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Preparation process and mechanism of ultra-fine spherical cobalt powders by hydrogen reduction of calcium cobaltite



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ABSTRACT

For the improvement of the properties of cemented carbides, ultra-fine spherical cobalt powders as binder were prepared using calcium cobaltite. The effects of the ratio of CaO to CoO, the calcination temperature and the reduction temperature on particle size and morphology of cobalt powders were studied. The results show that the average particle size of cobalt powders decreases with increasing the weight ratio of CaO to CoO, but increases with the calcination temperature and reduction temperature. The spherical cobalt powders with the mean particle size of 84 nm are obtained when the weight ratio of CaO to CoO is 7:4 and the calcination temperature and reduction temperature are 1000 °C and 700 °C, respectively. In addition, CaO regarded as the blocking agent can refine cobalt powders during the hydrogen reduction process.

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1. Introduction

Cobalt and its alloys have been widely used in superalloy, magnetic materials [1,2], rechargeable alkaline batteries [3], heterogeneous catalysis [4], cemented carbide and diamond tools [5], because of their high-density magnetic property, sintering reactivity, hardness levels and excellent impact resistance property [1,2]. Cobalt powders have a strong influence on the formation of homogeneous microstructure and the improvement of mechanical properties of WC-Co cemented carbides. Ultra-fine spherical cobalt powders are favorable to the development of high-quality WC-Co cemented carbides [6]. Physical and chemical properties of cobalt powders strongly depend on their size and morphology [7,8], therefore the improvement of fabrication methods may be used for enhancing the properties of cobalt powders [9–11]. At the present, cobalt powders may be prepared by several methods, such as hydrothermal reduction [12], vacuum pyrolytic decomposition [13], ultraviolet-irradiation [14], chemical vapor condensation [15], xirradiation [16], polyol process [17], and liquid phase reduction [18]. However, the disadvantages of these methods are apparent, such as the high cost that retards industry applications, and the difficulty to achieve ultra-fine spherical cobalt powders.

In this paper, we exploit a two-stage procedure for preparing

* Corresponding author. E-mail address: tangjiancheng@ncu.edu.cn (J. Tang). ultra-fine spherical cobalt powders. During the hydrogen reduction process, CaO plays an important role in controlling the shape and size of Co powders. The effects of the ratio of CaO to CoO, the calcination temperature and reduction temperature on the size and morphology of cobalt powders were investigated. The role of CaO during the preparation process of cobalt powders was discussed.

2. Experimental

2.1. Preparation of calcium cobaltite

CaO (purity \geq 98.0%) and CoO (purity \geq 99.5%) were used as raw materials. The raw materials were uniformly mixed at room temperature. The total mass and its weight ratio were summarized in Table 1. These materials were placed into three agate grinding cylinder with volume 500 ml. Agate ball was used as milling ball (diameter 5–12 mm) and the weight ratio of ball to powders was 3:1. The homogenous mixtures were obtained after milling for 7 h at 500 rpm, then placed into three corundum boats and, respectively, calcinated at 900 °C, 1000 °C and 1100 °C for 5 h in air to obtain precursor powders. The 5 g precursor powders were placed into three railbaots and, respectively, reduced in hydrogen atmosphere at 600 °C, 700 °C, 800 °C and 900 °C for 2 h. To avoid the influence of oxygen on the cobalt, the powders were cooled in hydrogen atmosphere. Finally, the prepared mixtures were washed by NH₄Cl solution to remove the excess CaO and obtain the cobalt powders.

Table 1

The quantity and weight ratio of raw materials used in the experiment.

	1	2	3
Quantity(CaO + CoO)/g	100	100	100
Weight ratio(CaO/CoO)	6:4	7:4	8:4

2.2. Characterization of powders

The phases of calcium cobaltite powders were determined by X-ray diffraction (XRD, Bruker D8 X-ray diffractometer Focus) using Cu K α radiation. The morphology and average size of cobalt powders were observed using scanning electron microscopy (Nova Nano SEM450).

3. Results

Calcium cobaltite as the precursor was prepared by calcining the CaO and CoO at 1000 °C and its patterns are shown in Fig. 1. As can be seen in Fig. 1(a), the precursor consists of CoO, CaO and Ca₃Co₂O₆ phases. The phase of CoO appears in the precursor, indicating that CaO and CoO have not been reacted completely. When the weight ratio of CaO to CoO increases to 7:4, the phase of CoO disappears, as shown in Fig. 1(b). With the ratio further increases to 8:4, the phase of Ca₃Co₂O₆ transforms into Ca₂Co₂O₅. However, due to the irregularly shape of Ca₂Co₂O₅, it is difficult to use Ca₂Co₂O₅ as precursor for obtaining spherical cobalt powders in the process of reduction [5,19]. Therefore, it can be concluded that the optimum weight ratio of CaO to CoO is 7:4.

Fig. 2 shows the XRD patterns of the calcined powders at different temperatures. From Fig. 2(a), it can be seen that the calcined powders at 900 °C are consisted of $Ca_3Co_2O_6$ and Co_3O_4 phases. The presence of Co_3O_4 phase indicates that the CoO phase just transformed into Co_3O_4 , and the reaction between CaO and CoO is not completed. When the calcination temperature reaches 1000 °C, the powders are identified to be $Ca_3Co_2O_6$, as shown in Fig. 2(b). With further increase of the calcination temperatures, the $Ca_3Co_2O_6$ phase transit into $Ca_9Co_{12}O_{28}$ phase (Fig. 2(c)). It is indicated that when the calcination temperature is above 1000 °C, CaO and CoO have been reacted completely. In view of that the high



Fig. 1. XRD patterns of precursors produced at different ratio of CaO and CoO: (a) 6:4; (b) 7:4; (c) 8:4.



Fig. 2. XRD patterns of precursor produced at different temperatures: (a) 900 $^\circ C$; (b) 1000 $^\circ C$; (c) 1100 $^\circ C$.

temperature can lead to the grains of calcium cobaltite growth and aggregation and accelerate the reaction. As mentioned above, the product consists of three phases (Co₃O₄, Ca₂Co₂O₅ and CaO). This leads to the cobalt powders non-uniform in the hydrogen reduction process in low temperature. Therefore, it can be concluded that the optimum calcination temperature is 1000 °C.

Fig. 3 shows the XRD patterns of the reduced powders at different temperatures. As seen in Fig. 3(a), the reduced powders at 600 °C still consist of $Ca_3Co_2O_6$ phase, indicating that $Ca_3Co_2O_6$ is not converted into CaO and Co completely. With the temperature increasing, the patterns only contain peaks corresponding to Co, CaO and Ca(OH)₂ phases, as shown in Fig. 3(b–d), and the peaks of cobalt shows sharp, which indicates that the cobalt powders have a good crystallinity state.

SEM images of cobalt powders are shown in Fig. 4(a-c). It is



Fig. 3. XRD patterns of reduced cobalt powders at different temperatures: (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 900 °C.





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seen that the increase in the hydrogen temperature leads to the grain growth and slight aggregation. The reason for this is due to



Fig. 5. XRD pattern of cobalt powders.

the fact that the hydrogen temperature determines the rate for both nucleation and growth of the cobalt powders. The possible mechanism is as follows. In low temperature, $\Delta G_v - \Delta G_k > 0$ (ΔG_v and ΔG_k represent dynamic barrier and thermal barrier, respectively), beneficial for the nucleation of Co powders during the process. However, in high temperature, $\Delta G_v - \Delta G_k < 0$ is favored for the grain growth of Co powders, resulting in the formation of large particles. Based on such an assumption, it can be concluded that the optimum temperature of the hydrogen reduction is 700 °C.

XRD pattern of Co powders is shown in Fig. 5. The pattern only contains the peaks corresponding to Co without other impurities. This indicates that $Ca_3Co_2O_6$ have been transformed into Co powders completely. Additional, CaO and Ca(OH)₂ disappear after washing by NH₄Cl solution.

In order to understand the effects of CaO on Co powders growth, two processes for preparing cobalt powders are compared. One is that Co powders are prepared by reducing cobaltous oxide (CoO) with hydrogen directly, and the other is that CaO and CoO are calcined into calcium cobaltite (Ca₃Co₂O₆) and then reduced under hydrogen atmosphere. It is observed that the cobalt powders are of irregular shape with the average particle size of 390 nm, as shown in Fig. 6 (a). While in Fig. 6 (b), the morphology of cobalt powders is nearly spherical with the average particle size of 84 nm. CaO plays an important role in refining cobalt powders. The specific mechanism will be explained in the next section.

4. Discussion

4.1. Thermodynamics analysis of the reaction for preparing calcium cobaltite

The basic condition for solid-phase reactions is that the Gibbs free energy changes of the reaction is smaller zero, i.e., $\Delta G_m < 0$. In this experiment, the possible reaction equation during the process for preparing calcium cobaltite is [21].

$$6CaO(s) + 4CoO(s) + O_2(g) = 2Ca_3Co_2O_6(s)$$
(1)

According to thermodynamic law, Gibbs free energy of the reaction can be calculated by

$$\Delta_{\rm r} G^{\theta}_{{\rm m},1} = 2\Delta_{f} G^{\theta}_{{\rm m},T_{1}} (Ca_{3}Co_{2}O_{6}) - 6\Delta_{f} G^{\theta}_{{\rm m},T_{1}} (CaO) - 4\Delta_{f} G^{\theta}_{{\rm m},T_{1}} (CoO) - \Delta_{f} G^{\theta}_{{\rm m},T_{1}} (O_{2})$$
(2)



Fig. 6. SEM images of cobalt powders reduced of: (a) CoO; (b) Ca₃Co₂O₆.

$$\Delta G_{m,1} = \Delta_{\rm r} G_{m,1}^{\theta} + RT_1 \ln \frac{[CaO]^6 [CoO]^4}{P_{O_2}}$$
(3)

where $\Delta G_{\rm m}$, $\Delta_{\rm r} G_m^{\theta}$ and $\Delta_{\rm f} G_m^{\theta}$ represent the actual change values of Gibbs free energy, the changes value of standard Gibbs free energy and standard Gibbs free energy of formation at reaction temperature (T_1), respectively, R is ideal gas law constant, $P_{\rm O2}$ is partial pressure of oxygen.

At T₁ temperature (1000 °C), the standard Gibbs free energy of formation of each compounds in Eq. (2) are listed in Table 2. By substituting these data into Eq. (2), we have $\Delta_r G_{m,T_1}^{\theta} = -33.941$ kJ mol⁻¹. Because the activity of solid is 1 and the partial pressure of the gas is very small during the solid reaction, the actual change values of Gibbs free energy ($\Delta G_{m,1}$) calculated from Eq. (3) is approximately -33.941 kJ mol⁻¹. According to

Table 2	
Standard Gibbs free energies of formation of compounds [20].	

Compounds	CaO(s)	CoO(s)	Ca ₃ CoO ₆ (s)
$\Delta_{f}G_{\mathrm{m}}^{\theta}$ (KJ mol ⁻¹)	-679.7	-296.51	-2615.18

the laws of thermodynamics, $\Delta G_{m,1} < 0$, the solid reaction of synthesizing calcium cobaltite will occur, as described in Eq. (1).

4.2. Thermodynamics analysis of the reaction for preparing cobalt powders

During the hydrogen reduction process, the thermodynamic behavior of $Ca_3Co_2O_6$ and CaO is analyzed. The possible reduction process of $Ca_3Co_2O_6$ into Co and CaO into Ca can be generalized as follows

$$Ca_{3}Co_{2}O_{6}(s) + 3H_{2}(g) = 3CaO(s) + 2Co(s) + 3H_{2}O(g)$$
(4)

$$CaO(s) + H_2(g) = Ca(s) + H_2O(g)$$
 (5)

According to thermodynamic laws, the Gibbs free energy changes ($\Delta G_{\rm m}$) of the reaction (4) and (5) can be calculated according to Eq. (6) and Eq. (7), respectively.

$$\Delta G_{m,2} = \Delta_r G_{m,2}^{\theta} + RT_2 \ln \frac{a_{CaO}^3 \cdot a_{Co}^2 \cdot a_{H_2O}^3}{a_{Ca_3 Co_2 O_6} \cdot a_{H_2}^3}$$
$$= \Delta_r G_{m,2}^{\theta} + RT_2 \ln \frac{[CaO]^3 \cdot P_{H_2O}^3}{P_{H_2}^3}$$
(6)

$$\Delta G_{m,3} = \Delta_r G_{m,3}^{\theta} + RT_2 \ln \frac{a_{Ca} \cdot a_{H_2O}}{a_{CaO} \cdot a_{H_2}} = \Delta_r G_{m,3}^{\theta} + RT_2 \ln \frac{[Ca] \cdot P_{H_2O}}{P_{H_2}}$$
(7)

where $\Delta G_{\rm m}$ and $\Delta G_{\rm m}^{\theta}$ represent the actual change values of Gibbs free energy and the changes value of standard Gibbs free energy at reaction temperature (T_2), respectively, R is ideal gas law constant, $P_{\rm H2O}$ and $P_{\rm H2}$ are partial pressure of water and hydrogen, respectively. In order to simplify the calculation, we assume that most of the water vapor are moved out of the camber by the hydrogen flow and $P_{\rm H2O}/P_{\rm H2}$ is 0.01. $T_2 = 700$ °C is taken for calculation.

Based on Eqs. (6) and (7), the actual change values of Gibbs free energy for $\Delta G_{m,2}$ and $\Delta G_{m,3}$ is -94.79 kJ mol⁻¹ and 345.95 kJ mol⁻¹, respectively. Therefore Ca₃Co₂O₆ are reduced to Co powders by hydrogen as Eq. (4) and the reaction of Eq. (5) will not be occurred.

4.3. Refinement mechanisms

In the solid-phase reaction, two reactions are included, namely contact reaction and diffusion reaction. Oxygen (O) ions are difficult to diffuse because of its larger atomic radius than that of Co and Ca. The charge balance is remained through the transmission of oxygen at high oxygen partial pressure. At high temperature, diffusion reaction is the primary mechanism, due to the mutual diffusion of Co and Ca ions. This process can lead to numerous of defects, and is beneficial for accelerating reaction rate.

The corresponding reactions are analyzed as follows: At the beginning CoO is oxidized to Co_2O_3 with the calcination temperature increasing, according to Eq. (8). The further increase in the temperature can promote the homogeneous mixing of the Ca and Co ions. As a result, $Ca_3Co_2O_6$ are obtained at the interface of $Co_2O_3/$ CaO, and $Ca_3Co_2O_6$ grains grow with the holding time. The corresponding reaction equation is described as follows

$$4Co0 + O_2 = 2CO_2O_3 \tag{8}$$

Diffusion occurs at interface of Co₂O₃/Ca₃Co₂O₆ by

$$Co_2O_3 + 3Ca^{2+} + 3O^{2-} = Ca_3Co_2O_6 \tag{9}$$

Diffusion occurs at interface of Ca₃Co₂O₆/CaO by

$$2Co^{3+} + 3CaO + 3O^{2-} = Ca_3Co_2O_6 \tag{10}$$

During the hydrogen reduction process, Ca₃Co₂O₆ decomposes into CaO and Co₂O₃ with the increase in temperature. The Co₂O₃ powders and be quickly reduced into Co powders, and CaO homogeneously disperses on the surface of Co particles as blocking agent. In the meantime, the blocking agent keeps the enclosed Co particles isolated, impeding the aggregation of Co particles and restricting the size of Co particles to the nanometre scale. In addition, the homogeneous distribution of CaO on the surface of Co particles suppress anisotropic grain growth of cobalt, which may be conductive to the Co particles maintain the spherical shape. In comparison, Co powders are directly reduced from Co₂O₃ or other precursor powders without blocking agent in conventional hydrothermal reduction. The small Co particles may aggregate through physical bonding and its grains grow though Ostwald ripening [22].

5. Conclusions

Spherical cobalt powders with the mean particle size of 84 nm are obtained when the weight ratio of CaO to CoO, the calcination temperature and the reduction temperature are 7:4, 1000 °C and 700 °C, respectively. The average size of cobalt powders decreases with increasing the ratio of CaO to CoO, but increases with increasing the calcination temperature and the reduction temperature. CaO can be regarded as the blocking agent that can refine cobalt powders during the reduction process.

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