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Mechanochemical Treatment of Quartz for Preparation of EMC Materials

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Abstract

Mechanochemical effects that occurred in the fine grinding process of quartz particles using planetary ball mill was investigated. Quartz particles have been frequently utilized for optical materials, semiconductor molding materials. We determined that grinding for a long time can be create amorphous structures from the crystalline quartz by Mechanochemical effects. But, to be produced nano-composite particles that the critical grinding time reached for composite materials in a short time. Henceforth, a qualitative estimation must be conducted on the filler for EMC(Epoxy molding compound) materials. It can be produced mechanochemically treated composite materials and also an integrated grinding efficiency considering of the nano-composite amorphous structured particles.

The mechanochemical characteristics were evaluated based on particle morphology, size distribution, specific surface area, density and the amount of amorphous phase materials into the particle surface. The grinding operation in the planetary ball mill can be classified into three stages. During the first stage, initial particle size was reduced for the increase of specific surface area. In the second stage, the specific surface areas increased in spite of the increase in particle size. The final stage as a critical grinding stage, the ground quartz was considered mechanochemically treated particles as a nano-composite amorphous structured particles. The development of amorphous phase on the particle surface was evaluated by X-ray diffractometry, thermal gravity analysis and IR spectrometer.

The amount of amorphous phase of particles ground for 2048 minutes was 85.3% and 88.2% by X-ray analysis and thermal gravity analysis, respectively.

Keywords: Mechanochemical characteristics, Quartz, Fine grinding. Planetary milling, Amorphous phase

Introduction

The grinding operation, a tool for mass production of solid particles, has been applied in various fields such as mineral processing, precision chemistry and material industry. One of the most important point in the conventional handling of this process was the establishment of the relationship between amount of production and energy consumed by grinding. As for this, there has been many studies on the principle of grinding energy and most of that presented production sizes with the specific surface area comparing of the grinding energy. That is, earlier studies were almost limited to estimate the grinding efficiency with surface area increasement or new surface generation.

On the other hand, as a grinding is progressed in a long time, mechnochemical phenomena cannot be neglected, which is generated not only from the new created surface but also solid surfaces or bulk interior changed their structure during the grinding. The mechanochemical effects can be defined as physico-chemical changes in particles by grinding in a long time; these changes can occured when the particle sizes do not decrease any longer. By the way, the mechanical energy working after the yield of grinding is consumed to break crystal structures of particles and their activities such as the increased of a solubility and a sintering effects though the particle sizes are not reduced any more. Moreover, these phenomena are generated the energy consumption during the excessive grinding time compared with the grinding energy solely consumed in creating new surfaces.

In this study, quartz was chosen as a sample. It has been frequently utilized for optical materials, semiconductor instrument materials, heating materials, and filling materials. The mechanochemical effects were investigated which were generated new surface and consumed mechanical energy in a grinding. The mechnochemical effects were estimated by analyzing of the ground sample surface of their amorphization and phase conversion of grinding time, as well as the basic particle characteristics such as the particle sizes, specific surface areas and particle density.

Materials and experimental apparatus

For the sample was prepared, ore was produced from a quartz mine located in Jangsu-kun, Chunbok, mineral processing treatment, and then, utilized as the sample for grinding. Table 1 shows the chemical analysis of the sample. The purity of this is up to SiO2 99.8%. The planetary ball mill(PM-400, Retsch co. Germany) was used for this study. This, which had been frequently utilized for fine grinding, consists of four cylinder type mills of each 250ml volume vessel installed four directions as shown in Fig.1: these mills are rotated and revolved simultaneously. Other apparatus for chemical analysis are as follows: a particle size analyzer by light diffraction(Sald 2001, Shimasu co. Japan), a BET measurement apparatus(Nova 1000, Quantachrome co. USA), IR(FTS-375c, Bio-Rad co. USA), X-ray(X'pert type, Phillips co. Germany), DTA(SDT 2960, TA instrument co. USA), and SEM(JEOL co. Japan)..

Experimental method

The carrier length of a turning radius(R1) of the mills was 130mm, and the rate of revolution(N1) of these was 400rpm. Zirconia balls with a diameter of 3mm was used for media. The value of filling ratio of 0.45, and that of the sample filling ratio was 1.0. The sampling was taken at the time of t=2nmin(n=1,2,...,11). The operation condition of equipment was in the atmospheric condition of the changes in physical properties of ground products. Characteristics were evaluated based on particle morphology, size distribution, specific surface area, density and the amount of amorphous phase materials on the particle surface for making the nano-composite amorphous structured particles.

Results and Discussion

Particle sizes and shapes

Fig. 2. presents SEM photographs of the productions ground for different time respectively. The raw material is of the irregular shape but, as grinding is progressed for t=128min, the particle sizes are reduced and the particle shapes are closed with round. Upto t=512min, the particle sizes rather increase for generation of secondary particles due to agglomeration compare of the primary particles. Consequently, it can be determined that approximately 2 hours are chosen as the yield of grinding at which the particle sizes are not reduced any more, although in grinding. Especially, the case of grinding for t=2048min can be appeared that huge tertiary particles are created by mechanochemical cohesion because of activation of the primary particles with sizes of 100-150nm as calulated by SEM image, which is influenced by excessive energy during grinding. The tertiary particles have the surface activities increased with their amorphized phenomena.

Fig.3 shows each grinding stage classified by the results of investigating the SEM photographs. All grinding process is divided into three stage: the size reduction stage-I(upto t=128min), size enlargement stage-II(upto t=512min) by excessive grinding and mechanochemical agglomeration stage-III (after t=512min). To verify this investigation, we measured the average sizes and specific surface areas of the sample ground, which is presented in Fig.4.

As referred above, initially average sizes are inclined to decrease, but, from II stage after 2 hours around, they are to increase so that one can find yield of grinding is reached. But, the specific surface areas are also increasing in stage-II though the average particle sizes are increasing. This is probably due to weak agglomeration of the primary particles cause by attraction or friction heat energy. In stage-III , the particle sizes are increasing with decreasing the specific surface areas. Consequently, it can found that the production of this stage is coarse particles by real agglomeration with the inter-particle porous voids are compaction by grinding effects. These coarse particles can be called "produced by mechanochemical reaction", since the crystalline structures are disturbed and penetration of amorphization layer into the particles.

Particle density

In general, the density values of quartz are ranged from 2.21(cristobarite) to 2.65g/cm^3(β-quartz). For this difference, the particle density must be measured to estimate the change in crystalline structure by grinding.

Fig.5 gives the density variation of the particles as a function of the grinding time. The density of the raw sample is equal to 2.68g/cm^3, but the density value decreases into 2.24 g/cm^3 at the time of t=2048min. So we can find that the density decrease reflects the defects generated into the crystalline structures directly, and the large extent of the defects can create the amorphous structure in the surface of the particles.

X-ray diffraction analysis

Fig.6 shows results of the X-ray diffraction analysis on the sample particles ground at the filling ratio equal to 1.0. The peak intensity on X-ray diffraction line decreases and peak width broaden with increasing grinding time. Moreover, the decrease in peak intensity after 2 hours, which was determined as the yield of grinding, reflects the progress of the amorphization in the particle surfaces. The particles are activated by continual mechanical impacts even after the particle sizes do not decrease any more. As the results of this, we can find that amorphous layers are generated in the surfaces, as well as strain energy being accumulated.

IR analysis

A quartz crystal has a pyramid structure in which four O2- are combined by a Si4+, and, consequently, its structure unit is Si4+(O...). During the grinding, newly created surfaces are produced according to the defect formation of Si-O-Si bonding.

Fig.7 presents the results of IR(infrared absorption spectroscopy) analysis for examining the bonding structure of the crystalline quartz and the generation of the surface functional group. The analysis showed that formation of silanol radicals which was produced by the rupture of Si-O-Si bond of quartz. The amorphous layer, transition layer and crystal layer were confirmed to be present on the surface of ground particles by examining leached products by 1M of NaOH solution.

That formation of silanol radicals which was produced by the rupture of Si-O-Si bond of quartz. As grinding is progressed, it can be found that the absorption peak is widened in the absorption band of the Si-O bonding(800～1200cm-1), and an absorption band of -OH functional group(3300-3750cm-1) is created in together. This creation is derived probably by hydration of the new surfaces with moistures in the atmosphere.

DTA

In Fig.8, the DTA results of the endothermic reaction generated by the α to β conversion of the sample. The area of the peak reflects the volumetric amount of the crystalline α -quartz to be converted. The reduction of the endothermic peak intensity is derived from increasement of the amorphous layers with decreasing the crystalline α -quartz part. The activity of the particles are also detected from the conversion temperature down with increasing grinding time.

Analysis of the nano-composite amorphous structured particles

In Fig. 9 shows that the nano-composite amorphous structured particles and the ratio of amorphization increased noticeably at about 128 minutes of grinding time as the start of the nano-composite materials and the critical grinding stage where extremely mechanochemically treated products after 512 minutes of grinding. The amorphization ratio of totally mechanochemically produced particles for 2048 minutes was 85.3% and 88.2% by X-ray analysis and thermal gravity analysis, respectively.

Conclusion

We investigated mechanochemical effects that occurred in ground quartz using a planetary ball mill. It has been conformed that surface of particles were transformed into amorphous forms during the grinding by density, specific surface area and XRD patterns. These effects can be estimated by the amorphization on the particle surfaces as the phase conversion with grinding and variation of the fundamental characteristics such as particle size, density and specific surface area.

1. We determined that grinding for a long time can create amorphous structures in the crystalline quartz by mechanochemical reaction in a planetary ball mill. This can be examined by measuring particle density, size and specific surface area and by analyzing X-ray diffraction , DTA and IR spectrometer.

2. The yield of grinding is reached short time(within 2 hours) in the planetary ball mill, the high energy type grinding machine and grinding process is divided into three stages: the size reduction stage, weak agglomeration stage and strong agglomeration stage.

3. Henceforth, a qualitative estimation must be conducted on the amorphous structure by mechanochemical effects, and also an integrated grinding efficiency considering the generation of the amorphous structure must be produced the nano-composite amorphous structured particles .

4. It is considered that mechanochemically treated quartz contains amorphous and transition layers of about 400nm and 50～60nm thick. And at the same time, the amorphization part with a radius of average particle is created 40.6% of length ratio after 2048minutes of grinding.

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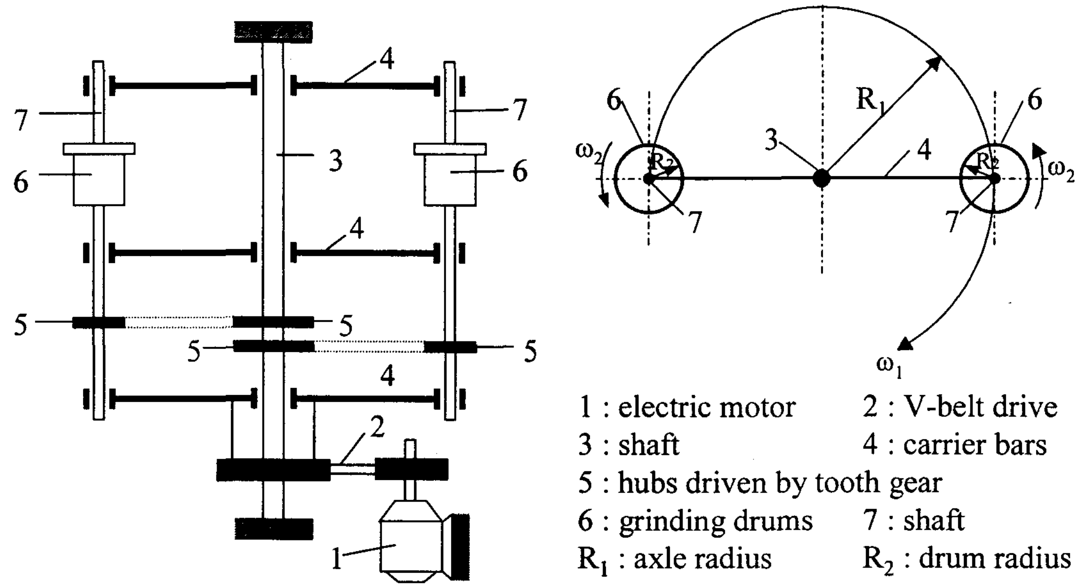


Fig. 1. Schematic representation of a planetary mill

Table 1. Chemical Composition of feed material

COMP.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Ig
wt [%]	99.8	0.01	0.01	tr	tr	tr	0.5

Ig. : ignition loss
tr : trace amount

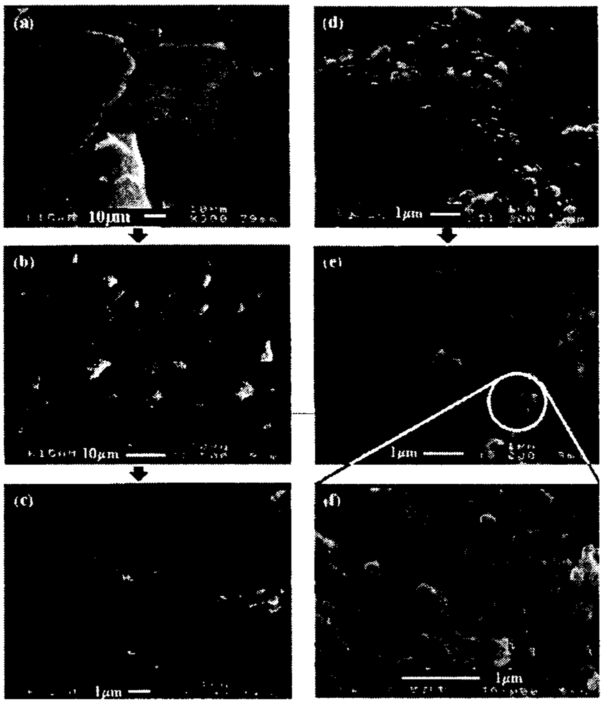


Fig. 2. SEM micrographs of progeny particles for different grinding times, (a) 2min, (b) 8min, (c) 128min, (d) 512min, and (e) 2048min.

grinding stage	ground particle	extent of mechanochemical treatment
Stage Ⅰ : Size reduction	Feed primary particles	low
Stage Ⅱ : Aggregation	secondary particles	Medium
Stage Ⅲ : Agglomeration (mechanochemical reaction)	tertiary particles	high

Fig. 3. Schematic illustration of grinding stage Ⅰ, Ⅱ and Ⅲ.

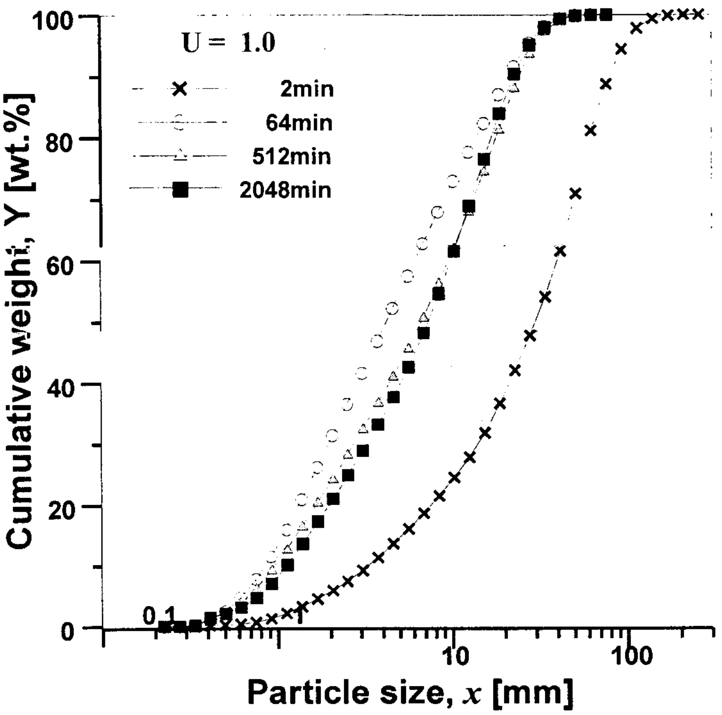


Fig. 4. Particle size distribution of ground quartz with various grinding time

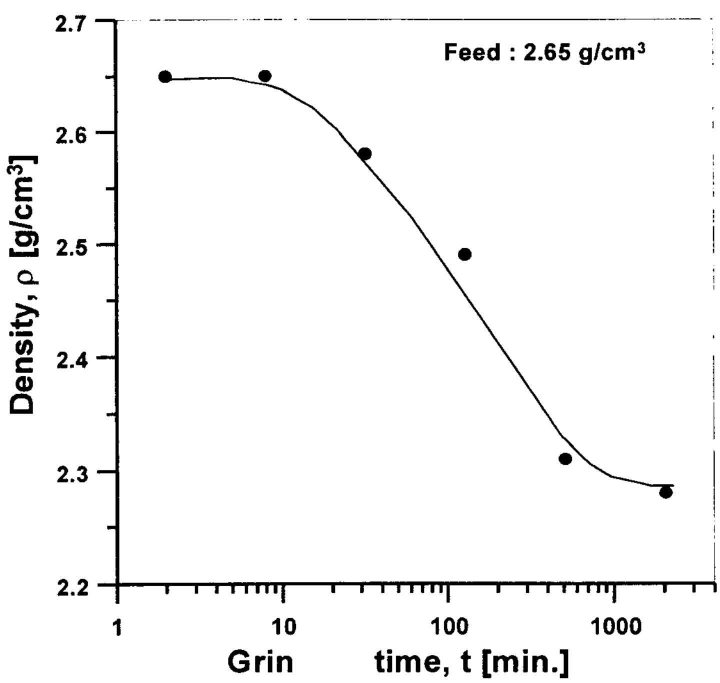


Fig. 5. Variation of particle density with grinding time.

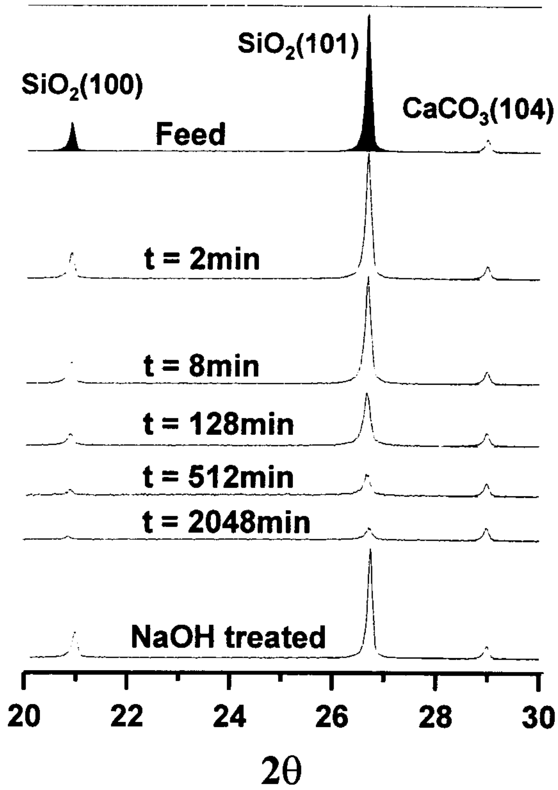


Fig. 6. XRD patterns of ground quartz.

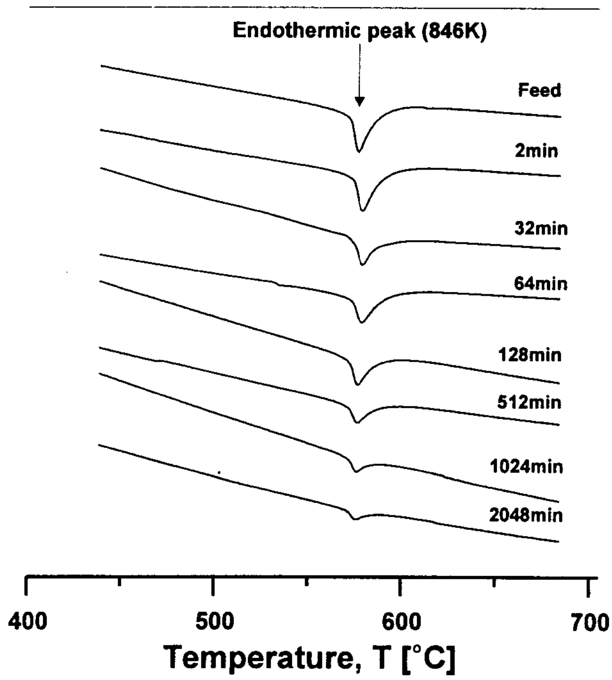


Fig. 8. DTA endothermic peak for various ground quartz

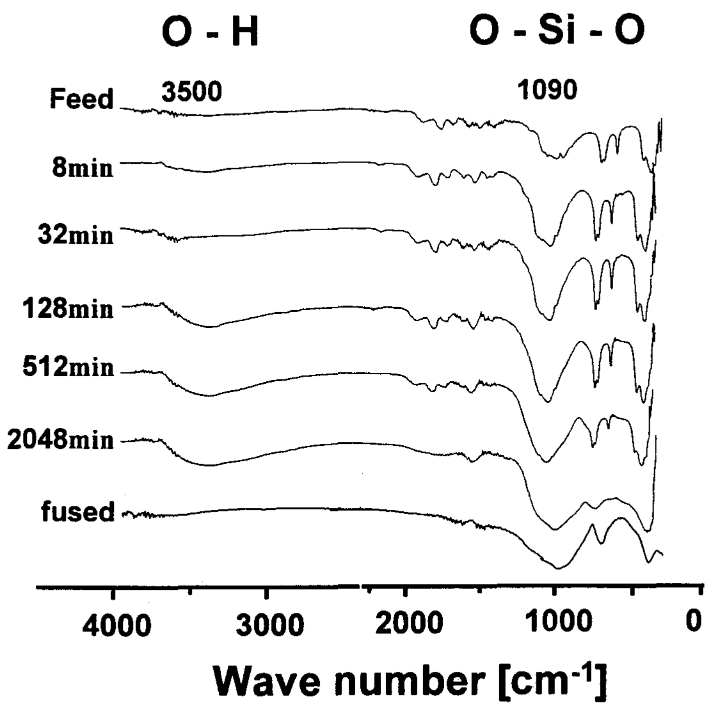
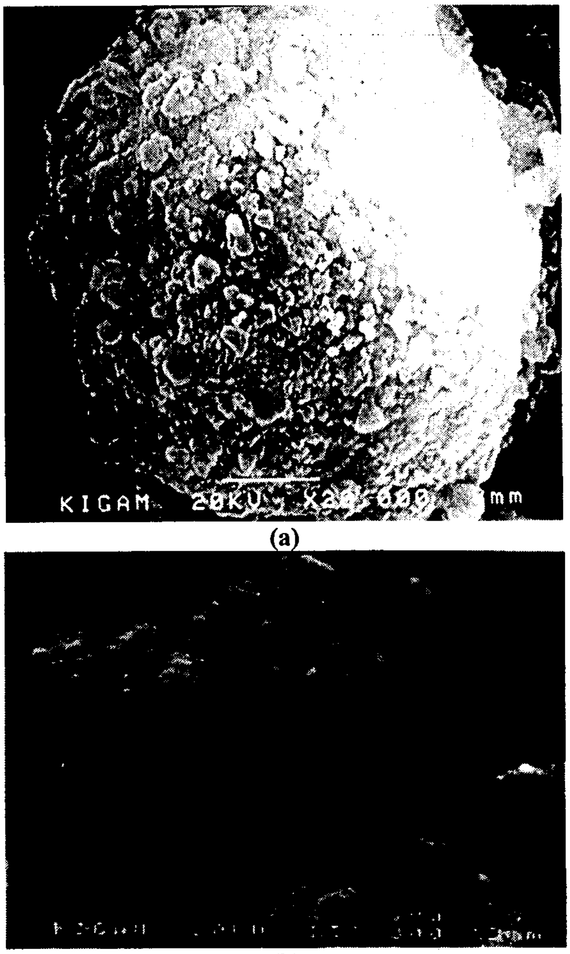


Fig. 7. FTIR spectra of the ground quartz with varying grinding time



(a)

(b)

Fig. 9 Nano-composite amorphous structured particles (a: Unit particle, b: Inner side)