Liquid phase synthesis: preparation of Co microspheres by hydrazine reducing method

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Abstract. The study synthesizes Co microspheres with perfect spherical shape by use hydrazine hydrate as reducing agent to reduce CoCl2 in alkaline conditions at room temperature, the influence of NaOH addition amount on crystal morphology and structure of cobalt particle were studied. The results show that, under the condition of concentration of NaOH, 0.030g ml-1 and having ethylene glycol as solvent, are the best choice to synthesize Co microspheres, and the grain is smaller, suitable for industrial production. At the condition of less amount of NaOH, cobalt particle's surface is smooth spherical, and with the increase of NaOH, particles will deviate from the spherical morphology and the surface become rough.

1. Introduction
Cobalt is a kind of strategic metals, which is the main material of metal composite material with its ductility property. [1] Studies show that spherical morphology cobalt particle is more suitable for metal composite materials due to its small contact surface, which make particles not easy adhering and disperse well. [2] Anymore, it can significantly reduce the aggregation, reduce cobalt pool of composite, therefore the spherical cobalt particle is the best shape of metal composite material application. [3] There are many methods to synthesize spherical cobalt particles, such as the adding of nodulizing agent and surfactant, spray, plasma method and so on. [4] But neither chemical nor physical method, the spheroidization rate is lower, making the shape come to spherical-like, resulting the particle contact area increasing, unfavorable to disperse. [5] In recent years, it was found that hydrazine hydrate reduction (HHR) method can synthesize perfect spherical metal particles, [6] based on it, this study discusses the condition of hydrazine hydrate method to synthesize cobalt microspheres, in order to contribute to the batch production of spherical cobalt particle.

2. Experiments

2.1. Reagents
Cobalt dichloride (CoCl2), absolute ethyl alcohol, ethylene glycol, glycerol, Sodium hydroxide, polyvinylpyrrolidione (PVP), hydrazine hydrate. All the chemical reagents used in this study were of analytical grade, and used as received without further purification.
2.2. Experimental Procedures

Adding an appropriate amount of sodium hydroxide and surfactant PVP to 30 ml of hydrazine hydrate, made PVP, sodium hydroxide dissolved in hydrazine hydrate by ultrasonic stirring, so got a uniform mixed solution; Weighing 2.9g CoCl$_2$ and dissolved it in four 30ml solvent separately (water, alcohol, glycol, glycerol) to get B which is Co ions solution; Ultrasonic dispersing solution A, meanwhile, dropped the solution B to the solution A at the rate of 20 drops/min. after dropping, continued ultrasonic dispersing the mixing solution 20 min and then static. Finally, the mixing solution was divided into two layers, of which the upper was transparent liquid, and the precipitation of bottom were black particles sample. Then separated the precipitation by centrifuge, and vacuum dried the sample to obtain the target particles.

3. Results and Discussion

3.1. The influence of PH value

We can observe from the HHR reaction experiment, with the different of PH values and solvents using, the morphology and the size of cobalt particles are different, but the crystal structure of them are similar. Studies show that, [7] with the increase of PH, hydrazine hydrate reduction ability will be enhanced at alkaline conditions. Smoluchwski’s Particle Collision Theory pointed out that the collision frequency of primary grains and other particles, will increase with the increase of the number of crystal nucleus of per unit volume, it lead the primary grains size smaller. [8]

Figure 1 shows the SEM imagines of cobalt particles from HHR with different NaOH adding. From the figure, it can be observed that, with the increase of PH value adding, the particles size decreased, and the surface was more and more rough. This is because of the HHR ability will increase with the PH value adding, while the number of nuclei of Co increases. This will results that the collision and aggregation of grains occurs easier, and limit the free growth of grains, finally get smaller cobalt particle particles with rough surface.

Figure 1. SEM images of Co prepared by HHR with the different NaOH adding

3.2. The influence of the solvent

Studies have shown that, Co tends to priority form small pieces shape in the process of liquid phase synthesis. [9] Adding polyols in HHR course, it will gather together to form micro spherical reactor, and the reaction of HHR will be limited to a small space, small cobalt pieces will gather to form spherical particles. The formation of micro reactor requires a sufficient number of hydroxyl (OH), and hydroxyl numbers will influence the sphericity of particles. In the solvent of HHR, the largest number of hydroxyl is glycerol, followed is ethylene glycol, ethanol and water. Figure 2 shows the SEM imagines of Co particles from different solvent systems of HHR. It can be clearly seen from the figure
that, the best sphericity degree of particles is from the glycol, followed is glycerol, and the shapes of Co particles are irregular which from water and ethanol solvent systems, especially the water solvent makes the Co shape to pieces. This indicates the role of the hydroxyl reactor, which is only proper quantity of hydroxyl numbers can form complete spherical cobalt particles, such as ethylene glycol.

![Figure 2. SEM images of Co prepared by HHR from the different solvent systems](image)

Figure 2. SEM images of Co prepared by HHR from the different solvent systems
a. water b. alcohol c. glycerol d. glycol

![Figure 3. XRD images of Co prepared by HHR](image)

Figure 3. XRD images of Co prepared by HHR
①-② water and alcohol as the solvent, NaOH conc. 0.030g·ml⁻¹
③-④ NaOH conc. 0.030/0.004g·ml⁻¹, glycolic as the solvent

3.3. Structure of Co crystal
Figure 3 shows the XRD patterns for Co particles from HHR course. ①-② of the figure are the samples from water and glycol separately, and the concentrate of NaOH is 0.030g·ml⁻¹, while ③-④ are from glycerol and the concentrate of NaOH is 0.030/0.004g·ml⁻¹ separately. Compared the patterns of figure 3 to standard PDF card of Co, we can conclude that the Co particles from all HHR course are pure Co with fcc and hcp structures, the reaction of HHR can synthesize pure Co particles with perfect spherical shape.
4. Conclusions
(1) Hydrazine hydrate reduction can be used to synthesize Co particles with perfect spherical shape by using glycol as solvent with 0.030g·ml⁻¹ NaOH adding. The particle from it is greater than 1 μm, and suitable for the batch production of metal composite material;
(2) NaOH adding can influence the morphology of the cobalt powders: lower amount of NaOH will produce spherical Co particle particles with smooth surface; with the increase of NaOH, the particle of Co deviates from the spherical shape and become irregular, and its surface become coarse;
(3) Only proper quantity of hydroxyl numbers can form complete hydroxyl reactors, by using glycol as solvent, it can produce suitable spherical reactors and results spherical Co particles forming.

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