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Letter

Ultrafine Cu particles prepared by mechanochemical process

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Abstract

The solid-state displacement reaction of $CuCl_2 + 2Na = Cu + 2NaCl$ induced by mechanical milling has been studied. Ultrafine Cu particles have been produced after removing the by-product NaCl from the as-milled mixture in a washing process. Two different morphologies of Cu particles were observed by transmission electron microscopic examinations. Cu particles of uniform size in the range of 20–50 nm were found after a steady-state reaction during mechanical milling, whereas larger particles were observed when combustion had occurred.

Keywords: Ultrafine Cu particles; Mechanochemical process

1. Introduction

Mechanical milling has been widely applied for the synthesis of nanocrystalline materials in recent years [1,2]. Using appropriate milling conditions, this technique results in the formation of aggregates of nano-sized grains within micro-sized particles. Schaffer and McCormick [3,4] have demonstrated the use of mechanical milling to initiate solid-state displacement reactions. Recently, we have reported the synthesis of ultrafine Fe particles by a novel mechanochemical process. A nanocomposite of Fe and NaCl was prepared through the solid-state displacement reaction of $FeCl_3 + 3Na = Fe + 3NaCl$ during mechanical milling. Removal of the chloride by-product yielded separated Fe particles, about 10 nm in size [5]. The result showed that the mechanochemical process is a promising method for producing ultrafine powders in an economical and efficient way [5,6]. In this work, we have synthesised ultrafine Cu powders by the mechanochemical process. The influence of milling conditions on the structure and particle size of Cu particles is reported in this letter.

2. Experimental process

For the production of Cu particles, dried $CuCl_2$ and NaCl powders (~100 mesh) and small Na pieces ($\leq$0.5 mm) were used as starting materials. 5 g charges of the mixture of the $CuCl_2 + Na$ were loaded and sealed in a hardened steel vial together with several steel balls in a high-purity argon filled glove box. Steel balls of different sizes varying between 3.2 and 12.6 mm in diameter were used. The powder to ball mass ratio was 1:3. Milling was performed for 16 h with a Spex 8000 mixer/mill. The temperature of the vial during milling was measured using a thermocouple attached to its outside surface. For a milling using 4.8 mm diameter steel balls, 5 g of NaCl was added to the starting material. The as-milled powders were washed several times with deionised water and finally rinsed with methanol, using an ultrasound cleaning bath. The washed powders were dried under vacuum and directly transferred to the argon glove box.

The powders were examined using a Siemens D5000 X-ray diffractometer with the Cu–K_α radiation (XRD) and a Philips 430 transmission electron microscope (TEM) equipped with an energy dispersive spectroscopy (EDS) facility for composition analysis. Sealed sample holders were used for the measurements mentioned above.

3. Results and discussion

It has been reported earlier [3,4,7] that a solid-state displacement reaction during mechanical milling can

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occur either in a steady-state manner or via unstable thermal combustion, depending on the enthalpy change and other reaction parameters, as well as the milling conditions. In this work, combustion was always observed during the milling of $CuCl_2 + 2Na$. The combustion was characterised by an abrupt increase of the temperature measured on the outside surface of the vial [7]. The reaction of $CuCl_2 + 2Na = Cu + 2NaCl$ has a reaction enthalpy change of $-575\ kJ\ mol^{-1}$ of $CuCl_2$ at room temperature. The large negative enthalpy change can increase local temperature significantly [3,4]. In addition, mechanical milling can lead to the reduction of particle size and intimate mixing of the reactants [3,4,7], which can lower the ignition temperature of combustion [3,4,7].

Fig. 1 shows the critical milling time for the onset of combustion as a function of ball size for the milling of $CuCl_2 + 2Na$. It can be seen that the critical time decreased with increasing ball size. An increase of ball size results in an increase of collision energy. A higher collision energy can lead to reduction of particle size more efficiently. Therefore, an increase of ball size favours the occurrence of combustion. Similar results have been reported previously [4,7].

The occurrence of combustion is not desirable for the production of ultrafine particles, because the combustion can cause significant temperature increase, resulting in melting and varporisation [4,7]. Therefore, suppression of combustion is important for the production of uniform particles by mechanochemical processes [5]. Reduction of collision energy and dilution of reactants are possible methods for avoiding combustion. Reduction of collision energy can be achieved by using smaller ball size, reduced powder/ball mass ratio and lower vibration intensity. Dilution of reactants can result in an enhancement of the ignition temperature because of the separation of reactants. In this work, combustion was suppressed by adding 50 wt.% of NaCl into the starting material and using 4.8 mm diameter steel balls. Adding NaCl leads to the dilution of reactants and the reduction of the powder/ball mass ratio.

X-ray diffraction results showed that the displacement reaction could be completed in a steady-state manner for milling with adding NaCl in the starting material. As shown in Fig. 2, the as-milled powder had a mixture of NaCl and Cu after milling for 16 h. For milling with combustion, traces of metallic Cu and NaCl were observed in X-ray diffraction patterns before the combustion had occurred, indicating that the displacement reaction took place in a steady-state manner. As soon as combustion occurred, a large amount of Cu and NaCl was found, showing that the displacement reaction occurred abruptly during combustion. However, completion of the displacement reaction required a further milling, especially if smaller balls were used. All as-milled samples were found to consist of NaCl and Cu after milling for 16 h.

After washing, all samples were found to consist of Cu and a small amount of Cu_2O, as shown in Fig. 2, probably due to oxidation during the washing process. Using the Scherrer method, an average particle size of 25–30 nm was calculated for Cu particles after milling with adding NaCl in the starting material, wherein the Cu particles were formed in a steady-state manner. The average particle size of Cu was about 50 nm, if combustion occurred during milling. These results showed that combustion led to an increase of particle size.

A TEM micrograph of Cu particles is shown in Fig. 3. Washed samples were found to consist of individual Cu particles. No trace of Na and Cl was detected by EDS. For the sample milled with adding NaCl in the starting material, the size of Cu particles was fairly uniform, ranging between 20 and 50 nm (Fig. 3), in a

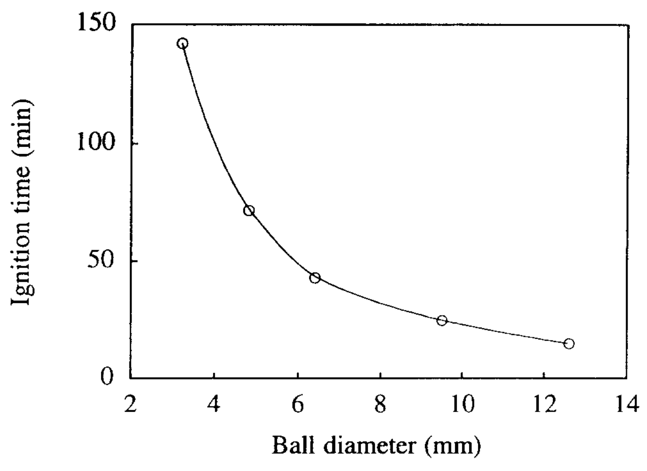

Fig. 1. The critical time of the onset of combustion as a function of ball size.

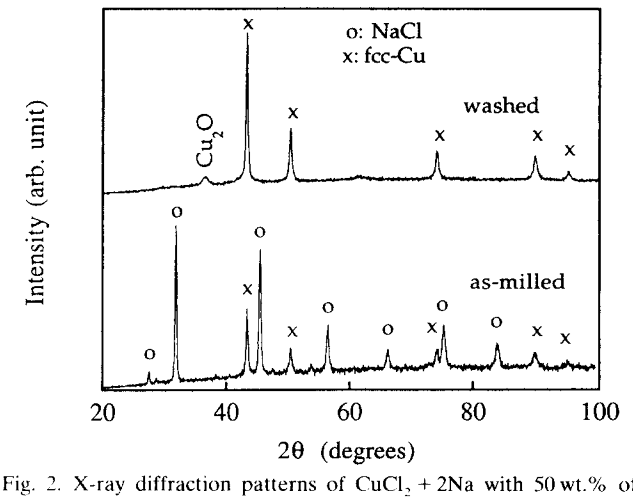

Fig. 2. X-ray diffraction patterns of $CuCl_2 + 2Na$ with 50 wt.% of NaCl added in the starting material milled for 16 h using 4.8 mm diameter balls and subsequently washed.

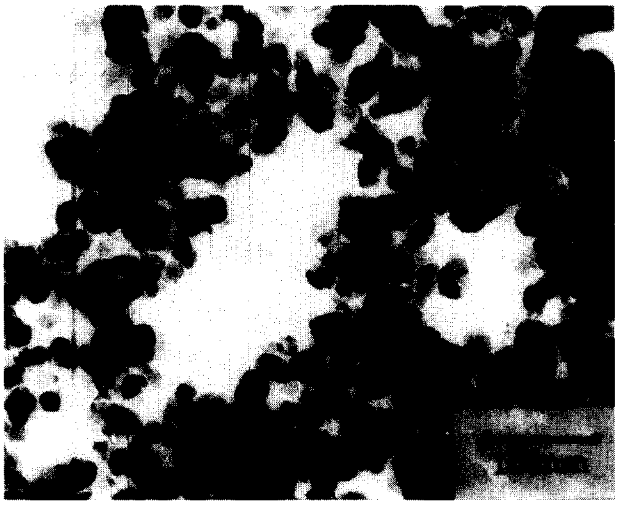

Fig. 3. TEM micrograph of Cu particles after milling with NaCl added in the starting material and subsequently washed.

good agreement with the particle size estimated from X-ray diffraction results.

If combustion occurred, washed samples consisted of Cu particles which could be classified into two groups by TEM studies; one comprised the particles having a size of 20–50 nm, and the other the particles with a size of about 100 nm. The 20–50 nm particles were probably formed in a steady-state manner and larger particles with a size of about 100 nm were the consequence of combustion.

4. Conclusion

Mechanical milling of $CuCl_2 + 2Na$ resulted in the formation of the nanocrystalline mixture of $Cu + 2NaCl$. When $CuCl_2 + 2Na$ was used for the starting material, combustion was observed. The suppression of combustion was achieved by adding NaCl in the starting material, diluting the reactants and decreasing the powder/ball mass ratio.

X-ray diffraction and TEM studies showed metallic Cu particles of a size as small as 30 nm. This work shows that the synthesis of ultrafine Cu powder can be achieved by low-energy milling and a simple washing process. Therefore, mechanochemical processing has significant potential for large scale production of metallic ultrafine powders [5,6].

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