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### Nanoparticles of silver powder obtained by mechano-chemical process

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## Nanoparticles of silver powder obtained by mechano-chemical process

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The silver (Ag) powder was synthesised in a mechano-chemical (MC) process by inducing a solid-state displacement reaction between silver chloride (AgCl) and copper (Cu). The AgCl and Cu were ground in atmosphere conditions using a planetary ball mill. The reaction caused the mixture of AgCl and Cu to change the composition of the mixture, such as Ag and copper chloride (CuCl). CuCl was separated from MC product by leaching with ammonium hydroxide and we obtained Ag powder as the final product. Moreover, ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) was used as the additive to improve dispersion of Ag powder during MC process. The ground powders, formed in the presence 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 complete in almost all the experiments carried out. SEM 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; chemical reduction; ascorbic acid

### 1. 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 nonagglomerated 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 them, the chemical process can be considered as more lucrative than the others as it offers both

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sound powder morphology and efficient scale-up for mass production [6,7]. Therefore, an alternative process for the preparation of Ag powder has been strongly demanded, which is much simpler. One alternative is the mechano-chemical (MC) process, which enables us to prepare fine powder with simple instruments and procedures [8,9].

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. ascorbic acid. The reactions were conducted using silver chloride (AgCl) and copper (Cu), with subsequent leaching treatment with ammonium hydroxide (NH<sub>4</sub>OH).

## 2. Experiment details

All the experiments were carried out by taking analytical grade AgCl (Kojima Chemical Co., Japan) and Cu (325 mesh, Cerac Inc., USA) as starting materials. Ascorbic acid (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>, Junsei Chemical Co., Japan), in its solid form, was used as an additive for improvement of anti-oxidation of powder surface and dispersion degree. The two starting materials were mixed at equivalent molar ratio, and the mixture was kept in a desiccator. A planetary mill (Pulverisette 7, Fritsch, Germany) was used for grinding the mixture. The mill was composed of a pair of pots made of zirconia installed on a rotating disc being driven by an electric motor. Four grams of the mixture were put in the pot (45 cm<sup>3</sup> inner volumes) with seven zirconia balls of 15 mm diameter. The mixture was subjected to grinding in air at 700 rev min<sup>-1</sup>. Leaching treatment of the ground samples was carried out with NH<sub>4</sub>OH. One gram of the ground sample was dispersed in 100 mL of 1.0 M NH<sub>4</sub>OH solution in a 300 mL conical flask, and the slurry was stirred by magnetic bar to extract Cu 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 μm, Advance MFS Inc., Japan). The phases of solids were analysed by X-ray diffraction (XRD) using Cu-Kα radiation (RTP 300RC, Rigaku, Japan). Specific surface area measurement of the powder was carried out by using nitrogen adsorption BET surface area analyser (TriStar 3000). The morphology of Ag powder prepared in this investigation was observed by scanning electron microscopy (SEM, JSM-6380LA, Jeol, Japan).

## 3. Results and discussion

### 3.1. Characterisation of powder sample after milling

The XRD patterns of the mixture of AgCl and Cu, which was ground for 6 h in absence of additive (ascorbic acid), are shown in Figure 1(a). The displacement reaction during the synthesis can be written as:



As can be seen from the figure, the peaks of Ag and CuCl are clearly detected in the ground mixture; however, we still observed a small remnant of starting material AgCl in the XRD diagram. This suggested the possibility of an incomplete reaction between the starting materials.

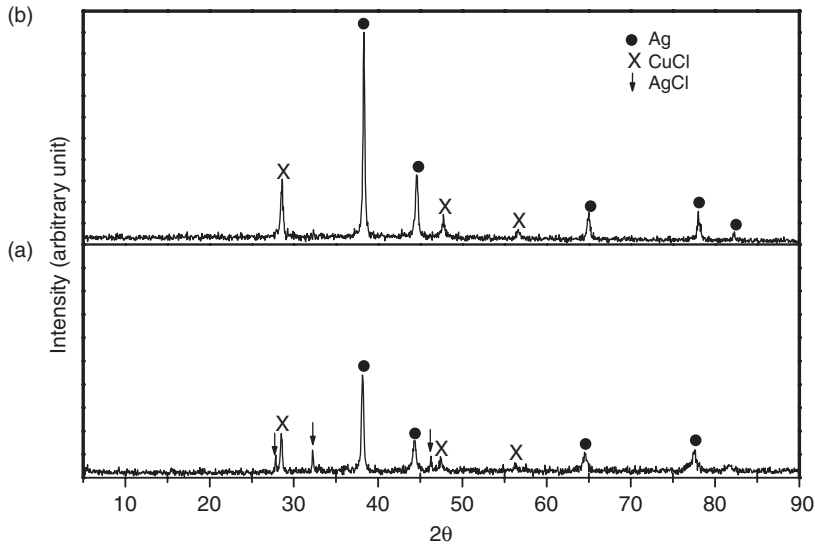
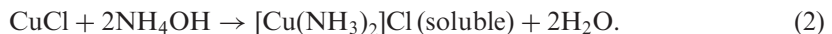


Figure 1. X-ray diffraction patterns of AgCl+Cu mixture ground for 6 h (a) without additive, (b) ascorbic acid additive.

On the other hand, when we added ascorbic acid as an additive in the starting materials, after 6 h of milling we observed the disappearance of AgCl in the final ground mixture (Figure 1(b)). In this case, the peaks showed Ag and CuCl distinctly in the final mixture. Addition of ascorbic acid has also increased the peak intensity of Ag in the final mixture compared to the peak intensity of Ag in Figure 1(a). Ascorbic acid, being a reducing agent, helped complete the reaction between the starting materials of AgCl and Cu. That is why our further experiments were carried out taking ascorbic acid as an additive agent with the AgCl and Cu.

### 3.2. Characterisation 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 [10]:



In the absence of additive, the small remnant of AgCl present in the mixture reacted with  $\text{NH}_4\text{OH}$  during the leaching process and formed the following complex [10]:

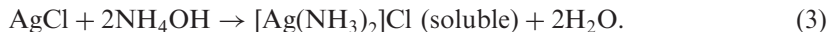


Figure 2 shows the XRD pattern of the separated Ag powder from liquid during the leaching process. The diffraction peaks correspond to the (111), (200), (220), (311) and (222) planes, respectively. All reflections on the XRD pattern can be indexed to a face centred cubic (fcc) structure according to 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

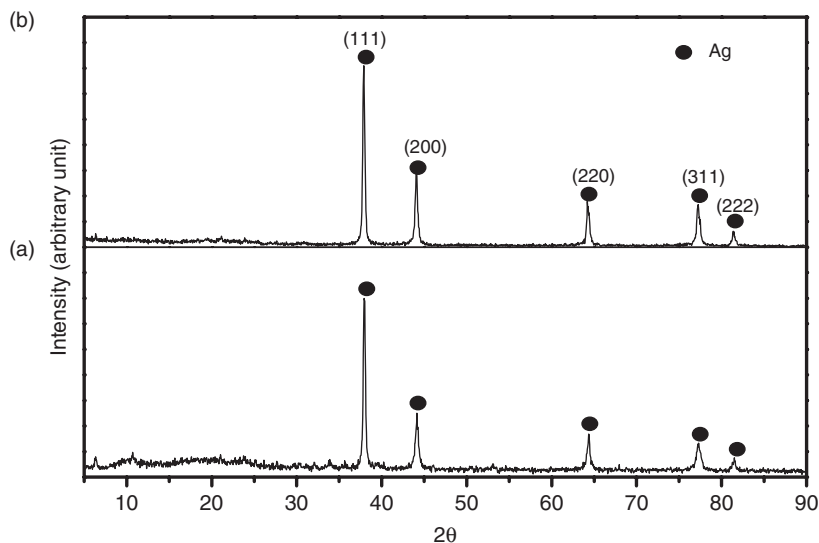


Figure 2. X-ray diffraction patterns of AgCl+Cu mixture ground for 6 h (a) without additive, (b) ascorbic acid additive, after leaching by  $\text{NH}_4\text{OH}$  solution.

synthesised during the leaching process is pure Ag powder. Previously, similar highly pure Ag powder had been obtained by the MC process using PVP as an additive [9].

The broadening of the peaks of the pattern correlates to the fineness of the Ag particle. The crystallite size of the powder was calculated by line broadening of (111) peak of the XRD pattern using Scherrer's formula:

$$\text{Crystallite size} = \frac{0.9\lambda}{\beta \cdot \cos \theta} \quad (4)$$

The width  $\beta$  is usually measured in radians, at intensity equal to half the maximum intensity. The crystallite size of Ag powder with and without additive is found to be 32.3 and 38.2 nm, respectively.

The BET surface area of the powder produced through the MC process is shown in Table 1. With the assumption of monodispersed spherical-shaped crystal particles, the particle size ( $\mu\text{m}$ ) was calculated based on the relation:

$$\text{Particle size} = \frac{6}{\rho \cdot S_{\text{BET}}}, \quad (5)$$

where  $\rho$  is density of Ag ( $\text{g cm}^{-3}$ ), and  $S_{\text{BET}}$  is the measured value of specific surface area in square metre per gram. The particle size and the crystallite sizes of the Ag powders were calculated from specific surface area data as shown in Table 1. This indicated that the particle size of Ag powder without additive (247 nm) is bigger than with additive (152 nm). The difference in particle size can be attributed to the agglomeration that occurred during the reaction in the absence of additive.

The SEM photomicrographs of the Ag powders produced through this route are shown in Figure 3. Figure 3(a) shows the photomicrograph of the powder prepared

Table 1. BET surface area measurement, calculated particle size and crystallite size of Ag powders produced through MC process.

	BET-specific surface area ( $S_{\text{BET}}$ ) (metre) <sup>2</sup> per gram	Calculated particle size from $S_{\text{BET}}$ (nm)	Calculated crystallite size form XRD (nm)
Without additive	2.316	247	32.3
With additive ( $\text{C}_6\text{H}_8\text{O}_6$ )	3.742	152	38.2

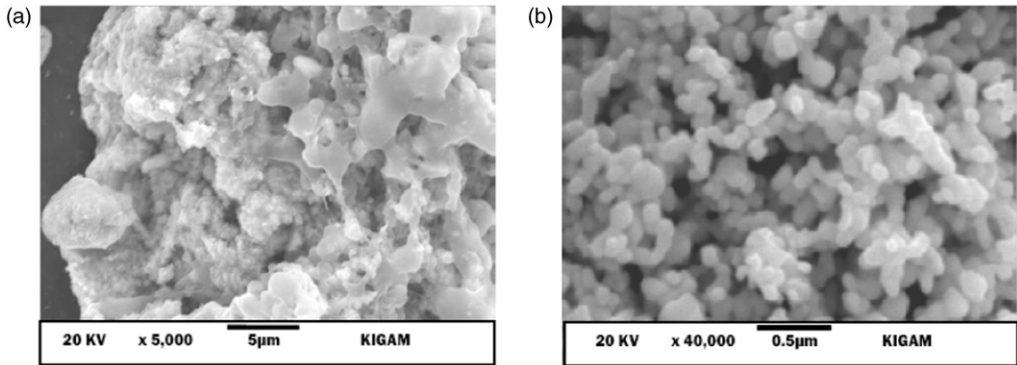


Figure 3. Scanning electron micrographs of silver particles formed for the prepared sample presented in Figure 2(a) and (b).

without additive. This reveals that the powder particles are densely agglomerated and it is difficult to distinguish them clearly. Figure 3(b) shows the photomicrograph of the Ag powder prepared using ascorbic acid additive. The powder is more dispersible than in the case without additive, where the size of particle remains in the range of 30–300 nm because of the reducing nature of ascorbic acid.

The above results suggested that addition of ascorbic acid plays an important role during Ag powder synthesis. This additive not only behaves as a dispersant, but it also plays a role as a reducing agent in the MC process. As per the effect of ascorbic acid, there is no clear evidence that would show its reaction mechanism during Ag powder synthesis. However, we expect there may be the possibility of the formation of an outer-sphere or a surrounding layer of ascorbic acid that covers the dispersed Ag particles in the mixture. This helps prevent agglomeration of the Ag particles.

#### 4. Conclusions

We have synthesised Ag powder by MC process with AgCl and Cu as starting materials and reactions were carried out in the absence and presence of ascorbic acid, an additive. The SEM images and XRD data could reveal much about the effective nature of ascorbic acid in formation of Ag powder during the MC process. Using ascorbic acid, we were able to get well-dispersed Ag powder with 30–300 nm size. The ascorbic acid acted as a reducing agent in the MC process and it also helped to control the particle size of the Ag powder.

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