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Synthesis of silver powder using a mechanochemical process†

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Fine silver powder was synthesized in a mechanochemical process by inducing a solid-state displacement reaction between AgCl and sodium. The process employed was ball milling in a planetary-type ball mill. The reaction products were elemental silver and NaCl in powder form. The silver particles were separated out by washing the NaCl by-product from the milled powder mixture. The milled powders were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD determination showed that the reaction between AgCl and sodium was complete in almost all the experiments carried out. In some cases a minor quantity of Ag_2Na was formed. SEM and TEM examinations revealed that, depending on the milling parameters employed, the size of the particles in the synthesized metallic silver powder was in the range 50–1000 nm. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: silver; mechanical alloying; mechanochemical processing; displacement reaction; X-ray diffraction

1 INTRODUCTION

Modified electrical, thermal, mechanical, optical or magnetic properties can be achieved when powder particle sizes fall within the sub-micrometre (100–1000 nm) or nanoscale (1–100 nm) range. Although several methods of producing such powders exist, they often feature relatively slow rates of synthesis, which makes commercial use unrealistic.[1]

One scalable method for the production of fine powders that can be employed at an industrial scale is mechanochemical processing, a process that is comparable to mechanical alloying (MA). This is a solid-state powder metallurgy process that consists of repeated welding and fracturing in a high-energy ball mill. Though MA is quite widely used in the preparation of nanocrystalline materials, relatively few experiments have been reported in which the technique is used for the manufacture of fine particles. Ding *et al.*[2–4] have prepared ultrafine iron, copper, cobalt and nickel particles using mechanochemical processing to reduce of $FeCl_2$, $CuCl_2$, $CoCl_2$ and $NiCl_2$ using sodium. Nickel particles can also be made by a displacement reaction in which $NiCl_2$ is reduced by magnesium.[5] The results of these experiments have shown that the mechanochemical process is an economical and efficient way of producing fine powders.

Silver-based conductive composite materials can be used as conductive coatings, conductive adhesives and thick-film conductors. When the particle size is small enough and forms a porous structure, the amount of silver powder required decreases.[6] The aim of this research work was the synthesis of silver powders with a particle size small enough to make it possible to reduce the concentration of silver in conducting composite materials.

2 EXPERIMENTAL DETAILS

The mechanochemical processing of AgCl and sodium was performed in an argon atmosphere. The AgCl was used in powder form and the sodium was cut into pieces before being placed in the milling vial.

A planetary-type ball mill was used. The milling vials and balls were of hardened steel. The starting

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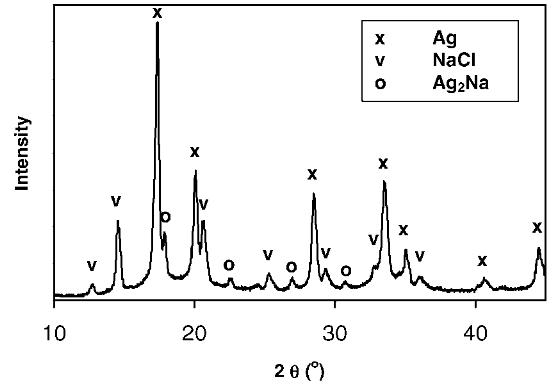

Figure 1 X-ray diffraction curve of a sample of AgCl and sodium milled for 2 h.

materials were loaded into the vials in an argon-filled glove box. Two types of milling vial were used. In the case of the smaller vial, the total weight of the 10 mm diameter balls was 200 g and a 20 g batch of AgCl and sodium was used. The AgCl to sodium ratio was selected to result in silver and NaCl following the displacement reaction. In the case of the larger vial, 500 g of balls and a 100 g batch of AgCl and sodium was used. Milling times ranged from 10 min to 2 h. After milling, the powders were washed using deionized water, dried under a vacuum and moved to an argon-filled glove box.

The microstructure of the powders was studied using scanning electron microscopy. The crystal structure was defined by X-ray diffractometry using

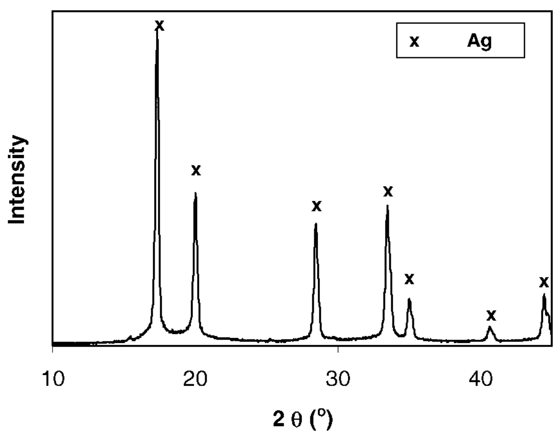

Figure 2 X-ray diffraction curve for the sample used to obtain the curve in Fig. 1, but measured after washing the milled powder with deionized water.

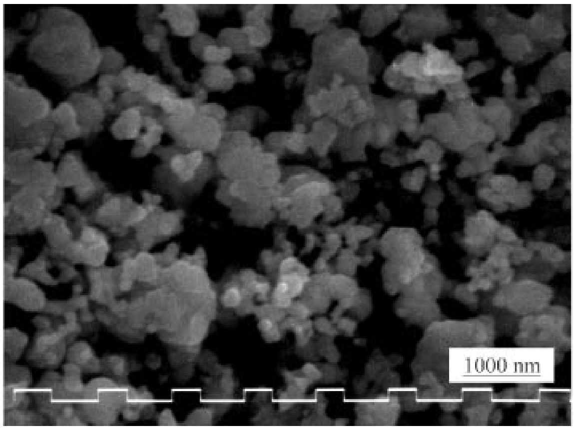

Figure 3 Scanning electron micrograph of the washed powder.

Mo–Kα radiation and by transmission electron microscopy (TEM).

3 RESULTS AND DISCUSSION

The displacement reaction used in the synthesis of silver was

$$AgCl + Na \rightarrow Ag + NaCl$$

The enthalpy change in this reaction is -284 kJ mol^{-1} at room temperature [7] and this exothermal reaction makes it possible to achieve combustion during milling.

Figure 1 shows the X-ray diffraction curve for a sample that has been milled for 20 min in a planetary ball mill. The peaks characteristic of silver and NaCl can be seen distinctly, but the peaks belonging to AgCl and sodium cannot be found, indicating completion or near completion of the reaction. In addition to these expected changes, the curve shows traces of an intermetallic Ag_2Na phase.[8] Though these peaks existed in most of the samples, the amount of Ag_2Na appeared to depend on the milling time and increased when the milling process was prolonged. After milling for only 10 min the Ag_2Na peaks were hardly detectable.

Figure 2 shows the X-ray diffraction curve of the sample used to obtain the curve presented in Fig. 1 after the as-milled powder had been washed using deionized water. This curve indicates that the sample consists of only a single phase, i.e. crystalline silver.

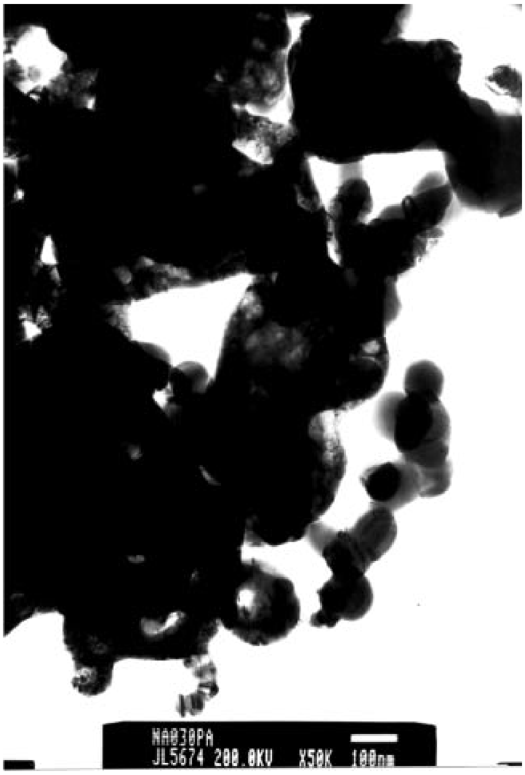

Figure 4 Transmission electron micrograph of the washed powder.

The microstructure of the washed silver powder can be seen in Figs 3 and 4. The scanning electron micrograph shows that the particle shape is irregular, as is normally the case with mechanically alloyed powders. The smallest particles that can be found in the transmission electron micrograph are below 50 nm. The scanning electron micrograph shows some particles that are as large as 1000 nm. In the main, the size of the particles falls in the range 100–500 nm.

4 CONCLUSIONS

A mechanochemical displacement reaction in a planetary ball mill was used to produce silver particles from AgCl and sodium. In the ball mill, the AgCl and sodium reacted to form silver and NaCl. After washing the NaCl out of the mixture, pure silver powder was obtained. Examination of the silver particles using X-ray diffraction revealed no traces of chlorides, sodium or other impurities. The synthesized powders had a particle size range of 50–1000 nm.

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