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ARTICLE

Preparation of Spherical Cu Nanoparticles by Gaseous Detonation and Their Formation Mechanism

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Abstract: Face-centered cubic (fcc) copper nanocrystal particles (Cu NPs) were synthesized by the gaseous detonation method using hydrogen-oxygen mixed gases as the explosion source and copper (II) acetylacetonate as the precursor. The morphology, phase composition and microstructure of the as-obtained products were analyzed by XRD, TEM, SAED and EDX. Meanwhile, to predict the growth characteristics of the Cu NPs, the Kruis model was tentatively integrated in reaction condition of gaseous detonation. The results show that the as-synthesized fcc structural nanocrystalline copper with good dispersibility is coated with thinner graphite layer and the average size of particles is 24 nm. In addition, the growth characteristic of spherical Cu NPs is consistent with the obtained experimental data based on Kruis model, providing a reliable theoretical guidance for the controllable synthesis of Cu NPs.

Key words: gaseous detonation; copper nanocrystal particles; fcc; Kruis model; growth characteristic

As a new kind of functional nanomaterial, nanoscale metal crystal has recently attracted increasing attention because of its unique size effect, dimensionality-dependent physical and chemical properties. As an promising metal, Cu NPs have been widely applied in catalysis[1-3], lubricants[4,5], antibiosis[6], biological medicine[7], printing electronics[8], sensors[9], etc. Up to now, researchers have actively carried out researches on different preparation methods for Cu NPs. Most commonly used methods amongst them are chemical reduction[10,11], microwave techniques[12], thermal decomposition methods[13,14], micro emulsion methods[15], etc. In addition to these methods, the gaseous detonation method is a novel one and emerges in recent years for the synthesis of nanomaterials. The method is simple, fast, green and easily controlled; therefore, many nanoscale materials such as onion-like carbons[16], nanotubes[17], nano-diamond/alumina[18], and nano-TiO_2[19] have been successfully prepared by this method. However, accurately numerical simulation of nanosized grain growth in gaseous detonation field is still a difficult problem. The Kruis model is a theoretical model describing simultaneous aggregation and sintering in an aerosol flow reactor that is very similar to the gaseous detonation field[20]. In our previous reports[21,22], the model was used to predict the trend of the spherical particles under different reaction conditions. Therefore, we tentatively introduced Kruis model to simulate the growth characteristics of spherical Cu NPs, providing guidance for the crystal growth of nanoparticles.

In this paper, the Cu NPs were successfully prepared by the rapid gaseous detonation using copper acetylacetonate, hydrogen and oxygen as raw materials. Through the introduction of Kruis model, the growth characteristics and formation mechanism of the spherical Cu NPs during the gaseous detonation process were mainly discussed.

1 Experiment

The gaseous detonation was performed in a device described in Ref.[23]. Before the experiment, the detonation tube was pumped into vacuum state and heated to 430~450 K.

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Then, 0.005 mol copper acetylacetonate ($C_{10}H_{14}CuO_4$, sublimation point 433 K, AR, Sinopharm Chemical Reagent Co., Ltd, China) was injected into the tube through the feed port and gasified. Hydrogen, oxygen and nitrogen was filled into tube until the pointer of the barometer reached ordinary pressure (mole ratio of H_2:O_2:N_2 was 2:1:3.76), held for 3~5 min and the gaseous mixture was ignited with a 40 J high-energy igniter. After the detonation tube was cooled to room temperature and the end gas was removed, the black product was collected from the inner tube for subsequent analysis. The chemical reaction is very fast and complex in which the maximum values of temperature, pressure and spread velocity were higher than 2000 °C, 3~4 MPa, and 1100~1300 m/s, respectively.

The X-ray diffractometer (XRD, BRUKER, D8 ADVANCE, λ=0.154 06 nm, 40 kV voltage, 30 mA current) was used to test phase composition of detonation products, operated at a step size of 0.02° in a range of 15°~85° with Cu Kα radiation. The morphology of the synthesized products was investigated by transmission electron microscopy (TEM, FEI, Tecnai G2 F20, operated at 200 kV, 0.24 nm point resolution, 0.102 nm line resolution) and the chemical composition of products was analyzed by the equipped energy-dispersive X-ray spectrometer (EDX, 136 eV energy dispersive resolution).

2 Kruis Model Theories

The simple monodisperse Kruis model was employed to estimate particle growth by coagulation using the formulas. Assuming that all the aggregated particles contain the primary particles with the same number and equal size, the formula for the particle size distribution of the aggregated particles is:

$$\frac{\mathrm{d}N}{\mathrm{d}t}=-\frac{1}{2}\beta N^2 \tag{1}$$

$$\frac{\mathrm{d}v}{\mathrm{d}t}=-\frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}t}v \tag{2}$$

$$\frac{\mathrm{d}a}{\mathrm{d}t}=-\frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}t}a-\frac{1}{\tau}(a-a_\mathrm{s}) \tag{3}$$

$$a_\mathrm{s}=(\frac{v}{v_0})^{\frac{2}{3}}a_0 \tag{4}$$

where N is number fraction of the aggregates, v is volume of aggregates which is only affected by coagulation, β is monodisperse collision frequency for coagulation spanning over the free-molecular, transition and continuum regimes, τ is the characteristic sintering time, a is surface area of aggregate particles increased by coagulation and decreased by sintering, a_s is surface area of completely melt spherical particle, a_0 and v_0 are monomer particle surface area and volume, respectively[24]. In addition, primary particle diameter d_p and primary particle number in aggregates n_p are calculated as (v_p is the volume of primary particles):

$$d_\mathrm{p}=\frac{6v}{a},\ n_\mathrm{p}=\frac{v}{v_\mathrm{p}} \tag{5}$$

The characteristic time is given by the expression proposed by Friedlander et al[25]:

$$\tau=\frac{3k_\mathrm{b}Tv_\mathrm{p}}{64\pi\sigma D(T)v} \tag{6}$$

where k_b is Boltzmann's constant, σ is surface tension, D is solid state diffusion coefficient and can be represented by $D(T)=A\exp(-Q/T)$. The collision radius of the primary particle r_c is defined as:

$$r_\mathrm{c}=r_\mathrm{p}(\frac{v}{v_\mathrm{p}})^{\frac{1}{D_\mathrm{f}}}=r_\mathrm{p}(n_\mathrm{p})^{\frac{1}{D_\mathrm{f}}} \tag{7}$$

where r_p is the radius of the primary particle, and D_f is the quality of the fractal coefficient. The monodisperse collision frequency for coagulation is thus calculated as:

$$\beta=8\pi D_\mathrm{d}r_\mathrm{c}(\frac{r_\mathrm{c}}{2r_\mathrm{c}+\sqrt{2}g}+\frac{\sqrt{2}D_\mathrm{d}}{cr_\mathrm{c}})^{-1} \tag{8}$$

where D_d is particle diffusion factor, and

$$D_\mathrm{d}=\frac{kT}{6\pi\mu r_\mathrm{c}}[\frac{5+4K_\mathrm{n}+6K_\mathrm{n}^2+18K_\mathrm{n}^3}{5-K_\mathrm{n}+(8+\pi)K_\mathrm{n}^2}]$$
$$K_\mathrm{n}=\frac{\lambda}{r_\mathrm{c}},\quad \lambda=\frac{1}{4\sqrt{2}\pi nr_\mathrm{c}} \tag{9}$$

where λ is the mean free path of gas molecules, and

$$g=\frac{1}{6r_\mathrm{c}l}[(2r_\mathrm{c}+l)^3-(4r_\mathrm{c}+l^2)^{\frac{3}{2}}]-2r_\mathrm{c}$$

$$l=\frac{8D_\mathrm{d}}{\pi c},\quad c=\sqrt{\frac{8k_\mathrm{b}T}{\pi\rho_\mathrm{p}v}} \tag{10}$$

where ρ_p is the density of primary particles. To calculate the Fuchs polymeric particle collision coefficient, the relationship between the collision radius and the volume and area of the polymeric particles needs to be determined.

$$r_\mathrm{c}=\frac{3v}{a}(\frac{a^3}{36\pi v^2})^{\frac{1}{D_\mathrm{f}}} \tag{11}$$

Here, it is assumed that the fractal coefficient of coalescence of particles does not arise from sintering.

3 Results and Discussion

3.1 Microstructure of the as-received products

Fig.1 shows the XRD pattern of Cu NPs with diffraction angles of 15°~85°. It is clear that 3 obvious diffraction peaks appear at 2θ=43.0°, 50.2°and 73.9°, corresponding to (111), (200) and (220) planes of fcc Cu, respectively. Besides the copper peak in the samples, there are no peaks of other impurities in the figure. By use of Scherrer's formula, the crystalline sizes of Cu NPs were calculated from the major diffraction peak, approximately 25.89 nm.

TEM analysis and EDX spectrum images of the synthesized Cu NPs samples are shown in Fig.2. It can be seen from Fig.2a that the Cu NPs are spherical or ellipsoidal shapes with good dispersibility. Almost all the nanoparticles range from 8~50 nm and the average size is about 24 nm (Fig.2b). The

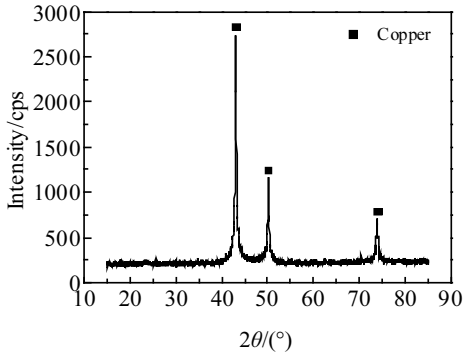

Fig.1 XRD pattern of Cu NPs

HRTEM image (Fig.2c) reveals that the graphite layer tightly encapsulate spherical black fcc-Cu cores without obvious voids between the core and coating layers, and the crystal spacing is 0.209 nm. Fig.2d shows that a certain amount of amorphous carbon-coated Cu NPs form a coating layer of about 1 nm, and based on selected area electron diffraction (SAED) pattern, the characteristic spot array can be indexed to (111), (200), (220) and (311) of the fcc-Cu lattice structure. The EDX data show that the as-obtained products mainly consist of copper, carbon and a little oxygen, which is consistent with the XRD and TEM results.

3.2 Formation mechanism analysis

During the whole reaction process, the molar mass and released heat of copper acetylacetonate are very small, so when calculating the detonation temperature, only the exothermic of gas is considered. According to the first laws of thermodynamics, the thermodynamic energy of combustible gas under constant volume (closed system) remains unchanged before and after reaction. The properties of the state function are as follows:

$$\Delta U = \Delta U_1 + \Delta U_2 \quad (12)$$

$$\Delta U_1 = \Delta H_1 - \sum n_1 RT \quad (13)$$

$$\Delta U_2 = \sum n_2 C_{v,m} \Delta T \quad (14)$$

where ΔU is the thermodynamic energy increment of matter system, ΔU_1 is the energy increment of constant temperature and constant volume reaction process, ΔU_2 is the energy increment in constant volume temperature rise process. $C_{v,m}$ is average constant volume specific heat. The related detonation reaction equation and constant volume specific heat of reactive material are as follows:

$2H_2(g)+O_2(g)+3.76N_2(g)\rightarrow 2H_2O(g)+3.76N_2(g)+483$ kJ/mol

$C_{10}H_{14}CuO_4(g)\rightarrow Cu(s)+10C(s)+4H_2O(g)+3H_2(g)$

By calculating enthalpy and specific heat, the detonation temperature is about 2482 K under the premise of ignoring the

Table 1 Average constant volume specific heat of reactive material ($J\cdot K^{-1}\cdot mol^{-1}$)

$H_2O(g)$	N_2	H_2
37.66	25.1	24.6

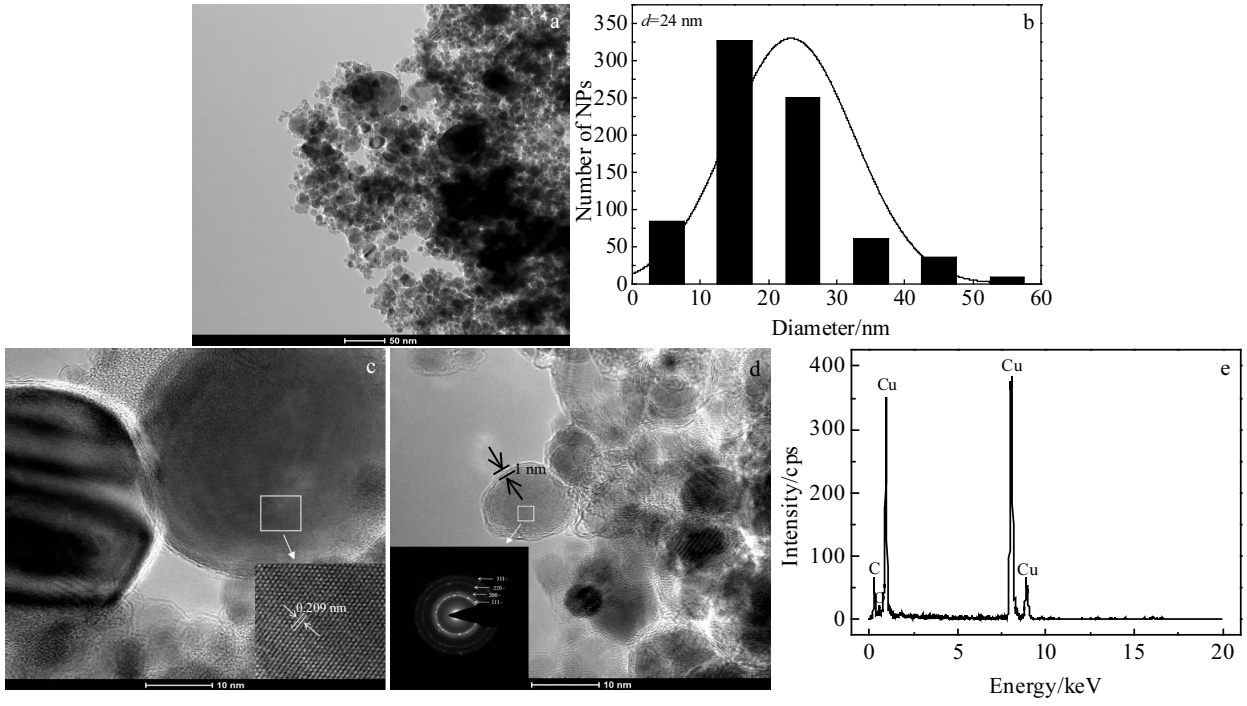

Fig.2 TEM image of the Cu NPs (a), bar chart of diameters of products (b), crystal spacing of 0.209 nm of Cu NPs (c), selected area electron diffraction pattern of Cu NPs (d), and EDX spectrum of the obtained product (e)

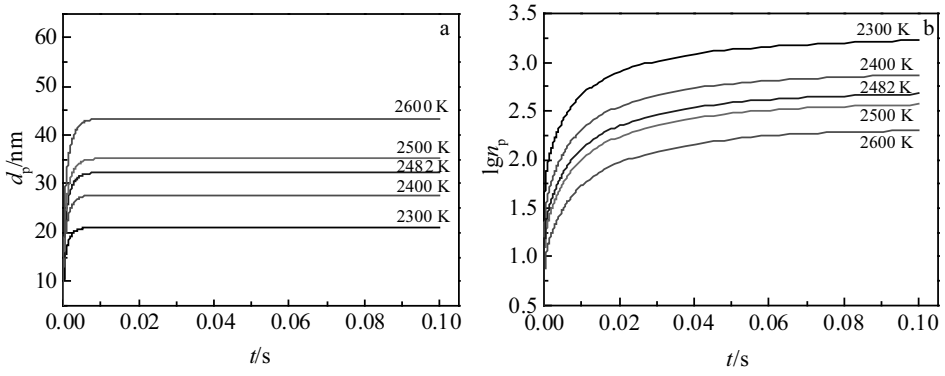

Fig.3 Evolution of diameter d_p (a) and number n_p (b) of primary particles with time at different temperatures (2300~2600 K)

energy loss and constant temperature-volume.

Through the observation of the numerical analysis results in Fig.3a, it can be found that the growth process of the crystal particle is basically completed at 5 ms, and the primary particle diameter d_p increases with temperatures. Fig.3b shows the contrast of number of primary particles n_p when the temperature is changed. It can be apparently seen that the curves increase exponentially when the temperature rises. From the comparison of calculated and experimental results, the particle size from the numerical analysis almost match with growth characteristics of experimental data, which can provide a reliable theoretical basis for the nanoparticle growth characteristics under the gaseous detonation condition to a certain extent.

4 Conclusions

1) The spherical and near-spherical fcc-Cu NPs are synthesized by the gaseous detonation method with copper acetylacetonate as metal source and mixed gases as the explosive source.

2) The nanoparticle is coated with graphite layer and the average size is 24 nm. The Kruis model is tentatively applied to simulate the characteristics of Cu NPs and the calculation results can fit the experimental results well.

References

1 Gawande M B, Goswami A, Felpin F *et al*. *Chemical Reviews*[J], 2016, 116(6): 3722
2 Alonso F, Moglie Y, Radivoy G. *Accounts of Chemical Research*[J], 2015, 48(9): 2516
3 Zhu R, Buchwald S L. *Journal of the American Chemical Society*[J], 2012, 134(30): 12 462
4 Zhang B, Xu B, Xu Y *et al*. *Tribology International*[J], 2011, 44(7-8): 878
5 Guzman Borda F L, Ribeiro De Oliveira S J, Seabra Monteiro Lazaro L M *et al*. *Tribology International*[J], 2018, 117: 52
6 Hajipour M J, Fromm K M, Akbar Ashkarran A *et al*. *Trends in Biotechnology*[J], 2012, 30(10): 499
7 Lei R, Wu C, Yang B *et al*. *Toxicology and Applied Pharmacology*[J], 2008, 232(2): 292
8 Magdassi S, Grouchko M, Kamyshny A. *Materials*[J], 2010, 3(9): 4626
9 Huang M, Zhang Y, Du C *et al*. *Plasmonics*[J], 2016, 11(5): 1197
10 Priya C S, Velraj G. *Materials Letters*[J], 2012, 77: 29
11 Wen Y, Huang W, Wang B *et al*. *Materials Science and Engineering B*[J], 2012, 177(8): 619
12 Yallappa S, Manjanna J, Sindhe M A *et al*. *Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy*[J], 2013, 110: 108
13 Salavati-Niasari M, Davar F, Mir N. *Polyhedron*[J], 2008, 27(17): 3514
14 Salavati-Niasari M, Davar F. *Materials Letters*[J], 2009, 63(3-4): 441
15 Luo N, Li X J, Liu K X. *Journal of Particle Research*[J], 2013, 15: 614
16 Luo N, Jing H, Ma Z *et al*. *Mendeleev Communications*[J], 2017, 27(2): 195
17 Luo N, Jing H. *Fullerene Science & Technology*[J], 2016, 24(8): 494
18 Yan X, Li X, Wang X *et al*. *Diamond & Related Materials*[J], 2017, 77: 79
19 Luo N, Jing H, Ma Z *et al*. *Materials Letters*[J], 2014, 137: 164
20 Einarkruis F, Kusters K, Pratsinis S *et al*. *Aerosol Science & Technology*[J], 1993, 19(4): 514
21 Luo N, Jing H, Ma Z *et al*. *Particuology*[J], 2016, 26: 102
22 Luo N, Shen H, Jing H *et al*. *Particuology*[J], 2017, 35: 78
23 Luo N, Xiang J, Shen T *et al*. *Fullerenes, Nanotubes and Carbon Nanostructures*[J], 2018, 26(2): 87
24 Wang C, Shu C, Han W *et al*. *Combustion and Flame*[J], 2013, 160(2): 447
25 Friedlander S K, Wu M K. *Physical Review B*[J], 1994, 49(5): 3622

气相爆轰法制备球形铜纳米粒子及其形成机理

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摘　要：以氢氧混合气体为爆炸源，乙酰丙酮铜(II)为前驱体，采用操作简单、高效的气相爆轰方式合成了类球形的铜纳米晶颗粒。进一步采用 XRD、TEM、SAED 和 EDX 对所获得产物的形貌特征、物相组成和微观结构进行了表征和分析。同时为了预测气相爆轰流场中铜纳米颗粒的生长特性，将 Kruis 模型引入气体爆轰反应程序中。结果表明：实验合成的类球型 fcc 结构纳米铜晶体分散性良好，平均粒径在 24 nm 左右且纳米铜晶体外包覆了 1 nm 左右的较薄石墨层。基于 Kruis 模型对球形铜纳米粒子的生长特性预测结果与实验数据吻合较好，为可控合成铜纳米粒子提供了可靠的理论指导。

关键词：气相爆轰；铜纳米晶体颗粒；fcc；Kruis 模型；生长特性

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