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Original Research Paper

An investigation on the application of process control agents in the preparation and consolidation behavior of nanocrystalline silver by mechanochemical method

Gholam Reza Khayati [a,*], Kamal Janghorban [b]

[a] Department of Material Science and Engineering, Shahid Bahonar University of Kerman, P.O. Box 76135-133, Kerman, Iran
[b] Materials Science and Engineering Department, School of Engineering, Shiraz University, Zand Avenue, Shiraz 7134, Iran

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ABSTRACT

In this paper, the effect of various amounts and types of process control agent (PCA), i.e., stearic acid (SA) and ethylene bis-stearamide (EBS), in the production and consolidation behavior of nanocrystalline silver prepared by mechanochemical reduction of Ag_2O by graphite was studied. The structural evolution and morphology of powders were investigated using XRD, HRSEM and particle size analyzer techniques. The results showed the nanocrystalline Ag formed after 25 h of milling and the addition of PCA prolonged the synthesis process time. Also, the effect of EBS on prevention of the excessive cold welding of ultra-fine Ag particles in the final stages of milling was more serious than SA. In fact, the presence of PCA effectively inhibited the creation of coarse Ag particles and finally decreased the crystallite size to 14 nm. Moreover, with the addition of PCAs, the Brinell hardness of sintered Ag samples was considerably increased.

1. Introduction

Due to widespread application, the commercial nanotechnology is forecasted to grow significantly to $3 trillion by 2015 [1]. It is predicted that within all the nanoparticles in user products, silver nanoparticle applications currently have the highest level of commercialization. A broad range of Ag nanoparticle applications has appeared in consumer products ranging from decontamination of medical devices and home appliances to water treatment. Furthermore, due to the unique physical and mechanical properties, Ag nanoparticles have also been used in potential catalysis, aerosol, filter, sensor, magnetic, biomedical, optoelectronic, dielectric ceramics, hygienic and healing purposes [2,3].

As reported by Zheng Min et al. [4], a wide variety of synthesis methods such as gas reduction process, precursor pyrolysis, microwave plasma synthesis, and laser ablation have been successfully employed in the preparation of silver nanoparticles. Nevertheless, there has been little research directed to the mechanochemical synthesis of silver nanoparticles yet.

Mechanochemical synthesis is a novel technique for preparation of nano-sized materials. Studies show that improved reaction rates can be achieved and dynamically maintained during the mechanical activation by different mechanisms, such as repeated fracture, welding, deformation of particles, microstructural refinement and mixing processes [5–13]. Depending upon which mechanism is dominant during the milling, the size of prepared powder may grow through agglomeration by cold welding, or become smaller through the fracture phenomenon. Mostly, to generate the balance between the fracturing and welding phenomena, a process control agent (PCA) applied in the milling process [14,15]. PCAs are generally organic materials, which invariably lowers the surface tension of deformed particles and consequently impeding the clean metal-to-metal contact essentially for cold welding [16]. Majority of PCAs decompose during milling, introducing carbon and/or oxygen into the powder particles, resulting in the formation of carbides and oxides which are uniformly dispersed in the matrix [14].

In our pervious works, the preparation of nanocrystalline silver through the mechanochemical reduction of Ag_2O with graphite according to Reaction (1) was investigated [11].

$$2Ag_2O + C \rightarrow 4Ag + CO_2 \uparrow \quad (1)$$

To the best of our knowledge, the effects of process control agents in mechanochemical reduction of Ag_2O have not been thoroughly investigated. These investigations are appreciated for the ability to control the solid-state reactions. In this paper, a novel technique for synthesis of highly spherical silver nanoparticles using mechanochemical reduction of Ag_2O in the presence of stearic acid and ethylene bis-stearamide as PSAs has been proposed.

The main advantages of the mechanochemical method in comparison with the traditional technological procedures are: decrease in the number of technological stages, excluding the operations that involve the use of solvents and stabilizing agents, simplification of the process, mass production capability and easy handling of process, environmental health and safety. These items characterize

* Corresponding author. Tel.: +98 915 1903477; fax: +98 711 2307293.
E-mail address: khayati@uk.ac.ir (G.R. Khayati).

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the mechanochemical approach method for production of Ag nanoparticles. Furthermore, the sintering behavior of silver powders prepared under various conditions for mechanochemical synthesis compared with the micro-grained Ag powder produced through conventional method.

2. Experimental procedure

Starting materials were Ag_2O powder (99% purity, 5–40 μm, Merck), graphite (99.9% purity, 10–50 μm, Merck), SA (99% purity, Merck), EBS (99% purity, Nanjing Xinxu Industry & Trade Co., Ltd.) and micro-grained Ag (99% purity, Iran Industry & Trade Co., Ltd.). The powder samples were prepared in a high energy planetary ball mill. Mixture of Ag_2O together with 40 mol% of extra carbon according to the Reaction (1) was subjected to intense mechanical treatment in an argon atmosphere for various times. The excess carbon was used to perform as a diluent and prepared maximum contact area between the reacting particles during milling. Moreover, graphite has a layered, planar structure and due to the loose interlamellar coupling between sheets, is valued for its self-lubricating and dry lubricating properties. The contamination due to the milling media was significantly suppressed in the presence of excess carbon. To find the suitable ball to powder weight ratio and speed of milling, similar experiments performed in three steps without the presence of PCA. The first step carried out at the ball to powder weight ratio of 10:1 with milling speed of 5.83 s^{-1}. In this case, no detectable reaction took place to prepare any new compounds after 50 h of milling. This was could be an indication of inadequate collision energy supplied in the mill. The second step conducted at the ball to powder weight ratio of 20:1 with milling speed of 7.5 s^{-1}. The results show that the mechanochemical reduction of Ag_2O occurred gradually as a function of milling time. The third step performed at the ball to powder weight ratio of 30:1 with milling speed of 9.17 s^{-1}. In this case, after passing 2.5 h of milling, suddenly the internal pressure was increased and Ag_2O completely reduced to metallic Ag by a self-sustaining reaction mechanism. Accordingly, the milling operations parameters of the second step were selected as suitable conditions. Details of ball milling machine and milling conditions were summarized in Table 1.

Studying the effect of PCA was separately performed by the addition of SA and EBS during the milling operation. The main properties of SA and EBS are given in Table 2 [17,18]. Table 3 summarizes the various conditions of mechanochemical synthesis. The first set of experiments was performed with the addition of PCAs from the start of the milling. In the second set the PCAs were added after passing 12 h of milling. Ag powder prepared by the mechanochemical process and micro-grained sample were isostatically cold-pressed at 750 MPa into cylinders with 10 mm diameter and 5 cm height. The compacts were then sintered at 723 K for 1.5 h in an argon furnace. The density of the sintered samples was calculated using Archimedes' principle in accordance with ASTM B328. Micro-hardness was measured on the polished samples.

Table 1
Details of planetary ball mill machine and milling conditions.

Parameter	Value
Rotation speed of vial (s^{-1})	7.50
Rotation speed of disc (s^{-1})	4.17
Diameter of disc (m)	350×10^{-3}
Diameter of vial (m)	90×10^{-3}
Vial material	Hardened chromium steel
Capacity of vial (m^3)	150×10^{-6}
Ball material	Hardened carbon steel
Diameter of ball (m)	20×10^{-3}
Number of balls	6
Ball to powder weight ratio	20:1
Times of milling (h)	0–25
Process control agent	SA and EBS
Types of milling	Dry
The atmosphere of milling	Ar
Total powder mass (g)	9.75

Table 2
The main properties of stearic acid (SA) and ethylene bis-stearamide (EBS) [17,18].

Properties	SA	EBS
Molecular formula	$C_{18}H_{36}O_2$	$C_{38}H_{76}N_2O_2$
Molar mass (g/mol)	284.48	593.02
Density (kg/m^3)	847	901
Melting point (K)	342	418
Boiling point (K)	634	997

Table 3
Various conditions for mechanochemical synthesis of samples.

Sample	PCA (wt.%)	Milling time (h)	Time of PCA adding (h)
W1	0	6	–
SA1	1	6	0
SA2	2	6	0
EBS1	1	6	0
EBS2	2	6	0
W2	0	12	–
SA3	1	12	0
SA4	2	12	0
EBS3	1	12	0
EBS4	2	12	0
W3	0	25	–
SA5	1	25	12
EBS5	1	25	12

The samples were characterized by HRSEM (Hitachi S-4160) equipped with an energy dispersive spectrometer (EDS) and XRD (Simens-D8 Advanced) using Cu k_α radiation. The line broadening due to the instrument was calculated from Warren's method [19]. The average crystallite size and internal strain were estimated using Williamson–Hall plot [20]. Particle-size distribution was measured using a dynamic light scattering particle size analyzer (HORIBA LB-550).

3. Results and discussion

3.1. Characteristics of nanocrystalline silver powders

XRD analysis of prepared powders (Fig. 1) obviously shows that the addition of PCA caused a delay in the reduction reaction. As shown in Fig. 1(a) Ag_2O was a dominant phase of samples milled for 6 h and there was no distinct difference in the phase composition of W1 and SA1 samples, while the presence of organic PCAs in SA2, EBS1 and EBS2 samples significantly changed the displacement reaction during the mechanical milling.

Much different XRD diffraction spectra of samples milled for 12 h with and without the addition of PSAs are shown in Fig. 1(b). Even after 12 h of milling with EBS, only very weak Ag peaks was formed. However, although only a little amount of Ag was prepared, both Ag and Ag_2O crystalline sizes were decreased by the indication of broadening of diffraction peaks. As shown the intensities of Ag peaks increased by milling up to 12 h in SA3, SA4, EBS3 and EBS4 samples whereas the Ag_2O peaks intensities decreased. It seems that the presence of PCAs significantly changed the behavior of reactants within the milling and delayed the reduction reaction. Moreover, using a greater amount of PCAs led to a drastic change in the mechanisms of reaction. This effect is originally related to the decrease in contact area of powder mix-