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Microhardness studies of nanocrystalline lead molybdate

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ABSTRACT

Nanocrystalline lead molybdate ($PbMoO_4$) of four different grain sizes were synthesized through chemical precipitation technique and the grain sizes and crystal structure are determined using the broadening of X-ray diffraction patterns and transmission electron microscopy. The microhardness of nanocrystalline lead molybdate ($PbMoO_4$) with different grain sizes were measured using a Vicker's microhardness tester for various applied loads ranging from 0.049 to 1.96 N. The microhardness values showed significant indentation size effect at low indentation loads. The proportional specimen resistance model put forward by Li and Bradt and energy balance model put forward by Gong and Li were used to analyze the behaviour of measured microhardness values under different indentation loads. The microhardness data obtained for samples of different grain sizes showed grain size dependent strengthening obeying normal Hall–Petch relation. The dependence of compacting pressure and annealing temperature on microhardness of the nanostructured sample with grain size of ~18 nm were also studied. The samples showed significant increase in microhardness values as the compacting pressure and annealing time were increased. The variation of microhardness of the material with pressure of pelletization and annealing time are discussed in the light of change of pore size distribution of the samples.

1. Introduction

Nanocrystalline materials exhibit peculiar physical, mechanical and chemical properties compared to coarse grained materials which make them highly significant in technological applications [1,2]. The outstanding properties of nanograined materials arise from the interface and nanoscale effects connected with their structural features. The exceptional mechanical and diffusional properties linked with nanocrystalline materials are due to the presence of a large number of atoms in the grain boundaries and the nanoscale structuring of building blocks [3,4]. Reports on the study of mechanical properties through a determination of microhardness of nanocrystalline materials, nanostructured thin films and nanocrystalline composite coatings are available in the literature [3–7]. Out of the different methods to determine the microhardness of a material, Vickers method is the most simple and widely used one. Several studies on microhardness of metals, alloys, glasses and ceramic materials are reported in the literature [4,8–13]. The microhardness of a material either decreases with increase in indentation load, a phenomenon called indentation size effect (ISE) [8,9,11,12] or increases with increase in indentation load called reverse indentation size effect (RISE) [7,11,14,15]. Indentation size effect is often observed in metallic, ceramic and non-crystalline materials [8,9,12,16] while some studies report reverse indentation size effect on glasses and certain ceramic materials [11,14,15,17,18]. The ISE behaviour has been explained on the basis of dislocation produced during indentation [4,19–21] and RISE behaviour is ascribed to the predominance of nucleation and multiplication of dislocations and activity of slip mechanisms [4].

Several reports are available in the literature where the dependence of microhardness on grain size of nanocrystalline materials is investigated [7,22–27]. The grain size and microhardness of a material can be related using the well known Hall–Petch relation (HP) [28,29] which predicts a linear relationship between grain size and microhardness. Several studies on nanocrystalline materials have reported that the microhardness increases with decrease in grain size showing a normal HP behaviour [24–27,30,31] while some studies indicate an increase in microhardness with increase in grain size, a phenomenon known as inverse HP behaviour [4,6,7,32–36]. Variations in hardness can occur with temperature, compaction pressure, porosity, and depth of penetration [4–7,11,12,22,27].

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The present paper reports the results of a detailed study of the microhardness of consolidated nanoparticles of lead molybdate ($PbMoO_4$). $PbMoO_4$ belongs to scheelite family characterized by the tetragonal space group C_{4h}^6. Nanoparticles of $PbMoO_4$ were synthesized using chemical precipitation technique and the samples were characterized using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The porosity of as-compacted samples was determined using mercury intrusion porosimetry. The dependence of microhardness on the grain size of the samples, compaction pressure and annealing of the pellets is investigated. The validity of Hall–Petch [28,29] relation is examined using the measured microhardness values of the samples of different grain sizes.

2. Experimental

Nanoparticles of lead molybdate of four different grain sizes were synthesized through chemical precipitation technique. Analar grade $Pb(NO_3)_2$, $Na_2MoO_4{\cdot}2H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were used for the synthesis. The details of the synthesis of the samples with different grain sizes are shown in Table 1.

The reactants were dropped into the reaction medium kept under rigorous stirring. The precipitate obtained was separated from the reaction medium and air-dried. The crystal structure and grain size of nanocrystalline $PbMoO_4$ samples were determined using XRD and transmission electron microscopy (TEM). The XRD patterns of the samples were recorded using Philips XPERT PRO diffractometer with Cu K_α radiation (λ = 1.5406 Å) source. Further, the samples were analyzed using JEOL 3010 high resolution transmission electron microscope (HR-TEM) operated at 300 keV. For the study of microhardness, the nanoparticle samples of $PbMoO_4$ of different grain sizes with sample codes L1, L2, L3 and L4 were compressed into pellets of diameter 13 mm and thickness approximately 2 mm using KBr pellet die in a PERKIN-ELMER press by applying uniaxial pressure of 0.77 GPa. The compaction time was kept constant at 5 min. To study the effect of compaction pressure on microhardness, nanoparticles of grain size ~18 nm (sample code L2) were compacted at two other pressures of 0.62 and 1.08 GPa (sample codes – L21 and L22, respectively). In order to study the effect of annealing of the samples on microhardness of the pellets, pellets of grain size ~18 nm compacted at a pressure of 0.77 GPa were annealed at a temperature of 300 °C for 1, 2, 3 and 4 h (sample codes – L21H, L22H, L23H and L24H, respectively). The annealing temperature was kept low at 300 °C in order to ensure that no appreciable growth in grain size occurred as a result of annealing.

The microhardness of the pelletized samples of nanocrystalline lead molybdate ($PbMoO_4$) was determined using Shimadzu HMV-2000 Vickers microhardness equipment. In this method a hardness tester with a diamond pyramidal indenter and a microscope was used for the study. The indentations were made perpendicular to the surface of the pellet at different sites where no surface defects were visible. The load P was varied from 0.049 to 1.98 N and the time of indentation was kept a constant at 12 s. The diagonal lengths were measured using an optical head having a linear encoder having a resolution of 0.1 μm. The distance between any two indentations was kept more than five times the diagonal length of the indentation, to avoid any mutual influence of the indentations. Indentations that did not appear symmetrical were not considered for diagonal measurement. All the indentation measurements were carried out at room temperature. For each load, 10 trials of indentations were carried out and the average values of diagonal lengths of indentation in each measurement are taken to determine the value of microhardness. To study the effect of pore sizes and their distribution on the microhardness of the pellets of nanostructured $PbMoO_4$, mercury intrusion porosimetry measurements were performed on the pellets using Quantachrome Poremaster. This measurement yielded the pore volume and pore size distribution in the pellets. In Vickers method microhardness is expressed as Vickers hardness number (H_V) which is calculated from the relation [4],

$$H_V = \frac{KP}{d^2} \quad (1)$$

where P is the applied indentation load, d the diagonal length of the indentation and K is a constant equal to 1.8544 for a Vickers indenter.

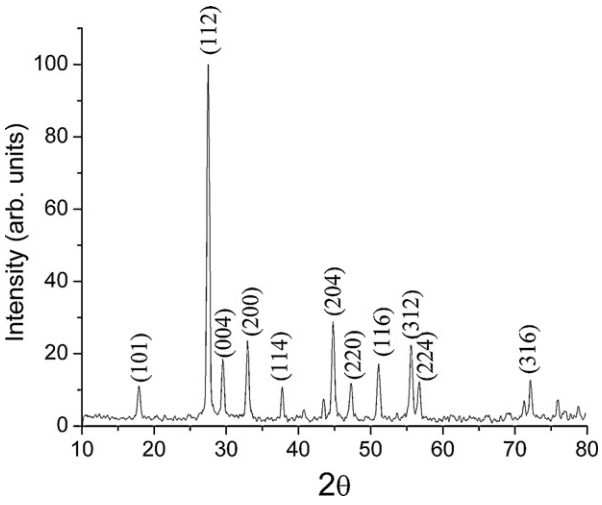

Fig. 1. XRD pattern of nanocrystalline $PbMoO_4$.

3. Results and discussion

3.1. Determination of crystal structure and grain size

Fig. 1 shows the XRD pattern of one sample of nanostructured $PbMoO_4$. The diffraction peaks agree with ICDD file no. 44-1486 which correspond to $PbMoO_4$ belonging to scheelite structure. The XRD pattern showed typical interplanar spacings corresponding to body centered tetragonal phase of scheelite structure characterized by space group C_{4h}^6. The grain sizes of nanocrystalline samples were determined using Hall–Williamson method [7,37]. Hall–Williamson method is the simplest method to separate the effects of strain and grain size on the broadening of XRD peaks [37]. The effects of strain and particle size on full width at half maximum (FWHM) are additive and can be expressed using Hall–Williamson

Table 1
Details of preparation conditions of nanocrystalline $PbMoO_4$.

Reaction medium	Reactants	Temperature	Grain size (nm)	Sample code
60 ml propanol + 20 ml distilled water	1 M 10 ml aqueous $Pb(NO_3)_2$ and $Na_2MoO_4{\cdot}2H_2O$	Ice temperature	14	L1
50 ml propanol	0.25 M 25 ml aqueous $Pb(NO_3)_2$ and $Na_2MoO_4{\cdot}2H_2O$	Ice temperature	18	L2
80 ml distilled water	0.25 M 10 ml aqueous $Pb(NO_3)_2$ and $Na_2MoO_4{\cdot}2H_2O$	Ice temperature	24	L3
80 ml distilled water	1 M 10 ml $Pb(NO_3)_2$ and 0.25 M 10 ml $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$	Room temperature	52	L5