Mechanochemical Synthesis of Silver Nanoparticles

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Abstract
The silver (Ag) powder was synthesised in a Mechanochemical (MC) process by inducing a solid-state displacement reaction between silver chloride (AgCl) and copper (Cu). This process was done in Argon atmosphere conditions using a planetary ball mill. The reaction caused the mixture of AgCl and Cu to change the composition of the mixture, of Ag and copper chloride (CuCl). CuCl was separated from MC product by leaching with ammonium hydroxide and Ag powder was obtained as the final product. Stearic acid (C17H35COOH) was used as the additive to improve dispersion of Ag powder during MC process. The ground powders, formed in the presence and absence of additive, were characterised by X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD determined that the reaction between AgCl and Cu was completed in 18 h milling. SEM and particle size analysis (PSA) examinations revealed that the size of the particles in the synthesised metallic Ag powder was in the range of 30-300 nm.

Keywords: Silver powder; Mechano-chemical processing; Solid-state displacement reaction; Stearic acid

Introduction
Silver (Ag) powder has been extensively applied in the electronic industry over the last three decades, particularly in the field of making conducting inks and paste for thin/thick films. Conductive Ag paste forms the basis for electronic components such as hybrid microcircuits and the internal electrodes of multi-layer ceramic capacitors. A specific morphological feature of Ag powder is needed for such applications. The powders should be composed of crystalline non-agglomerated micron/submicron particles with narrow size distribution [1]. To date, preparation of Ag powder has involved many routes, such as chemical reduction of Ag ion on aqueous solution with or without stabilising agent [2-4], radiation chemical reduction [5], polyol method, physical and electrochemical processes, and each of these processes generates Ag powder with unique morphological properties. Among the methods, mechnochemical (MC) process due to the low cost and simplicity is highly regarded [6,7]. The main purpose of this investigation is to make a comparative study of the morphological characteristics of fine Ag powder prepared by MC reactions in the presence and absence of an additive, i.e. stearic acid.

Experimental Procedure
All the experiments were carried out by taking analytical grade AgCl (purity: >99%, <100 μm) (Fluka Chemical Co.) and Cu (purity: >99.9%, <100 μm) (Merck Chemical Co.) as starting materials. To prevent agglomeration, 1 wt.% stearic acid was added to the initial powders. The two starting materials were mixed at equivalent molar ratio, and the mixture was kept in a desiccator. A high-energy ball milling Fritsch P-5 planetary mill (Fritsch, IdarOberstein, Germany) using stainless steel containers and balls of different diameters was used for grinding the mixture. The mixture was subjected to grinding in Argon atmosphere at rotation Speed of 400 rpm and ball-to-powder ratio (BPR) of 20 for different times: 9, 12, 15 and 18 h. Leaching treatment of the ground samples was carried out with NH4OH. One gram of the ground sample was dispersed in 100 mL of 1.0 M NH4OH and the slurry was stirred by magnetic bar to extract Ag from CuCl in the ground mixture. After leaching, it was filtered to separate solid from slurry by using membrane filter (cellulose acetate, pore size 0.2 mm, Advance MFS Inc., Japan). The phases of solids were analyzed by X-ray diffraction (XRD) using Cu-Kα radiation (Siemens Corporation, Cherry Hill, NJ, USA). The morphology of Ag powder prepared in this investigation was observed by scanning electron microscopy (SEM).

Results and Discussion
Characterization of time effects on the MC reaction
The XRD patterns of the mixture of AgCl and Cu, for the different milling times in absence of additive (steearic acid) are shown in Figure 1. The displacement reaction during the synthesis can be written as:

AgCl + Cu → CuCl + Ag

According to Figure 1, it is observed that the appearance of Ag and CuCl in the final ground mixture after 9 h milling reveals that the displacement reaction has partially taken place during MC process. With the increase of milling time to 18 h, the diffraction peaks of remaining AgCl and Cu is completely disappeared, and only the diffraction peaks of crystalline Ag and CuCl exist. It is also seen that increasing the milling time broaden width of the peaks. This represents a decrease in crystallite size of the powder particles.

Characterization of additive effects on the MC reaction
To determine additive effects, two samples were prepared with similar milling conditions. As seen in Figure 2, when stearic acid added as an additive in the starting materials, after 18 h of milling, AgCl in the final ground mixture (Figure 2b) was observed. This represents the role of controller of stearic acid in MC reaction.

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Characterization of powder sample after leaching

Leaching process formed the single phase of Ag powder in the residue. The process can be explained by the following reaction [8]:

$$\text{CuCl} + 2\text{NH}_4\text{OH} \rightarrow [\text{Cu} (\text{NH}_3)_2] \text{Cl} \text{(soluble)} + 2\text{H}_2\text{O}$$  \hspace{1cm} (2)

In the presence of additive, the small remnant of AgCl present in the mixture reacted with NH$_4$OH during the leaching process and formed the following complex [8]:

$$\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow [\text{Ag} (\text{NH}_3)_2] \text{Cl} \text{(soluble)} + 2\text{H}_2\text{O}$$  \hspace{1cm} (3)

Figure 3 shows the XRD pattern of the separated Ag powder from liquid during the leaching process. The diffraction peaks correspond to the (111), (200), (220), (311) and (222) planes, respectively. All reflections on the XRD pattern can be indexed to a face centered cubic (fcc) structure according to the literature pattern (JCPDS, file no. 04-0783). The phases in Figure 2 show the existence of Ag only. Thus, it confirmed that the material synthesized during the leaching process is pure Ag powder. The broadening of the peaks of the pattern correlates to the fineness of the Ag crystallite. The crystallite size of the powder was calculated by line broadening of (111) peak of the XRD pattern using Scherrer’s formula:

$$\text{Crystallite size} = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (4)

The width $\beta$ is usually measured in radians, at intensity equal to half the maximum intensity. The crystallite size of Ag powder is found to be 38 nm. The SEM photomicrographs of the Ag powders are shown in Figure 4. Figure 4a shows the photomicrograph of the powder prepared without additive. This reveals that the powder particles have densely agglomerated and it is difficult to distinguish them clearly. Figure 4b shows the photomicrograph of the Ag powder prepared using stearic acid additive. The powder is more dispersive than the sample without additive, where the size of particle remains in the range of 30-300 nm.
SEM images in Figure 4. Suggest that addition of stearic acid plays an important role during Ag powder synthesis. This additive behaves as a dispersant in the MC process due to the possibility of the formation of an outer-sphere or a surrounding layer of stearic acid that covers the dispersed Ag particles in the mixture. This helps to prevent the agglomeration of the Ag particles. Figure 5 shows results of particle size analysis (PSA) for Ag powder in the presence of stearic acid as additive. It can be observed that the size of particles remains in the range of 30-300 nm and verifies the SEM photomicrographs, also according to the diagram the average size of particles is obtained 85.4 nm.

Conclusions

Silver nanoparticles were synthesized by MC process with AgCl and Cu as starting materials and reactions were carried out in the absence and presence of stearic acid as additive. The SEM images, XRD and PSA data reveals the effective nature of stearic acid in formation of silver nanoparticles during the MC process. Using stearic acid controlled the particle size and led to get more dispersed Ag powder with the range of 30-300 nm.

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