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Effect of Addition of Process Control Agent (PCA) on the Nanocrystalline Behavior of Elemental Silver during High Energy Milling

P. B. JOSHI[1], G. R. MARATHE[1], ARUN PRATAP[2,*] and VINOD KURUP[3]
[1]*Department of Metallurgical Engineering, M. S. University of Baroda, Vadodara 390 001, India*
[2]*Department of Applied Physics, M. S. University of Baroda, Vadodara 390 001, India; e-mail: apratapmsu@yahoo.com*
[3]*Electrical Research and Development Association, Vadodara 390 010, India*

Abstract. Mechanical Alloying (MA) or High Energy Milling has been a subject of great interest for last few decades. However, in the majority of the cases the investigations are confined to areas like alloying in binary or multi-component systems from premixed powders. Very little work has been reported on high-energy milling of pure metals. There are some reports on mechanical alloying of pure metals that undergo polymorphic transformation on milling, but relatively few papers have been reported in the literature pertaining to attrition milling of pure metals, which do not fall under this category. One such attempt has been made in this investigation by subjecting a noble metal like silver with fcc crystal structure to attrition milling. The present work deals with the investigation of the effect of addition of a process control agent (PCA) on the nanocrystalline behavior of elemental silver powder subjected to high energy milling in an attritor. Elemental silver powder was subjected to attrition milling with and without addition of stearic acid as PCA. The powder samples drawn at periodic intervals during the course of milling were subjected to characterization using techniques like XRD, SEM and DSC. The variation in particle shape morphology, crystallite size and lattice strain as a function of PCA was studied.

Key Words: effect of PCA, mechanical alloying, silver powder.

1. Introduction

Nano-crystals are ultrafine single or multiphase mono/polycrystalline materials with nanometric grain size (typically <20 nm). Nano-crystals are subject of intense research due to many attractive mechanical (hardness, elastic modulus, etc.) and functional (heat capacity, magnetic, catalytic, chemical reactivity and electrical resistivity) properties and associated applications of them [1–3]. Among the possible routes of synthesis of nanocrystalline metallic and ceramic materials, mechanical alloying/milling offers an easy, flexible and inexpensive option capable of producing materials with interesting microstructure in large

* Author for correspondence.

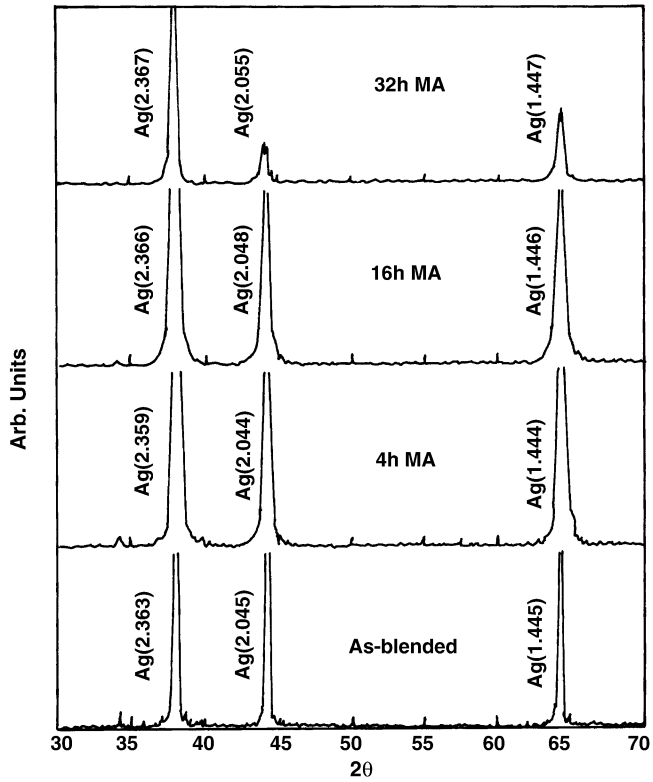


Figure 1. Variation of the peak intensity of the silver powder containing PCA for various milling times.

quantity. Mechanical alloying/milling mostly involves multi-component powder blends, which leads to intermixing of two atomic species on an atomic scale with a large negative heat of mixing [4–6]. Very little work has been reported on high energy milling of pure metals. There are some reports on mechanical alloying of pure metals which undergo polymorphic transformation on milling revealing some fundamental aspects of phase transformation [7].

In the present work, high energy milling of elemental silver powder (fcc) was taken up. Silver nano powders are on the edge of becoming commercial filler materials for electrically conducting polymer matrix composites. The morphology of the powder as such contributes to the electrical and mechanical properties [8, 9]. The study presents the effect of PCA additions on the behavior of elemental silver powder during milling.

2. Experimental

Pure silver powder (less than 5 micron particle size and 99 percent purity) was milled in an indigenously fabricated high energy attrition mill. Two independent

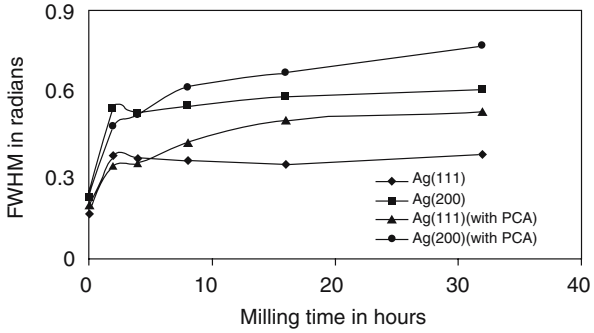


Figure 2. Variation of full width at half maximum intensity for the silver peaks with respect to milling time.

batches of 30 g each of silver powder, one with stearic acid as process control agent (PCA) and the other without PCA, were run. The ball to charge ratio was 20:1. Approximately 3 g of sample was drawn at definite time intervals of 2, 4, 8, 16, 32 and 48 hours during the course of milling.

The milled samples with and without PCA were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in secondary electron imaging (SEI) mode. The change in thermal behavior of powder samples due to milling was investigated using SHIMADZU DSC−50 (Differential Scanning Calorimetry) at a heating rate of 10°C / min.

3. Results

The X-ray diffraction patterns of the samples milled with and without PCA and drawn at different time intervals show a broadening of peaks with increasing milling time. Representative multiple XRD plots for powders milled with PCA are shown in Figure 1. The variation of the full width at half maximum intensity for the silver peaks with different milling duration is shown in Figure 2.

This is a general trend with regard to the broadening of diffraction peaks that follows due to mechanical disordering as well as particle refinement, but the degree of broadening is larger in the case of samples milled with PCA. The crystallite size was calculated from the broadening of the X-ray peaks using the Hall–Williamson method. The crystallite size variation with milling duration is shown in Figure 3. The crystallite size decreases sharply to around 30 nm during the initial period of milling (4 hrs) and later on it stabilizes between 20 to 30 nm and remains constant as milling proceeds. This phenomenon is observed in samples with and without PCA; however the crystallite size is finer in samples milled with PCA.

Figure 4 shows the variation of micro-strain with respect to milling time. As apparent from the figure, the lattice strain increases sharply up to 4 hours and

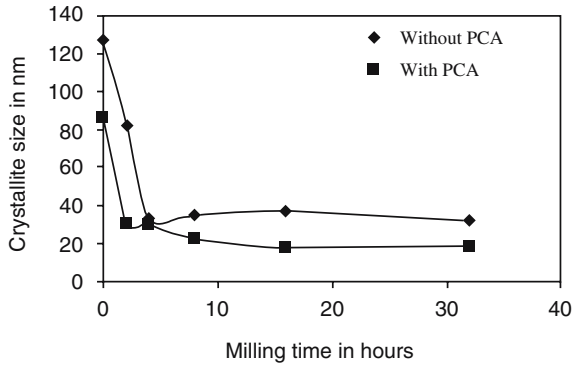


Figure 3. Variation of crystallite size of silver nano particles with respect to milling time.

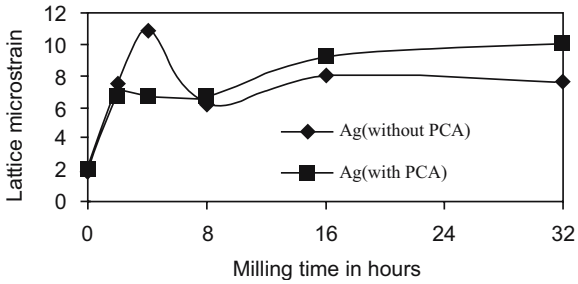
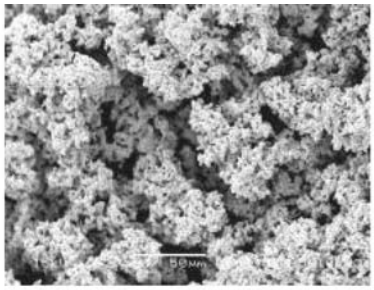


Figure 4. Variation in lattice micro strain of silver nano particles with respect to milling time.

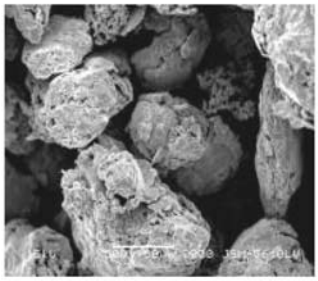
then decreases gradually and finally becomes constant. This is attributed to the sudden increase in density of defect structures such as dislocations and grain boundaries [10]. Prolonged milling leads to an increase in temperature which results in re-crystallization and annealing. Thus the decrease in lattice strain can be said to be due to the re-crystallization and annealing phenomenon.

The change in particle morphology of Ag powder for two different conditions (i.e., with and without PCA) was evaluated by subjecting the representative powder samples to scanning electron microscopy (SEM). Figure 5 indicates the tendency towards coarsening of particles with progressive milling. At intermediate stages of milling excessive flattening of silver particles is observed, this happens more in case of powder without PCA. The initially round particles having an agglomerated chain like structure change their morphology to a flat flaky type with increasing milling time.

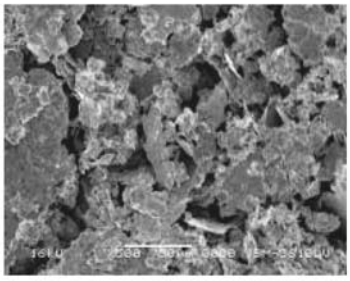
In view of noticeable changes in crystallite size and lattice strain, the starting powder and sample drawn after 4 hours of milling were subjected to DSC scans shown in Figure 6. The DSC plot in Figure 6(a) shows two small exothermic humps corresponding to the relaxation of the small amount of strain present in the starting material. However, a predominant exothermic peak at 626°K is ob-



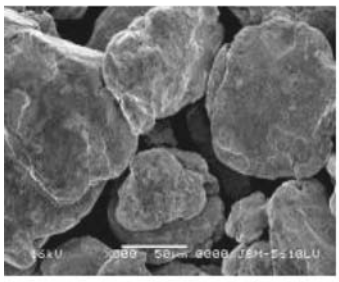
(a) Elemental silver



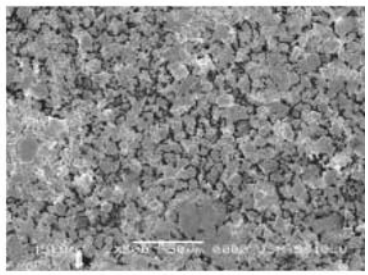
(b) Silver-2hrs milled (without PCA)



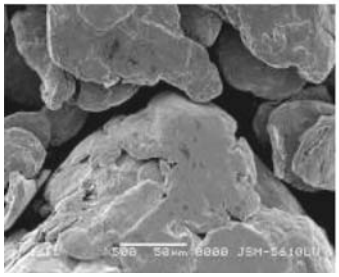
(e) Silver-2hrs milled (with PCA)



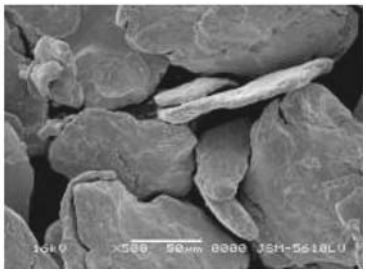
(c) Silver-16hrs milled (without PCA)



(f) Silver-16hrs milled (with PCA)



(d) Silver-32hrs milled (without PCA)



(g) Silver-32hrs milled (with PCA)

Figure 5. SEM Photomicrographs for (a) elemental silver powder, (b–d) Mechanically Alloyed powders without PCA and (e–g) Mechanically Alloyed powders with PCA.

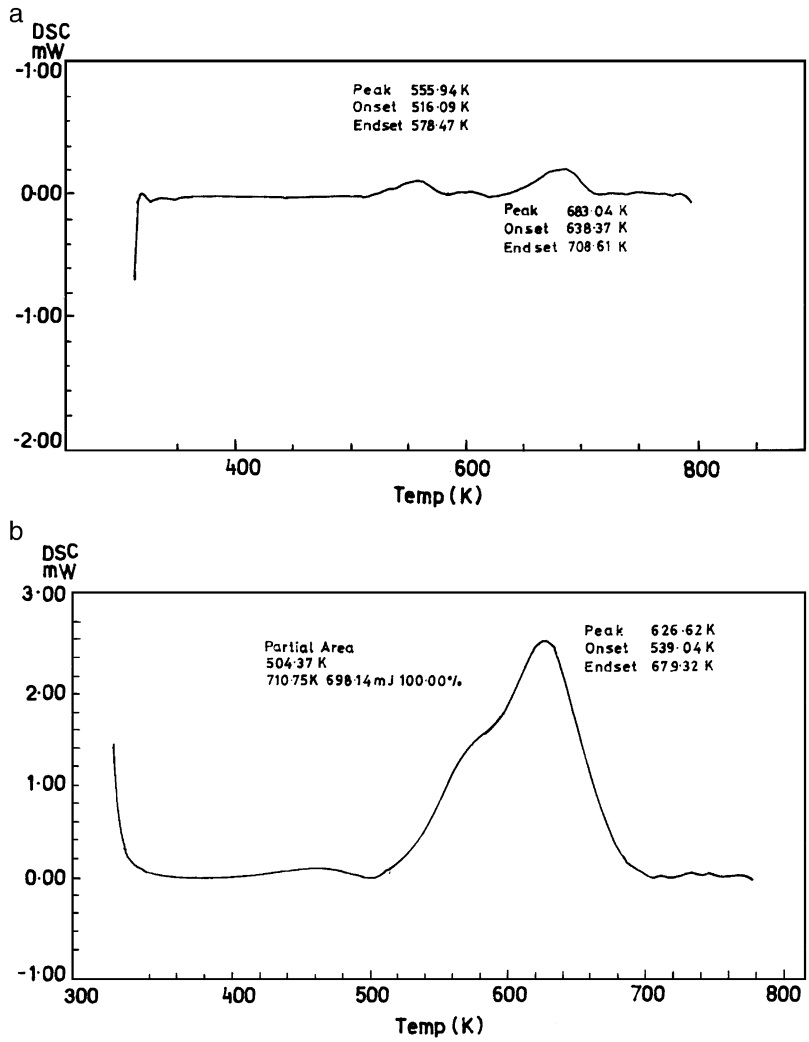


Figure 6. (a) DSC thermogram of initial silver powder before milling, (b) DSC scan for the same silver powder after 4 hrs of milling.

served for 4 hrs milled sample (Figure 6(b)), which may be due to recovery, i.e., grain growth and strain relaxation.

4. Discussion

The peak broadening at half maximum intensity of the X-ray diffraction lines is due to a reduction in crystallite size, flattening and micro-strains within the diffracting domains. The broadening is larger in samples milled with PCA, which indicates crystallite size reduction and increase in lattice strain as shown

in Figures 3 and 4. In general, plastic deformation proceeds by slip and twinning at low and moderate strain rates, whereas at high strain rates the formation of a dense network of dislocations becomes the dominant mechanism [11, 12]. Plastic deformation by ball milling occurs via shear bands. In early stages of milling, the average strain increases due to an increase in dislocation density. At a certain dislocation density within the heavily strained region, the crystal disintegrates into sub-grains. This leads to a decrease in lattice strain after 5 hours of milling. With further processing, deformation occurs in shear bands located in previously unstrained parts of the material. The size of sub-grains in existing bands is further reduced reaching a steady condition as shown in Figure 3 at a later stage. The PCA on being absorbed on the surface of particles helps in inhibiting excessive cold welding and thereby agglomeration, by lowering the surface tension of the solid. Because the energy required for milling is a function of plastic deformation of powder particles and new surface area generated times the surface tension, a reduction in surface tension by absorption of PCA results in a finer crystallite size.

The SEM micrographs indicate a trend towards coarsening along with a tendency to convolution as milling progresses. This change in particle morphology is as expected due to the high ductility of silver [13]. The effect of PCA in reducing the cold welding tendency can be clearly observed. If we critically compare the SEM micrographs for 16 hours milled samples (with and without PCA), we observe large flattened particles with smooth surfaces due to excessive cold welding in case of the sample without PCA where the particle diameter tends to increase in one dimension. However, for the sample milled with PCA cold welding is suppressed, therefore we are able to attain a finer particle size. Cold welding and fracturing processes help the powder particles to be in contact with each other with atomically clean surfaces. The degree of cold welding depends on the ductility of the powder. PCA impedes the clean metal-to-metal contact by being absorbed on the surface of the particles and helps to inhibit cold welding. However, as the milling is continued, the particle sizes become larger as seen in samples milled for 32 hours. This is due to the decomposition of the process control agent (PCA) leading to diminishing effect of the same. Thus in the 32 hrs milled sample we get a flat and flaky morphology with excessive cold welding.

The thermal behavior of the samples was investigated with the help of DSC. DSC plot for starting material exhibits two small exothermic humps shown in Figure 6(a). These may be attributed to (i) relaxation phenomena of small amount of pre-existing microstrains associated with the starting material; and/or (ii) tarnishing of silver. This is also evidenced by Figure 4 for lattice microstrain vs. milling time wherein some amount of microstrain is clearly indicated for unmilled sample. Such small initial microstrain in the starting sample seems to be a result of the specific manufacturing practice for the silver powder used as starting material in this investigation. It is due to this that the heats of enthalpy for these two small exothermic events are 28.23 mJ and 59.16 mJ, respectively.

The DSC thermogram of the elemental silver after 4-hrs of milling shows that higher heat of enthalpy is associated (698.14 mJ) and the broad exothermic peak at ~626°K is due to grain growth and strain relaxation, which is confirmed by XRD peaks after isothermal annealing heat treatment.

5. Conclusion

The high energy milling of elemental silver does not involve any polymorphic transformation even after prolonged milling, as indicated by the X-ray diffraction. The broadening of diffraction peaks and reduction in peak intensities is attributed to crystallite size reduction and an increase in the micro-strain level. The addition of PCA helps in retarding the excessive tendency to cold welding and thus is able to offer finer crystallite sizes. The SEM studies bring out the tendency of silver powder to extensive flattening/leafing with prolonged milling. This has a direct influence on the ratio of surface area to volume of the powder produced.

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