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ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) s240−s244

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Preparation of copper nanoparticles by chemical reduction method using potassium borohydride

ZHANG Qiu-li(张秋利)[1], YANG Zhi-mao(杨志懋)[2], DING Bing-jun(丁秉钧)[2],
LAN Xin-zhe(兰新哲)[1], GUO Ying-juan(郭莹娟)[1]

1. School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China;
2. School of Science, Xi'an Jiaotong University, Xi'an 710049, China

Received 6 July 2009; accepted 30 December 2009

Abstract: High dispersive copper nanoparticles were prepared by chemical reduction method using potassium borohydride as reducing agent. The effects of reactant ratio, concentration of $CuSO_4$, reaction temperature, and dispersant on the size of product and conversion rate were studied. The morphologies of copper nanoparticles were characterized by scanning electron microscopy. The results show that the optimum process conditions are as follows: the molar ratio of KBH_4 to $CuSO_4$ is 0.75 (3:4), concentration of $CuSO_4$ is 0.4 mol/L, reaction temperature is 30 ℃, and dispersant is *n*-butyl alcohol. The average particles size of copper powders with spherical shape gained is about 100 nm.

Key words: copper; nanoparticles; potassium borohydride; chemical reduction

1 Introduction

In the past few years, considerable interest has been focused on metal nanoparticles due to their special properties and potential applications in diverse fields. Among various metal particles, copper nanoparticles have attracted considerable attention because of their catalytic, optical, and electrical conducting properties. Several methods were developed for the preparation of copper nanoparticles, including thermal reduction, metal vapor synthesis, radiation methods, microemulsion techniques, laser ablation, mechanical attrition, and chemical reduction[1−9].

Most of the preparation methods have some factors that impede the use and development of the copper nanoparticles. For example, gas evaporation method presents the high cost of raw materials and complicated equipment. Copper nanoparticles synthesized by mechanical chemical method have wide particle size distribution and low purity. Among these methods, the solution method is simple and the most versatile for copper nanoparticles. Liquid reduction has its unique advantages such as simple equipment, short process and easy industrial production. Reducing agent is often used in present methods, including formaldehyde[10], ascorbic acid[11], sodium hypophosphite[12−13], and hydrazine hydrate[14].

However, some reducing agents are toxic and expensive, some have poor reducing ability, some have high costs, and some are easy to introduce other impurities to the process. Therefore, it is important to research more appropriate reducing agent and to study the chemical reaction system.

In the present study, potassium borohydride was used as the reducing agent to investigate the preparation of copper nanoparticles. Furthermore, the affecting factors were researched, including reactant ratio, copper sulfate concentration, reaction temperature, and dispersant.

2 Experimental

2.1 Preparation of copper particles

$CuSO_4·5H_2O$ and KOH are analytical reagents, and KBH_4 is chemical pure. The main equipment has an HH−4 type digital pot at a water bath temperature, a JJ−1 type blender from time to time, and a DZF−6050 vacuum drying oven.

$CuSO_4$ and EDTA were dissolved in distilled water.

Foundation item: Project(50834003) supported by the National Natural Science Foundation of China; Project(09JK561) supported by Educational Commission of Shaanxi Province of China
Corresponding author: ZHANG Qiu-li; Tel: +86-29-82201248; E-mail: qiulizhang@126.com

KBH_4 was added to the above solution as reducing agent, and then the solution was heated to reaction temperatures. After stirring at different temperatures for a certain time, the aqueous solution was spilled out and filtered. After that, the product was washed 3 times with ethanol and acetone separately, and finally dried in a vacuum drying oven.

2.2 Characterization

The morphologies of the copper particles were investigated via scanning electron microscope (SEM, TESCAN VEGA), and the particle size distributions were obtained by laser particle size analyzer (OMEC LS800).

3 Results and discussion

3.1 Effects of molar ratio of KBH_4 to Cu^{2+}

KBH_4 is a strong reducing agent, stable in air and alkaline solution, and has the risk of burning when exposed with acid or oxidants. Hydrogen will be slowly emitted when KBH_4 contacts with water. So, copper powder should be synthesized in alkaline environment when KBH_4 is used as reducing agent.

KOH is used as alkaline medium in the experiment, and EDTA is added as ingredient agent in order to avoid the formation of copper hydroxide precipitate in alkaline medium.

The equation of KBH_4 reacting with Cu^{2+} under alkaline conditions is as follows:

$$4CuSO_4+KBH_4+8KOH=4Cu+4K_2SO_4+KBO_2+6H_2O$$

It can be seen from the reaction that the theoretical molar ratio of KBH_4 to Cu^{2+} is 1:4. Different molar ratios are selected in the experiment, with reaction time fixed to 0.5 h. Therefore, the effects of particle size of copper powder on the conversion rate are investigated. The results are shown in Figs.1 and 2.

From Figs.1 and 2, it can be seen that reaction

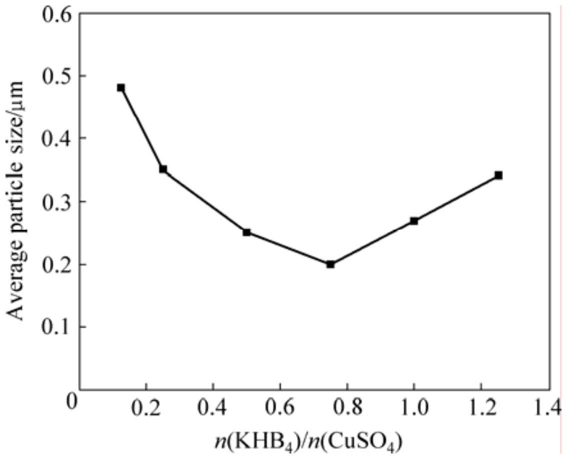

Fig.1 Effect of molar ratio of KHB_4 to $CuSO_4$ on average particles size

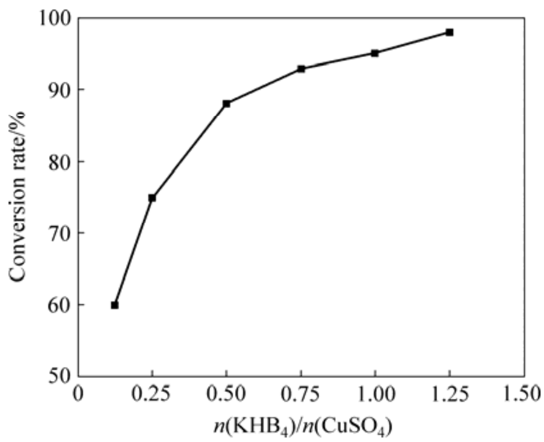

Fig.2 Effect of molar ratio of KHB_4 to $CuSO_4$ on conversion rate

conversion rate of copper sulfate increases with the increase of molar ratio of KBH_4 to $CuSO_4$, that is, the increase of KBH_4 amount. The reaction conversion rate is about 95% when the molar ratio is around 0.75 (that is 3:4), and then the increasing trend is not distinct. And size of copper is the smallest simultaneity. So, it has higher conversion rate and the KBH_4 consumption is less when the molar ratio is around 0.75. Therefore, the optimal molar ratio of KBH_4 to $CuSO_4$ is 0.75.

3.2 Effects of initial concentration of Cu^{2+}

There are two stages when copper nanoparticles generate in the solution. The first stage is to generate copper nuclei, and the second stage is the growth of copper. So, it is important to control preparation process that copper nuclei must generate faster and grow up slower, which requires better control of the initial concentration of Cu^{2+}.

The molar ratio of KBH_4 to $CuSO_4$ is fixed to be 0.75 in the experiment, and the initial concentration of Cu^{2+} is changed. The effect of concentration of Cu^{2+} on the average particle size is studied. The results are shown in Fig.3.

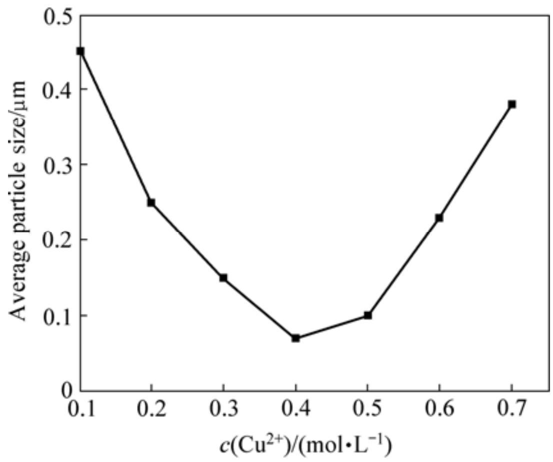

Fig.3 Effect of concentration of copper ions on average particle size of copper

It can be seen that reaction conversion rate increases with the increase of initial concentration of Cu^{2+}. With the increase of reaction conversion rate, the amount of the copper nuclei rises, and smaller particle size powders are obtained correspondingly. But an excess number of nuclei will be generated when the reactant concentration is too high. This results in the agglomeration of the nuclei and the growth of the particle size. So, the optimal initial concentration of Cu^{2+} is 0.4 mol/L.

3.3 Effects of reaction temperature

Fixing the molar ratio of KHB_4 to $CuSO_4$ to be 0.75, and the concentration of copper sulfate of 0.4 mol/L, we investigated the preparation of copper powders under different reaction temperatures. The results are shown in Fig.4.

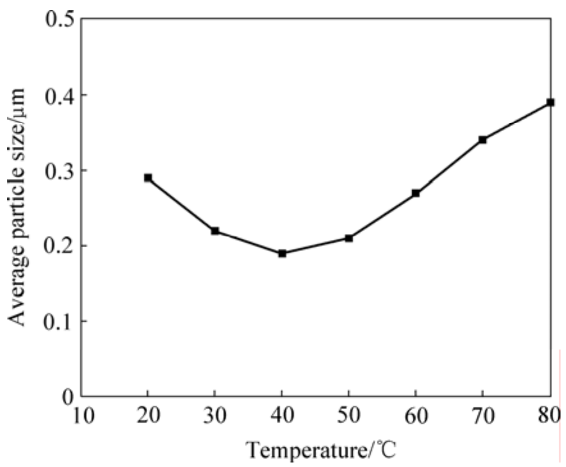

Fig.4 Effect of reaction temperature on average particle size of copper

It can be seen from Fig.4 that the size of copper powder decreases when the temperature goes up, but the gained size grows up when increasing to a certain temperature. In the reaction system, the effect on the nucleation rate by temperature is greater than that on the growth rate, so the nucleation rate of growth is faster than the growth rate when the temperature increases, and the smaller powder particle size is gained. But the nuclei surface activity is enhanced when the temperature is too high, which makes that the nuclei are prone to collide and reunite.

HUANG and REN[1] indicated that the purity of product would be increased and the oxidation of copper powder will be reduced when reacting at a lower temperature. Therefore, the optimal reaction temperature is 30 ℃.

3.4 Effects of dispersing agent

It is a key point to disperse effectively in the process of nanoparticle preparation. The surface activity of nanoparticles makes reunite and form a larger size group with number of weak interfaces easily. Adding dispersing agent, which is a kind of polymer, can prevent their reunion. Dispersing agent has two base groups: its hydrophilic group is attached to the surface of copper powder particles, while the other queue hydrophobic group is exposed to the solution. So, the surface of copper is covered with a layer of organic thin film, which can reduce collision between the powder cores. Then it prevents the growth of reunion particles and improves the dispersion of particles. At the same time, it can hinder copper from contacting with oxygen and prevent them from being oxidized.

There are four dispersing agents chosen in the experiment, namely polyvinyl pyrrolidone (PVP), glycerol, *n*-butanol and PEG−400. The results are shown in Table 1.

Table 1 Effect of dispersing agents on average particle size

No.	Dispersant agent	Average particle size/μm
1	Polyvinyl pyrrolidone	0.23
2	Glycerol propanetriol	0.61
3	*n*-butyl alcohol	0.15
4	PEG−400	0.42

It can be seen from Table 1 that *n*-butanol and PVP are more suitable for dispersing agent in this system, and smaller particles are gained using *n*-butyl alcohol. Therefore, *n*-butanol is chosen as dispersing agent.

3.5 SEM images of samples

The optimal conditions for the experiment are as follows: molar ratio of KBH_4 to $CuSO_4$ is 0.75, concentration of $CuSO_4$ is 0.4 mol/L, and reaction temperature is 30 ℃. Copper powders are synthesized using different dispersing agents respectively. The SEM images are shown in Fig.5.

It can be seen from Fig.5 that the gained powders reunite seriously but have some particles with smaller size when PVP is chosen as dispersing agent (shown in Fig.5(a)). When glycerol and PEG−400 are used as dispersing agent separately, the copper powders have a larger particle size and reunite seriously (Figs.5(b) and (d)). When *n*-butyl alcohol is used, the product possesses small size about 100 nm and even dispersive (Fig.5(c)). According to Ref.[15], copper nanoparticles can be gained when KBH_4 is used as reducing agent and PVP and sodium dodecyl sulfate are used as dispersing agents, the gained powder will be both spherical and non-aggregation[15]; when formaldehyde is used as reducing agent, the prepared powders reunite seriously and the size is in the range of 20−400 nm. Although spherical-similar copper powders with size of 35 nm can be prepared by the use of hydrazine method[14], the method has the disadvantage of toxic resource materials

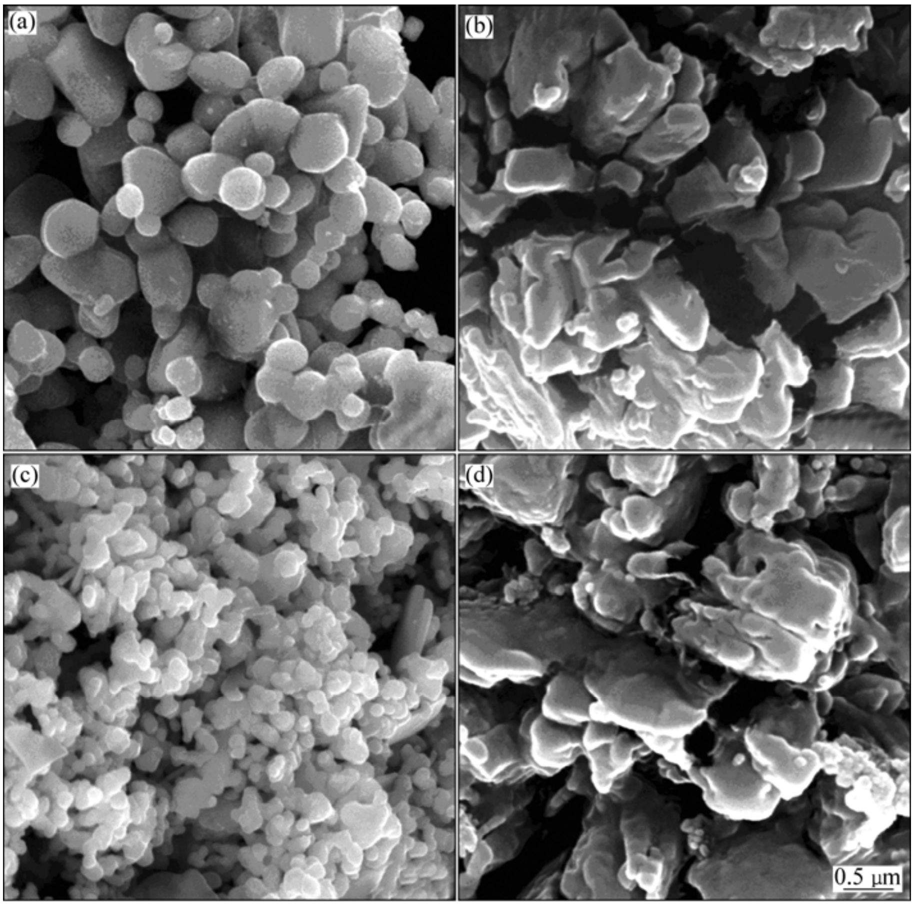

Fig.5 SEM images of copper powders prepared with different dispersing agents: (a) Polyvinyl pyrrolidone; (b) Glycerol propanetriol; (c) *n*-butyl alcohol; (d) PEG−400

and is unsuitable for large-scale application[1].

4 Conclusions

1) The present study illustrates simple, convenient and significant methods for the synthesis of copper nanoparticles through the reduction of copper salts using KBH_4 as reducing agent. Relatively monodisperse copper nanoparticles with a size range of 100 nm are obtained under optimum conditions.

2) The optimum conditions are as follows: the molar ratio of KBH_4 to $CuSO_4$ is 0.75 (3:4), concentration of $CuSO_4$ is 0.4 mol/L, and reaction temperature is 30 ℃. The dispersing agent plays an important role in determining the copper particle size distribution and inhibiting the agglomeration.

References

[1] HUANG Jun-sheng, REN Shan. Development on nanocrystalline powder copper preparation [J]. Materials Science and Engineering, 2001, 19(2): 76−79. (in Chinese)

[2] CHU Guang, TANG Yong-jian, LIU Wei, LUO Jiang-shan, LI Jun, YANG Tian-zu. The preparation technology and application of nanocrystalline copper powder [J]. Metallic Functional Materials, 2005, 12(3): 18−21. (in Chinese)

[3] CHEN Qing-chun. Hydrothermal conditions for fabrication of Cu nanorods and nanowires through reduction [J]. Fine Chemicals, 2005, 22(6): 417−419. (in Chinese)

[4] GENG Xin-ling, SU Zheng-tao. Research on preparation of nano-copper powder by liquid-phase method [J]. Applied Chemical Industry, 2005, 34(10): 615−617.

[5] WANG Xiao-li, XU Bin-shi, YU He-long, XU Yi. Preparation and tribological properties analysis of nano-Cu additive in lubricating oil [J]. China Surface Engineering, 2005, 18(5): 24−27. (in Chinese)

[6] HE Feng, ZHANG Zheng-yi, XIAO Yao-fu, WANG Wu-xiang, HAN Ya-fang, WANG Run. New electrolytic method of preparing ultrafine metal powder [J]. Acta Metallurgica Sinica, 2000, 36(6): 659−661. (in Chinese)

[7] WEI Qi-feng, ZHANG Qi-xiu. Preparation of copper powder by anion film electrolysis [J]. Non-ferrous Smelting, 2003, 6(3): 10−13. (in Chinese)

[8] HE Li-jun, HUO Cai-xia, WANG Yong-hong. Preparation of the nano sized Cu powders from the waste of electroless plating Cu solution [J]. Journal of Gansu Lianhe University: Natural Science, 2005, 19(4): 49−51. (in Chinese)

[9] TAN Ling-hua, LI Feng-sheng. Preparation of nanometer Cu powder and study on its catalytic characteristic of thermal decomposition of ammonium perchlorate [J]. Journal of Nanjing Institute of Technology: Natural Science Edition, 2005, 3(1): 6−10. (in Chinese)

[10] LIAO Rong, SUN Bo, TAN Hong-bin. Research of preparation of ultrafine copper powder using formaldehyde as reductive agent [J]. Journal of Chengdu University of Technology: Science and Technology Edition, 2003, 30(4): 417−421. (in Chinese)

[11] ZHOU Quan-fa, JIANG Ping-ping, ZHU Wen, ZHAO De-jian. Preparation and characterization of anti-oxidation copper nanopowders [J]. Rare Metal Meterials and Engineering, 2004, 33(2): 179−182. (in Chinese)

[12] ZHANG Zhi-mei, HAN Xi-jiang, SUN Miao-xin. Preparation of nano copper powder [J]. Fine Chemicals, 2000, 17(2): 69−71. (in Chinese)

[13] ZHANG Jing-chang, ZHU Fen-mei, CAO Wei-liang. Preparation of nano sized copper powder by supercritical drying technique [J]. The Chinese Journal of Nonferrous Metals, 2004, 14(10): 1741−1746. (in Chinese)

[14] CHEN Hui-yu, TANG Jiao-ning, XIN Jian, SU Wen-bin. Preparation of copper nanoparticles by reducing hydrazine [J]. New Chemical Materials, 2005, 33(11): 48−50. (in Chinese)

[15] LIN Rong-hui, FANG Liang, XI Ying-xin, SHAO Yan-xia. Preparation of nano-particle copper by chemical reduction [J]. Acta Chimica Sinica, 2004, 62(23): 2365−2368. (in Chinese)

(Edited by CHEN Wei-ping)