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...ctural defects in silica during high intensity grinding process

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...STRACT Ultra fine particles (below 5μm) is accomplished via comminution. However during ...h intensity grinding process the structure of the ground material will be distorted and this brings ...ualitative changes in the nature of the fine particles. Structural changes are clearly evident in fine ...rticles during fine grinding where the energy delivered by the mill is applied to bending or breaking of ...e crystal, which leads to structural alteration, by loss of regularity in the crystalline network. The degree ...f crystallinaty was characterised based on the XRD measurement. The presence of defects or random ...isorder was evident by the loss or reduction of peak intensity along the diffractograms with the ...roadening effect at the base of the peak. The percentage of crystallinity decreased from 100% before ...inding to 35.44% after 600s of grinding. The d_{50} value also plays an important role to the degree of ...ystallinity. When the particle size was 1.15μm, the degree of crystallinity was around 35.44%.

...Ultra fine grinding, Structural changes, Silica, Phase)

INTRODUCTION

Comminution plays an important role in various disciplines in terms of size reduction of the rocks from the mountains, in mining to the preparation of ultra fine particles (below 5μm) for the down stream process for the advance material application. The scope of comminution caters the size reduction and also the nature of the ground product that involves the structural changes during the high intensity grinding process. Recently the demand for superfine sub micron and nano scale particles increase drastically especially in the biomaterials, polymers, paint, coating, ceramics, composites, cement and also surface treatment industries [1]. Silica plays an important role as fillers, coating agents, abrasive materials and as feed stock for these disciplines. Besides particle size and purity, the phase of silica becomes an essential criterion in these disciplines. Nano scale silica particles in amorphous phase are in demand in the production of polymer electrodes industries where these materiasl are used as fillers [2].

Ultra fine silica is accomplished via comminution. Oscillating mill, planetary mill, attritor mill, vibratory mill and jet mill are used to accomplish ultra fine particles where the particle size distribution is in the micron range (below 10 microns). Ultra fine grinding is an intermediate case between cement grinding and mechanical activation. Similarly to any grinding process, it is intended for size diminishing but it has more complex background because the quantitative changes in the size reduction brings about qualitative changes in the nature of the ultra fine particles. The ultra fine particles technology demands a more fundamental understanding in the physico chemical properties of solid [3].

Crystalline structural changes are more clearly evident in solid when they are ground with equipment based on impact and friction among particles such as oscillating mill and planetary mill [4]. As a result of low conductivity characteristic of silica, the energy delivered by the mill is not stored in the particle as thermal energy, but applied to bending and/or breaking of the crystal. This kind of treatment apart from producing important changes in the physico chemical properties of solid, leads to structural alteration by loss of regularity in the crystalline network. The empirical of crystallinity has been established by characterisation mainly based on XRD measurement [5].

The presence of defects or random disorder is evident by the loss or reduction of peak intensity along the whole diffractograms with the broadening effect at the base of the peak [6]. In mineral processing industries, their objectives in comminution of ore are for liberation of valuable minerals from the gangue. It is a totally different scenario in the dry grinding of the industrial mineral where the fine grinding process not only causes size reduction but also structural changes from crystalline phase to amorphous. These structurally distorted particles are activated due to the high surface energy. Temuujin [7] found that mullite could be produce via fine grinding process between aluminum nitrate nanohydrate with silica due to the mechanical activation of these minerals. Zhang [8] reported that mechanochemically treatment of surpentine enhance the extraction process of magnesium and silicon due to the transformation of crystalline to amorphous.

EXPERIMENTAL

High-grade silica was used in this study. The SiO_2 content in the sample was around 99%. Mono size of the feed sample was used in this experiment. The fine grinding process was done in oscillating mill. This mill works through friction and impact caused by the relative movement of the ring and a concentric cylinder, packed within a casing containing the material to be ground. The amount of silica used in each experimental run was 100g. The samples were ground at different grinding period such as 0s, 15s, 30s, 60s, 120s, 240s and 600s. The obtained materials are identified in accordance to the period of treatment : S_0, S_{15}, S_{30}, S_{60}, S_{120}, S_{240} *and* S_{600}.

The X-Ray diffractograms were obtained using a Philips equipment model PW 1140/00. Radiation K_α of Cu (λ = 1.542 Å) was used for all analyses, at 40kV and 20 mA. One raw material and six ground samples at different grinding periods were chosen to investigate the structural distortion in silica during fine grinding process. The particle size analysis of the ground product was determined via the laser diffraction ray (The Malvern Mastersizer E Ver 1.2).

RESULTS AND DISCUSSION

Besides the drastic size reduction, up to 95% in 15s, the ground sample also exhibits crystal lattice distortion which has a major effect on the finely ground samples in the oscillating mill. As a result of structural changes in the silica, the XRD patterns showed a vast broadening effect at the base of the peaks and also the intensity reduction was observed in Figure 1. The XRD patterns shown in Figure 1 had different grinding periods ranging from 0s to 600s. The highest peak for silica sample was at 26.2^0 (2θ angle) and this peak was taken as a reference. The intensity of the peak after 15s of grinding the intensity was reduced by 2.79%. . A great intensity reduction up to 64.58% was observed after 600s of grinding. The broadening effect of the peak's base could be observed clearly in Figure 1. Table 1 shows the d_{50} values for the samples. As the particle size reduced, the broadening effect at the peaks base increased. The same XRD patterns were observed by Filio [5] for the talc sample where the reduction of peaks intensity and the broadening effects were observed.

Fine grinding is an intermediate case between coarse grinding and mechanical activation. Similarly to coarse grinding it is intended for size diminishing but it involves a more complex physical background. The maximum size reduction limit for a particle is equivalent to the size of tough-brittle transition size as observed by Filio [5]. Size reduction beyond the tough-brittle transition size will lead to plastic deformation rather than breakage of particle and it is accompanied by the growth of structure distortion. The same phenomenon was observed by Boldyrev *et al.* [3].

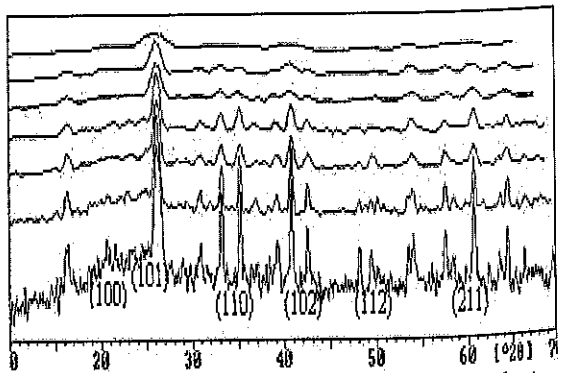

Figure 1. X-Ray diffractograms of silica obtained at different grinding period

Table 1: Intensity value and d_{50} at various grinding periods.

Sample	Grinding Period, s	d_{50}, μm	Intensity, counts	Degree of Amorphous, %
S0	0	64.00	70.56	0
S1	15	3.17	68.59	2.79
S2	30	2.61	57.76	18.14
S3	60	2.08	57.76	18.14
S4	120	1.25	40.96	41.71
S5	240	1.19	40.96	41.71
S6	600	1.15	25.00	64.56

Table 1 shows that the degree of amorphous in silica particle increases as the grinding period increases. The degree of crystallinity is only about 35.44% after 600s grinding. This shows a rapid distortion of crystal lattice in short grinding period due the high intensity grinding process. An important method employed for the investigation of distortion is the observation of line broadening in the X-Ray diffraction spectra. The intensity and the half width of the X-Ray lines in different patterns reflect the amorphous degree and lattice distortion of the particles.

The relation ship between the half-width and the lattice distortion is given by Hall formula as shown in equation 1.

$$\beta\cos\theta/\lambda = 1/D + \varepsilon \sin\theta/\lambda \quad (1)$$

where B is half width, θ is the diffraction angle, λ is the wavelength, D is sub-grain size and ε is relative lattice deformation. The intercept and slope of the straight line found by plotting $\sin\theta/\lambda$ versus $\beta\cos\theta/\lambda$ gives the values of sub-grain size and lattice distortion. Figure 2 shows the results calculated from equation 1 for the ground sample. The relative distortion of the lattice enhances as the grinding time increases. Figure 3 shows the sub grain size of silica particle at various grinding times. The sub grain size of silica particle decreases slowly as the grinding time increases. A slow decrement of the sub grain size observed may be due to the hardness of silica and the strong covalent bonding between the Si and O.

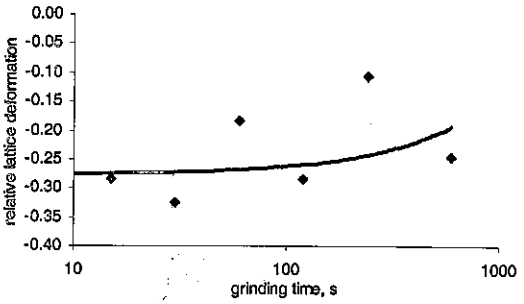

Figure 2. Relative lattice strain at different grinding time.

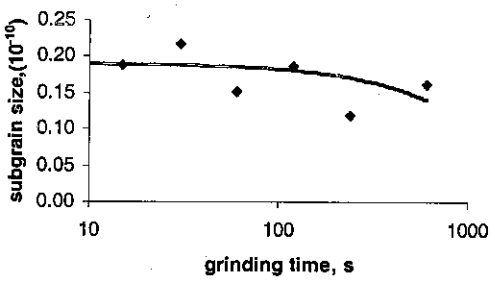

Figure 3. Sub-grain size at different grinding times.

CONCLUSION

The x-ray diffraction analysis showed that structural changes of silica particle to partially amorphous phase during fine grinding process were due to distortion of crystal lattice in the silica crystal structure. The percentage of crystallinity decreased from 100% before grinding to 35.44% after 600s of grinding. The d_{50} value also played an important role to the degree of crystallinity. When the particle size was 1.15μm, the degree of crystallinity was around 35.44%. The study of the structural changes during fine grinding process is very essential because structural changes will affect the silica usage as a feedstock material in vast applications, for example during the sintering process.

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