

PREPARATION AND MICROSTRUCTURE OF NANO-SIZED Cu PARTICLES BY MECHANOCHEMICAL REACTION^①

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ABSTRACT The nano-sized Cu particles have been prepared by a mechanochemical reaction. The structure of Cu particle has been investigated by means of X-ray diffraction (XRD), transmission electron microscope (TEM) and differential thermal analysis (DTA). The results showed that the Cu particle is around 20 nm in size, and it is so chemically active that Cu₂O is formed in the surface of the particle. The nano-sized Cu particles agglomerate if the temperature increases beyond 400 °C. In addition, the formation mechanism of nano-sized Cu particles was discussed.

Key words nanostructured material copper mechanical alloying nanoparticle

1 INTRODUCTION

The metal particle with size of 1~ 1000 nm is called superfine metal particle. Since the superfine metal particles have significant potential for a lot of applications, such as catalysts, medicine, electronic and optical instruments, many synthesis methods were studied, including physical vapor deposit^[1], thermal decomposition^[2, 3] and chemical reduction in liquid^[4-7], etc. Recently, mechanical alloying (MA) has been used to prepare the nano-sized Fe particles.

Mechanical alloying has been extensively applied for synthesis of nanostructured materials in the recent years. Although the grain size in particle prepared by MA can be refined to nanoscale, the particle size is larger than 1 μm. In 1995, Ding *et al*^[8] first reported that the nano-sized Fe particles had been synthesized by the mechanochemical reaction of the Na slices and the FeCl₃ powders. The mechanochemical reaction is considered as an effective and economic process for manufacturing nano-sized particles.

In the present work, the nano-sized Cu particles are prepared by mechanochemical reaction, and its structure is investigated, and the forma-

tion mechanism is also discussed.

2 EXPERIMENTAL

Elemental magnesium (< 150 μm, > 97%) and the dried CuCl powder (> 97%) were mixed in the mole ratio of 1: 2. The powder mixture was sealed in a hardened stainless-steel vial in an argon-filled glove box. The milling media were the steel balls of 10 mm in diameter. The mass ratio of the balls to the powder was 8: 1. Milling was conducted in a QM-1SP planetary ball mill with the planetary rotation speed of 230 r/min. Ball milling lasted for 50 h.

The as-milled powders were washed several times with deionized water and then resined and dried with ethanol. The powder samples were investigated by a Rigaku D/max-3B X-ray diffractometer with CuK_α radiation (λ = 0.15418 nm) and a JEM-100CX transmission electron microscope. The powders for TEM observation were pretreated with 5% HCl solution, then scattered in ethanol, and finally the suspended powders were mounted on a copper microgrid. The thermal stability of nano-sized Cu particles after pretreatment with 5% HCl solution were

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also studied by a Rigaku 8150 differential thermal analysis instrument with flowing argon at the rate of 20 K/min.

3 RESULTS AND DISCUSSION

3.1 XRD analysis

After the as-milled powders were washed several times with deionized water and then immersed in the 5% HCl solution for 1 min, the powders were found to be purplish red. And the XRD analysis showed that the powders were composed of elemental Cu with fcc structure (as shown in Fig. 1(a)). The broadened profile lines of Cu were corresponding to a particle size of 20 nm using the Vigot function. No trace of any other material except for Cu was detected. This indicates that the displacement reaction of Mg and CuCl was completed.

After the superfine Cu powder had been exposed in air for 5 h, the color of the powders became dull purple from purplish red. Fig. 1(b) demonstrates the XRD pattern of the powder exposed in air for 5 h. The result shows that Cu and Cu₂O existed in the exposed powders, implying that oxidation of Cu occurred. After this sample had been left in air for 1 month, the structures of the powders did not change.

3.2 TEM examination

Fig. 2 reveals the TEM micrograph of the powders after pretreatment in 5% HCl solution. The particle sizes were uniform and around 20 nm, which was in agreement with the estimated result of XRD analysis. The rings in the selected area electron pattern were correspondent to the Cu phase with fcc structure.

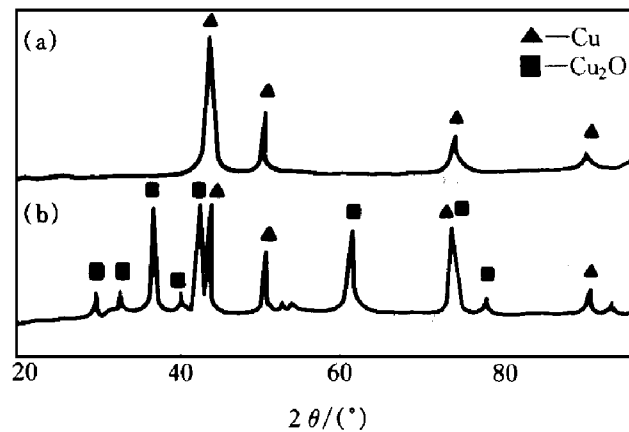


Fig. 1 XRD patterns of the nano-sized Cu particles

(a) —Pretreated with 5% HCl solution;
(b) —Exposed in air for 5 h

The powders after exposure to air were also examined by TEM. No diffraction pattern of Cu₂O was found. This indicated that the oxide layer of Cu₂O was very thin.

3.3 DTA analysis

The DTA curve for the nano-sized Cu particles is shown in Fig. 3. No sharp endothermic or exothermic peak was present in the curve. This indicates that no abrupt phase transformation occurred during heating. But the DTA curve presented a broad peak below 550 °C.

After the nano-sized Cu particles, which had been annealed in vacuum at 550 °C for 30 min, were exposed to air for 5 h, the Cu particles were found to be still purplish red rather than dull purple. This indicates that the Cu particles were not rapidly oxidized.

It is believed that the nano-sized Cu parti-



Fig. 2 TEM micrograph (a) and the selected area electron pattern (b) of the nanosized Cu particles

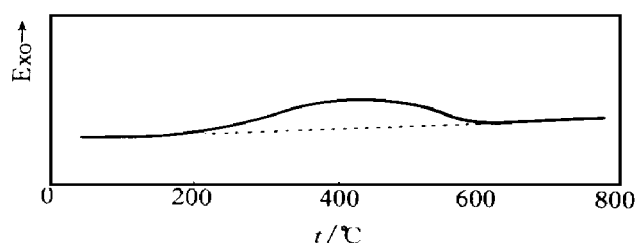
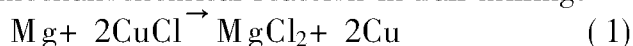


Fig. 3 DTA curve for the nano-sized Cu particles

cles are very active due to the large surface areas. During heating, the superfine Cu particles agglomerate, releasing the surface energy. As a result, an exothermic peak occurs in the DTA curve. After annealing at 550 °C, the agglomerate particles become less active.

3.4 Formation mechanism

The aim of the present work is to complete the mechanochemical reaction in ball milling:



Then the elemental Cu powders are obtained. Generally, the Mg powder can not react with the dried CuCl powder at the room temperature. However, this solid-state reaction may be triggered during high-energy ball milling. This kind of reaction mechanism has been described in the literature[9, 10].

In the present investigation, the reaction speed is a critical factor that controls the Cu particle size. If the reaction speed is high enough, the self-sustained (explosion) reaction will happen^[9, 11]. This explosion will result in significant temperature rise, leading to melting and solidification of Cu. As a result, the bulk Cu rather than the nano-sized Cu particles may be produced. According to Eq. (1), the formation heat of Cu is -183 kJ/mol ^[12]. Owing to the large formation heat of Cu, the explosion reaction will occur when the mixture of Mg and CuCl with the ratio of 1:2 is subject to ball milling. Therefore, the 15% NaCl is added into the starting material to act as a diluent. Dilution of reactants increases the ignition temperature for

explosion reaction and separates the reactants^[9, 13]. Consequently, the reaction speed can be remarkably reduced, and the explosion reaction can be suppressed. Thus superfine copper particles will be slowly precipitated.

If other materials aside from Cu are absent in the vial, the Cu powders will be subject to deformation, fracture and cold-welding. After attaining a dynamic equilibrium, the particle size of Cu is sustained in the range of 1~100 μm. Consequently, the nano-sized Cu particles can not be obtained. However, in the present experiment, since the produced Cu particles are immersed in the large amount of MgCl₂ and NaCl salts, the superfine Cu particles are separated each other. This reduces considerably the possibility of cold-welding. In addition, because the chlorides contacting with the Cu particles lower the surface energy of Cu, the nano-sized Cu particles do not agglomerate during ball milling.

REFERENCES

- 1 Zhang Lide and Mo Jimei. Nanostructured Materials, (in Chinese). Shenyang: Liaoning Scientific and Technological Press, 1994: 26.
- 2 van Wonerghem J, Morup S, Charles S W *et al.* Phys Rev Lett, 1994, 55(4): 410.
- 3 Morup S, Christensen B R, van Wonerghem J *et al.* J Magn Magn Mater, 1987, 67: 249.
- 4 van Wonerghem J *et al.* Nature, 1986, 322: 622.
- 5 Linderoth S *et al.* J Appl Phys, 1991, 69: 5256.
- 6 Sheng Jianyi, Hu Zheng, Zhang Lifeng *et al.* Acta Chemistry, (in Chinese), 1992, 50: 566.
- 7 Deng J F *et al.* Appl Catal, 1988, 37: 339.
- 8 Ding J, Miao W F, McCormick P G *et al.* Appl Phys Lett, 1995, 67: 3804.
- 9 Wu N Q, Lin S, Wu J M *et al.* Mater Sci Tech, 1998, 14(1), 287.
- 10 Wu N Q, Li Z Z. Materials Review, (in Chinese), 1997, 11(6): 20.
- 11 Schaffer G B and McCormick P G. Metall Trans, 1991, 22A: 3019.
- 12 Smithless C J and Boanderes E A. Metals Reference Book. London & Boston: Butterworths, 1978: 210.
- 13 Wu N Q *et al.* Mater Lett, 1997, 32: 259.

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