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Preparation of nanostructure silver powders by mechanical decomposing and mechanochemical reduction of silver oxide

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Abstract: The mechanical decomposing and mechanochemical reductions of silver oxide for preparation of nanocrystalline silver powders by high planetary ball mill was investigated. XRD and HRSEM techniques were used to characterize the structural evolution and morphological changes of products. The results show that the nanostructured silver with an average crystallite size of 14 nm and internal strain of 0.75% is synthesized by mechanical decomposing of Ag_2O after 95 h milling. While, the product of mechanochemical reduction of silver oxide using graphite after 22 h milling is nanostructured silver with an average crystallite size of 28 nm and internal strain of 0.44%.

Key words: nanocrystalline silver; silver oxide; mechanical decomposing; mechanochemical reduction

1 Introduction

Mechanochemistry is a branch of science referring to the chemical and physicochemical reactions of substances due to the influence of mechanical force [1]. Recently, mechanochemistry has been widely applied in many fields, such as preparation of intermetallic compounds, extractive metallurgy, crystal engineering, coal industry, composites and complex oxides, nanocrystalline substances, building industry, agriculture, pharmacy and waste treatment [2−6]. According to the literature, a broad variety of Ag nanoparticle applications were reported ranging from sterilization of medical devices and purifying appliances to water treatment. Furthermore, due to the unique characteristics, Ag nanoparticles have also been used in a broad variety of application such as magnetic, biomedical, optoelectronic, dielectric, hygienic and healing purposes [7,8].

In our previous work, mechanochemical reduction of Ag_2O was carried out in a planetary ball mill [9]. However, no information is available on the structural evolution of Ag_2O mechanical decomposing as well as the effect of graphite on reaction mechanism and product properties. In this study, nanostructured silver has been synthesized using mechanical decomposing of Ag_2O by high energy ball milling without any reducing agent, and the results are compared with the results of mechanochemical reduction of Ag_2O using graphite.

2 Experimental

Raw materials were commercially pure Ag_2O powder (99%, 5−40 μm) and graphite (99.9%, 10−50 μm). The powder samples were milled in a high energy planetary ball mill. Details of ball milling process for both mechanochemical reduction and mechanical decomposing are given in Table 1. The only difference between two types of reduction process was the composition of initial powder. Ag_2O powder in mechanical decomposing and a mixture of graphite-Ag_2O in mechanochemical reduction are used as initial materials.

The samples were characterized by high-resolution transmission electron microscopy (HRSEM, Hitachi S-4160) and X-ray diffraction (XRD, Philips PW-1730) using Cu K_α. The broadening owing to the instrument was computed from Warren's method [10]. Peak positions (2θ) and the full-width at half maximum (FWHM) were obtained from the XRD spectra by

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Table 1 Details of planetary ball milling process

Parameter	Value
Rotation speed of disc/(r·min^{-1})	250
Rotation speed of vial/(r·min^{-1})	450
Diameter of disc/mm	350
Diameter of vial/mm	90
Vial material	Hardened chromium steel
Capacity of vial/mL	150
Ball material	Hardened carbon steel
Diameter of balls/mm	20
Number of balls	6
Balls to powder mass ratio	20:1
Time of milling/h	0−95
Process control agent	−
Type of milling	Dry
Atmosphere of milling	Air
Total powder mass/g	9.75

OriginPro 8 from the Ag_2O planes selected for the profile analysis. The line broadening due to the instrument was calculated from Warren's method [11]. The average crystallite size and internal strain were estimated using Williamson-Hall plot [12].

3 Results and discussion

Figure 1(a) shows the XRD spectra of mechanical decomposing of Ag_2O milled for various times of 0, 10, 20, 21, 22, 25, 35, 50, 75, 90 and 95 h. Analysis of the XRD patterns shows that, up to 20 h milling, gradual refinement is the only considerable occurrence in Ag_2O powders, and no detectable transformation is happens to introduce any new phase. The traces of silver could be produced after 21 h milling. The XRD results also show that the Ag_2O peaks progressively disappear with increasing the milling time. In fact, they are well below the resolution limit of XRD after 95 h of milling, which suggests the completion of dissociation reaction as follows [13]:

$$Ag_2O(s)=2Ag(s)+1/2O_2(g),\ \Delta H=61080\ J \quad (1)$$

Figure 1(b) shows the XRD patterns of the mechanochemical reduction of Ag_2O together with 40% (molar fraction) of extra graphite as reducing agent according to Eq. (2) [13]:

$$2Ag_2O(s)+C(s)=4Ag(s)+CO_2(g),\ \Delta H=-363560\ J \quad (2)$$

The samples were milled for various times up to 22 h. It could be seen that Ag peaks appear after a relatively short milling time of 3 h in comparison with that of

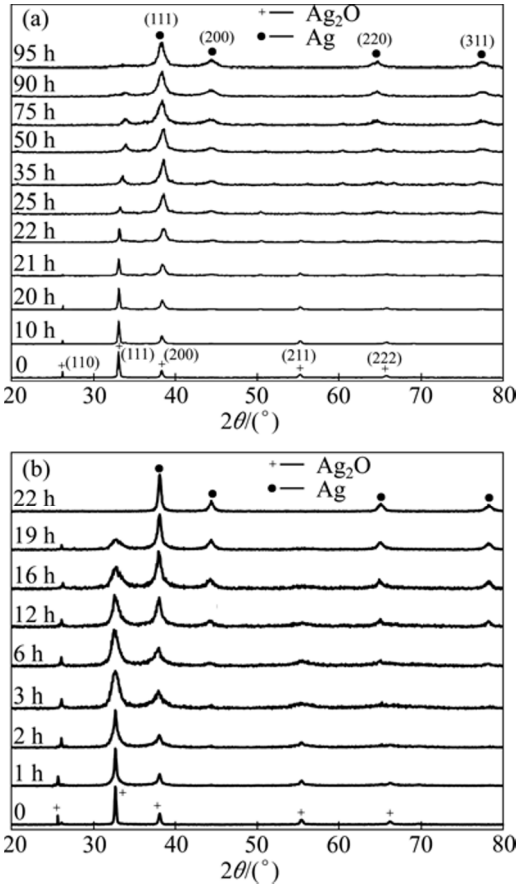

Fig. 1 XRD patterns as function of milling times: (a) Mechanical decomposing of Ag_2O; (b) Mechanochemical reduction of Ag_2O

mechanical decomposing of Ag_2O, where Ag peaks are first observed after 21 h milling. The XRD results also show that the Ag_2O peaks progressively disappear with increasing milling time. The fraction of Ag_2O reduced during milling, α, is estimated by considering the intensity of Ag_2O (111) peak as follows [5]:

$$\alpha=1-(I_t/I_0) \quad (3)$$

where I_t is the Ag_2O (111) peak intensity of sample milled for a certain time and I_0 is the intensity of Ag_2O (111) peak of unmilled sample. Figure 2 shows the calculated values of α as a function of milling time for mechanical decomposing and mechanochemical reduction of Ag_2O. An incubation time of approximately 22 h in mechanical decomposing and 3 h in mechanochemical reduction of Ag_2O are observed, then the rate of reduction reaction is increased. The presence of graphite in mechanochemical reduction performed as the reducing agent enhances the reducing potential of Ag_2O in comparison to the mechanical decomposing and consequently the time dependence of α is more drastic in mechanochemical reduction than in mechanical decomposing. It seems that the reduction energy barrier