt powder, that is, oxalate precipitation–calcination–hydrogen reduction. Through the use of new precipitation agents to replace the oxalate or oxalic acid, nanometer precursor as well as cobalt powder was obtained.

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Therefore, the majority of existing industrial production facilities can still be utilized, so the method has advantages of low capitalized cost and easy-expanded production capacity.

In this paper, liquid precipitation in Co(II)–$(NH_4)_2CO_3$–H_2O system combined with hydrogen reduction process for the preparation of nanometer spherical ε-cobalt powder was studied. Precipitation mechanism of Co-based precursor in the system and the effect of processing parameter of liquid-phase precipitation and hydrogen reduction process on particle size, oxygen content, phase composition and particle morphology of Co powder were discussed to develop a new manufacturing technique with low-cost of production and easily expanding of production capacity of nanometer spherical ε-cobalt powder.

2. Experimental

2.1. Preparation of nano-cobalt powder

Analytically pure cobalt salt $CoCl_2{\cdot}6H_2O$, precipitants $(NH_4)_2CO_3$, $(NH_4)_2C_2O_4$ and Na_2CO_3 were dissolved, respectively in deionized water to prepare the initial solution with appropriate mole ratio. Cobalt salt solution and precipitant solution were mixed sufficiently in 70–90 °C water bath and ammonia was used to adjust pH value to 8–9. When the precipitation reaction completed and gas bubbles give out, the blended liquid was aged for 20 min and filtered to separate the precipitation. After washing repeatedly by deionized water to remove the impurity ions adsorbed on the surface of precipitated precursor, drying under the temperature of less than 100 °C, grinding and sieving, the precursor powder was reduced at 350–500 °C in the hydrogen atmosphere to fabricate nanometer ε-cobalt powder with nearly spherical morphology.

2.2. Analysis and characterization

Cobalt ion concentration of the supernatant of precipitation reaction was measured by inductively-coupled plasma spectrometry (ICP-AES) in order to determine cobalt yield of precipitation reaction. Phase composition of cobalt powder was measured by X-ray diffraction (XRD). Pulse heating–infrared detection method was applied to determine the oxygen content of cobalt powder. The average particle size D50 of cobalt powder was analyzed by means of BET method. Scanning electron microscopy (SEM) was used to observe particle morphology and agglomerated degree of cobalt powder.

3. Results and discussion

3.1. Precipitation mechanism of nanometer Co-based precursor in Co(II)–$(NH_4)_2CO_3$–H_2O system

Mechanism of liquid precipitation has an important guiding significance on the parameters choice of deposition process and the preparation of nano-scale Co-based precursor. Although some reports indicated that the generated sediments was basic cobalt carbonate when soluble carbonate or hydrocarbonate was used as the precipitant of cobalt ions, the reaction mechanism and precipitation reaction formula did not point out yet [13,14]. Therefore, it is necessary to study the precipitation mechanism of the precursor in Co(II)–$(NH_4)_2CO_3$–H_2O system.

Commercial $CoCl_2$ is cobalt chloride containing six crystallization water ($CoCl_2{\cdot}6H_2O$). Hydrous Co (II) ion exists in aqueous solution in the form of pink $[Co(H_2O)_6]^{2+}$, and hydrolyzes weakly according to the following formula [16]:

$$[Co(H_2O)_6]^{2+} \Longleftrightarrow [Co(OH)(H_2O)_5]^{+} + H^{+} \tag{1}$$

When soluble carbonate reacts with metal ions in aqueous solution as a precipitating agent, due to the hydrolysis of the carbonate ion, the type of the product may be the corresponding salt, basic carbonate (hydroxy carbonate salt) or hydroxide, and can be determined by the solubility of the corresponding metal carbonate and hydroxide. If the solubility of carbonate is far less than the solubility of the corresponding hydroxide, the precipitating product will be the normal salt; If the solubility of the hydroxide is few and the hydrolysis of metal ions and CO_3^{2-} ions are fully happened, the product will be the hydroxide; If the solubility of the carbonate salt and the corresponding hydroxide are close, the reaction product will be the basic carbonate (hydroxy carbonate salt) [16].

At 298.15 K, the solubility product constant of $CoCO_3$ is 1.4×10^{-13}, and the solubility product constant of $Co(OH)_2$ (Pink, the new precipitation) is 1.6×10^{-15} [16]. The two are almost equal, thereby the product of precipitating reaction in Co(II)–$(NH_4)_2CO_3$–H_2O system is basic cobalt carbonate $Co_2(OH)_2CO_3$, and the reaction can be formulated as follows:

$$2[Co(H_2O)_6]^{2+} + 2CO_3^{2-} \Rightarrow Co_2(OH)_2CO_3(s) + CO_2(g) + 11H_2O \tag{2}$$

3.2. Effects of the type of the precipitant on the particle size of the precursor and cobalt powder

Three kinds of precipitant ($(NH_4)_2C_2O_4$, Na_2CO_3, $(NH_4)_2CO_3$) were chosen for liquid precipitation–hydrogen reduction experiments to prepare nanometer cobalt powder. The BET particle sizes of the precursor and cobalt powder prepared by three types of precipitating agent are compared in Fig. 1. It can be found that the particle size of the precursor and cobalt powder by using $(NH_4)_2CO_3$ precipitant is much finer than that by using $(NH_4)_2C_2O_4$ or Na_2CO_3 separately. And there is a particle size inheritance relationship between the precursor and cobalt powder.

From the above formula (2), it can be seen that there is a gas component, CO_2, in the products. And in the reaction process, it can also be observed that the reaction system, with a violent weltering up and down, was in the ‘‘false boiling" state due to a large number of bubbles. The state is beneficial to the refinement of precipitating products because it can effectively avoid the approach, gathering, merging and the growth of solid-phase particles. Therefore, compared with $(NH_4)_2C_2O_4$ precipitant applied in the traditional oxalate precipitation method [11], the use of $(NH_4)_2CO_3$ precipitant can be more conducive to preparing fine precursor powder theoretically. Similarly, particle size of the precursor powder by using $(NH_4)_2CO_3$ precipitant is finer than that by using

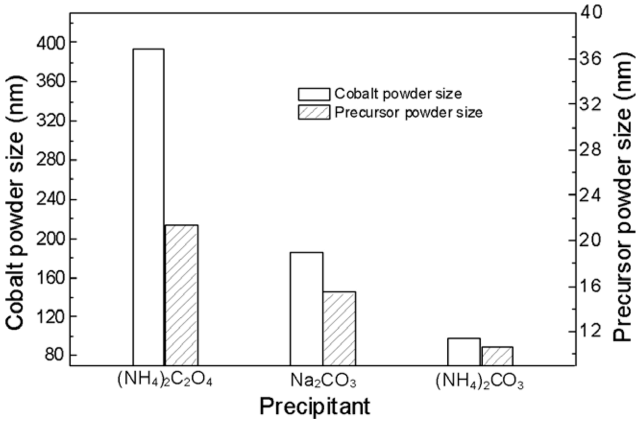

Fig. 1. BET particle size of the precursor and cobalt powder prepared by different precipitating agents.