Synthesis of Cubic Co Micro/Nano Powders by Mechanism-Chemical Method: The Influence of Reaction Complex and Mechanical Force

Ying DENG¹,²,a,*, Jin-Yu WANG¹,b, Fan XIE¹,c, Huan LIANG¹ and Ze-Qin LU¹

¹Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Chongqing 402160, PR China
²State Key Laboratory of Powder Metallurgy, Central South University Changsha 410083, PR China

a397194810@qq.com, b953557981@qq.com, c2595738661@qq.com

*Corresponding author

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Abstract. Cermet material is widely used in manufacturing, military and other fields. Co is a key component for cermets material, and can improve the strength and toughness of cermets because of its excellent ductility. Micro/nano structured spherical cubic-Co powder is the best structure for cermet with its special properties and internal structure. In this study, Oxalic acid and cobalt nitrate are used as raw materials to prepare cobalt oxalate Using mechanical solid-phase chemical reaction and thermal decomposition, a single phase spherical β-Co powder of around 200nm stable at room temperature is prepared. This study focuses on researching the interaction mechanism of the cobalt oxalate powders with the interaction of mechanical force, and the influence of reaction complex on the structure of Co powders.

Introduction

The cermets material is a metal composite material of hard and binder phase structure which is widely used in industry, military and other fields[1,2]. But because of the contradiction between its toughness and hardness, its application has been restricted. Metal Co has two structures β-Co and α-Co. Because of its excellent ductility, it has become a key component to improve the strength and toughness of the cermets material, β-Co has its robust performance superior to α-Co[3,4]. So far, the single-phase β-Co application has not been reported. So to carry on a research on it has scientific and practical significance.

The feature of micro/nano β-Co powders is stable at high temperature, to get stable β-Co at low temperature, first of all, the powder particles inside must reserve enough internal-energy, and make them stabilize at room temperature. At present, the preparation methods of Micro/nano crystalline are varied and most of them require high reaction temperature, which easily lead to particles become congregate and the size be bigger, and there have some deficiencies on controlling both crystal structure and dispersion of products effectively that cannot increase the internal energy of grains.[5,6] Mechanical solid-phase chemical method is the way to prepare micro/nano powders, its mechanism is reducing the reaction temperature to obtain compounds and get micro/nano size of products. Its characteristics are low reaction temperature, simple method and the mechanical force can increase the reaction energy, so it is suitable to prepare micro/nano powders for this study. This study focuses on researching the interaction mechanism of the cobalt oxalate powders with the interaction of mechanical force, and the influence of reaction complex on the structure of Co powders.
Experiments

Main Raw Material

Oxalic acid (H$_2$C$_2$O$_4$·2H$_2$O), cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O), cetyltrimethyl ammonium bromide (CTAB), sodium carbonate (Na$_2$CO$_3$), cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), polyethylene glycol (PEG) and absolute ethyl alcohol (CH$_3$CO$_2$OH). All the chemical reagents used in this study were of analytical grade, and used as received without further purification, manufactured by Chongqing Chemical Reagent Factory.

Experimental Procedures

Starting materials consist of cobalt salt ligands and weak acid, which is token corresponding quality respectively and the mole ratio is 1:1. Respectively mixing starting materials well and putting corresponding quality of surface active agent into agate ball-milling pot with the volume of it is 100 ml, then beginning to ball-grind. Experimental requirements are the ratio of grinding medias and materials ranges from 3 to 10:1, the speed of ball-grind is 500 rpm, times of ball-grind are 3 to 7 hours. Powdered materials is leached and washed 3 to 5 times after ball-grinding, then dried them in the environment of vacuum, the precursor samples are got.

Put precursor powder into ceramic crucible with controlling bilateral experimental temperature. First of all, rising temperature at 200°C in low temperature stage and keeping warm with one hour to exclude crystal water of precursor powder, then regulating temperature at 400 to 500°C with two to three hours after nitrogen being passed into furnace; last precursor powder is cool to room temperature with nitrogen protection for ensuring it is decomposed completely but not be oxidized.

Results and Discussion

Selection of Reaction Complex

Mechanical solid-phase chemical method is used high-energy mechanical ball milling as the mechanical force of evoked response, grinding balls squeeze, impact and mix strongly to reactant powder by ball mill running in high speed for promoting to produce activation point and evoking solid chemical reaction. In mechanical solid-phase chemical reaction, the complex is a metastable compound that formed by mechanical forces, which is different from liquid-phase reaction and traditional solid-phase reaction. Metastable compound easily resolves in the heat, it is smart choice for prepare metal precursor.[7] Co is an excessive metal element with not full of valence shell d orbit, its configuration of valence electron is 3d$^7$4s$^2$, it has 9 irregular valence electron configurations and higher charge and excellent polarization force. Co can easily prepare metastable complex, so it is fit to solid-phase reaction.

![Figure 1. a. Structure of C$_2$O$_4^{2-}$ b. Structure of CO$_3^{2-}$](image)

The data shows that metal Co powder prepared by thermolysis precursors, it will succeed the structure and morphology of precursors. Therefore, to get metal Co with stable structure, the needed complex of solid-phase chemical reaction demands higher solution rate and the product cobalt precursor should not only be insoluble but also have stable structure when solid-phase chemical method prepares Co precursor, which can enable reactants and products to separate effectively. Research has shown that the compound of chelated structure is the most stable structure. Oxalate and carbonate are the commonest chelated structure in metal compounds. Carbonate and metal ion
cooperate four-element chelated ring structure, but oxalate and metal ion cooperate five-element chelated ring structure, its electronic stability is particularly prominent due to containing one planar π system (8 electron). Two tooth ligands of oxalate and carbonate are shown in fig 1.[8] Thus oxalate and carbonate can be regard as solid-phase rectant ligands.

The solution rate of solid-phase reaction complexes by this study experiment chose as tab 1. We can know that solution rate of cobalt chloride and cobalt nitrate are high, they can be regard as Co ion ligands, even can response to oxalic acid and carbonate and the solution rate of formed cobalt oxalate and cobalt carbonate are low from some reports. [9] Therefore, complexes reactions by this study chose as follow:

\[
\begin{align*}
    &\text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} + \text{Co(NO}_3)_2\cdot6\text{H}_2\text{O} \rightarrow \text{CoC}_2\text{O}_4 \cdot2\text{H}_2\text{O} \downarrow + 2\text{HNO}_3 + 6\text{H}_2\text{O} \\
    &\text{CoCl}_2\cdot6\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \rightarrow \text{CoCO}_3 \downarrow + 2\text{NaCl} + 6\text{H}_2\text{O}
\end{align*}
\]

Both cobalt oxalate and cobalt carbonate are metastable compounds, which the cost of needed crude materials is low and have lower thermolysis temperature that can reduce the cost of follow-up. The by-products that are accompanied with precursor are easily separated from them, which can be easily removed in the process of decomposition and reduction. So cobalt oxalate and cobalt carbonate become the best choice of preparing stable structure metal Co by pyrogenic decomposition.

| Compounds       | Solubility (g/100ml, 20°C) |
|-----------------|-----------------------------|
| Co(NO₃)₂·6H₂O   | 97.4                        |
| CoCl₂·6H₂O      | 52.9                        |
| CoC₂O₄·2H₂O     | 0.0346                      |
| CoCO₃           | 0.046                       |

![a. cobalt oxalate](image1.png) ![b. cobalt carbonate](image2.png)

Figure 2. The SEM Images.

The SEM images of cobalt oxalate and cobalt carbonate by liquid-phase method prepared as fig 2. Obviously can be seen in the figure that cobalt oxalate crystal form is regular but cobalt carbonate’s is loose and amorphous particles. This just illustrates oxalic ion’s five-element chelated ring structure is more stable than nitrate radical’s four-element chelated ring structure. For stability of structure, cobalt oxalate is preferable to cobalt carbonate as precursor. In addition, the production costs of cobalt carbonate are exceed to cobalt oxalate because of the characters of cobalt carbonate being easily oxidized, hard filtered, difficult molding and so on in the air, so cobalt oxalate is the most frequently chosen raw material in industry. However, because Co has the charters of dependence and succession to precursor’s morphology, cobalt carbonate’s morphology is loose particles but cobalt oxalate is stick-like regular crystal, preparing global Co powder will usually choose cobalt carbonate as raw material. Consequently, it is premised on preparing global Co powder with stable structure by adopting appropriate preparation method to prepare to global cobalt precursor.
The Influence of Mechanical Force

The structure of cobalt oxalate is growing as rod-like crystal along the direction of [010]. This research adopts mechanical solid-phase chemical reaction to prepare global cobalt oxalate, solids are subjected by severe shock under the action of strong mechanical force, powder is repeated broken in the impact, the stacking layers of CoC$_2$O$_4$$\cdot$2H$_2$O gradually reduce along the direction of (100) and (001) crystal face and restrict $\beta$-CoC$_2$O$_4$$\cdot$2H$_2$O to grow along [010] direction to make limit the sizes of product particles. Performance is particles continuing to thinning and length-to-width ratio cutting down.

There are many ways of applying mechanical force, under given conditions, applying outside force such as trituration, ball-milling, squeeze and so on to touch off solid-phase reaction for specific solid-phase system. Figure a and b respectively indicates the product’s XRD image of high-energy ball milling solid-phase reaction and hand lapping solid-phase reaction in fig 3, their summit of X-ray diffraction are consistent with $\beta$-CoC$_2$O$_4$$\cdot$2H$_2$O in PDF JCPDS NO.25-0250, which proves hand milling and high-energy ball milling can enable solid-phase reaction to carry out and the product is $\beta$-CoC$_2$O$_4$$\cdot$2H$_2$O. We can see obviously from figure5 that the summit of sample a branch to low angle clearly and its peak width is large and crystalline grain are thinner, this proves that mechanical force of ball milling enables crystalline grain to reserve some internal energy for expanding the crystal lattices of cobalt oxalate and high mechanical force treatment enables crystalline grain to refine.

Sample a and b in fig 4 indicates respectively the XRD images for Co powder from $\beta$-CoC$_2$O$_4$$\cdot$2H$_2$O decomposed at 450°C and for 3hours in nitrogen atmosphere by high-energy ball milling and hand milling. We can observe from figure6 that Co powder from precursors preparing by hand milling in figure b is obvious mixed crystal type, this explains although hand mill enables reaction to happen, the product mechanical force can’t reserve enough energy to ensure precursors restore to Co powder with fcc structure. Co powder is fcc crystal type that precursor prepare it by high-energy ball milling.
Sample a, b and c in fig 5 respectively indicates the SEM images of $\beta$-CoC$_2$O$_4$·2H$_2$O prepared by high-energy ball milling, hand milling and liquid reaction at room temperature. From the figure it is clear that the strong mechanical force of high-energy ball milling enables $\beta$-CoC$_2$O$_4$·2H$_2$O crystalline grain to become short distinctly, the depth-diameter ratio of $\beta$-CoC$_2$O$_4$·2H$_2$O produced by hand milling is relatively larger, and the depth-diameter ratio of $\beta$-CoC$_2$O$_4$·2H$_2$O produced by liquid reaction at room temperature is the largest. This shows that the mechanical force can control the morphology of the reaction product and enable longer grain to share off and fracture. The mechanical force produced by high-energy ball milling process can produce the best crushing, shearing, extrusion and deformation effects for the reactions.

Fig 6-1,2,3 is the SEM images of cobalt samples from $\beta$-CoC$_2$O$_4$·2H$_2$O, the 1,2,3 in figure 6 correspond $\beta$-CoC$_2$O$_4$·2H$_2$O samples a, b and c separately, we can find clearly from the figure that Co powder commendably inherits the morphology of $\beta$-CoC$_2$O$_4$·2H$_2$O.

Fig 7 indicates the XRD image of product Co powder in the experiment of this chapter. It is seen from the figure that the 111, 200 and 220 crystal planes corresponding to the peak of the high-energy ball milling product are in agreement with the $\beta$-Co standard card (PDF 15-0806), which is fcc structure $\beta$-Co. But the product b of hand milling and the product c of liquid phase method are respectively fcc and...
hcp mixed crystal type. This proves that Co powder prepares by general method is mixed crystal type, but under sufficient mechanical force, the energy of the solid phase reaction reserve will make the $\beta$-CoC$_2$O$_4$·2H$_2$O decompose to produce fcc structure Co powder.

Conclusions

(1). Cobalt oxalate and cobaltous carbonate are not only double tooth structure chelate compound but also best choice of preparing Cobalt precursor by mechanical solid state reaction. Structure of cobaltous oxalate is five member chelate ring with best stability, which is good at formation and growth of crystals.

(2). Slight mechanical force can make a solid state reaction system, high energy ball milling can solid let reaction products store enough energy and expand crystal lattice of cobaltous oxalate, then continue reaction to generate face centered cubic crystal cobalt powder; in addition, mechanical force can enable reaction products to grain refining and control the appearance of reaction products to longer grain fracture and chip.

(3). Cobalt will succeed the appearance of cobalt oxalate precursor, adopting high energy ball milling solid phase reaction-thermal decomposition method to prepare around 200 nm spherical beta-cobalt powder.

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