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Morphological investigation on cobalt oxide powder prepared by wet chemical method

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Abstract

In this paper cobalt oxide has been prepared by wet chemical method using $Co(NO_3)_2$ sol (Co: 80 g/L) and $NaHCO_3$ sol (100 g/L) as starting materials. When organic reagent: ethanol, acetone, and Polyethylene glycol-400 (PEG-400) (all are 2 mL) or three sodium salts: sodium chloride, sodium sulfate and sodium acetate (all are 1 g) had been introduced into reaction as inert additives once every time, and the measurement of PH value, zeta potential and viscosity in all solutions retains on the same level of magnitude, but the SEM shows that specific shapes of cobalt oxide particle is obtained after firing of $CoCO_3$ at 300 °C for 2 h in air. The DLVO theory discloses effect of dielectric constant of organic reagent and steric hindrance effect is the main factor for big molecular PEG-400. By replacing partly $Co(NO_3)_2$ with $CoCl_2$, the behavior of Cl^- is studied in the process of nucleus growth, the results show that Cl^- existed in the structure of nucleus with the content from 1300 to 2400 ppm, the structure, which can stand several time washing in an ultrasonic bath after reaction, but collapse as soon as it is fired at 300 °C for 2 h in air. It is reasonable to conclude that there may be directed anion chemical adsorption existed in cobaltous carbonate structure, which results in corresponding cobalt oxide particle morphology via anisotropic growth of nucleus.

Keywords: Cobalt oxide; Particle morphology; Directed chemical adsorption; Anisotropic growth

1. Introduction

Cobalt oxide, a kind of transition metal oxide, has been widely used for cemented carbide, Lithium ion battery, catalyst, glass industry and many electronic components [1–4]. And for these electronic components such as ZnO varistor or NTC thermstor, cobalt oxide plays very important and indispensable roles [5,6].

In the research of preparation of cobalt oxide, only some properties of cobalt oxide, including particle size, specific surface area, contents, and impurity contents are taken into consideration and some techniques in these fields had been advanced [7–9]. On the other hand, the study on particle micrograph of cobalt oxide was seldom reported, and it is the particle shape that also plays an important role in electronic ceramics [10,11].

Nowadays, the main wet chemical process to fabricate cobalt oxide is to use ammonium oxalate or carbonate salt as precipitant [12,13], due to theirs simplicity, high efficiency and low cost. However the particle micrograph of cobalt oxide prepared by firing of cobalt oxalate in air is hard to be controlled, because the reaction mechanism of its firing in air includes two steps: at first, metallic cobalt and CoO are formed

Table 1
The PH, zeta potential and viscosity of after-reacted solutions after adding 2 mL of acetone, ethanol or PEG-400

Additive	Ethanol	Acetone	PEG-400
PH value	7.4	7.4	7.4
Zeta potential/mV	−17.2	−17.4	−18.6
Viscosity/mPa s	0.8	0.8	1.1

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for the decomposition of cobaltous oxalate, and then the metallic cobalt is easily fired with oxygen to cobalt oxide, the route of oxalate decomposition is strongly affected by the surrounding environment [14]. The two reaction steps always take place continuously. However, by firing cobalt carbonate, the cobalt oxide powders with specific particle shape can be obtained for metal oxide by firing its carbonate salt likely keeps its original shape [15,16]. The purpose of the present study is to clarify the morphological behaviors of cobalt oxide powder.

2. Experimental work

The cobaltous nitrate ($Co(NO_3)_2$) (chemical grade, Jinchuan company, China) aqueous solution (Co: 80 g/L) and sodium hydrogen carbonate ($NaHCO_3$, chemical grade) aqueous solution (100 g/L) were carefully prepared as starting materials. All additives are of analytical grade and deionized water was used in the experiment. All solutions were filtered through a 0.2 μm Millipore filter to remove any particulate contaminants before use.

300 mL of solution of $NaHCO_3$ was heated up to 50 °C in the 1000 mL glass beaker, and then the additive was introduced into the solution, followed by stirring the beaker at constant speed (160 rpm in all experiments) to obtain the homogeneous solution. Before solution of 120 mL $Co(NO_3)_2$ was dropped at 12 mL/min into the solution of $NaHCO_3$, it had been heated up to 50 °C. after having finished dropping of $Co(NO_3)_2$ solution, keeping stirring at 50 °C for 10 min. The cobaltous carbonate was prepared by suction filtration of the slurry and washed several times with deionized water to remove the ions possible remaining in the final product. And finally firing was conducted at 300 °C for 2 h in air with a heating rate of 5 °C/min to obtain cobalt oxide.

The morphology studies were carried out using a Scanning Electron Microscope (Cambridge S360). The measurement of PH value, zeta potential and viscosity in the solutions is done by PHS-25, Zetasizer (3000HS) and rotary viscometer (NDJ-8), respectively. The content of chloride ion in the powder is analyzed by the following steps [17]: A mixture of 1 g sample and 20 mL deionized water is treated in an ultrasonic bath for 1 min and then boiled up for 10 min, after filtration through a membrane with pore size 0.2 μm, the chloride ion in water is tested by spectrophotometer (UV-9100) with silver nitrate as indicator. The content of chloride ion in $CoCO_3$ is calculated by the result of cobalt oxide after firing of $CoCO_3$ in air at 300 °C for 2 h.

3. Results and discussion

When 2 mL of analytically pure reagents acetone, polyethylene glycol-400 (PEG-400) or ethanol, was added into 300 mL solution of $NaHCO_3$ respectively, the value of PH, zeta potential and viscosity of the three after-reacted solutions, as presented in Table 1, indicated that all three solutions have nearly the same level of magnitude (varying within 2%) after reaction. However, the SEM investigation (in Fig. 1a, b and c) showed totally differing powder shape, the ethanol additive yields needle-like powder, acetone stick-like and PEG-400 irregular ball respectively.

It is no doubt that acetone or ethanol or PEG-400 does not take part into the reaction with any ingredient in the initial aqueous solutions to form nucleus which affects nucleus growth much. And the comparison of PH values, zeta potential and viscosity in solutions after reaction is negligible, since organic reagents have been added. It is proved that these various morphological particles of cobalt oxide powders are attributed to the three different organic additives, and the experimental results can be repeated. Moreover, any individual particles of cobalt oxide with any above-mentioned organic additive retained the similar shape.

Specific shape of particles results from different coagulation process of nucleus in cobaltous aqueous sols. As we know, the dielectric constants of ethanol and acetone are 24 and 21.4, respectively, far below that of water 80, with the adding of these organic reagents, the dielectric constant of sols decreases without any doubt. According to DLVO theory, the potential U_t between two nucleuses could be expressed as follows [18]:

$$U_t = -\frac{A\alpha}{12H} + 2\pi\varepsilon\alpha\psi_0^2\exp(-KH) \quad (1)$$

Where, A is the Hamaker constant, α is the diameter of nucleus, ε is the absolute dielectric constant in aqueous media, H is the separation distance, Ψ_0 is the surface potential of nucleus, and K is the Debye–Huckel coefficient. The second term on the right hand side of the Eq. (1) describes the electrostatic repulsion. Here, we discuss that when diameter of nucleus and separation distance of two nucleuses are the same, and surface potential is measured as the same too. As a result, the lower dielectric constant of sols media is, the smaller static repulsive force between two nucleuses. The coagulation process would change according to variable dielectric constant of the solution. For big molecular inert additive of PEG-400, which is commonly used as steric hindrance reagent in preparation of monodispersed powder [19], the

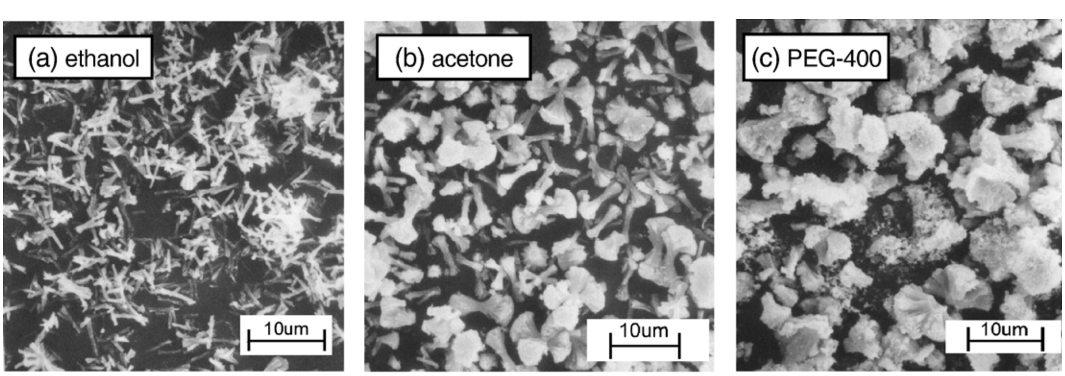

Fig. 1. SEM of cobalt oxide powder with different organic reagents additives: (a) ethanol, (b) acetone and (c) PEG-400.