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Role of process control agent on synthesis and consolidation behavior of nano-crystalline copper produced by mechano-chemical route

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Abstract

Nano-crystalline copper was synthesized by mechano-chemical reduction of Cu_2O with carbon. Influence of stearic acid addition as a process control agent (PCA) on characteristics of synthesized and consolidated copper samples was investigated. The structural evolution and morphology of powders were evaluated using XRD and SEM, respectively. It was found that the nano-crystalline Cu formed after 35 h of milling and addition of stearic acid prolonged the process. On the other hand, the use of stearic acid in final stages of the process prevented excessive cold welding of ultra fine Cu particles during milling. In fact, it successfully inhibited the formation of coarse Cu particles and eventually decreased the crystallite size of the product to 19 nm. The hardness of sintered Cu sample increased due to the reduction of mean crystallite size.

Keywords: Nanostructured materials; Mechano-chemical processing; Microstructure; X-ray diffraction

1. Introduction

Mechano-chemical processing is a novel technique for preparation of nanosized materials. It has been shown that enhanced reaction rates can be achieved and dynamically maintained during milling as a result of microstructural refinement and mixing processes accompanying repeated fracture, welding and deformation of particles during collision events [1]. Depending on which process is dominant during mechanical alloying, powder particles may grow in size through agglomeration by cold welding, or become smaller in size through the fracture process. A PCA is normally added in milling process in order to obtain a balance between fracturing and welding processes. Stearic acid is one of the most commonly used and effective PCA [2].

Chemical reduction of metal oxides could occur when milled with a suitable reductant [3]. Recently, copper nanopowder with various physical and mechanical properties has been used in electronics industry [4,5]. The reduction of copper oxide with a number of metallic reductants such as Fe, Al, Ti, Ni and Ca has been already investigated [2].

In our pervious works [6,7], synthesis of nano-crystalline Cu through following solid-state reaction between Cu_2O and graphite using mechano-chemical route was investigated.

$$2Cu_2O + C \rightarrow 4Cu + CO_2\uparrow \qquad (1)$$

Since the influence of PCA on this process has not been studied yet, the present research focuses on the influence of stearic acid as a PCA on the displacement reaction and Cu nanopowder formation. Furthermore, sintering behavior of copper powders produced through conventional and mechano-chemical routes was investigated.

2. Experimental procedure

Starting materials used in this research were commercially pure Cu_2O (99%, 5–30 μm) and graphite (99.9%, 10–50 μm). Mixture of Cu_2O together with 40 mol% of extra carbon according to the reaction (1) was subjected to intense mechanical treatment for various periods of time using a Fritsch P5 planetary ball mill with hardened steel balls and vial. A constant ball-to-powder weight ratio of 35:1 was maintained during the operation. The milling speed was also kept constant at 300 rpm.

To avoid the oxidation during milling, the vial was filled with pure argon before milling. Various amounts of stearic acid, $CH_3(CH_2)_{16}CO_2H$, were added in the beginning and final stage of the milling operation. Table 1 summarizes the milling conditions.

The morphology and phase identification of the products were examined by SEM (CamScan MV2300) equipped with an Energy Dispersive Spectrometer

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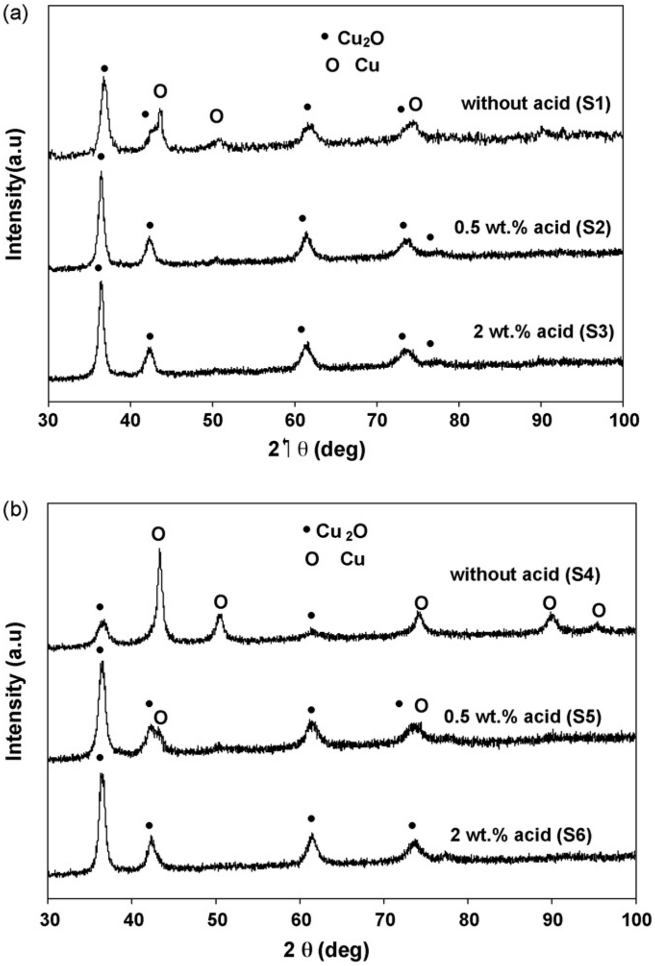

Fig. 1. XRD patterns of milled powders with 0, 0.5 and 2 wt.% of stearic acid for (a) 8 h and (b) 15 h.

(EDS) (Oxford Instrument) and XRD (Philips PW-1730) using Cu Kα radiation, respectively. The line broadening due to the instrument was calculated from Warren's method [8]. The mean crystallite size and internal strain of particles were obtained using Williamson–Hall plot [9].

Mechano-chemically produced Cu powders were isostatically cold-pressed at 600 MPa into cylinders with 20 mm diameter and 20 mm height. The compacts were then sintered at 550 °C for 1 h in a vacuum furnace at 100 Pa. For comparison, a Cu powder produced by conventional route, i.e., micro-grained sample, was also pressed and sintered under the same conditions.

The density of the sintered samples was measured by Archimedes' principle in accordance to ASTM B328. Brinell hardness was measured on the polished samples.

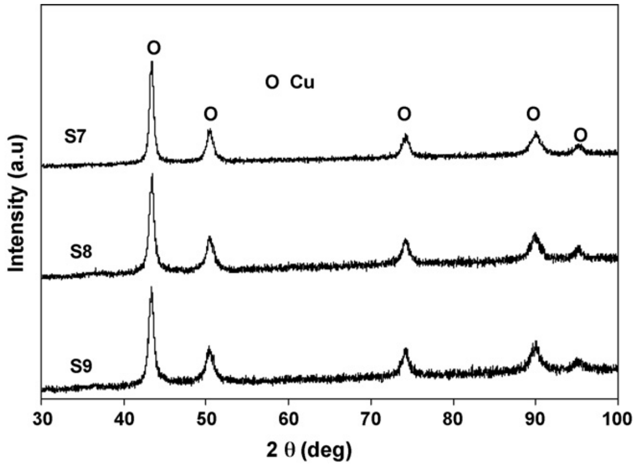

Fig. 2. XRD patterns of samples after 35 h milling.

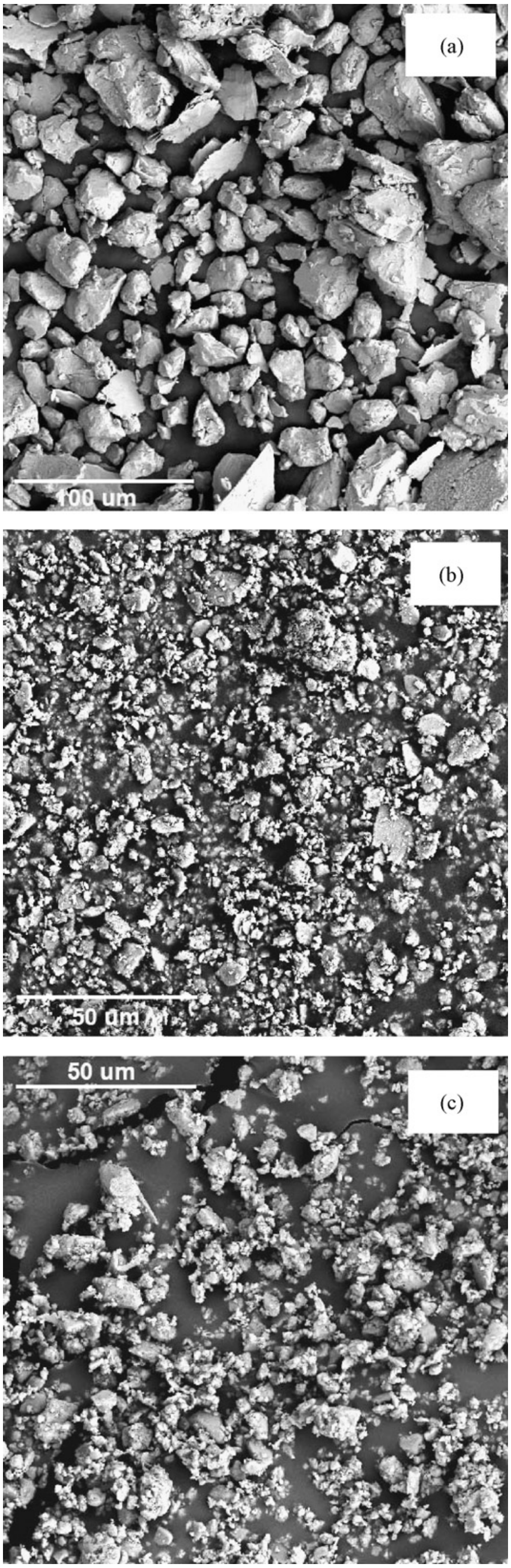

Fig. 3. SEM images of Cu powders in S7 (a), S8 (b) and S9 (c) samples.

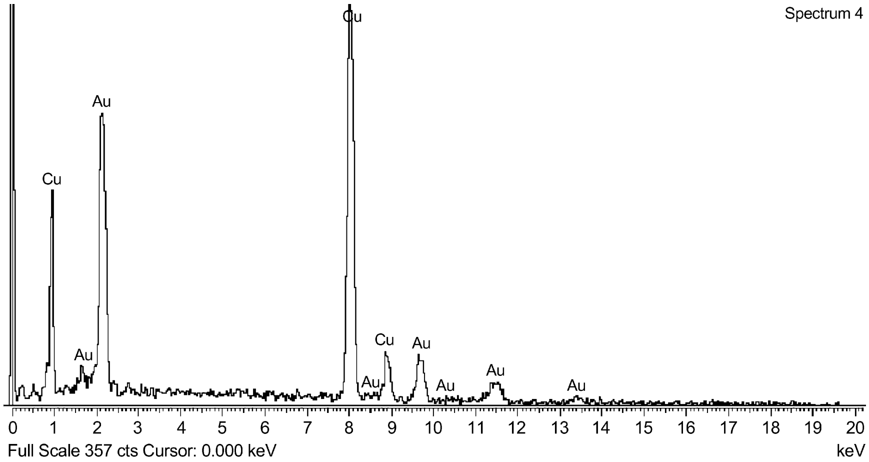

Fig. 4. EDS analysis of particles in S9 sample after 35 h milling.

Table 1
Milling conditions of the samples

Sample	PCA added (wt.%)	Time of PCA addition (h)	Milling time (h)
S1	0	–	8
S2	0.5	0	8
S3	2	0	8
S4	0	–	15
S5	0.5	0	15
S6	2	0	15
S7	0	–	35
S8	0.5	25	35
S9	0.5	30	35

Table 2
Mean crystallite size and internal strain of Cu particles in samples S7, S8 and S9

Sample	Crystallite size (nm)	Strain (%)
S7	27	0.41
S8	19	0.57
S9	22	0.49

3. Results and discussion

3.1. Characteristics of nano-crystalline Cu powders

Analysis of the XRD pattern of sample milled for 8 h without stearic acid indicates Cu_2O as a dominant phase and Cu as a minor phase. There is no distinct difference in the phase composition of samples milled for 8 h with 0.5 and 2 wt.% of stearic acid (Fig. 1(a)). XRD patterns in Fig. 1(b) show different spectra for samples milled for 15 h without and with stearic acid. The difference tends to be more evident when more stearic acid is used. The intensities of Cu peaks increased by milling up to 15 h in the absence of stearic acid whereas Cu_2O peaks intensities are decreased significantly. By addition of 0.5 wt.% stearic, Cu peaks appear after 15 h of milling whereas no detectable reaction takes place for Cu production in the sample milled with 2 wt.% stearic acid.

It seems that the addition of stearic acid alters the behavior of reactants significantly during the mechanical milling and delays the displacement reaction. The suppression of the reaction by stearic acid is primarily due to the decrease in contact area between reactants [2]. Also, enhanced lubrication because of higher acid content is believed to reduce the local temperature during collisions. Similarity of the XRD patterns of samples S1 and S5 confirms the above point and indicates that by addition of 0.5 wt.% stearic acid, the milling duration required for the reduction reaction is nearly doubled.

In the second set of experiments, 0.5 wt.% stearic acid was added in final stages of the milling process, i.e., after 25 (S8) and 30 h (S9). Fig. 2 shows XRD patterns of S7, S8 and S9 samples. Analysis of these patterns reveals that the reduction of Cu_2O to Cu for all three samples has been completed after 35 h and the reaction process has not been affected by the addition of stearic acid.

The mean crystallite size and internal strain of Cu particles in S7, S8 and S9 samples are presented in Table 2. As seen in the

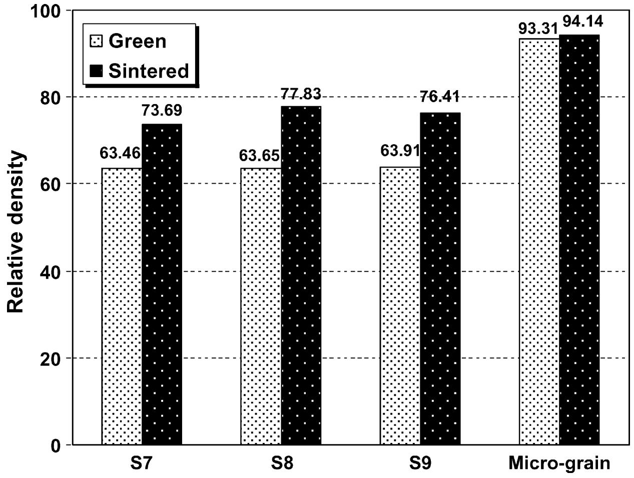

Fig. 5. Relative green and sintered densities of S7, S8, S9 and micro-grained samples.

table, the mean crystallite size is decreased and the internal strain increased by addition of stearic acid. The larger crystallite size calculated for sample S7 could be due to the relatively higher temperature obtained during milling in the absence of stearic acid.

Fig. 3 shows SEM images of S7, S8 and S9 samples. It is observed that the morphology of products processed in the presence of stearic acid differed considerably from that of processed without stearic acid. As shown in Fig. 3(a), large particles of copper exhibiting wide size distribution are formed in sample S7. The formation of large Cu particles may be attributed to its fcc crystal structure in which particles are easily deformed and cold welded to each other to form large agglomerates [10]. As could be seen in Fig. 3(b) and (c), the mean particle size of copper is considerably decreased in S8 and S9 samples. It seems that by addition of stearic acid, the cold welding process is suppressed.

EDS point chemical analysis of S9 sample after 35 h milling, Fig. 4, showed that the product is purely Cu and no impurity such as carbon and oxygen resulting from possible dissociation of PCA was detected. Au peaks in this pattern has come from the coating material. Similar results obtained from EDS analysis of S7 and S8 samples.

3.2. Characteristics of compacted and sintered samples

Fig. 5 shows relative green and sintered densities of S7, S8, S9 and micro-grained samples. In the micro-grained sample, green and sintered densities were found to be 93.31% and 94.14% of theoretical value, respectively. The sintered density in samples S8 and S9 are almost the same (∼77% of the theoretical density); this value for sample S7 is only 73.69%. It has been already shown that high green density in metal powders may be achieved when plastic yielding is occurred [11]. The high plasticity of micro-grained powders, based on the Hall–Petch dependence of yield stress on grain size, lead to higher density. However, work hardening due to the milling process resulted in lower green density in S7, S8 and S9 samples. Moreover, sliding and rearrangement in nanopowders are severely restricted owing to large frictional forces among powder particles [11]. As a result, lower green densities are likely to be achieved in mechano-chemically processed samples in comparison with micron size powders prepared conventionally. Lower sinterability of nanopowders in S7, S8 and S9 samples is probably due to their agglomerated nature and surface oxidation [11]. Less agglomeration in S8 and S9 samples due to the addition of stearic acid could be responsible for their relatively higher sintered density in comparison with

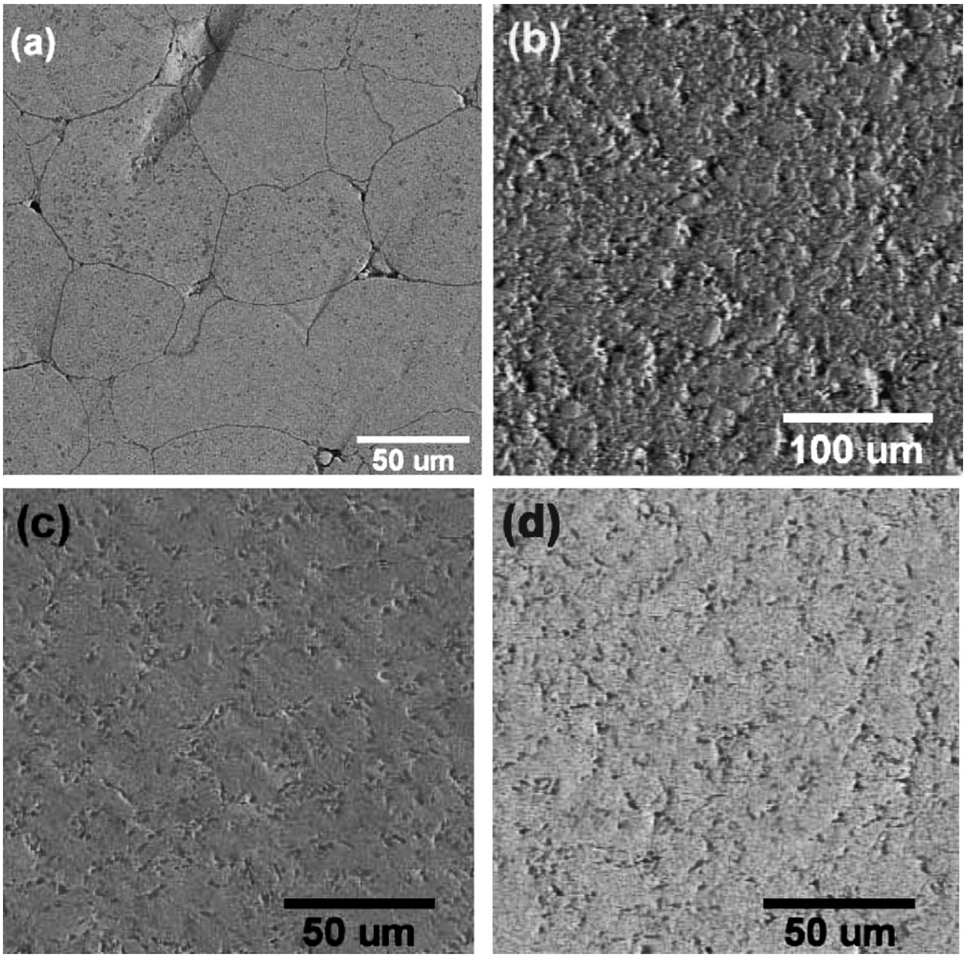

Fig. 6. SEM images of sintered micro-grained (a), S7 (b), S8 (c) and S9 (d) samples.

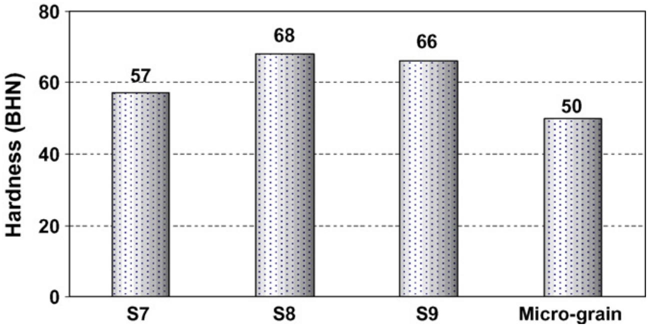

Fig. 7. Brinell hardness of sintered S7, S8, S9 and micro-grained samples.

S7 sample. Therefore, the influence of stearic acid on subsequent powder sintering is an indirect effect. On the other hand, as indicated before via EDS analysis, stearic acid does not affect the final chemical composition of the powders. Consequently, differences in powder sintering are not due to the direct effect of PCA.

SEM images of sintered micro-grained S7, S8 and S9 samples are shown in Fig. 6. Micro-grained sample shows a dense microstructure, whereas large pores are observed between particles of S7 sample. Microstructures of S8 and S9 samples indicating uniform grains together with some small pores confirm the positive role of stearic acid in densification process of these samples.

The Brinell hardness of sintered samples is shown in Fig. 7. It could be seen that S8 sample shows the maximum hardness of 68 BHN, which is 1.4 times higher than that of micro-grained sample. Increased hardness in S8 sample is due to its smallest crystallite size and highest remained strain (see Table 2). Moreover, higher hardness in S8 and S9 samples may be caused by the small amount of remained copper oxides due to the presence of the stearic acid during mechano-chemical process.

4. Conclusions

Nano-crystalline Cu powders were synthesized by mechano-chemical reduction of Cu_2O with graphite using high-energy ball milling with and without addition of the stearic acid as a PCA. It was found by XRD analysis that the mean crystallite size of the copper produced after 35 h of ball milling decreased from 27 nm in S7 sample to 19 nm in S8 sample. Moreover, the PCA strongly affects the formation process of copper. A fast reduction reaction occurred in the absence of PCA and presence of PCA delayed the reduction process. SEM results showed that addition of PCA efficiently reduced the particle size of Cu by suppression of excessive cold welding. Also, addition of stearic acid improved hardness of sintered nanopowder samples.

Acknowledgement

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