

Preparation of Nano-size Ceramic Particles by Cavitation Method

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Abstract : Nano-size TiO₂ and ZrO₂ particles were prepared using a shock wave which was generated by a nozzle cavitation in a mixture of their raw powders and a water. Their particle sizes were reduced to several tens nanometer after cavitation. The particles were preferentially fractured at the necks between the primary particles. And any deformations, lattice defects and strains were not introduced into particles. It is suggested that the fracturing of powders is the deaggregation, different from the pulverization by media such as a ball-milling.

In this paper the refinement of TiO₂ and ZrO₂ powders by a nozzle cavitation was studied by a X-ray diffraction, a field emission scanning electron micrograph, a transmission electron micrograph and a laser scattering method.

Keywords : TiO₂, ZrO₂, cavitation, shock wave, refinement, deaggregation, nano-particle

1. Introduction

There are many kinds of methods to prepare fine particles, for examples, vacuum evaporation, wet method as a sol-gel, atomizing and pulverization. These methods are classified to two categories. The first group is to prepare initial solid particles from the other phases as gas phase or liquid phase. Particles are prepared through gas phase in an evaporation method and through liquid one in an atomizing. The second is to prepare particles by some treatments, a mechanical one in particular, to raw powders. Crushing or ball-milling are representative of them and are called pulverization. These mechanical methods introduce deformations of particles, lattice defects as vacancies, dislocations, twins, strains and refine crystal grain besides the reduction of particle size. Many interesting phenomena and materials as super-saturated solid solutions, amorphous alloys, nanocrystalline alloys and mechanically induced chemical reactions have been studied with using mechanical milling. This method is available to prepare above-mentioned materials, but it is difficult to utilize only the refinement of particles in mechanical effects and prepare particles without deformations, lattice defects and strains.

It is known that the cavitation damage or the cavitation erosion occurs in a fluid. Propeller and water plane are damaged when they are moving at a high speed in a fluid. These cavitations are usually caused by the shock wave which is generated by the collapse of the cavity in a fluid. The supersonic washing and the dissolving of aggregates is based on this effect. The mechanism of cavitation is composed of four stages, (1) quick decompression of fluid, (2) origination and growth of cavity, (3) contraction and collapse of cavity and (4) rebounding of collapsed cavity. The shock wave is generated at the last stage. It is said that high shock wave, several thousands of atmospheric pressures, will be generated and several thousands of degrees will be increased at atomic level temperature for μ second. Erosion and damage of materials occur with the former, high pressure effect and non-equilibrium chemical reactions are induced with the

use of the latter, high temperature effect.

L. Rayleigh has firstly reported of the high pressure caused by the generation and the collapse of cavity [1]. R.T. Knapp estimated the maximum pressure at over several thousands kg/cm² [2]. W. Guth also calculated the maximum at over 10000 kg/cm² from photographical measurement [3]. Cavitations have been also studied in chemical engineering and called sonochemistry. T.J. Mason discussed about the principles and lots of applications to chemical reactions like organic synthesis, free radical reactions, heterogeneous catalysis and polymer chemistry [4].

Author tried the preparation of nanosize ceramic particles by shock wave, in particular using a nozzle cavitation apparatus [5]. It was shown that the cavitation method was available to reduce the particle size of ceramic powders. In this paper the refinement of TiO₂ and ZrO₂ powders with a cavitation method was studied for,

- (1) to prepare fine particles without deformation, lattice defect and strain
- (2) to prepare single crystalline particles
- (3) to study the polymorphic phase transformation

2. Experimental procedure

2-1. cavitation apparatus

Figure 1 shows the generator in a nozzle cavitation apparatus, in which the shock wave is generated in a fluid. The diameter of an injection hole is 0.12ϕ and the ejection one is 0.15ϕ . The tip of the orifice is made by diamond. The barrel of generator is made by tungsten carbide and its inside diameter is 5ϕ . Samples, the mixture of ceramic powder and water, are injected into a generator under high pressure from a right handside in the figure. Cavities are originated inside the generator when a mixture is quickly decompressed at passing through out the injection orifice, because the diameter changes from 0.12ϕ to 5ϕ . The higher the injection pressure is and the more quickly the pressure is released, the more easily the cavitation is originated. Particles are recovered as a suspension from a left handside in the figure. One cycle of the operation, the drawing and the discharging, is several seconds.

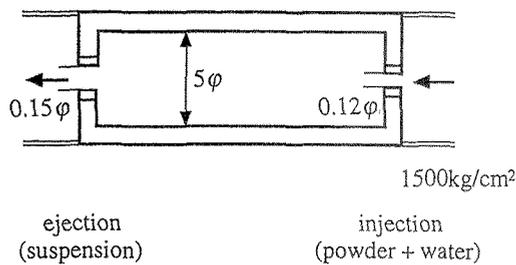


Fig.1 Generator in a nozzle cavitation apparatus.

2-2. experimental procedure

TiO₂ (99.9%, tetragonal, rutile) and ZrO₂ (99.9%, monoclinic, baddeleyite) powders were used for the cavitation. Their particle sizes are under 100μm for TiO₂ and under 40μm for ZrO₂. Powders were introduced to the apparatus after dispersed in a water by a supersonic wave. The injection pressure was 1500kgf/cm². The structures of powders were studied by a X-ray diffraction (XRD, CuKα 40kV, 200mA). Their morphological changes were observed by a field emission scanning electron micrograph (FESEM, 10kV) and by a transmission electron micrograph (TEM, 200kV). Particle size distributions were measured by a laser scattering method.

3. Results and discussions

3-1. TiO₂ oxide (rutile)

Figures 2 and 3 show the change of the particle size distributions of TiO₂ powder by one cycle of cavitation. The distribution was a log-normal one and the median diameter was 19.2μm before cavitation. The diameter decreased to 0.23μm by cavitation. The distribution de-

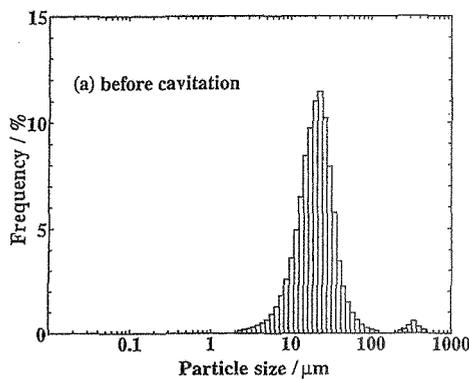


Fig.2 Particle size distribution of TiO₂ before cavitation.

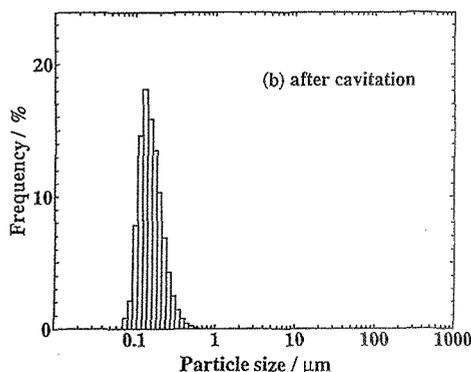


Fig.3 Particle size distribution of TiO₂ after cavitation.

viated from a log-normal one around 0.1μm, which is caused by (1) the limit to refine the particles by cavitation or (2) the limit to measure by a laser scattering method utilized. Figure 4 shows the XRD change of TiO₂ powder, (a) is before cavitation and (b) is after one. TiO₂ powder used is a rutile-type, so the diffraction of $2\theta_{(110)}=27.5$, $2\theta_{(101)}=36.1$, $2\theta_{(200)}=39.2$ and $2\theta_{(111)}=41.2$ are observed before cavitation. These diffractions did not change by cavitation both in their angles and half widths. The polymorphic phases were not obtained while TiO₂ had a monoclinic anatase, a orthorhombic brookite.

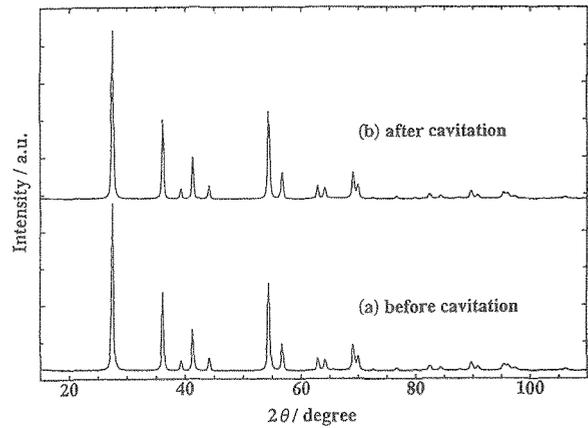


Fig.4 Change of XRD patterns for TiO₂ powder. (a) is before and (b) is after cavitation.

Figure 5 shows the SEM observation for TiO₂ powder after cavitation. The primary particle size was almost uniform and was about under 0.1μm. But these particles were con-

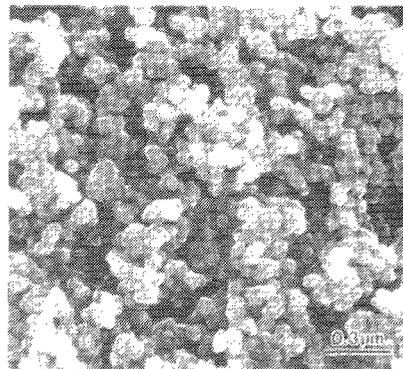


Fig.5 SEM image of TiO₂ powder after cavitation.

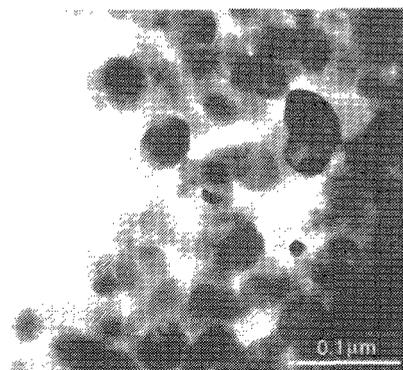
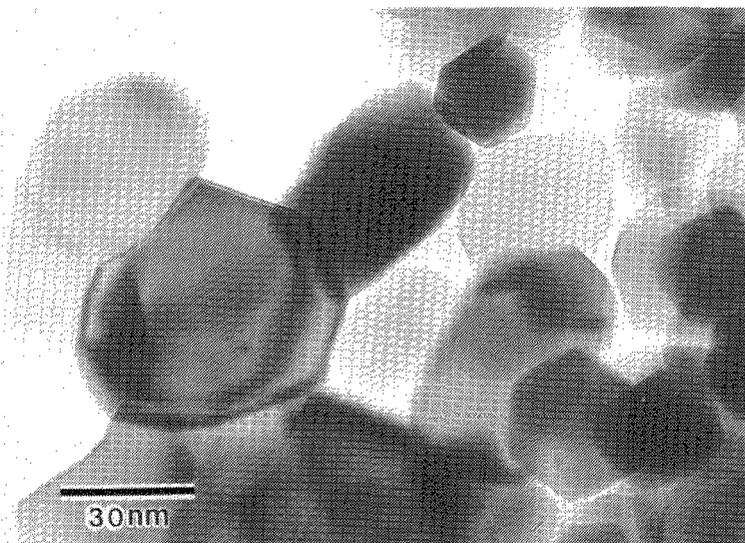


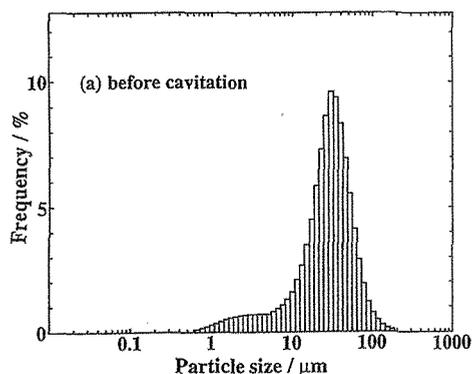
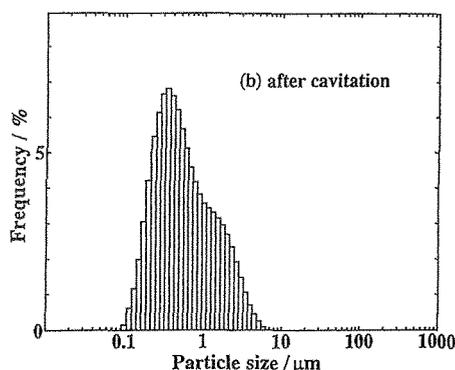
Fig.6 TEM image of TiO₂ powder after cavitation.

Fig.7 HRTEM image of TiO₂ powder fractured by cavitation(1500kg/cm²).

nected with other particles, in which the size distribution spreaded large from 0.1 μ m to 1 μ m by a laser scattering. Fig.6 shows the TEM image for TiO₂ after cavitation. Particles are complex ones, like aggregates, where components are connected with one another. The size of primary particle is about 50nm, which is less than the limit to measure by the laser scattering method utilized. Fig.7 shows the HRTEM image for TiO₂ after cavitation. Particles are connected and the interfaces between components are preferentially fractured by cavitation. These component particles were single crystals from their electron diffractions. Particles were not deformed and had no lattice defects. It is considered that the breakage of TiO₂ powders by cavitation is like a fracture at necks and not at interparticles.

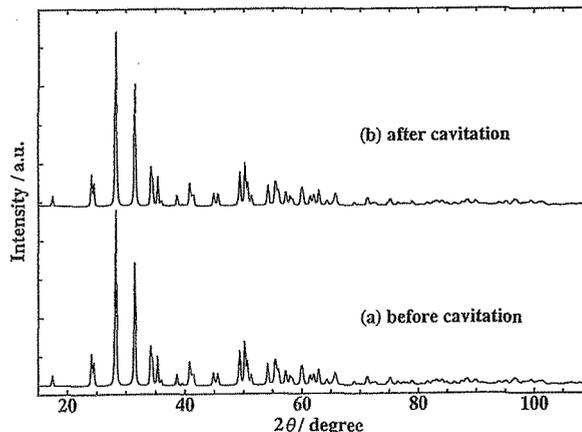
3-2. ZrO₂ oxide (baddeleyite)

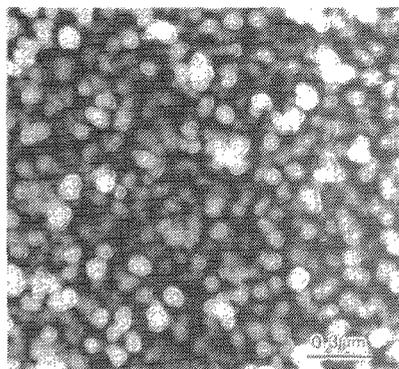
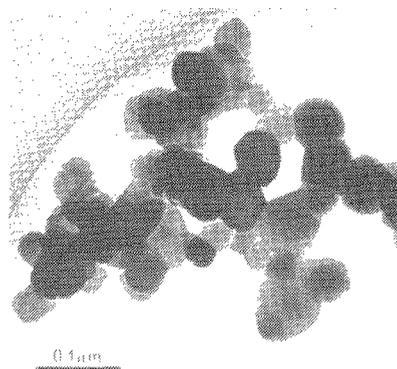
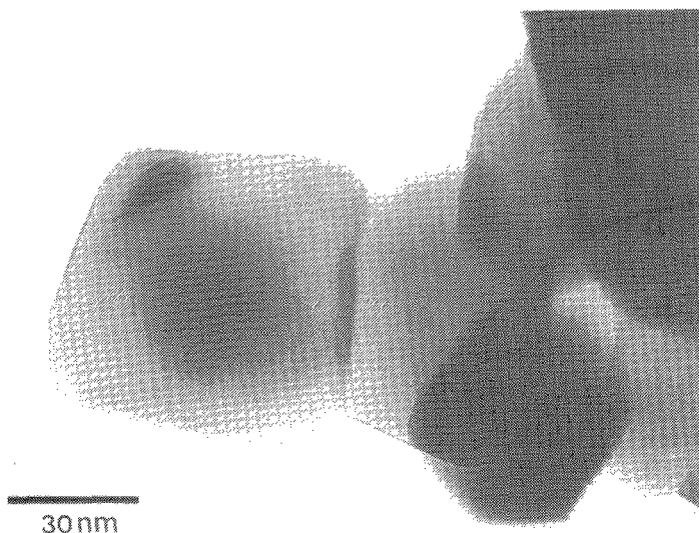
Figures 8 and 9 show the changes of the particle size distribution of ZrO₂ powder by one cycle of cavitation. The median diameter of raw powder was 26.8 μ m but it decreased to 0.46 μ m after cavitation, which was about one fiftieth of the initial value. The size reduction of ZrO₂ powder is a little difficult than TiO₂. The distribution deviated from a log-normal after cavitation, and seemed to be composed of two distributions. This suggests that the refinement of powders is not sufficient. Figure10 shows the XRD change of ZrO₂ powder, (a) is

Fig.8 Particle size distribution of ZrO₂ before cavitation.Fig.9 Particle size distribution of ZrO₂ after cavitation.

before cavitation and (b) is after one. ZrO₂ powder used is monoclinic, so the diffractions of $2\theta_{(100)}=17.5$, $2\theta_{(011)}=24.1$, $2\theta_{(110)}=24.5$ and $2\theta_{(111)}=28.2$ are observed before cavitation. These diffractions did not change in their angles and their half widths by cavitation. The polymorphic transformation did not occur while ZrO₂ has a tetragonal, a cubic structure.

Figure 11 shows the SEM image for ZrO₂ after cavitation. Particles were uniform and were about 0.1 μ m. Large particles, from 0.1 μ m to 10 μ m, measured by the laser scatter-

Fig.10 Change of XRD patterns for ZrO₂ powder. (a) is before and (b) is after cavitation.

Fig.11 SEM image of ZrO₂ powder after cavitation.Fig.12 TEM image of ZrO₂ powder after cavitation.Fig.13 HRTEM image of ZrO₂ powder fractured by cavitation (1500kg/cm²).

ing is caused by the aggregates. Fig.12 shows the TEM image for ZrO₂ powder after cavitation. It is indicated that primary particles are not isolated but are aggregates. The fracturing of ZrO₂ powder by cavitation is not complete to dash into components. The large size distribution is influenced by these aggregates. Fracturing of powders preferentially occurs at the necks and the transgranular fracturing was not observed. Component particles were about 50nm for their sizes and were not deformed by cavitation. Fig.13 shows the HRTEM image for ZrO₂ after cavitation. Lattice defects were not observed in particles, which were single crystals by their electron diffractions. It could be said that the straight planes of component particles were the necks before cavitation fracturing.

It is considered that a cavitation method, in particular a nozzle cavitation here, is available to refine ceramic particles without deformations and lattice defects. The refinement of powders is based on the preferential fracturing at the necks. A lot of applications will be expected, photo-catalytic particles, single magnetic domain ones and superparamagnetic ones for examples. However it is necessary to improve the apparatus and to estimate the pressure of shock wave, the distance between the cavities and particles and the soluted gas content in a water. Moreover it is also necessary to evaluate the notch angle

at the neck and the crystal structure at the interface.

4. Conclusion

The refinement of ceramic particles by a shock wave was studied using a nozzle cavitation. It was possible to prepare several tens nanometer TiO₂ and ZrO₂ particles. It is considered that the fracturing of powders is a disintegration by the preferential fracturing at the necks, different from the pulverization using media like the ball-milling.

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