Microhardness of nanocrystalline aluminium phosphate

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Nanocrystalline aluminium phosphate with different grain sizes was prepared by a simple and efficient method. Thermolysis of the precursor mass at external temperatures of around 900°C resulted in the required phase. The structural evolutions of the samples as a function of sintering temperature and time were monitored by XRD. The FTIR spectra of the samples were taken and the group bonds of their corresponding shifts were analysed. The microhardness of the samples compacted under different pressure ranges were studied. The variations of microhardness with change in grain size, compacting pressure, and density were studied. The microhardness of the sample did increase with increase of compacting pressure and density. Examination of the results also reveals that the microhardness is increased with reduction of grain size in accordance with the normal Hall-Petch relationship.

[Keywords: Microhardness, nanocrystalline material, Aluminium phosphate]

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1 Introduction

Aluminium phosphate (AlPO₄), which is isostructural with quartz (SiO₂), has been studied extensively, because of its potential application as a catalyst support and microwave substrate. Moreover, unlike quartz, AlPO₄ is found to behave as a ‘memory glass’, a term used for characterizing a group of materials which undergo an amorphous transition when subjected to high pressure, yet will recrystallize with the original crystallographic orientation upon quenching. As the grain size enters the nanometer regime, the fundamental properties of materials are significantly different from and sometimes superior to that of their bulk counterpart. Nanostructured metals and ceramics can have improved mechanical properties compared to conventional materials as a result of the ultrafine microstructure. Many authors studied the microhardness behavior of different nanostructured materials. For example, Nieman, Weertman and Siegel reported that nanocrystalline palladium samples (20 nm) show a four fold increase in hardness compared to coarse-grained (100 nm) palladium and a doubling in hardness for nanocrystalline copper samples (25 nm) over coarse-grained (50 nm) copper. The present study is to explore the properties of the nanosize range of aluminium phosphate. A series of tests were made to examine the Hall-Petch relationship, using hardness measurements on nanostructured AlPO₄.

2 Experimental Procedure

Nano-sized AlPO₄ powders are prepared from the thermolysis of a new polymer matrix based precursor solution. The resulting powder is nano-sized, and is of high purity. The details are given in the literature. In the present study, stoichiometric amounts of the reactants were taken such that the concentration of the reactants was 1.0 mol L⁻¹ to produce nanosized sample of about 30 nm grain size. Nano-sized powders of AlPO₄ with grain sizes about 24 nm and 20 nm were also prepared by changing the concentration of the reactants to 0.5 mol L⁻¹ and 0.1 mol L⁻¹ respectively. X-ray diffraction studies were made to analyze phase transformations and the dimensions of the crystallites. FTIR spectra were used to study the basic structural elements, the character of the chemical bonds, and also to analyse the shift in the bands because of micro structural formation.

The microhardness (HV) of the samples was measured using Vickers indentation method. The load P was varied from 0.1 N to 5 N, and the time of indentation was the same (30 s) for all trials and samples. For each sample, several trials of indentation with each load were made and the average values of the diagonal lengths of indentation marks were obtained. The Vickers microhardness number HV at each load was calculated using the relation

\[ HV = \frac{1.8544 P d^2}{2} \text{ (GPa)} \]

where P is the applied load in N and d is the diagonal
length of the indentation in m. In this study, the nanopowders of the samples obtained by chemical method as described earlier, were collected and compacted for 2 min under pressures of 0.3 GPa, 0.34 GPa, 0.38 GPa and 0.41 GPa. The specimens were disc shape, 13 mm in diameter and 1 to 2 mm in thickness. The density measurements of the specimen were made based on Archimedes principle.

3 Results and Discussion

Nano-sized AlPO₄ (n-AlPO₄) samples of different grain sizes were prepared and the effects of thermal treatments on these powders were studied. Fig. 1 presents the XRD spectra of 'as prepared sample' and samples with different heat treatment conditions. An examination of these spectra leads to the conclusion that the 'as prepared sample' and samples at low heat treatment conditions are amorphous in nature (a, b and c of Fig 1). The crystalline nature gradually increases as the annealing temperature and time are increased. The broad bands corresponding to the annealing temperature 900°C for 5 hours (d of Fig. 1) clearly indicate the crystalline nature of the sample at higher annealing conditions. The mean crystallite sizes of the samples were determined using Scherrer formula. It is estimated that the crystallite size of the sample is about 30 nm. By reducing the concentration of the reactants, nano samples of lower dimensions could be prepared. For the present study, nano-sized samples of AlPO₄ with grain sizes of 24 nm and 20 nm, were also prepared, in addition to the 30 nm size sample, by changing the concentration of the reactants.

The FTIR spectrum of the bulk sample shows that the basic structural elements of AlPO₄ are tetrahedral units, although there are two types of tetrahedra in the framework structure, that is, [AlO₄]⁴⁻ and [PO₄]³⁻. Thus, there are two different bonds present in the structure of AlPO₄: a stronger P-O, and a weaker Al-O. For a pure bulk AlPO₄ sample, the individual P-O symmetric stretching (1100 cm⁻¹), asymmetric stretching (1250 cm⁻¹), symmetric bending (480 cm⁻¹) and asymmetric bending (695 cm⁻¹) modes are expected in the IR spectrum. Thus, the band observed in the FTIR spectrum of the present sample (Fig. 2) around 1115 cm⁻¹ corresponds to the symmetric stretching mode of [PO₄]³⁻. This produces a blue shift of about 15 cm⁻¹ for the symmetric stretching mode. Similarly, the band observed around 1260 cm⁻¹ corresponds to the asymmetric stretching mode. A blue shift of about 10 cm⁻¹ is observed in this case. The bands observed around 485 cm⁻¹ and 725 cm⁻¹ are characteristic bending modes of [PO₄]³⁻, and the corresponding blue shifts are about 5 cm⁻¹ and 30 cm⁻¹ respectively. For a nano size grain, the atomic arrangements on the boundaries differ greatly from that of bulk crystals; both in coordination number and bond lengths, showing some extent of disorder. Crystal symmetry is thus degraded in nano size grains. The degradation in crystal symmetry results in the shifting of IR active modes. In the present case, all the IR active modes are shifted to the high frequency side, mainly because of the nano grain size of the sample.

The micro hardness behavior of the samples was studied in detail. Fig. 3 shows the variation of Vickers microhardness number Hv with indentation loads of the 30 nm size sample.
compacted under different pressures. The hardness shows an increase up to a load of about 2 N, and then becomes practically independent of load. The nature of variation of hardness is similar at higher compacting pressures but when the compacting pressure is gradually increased, the hardness also is seen to increase. It is found that the hardness for 0.45 GPa is about two orders greater than that for the same sample compacted under 0.3 GPa. This result indicates that the hardness of n-AlPO₄ is strongly related to compacting pressure. Fig. 4 gives the variation of Hv with indentation loads for different compacting pressures for the 24 nm size sample. Here also the nature of variation of Hv is similar to the 30 nm size sample, but Hv has a five-fold increase when the compacting pressure is increased from 0.3 GPa to 0.45 GPa. The increase of compacting pressure inevitably leads to further densification of the specimen. To prove this result, we measured the densities of the specimens compacted under different pressures. The density increases almost linearly with increasing pressure. In order to show the influence of density on microhardness, we plot the hardness as a function of density (see Fig. 5). It can be seen from Fig. 5 that the hardness of n-AlPO₄ increased from 0.38 GPa to 0.79 GPa as the density increased from 1.48x10⁶ kg/m³ to 1.55x10⁶ kg/m³. This increase of microhardness of n-AlPO₄ with increasing compacting pressure actually reflects the effect of density on hardness. This result indicates that the density of n-AlPO₄ specimen is an important factor affecting its hardness. The variation of microhardness with compacting pressure and density, is further intensified as the grain size of the sample is reduced. The Hall-Petch relationship connecting the microhardness number (Hv) with the grain size (d) is given by

\[ Hv = H_0 + k d^{-\frac{1}{2}} \]

Some authors⁶⁻⁹ reported that the microhardness of nanocrystalline materials increased with decreasing grain size which is consistent with a normal Hall-Petch relation, while some other authors¹₀⁻¹² have reported an inverse Hall-Petch relation, i.e. hardness decreased with decreasing grain size.

To investigate the effect of grain size on the hardness of n-AlPO₄, we plot the values of the microhardness number (Hv) with grain size (d¹/₂) of n-AlPO₄ as a function of indentation loads (Fig. 6). It can be seen from the figure that the plots are more or less straight lines with positive slopes, showing that microhardness of n-AlPO₄ increases with decrease of grain size in accordance with a normal Hall-Petch relationship.

Indentation is primarily due to densification of a volume of the sample in the vicinity of the indenter, and not by plastic flow¹⁰. The marked change in the hardness number for the change in loads from 0.1N to 2 N may be attributed to the generation of plastic deformation. The somewhat constant hardness values for loads above 2 N might be due to the workhardening of the sample.
4 Conclusion

1. Nanophase AIPO₄ microstructures of different grain sizes can be produced by varying the concentration of reactants. Reduction in the reactant concentration reduces the crystallite size of the sample.
2. The precursor powders are found to be X-ray amorphous. The crystalline phases are formed at higher heat treatment conditions. Measurements by XRD analysis showed that the samples with average crystallite sizes of 30 nm, 24 nm and 20 nm were obtained for the present study.
3. FTIR spectrums of the 30 nm size sample indicating shifts in the bands are attributed to nano grain size of the sample.
4. The variation of Vickers microhardness number (HV) of the specimens with indentation loads, shows an increase of hardness up to a load of about 2 N, and then remains practically constant, independent of load. The hardness shows an increase of two orders when the compacting pressure is increased from 0.3 GPa to 0.45 GPa for the 30 nm size sample, while the corresponding increase is five fold in the case of 24 nm size sample.
5. With increase in the densification of the sample there is corresponding increase in the hardness of the sample. When the grain size of the sample is reduced, the hardness increases indicating a normal Hall–Petch relationship.

References