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The Structural Change in Zinc Oxide in the Process of Mechanical Treatment

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The structural change in zinc oxide by mechanical treatment was studied. In the process of the mechanical treatment of zinc oxide, the crystallite size and the lattice distortion as measured by the X-ray diffraction method, the specific surface area as measured by the BET method, and the density as measured by a pycnometer changed monotonously with the treatment time. Such monotonous changes correspond to a primary structural change in zinc oxide.

Solid materials, when subjected to such mechanical treatments as crushing, grinding, rolling or impact, suffer a change in particle shape and size, and, in some cases, their physical and chemical properties become different from the intrinsic ones of the original crystals.[1] In the process of mechanical treatment, particularly the grinding of powder crystals, such changes as the formation of an oxide-layer or amorphous-layer on the surface of the particles,[2] a reduction in the crystallinity,[3] a structural disordering[4] or a polymorphic transformation[5] have been observed. Accompanying such structural changes, the powder crystal may have a new surface different from the original surface, which should be more active due to the structural distortion.[6] Such a mechanical effect on the solid materials appears to be caused largely by the shearing stress applied; it is different depending on the structural characteristics of the original material as well as on the procedure of the treatment.

In this paper, the structural change of zinc oxide in the process of mechanical treatment will be studied, particularly its crystallinity, crystallite size, particle size, density and specific

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[1] For example, S. R. Rao, *Ind. J. Phys.*, **6**, 24 (1931); S. S. Bhatnager, *Kolloid-Z.*, **78**, 9 (1937); H. Prasad and S. S. Dharmatti, *Ind. J. Phys.*, **11**, 393 (1938); J. W. Axelson and E. L. Piret, *Ind. Eng. Chem.*, **42**, 665 (1950); P. B. Dempster and P. D. Ritchie, *Nature*, **169**, 538 (1952).

[2] S. R. Rao, *Ind. J. Phys.*, **6**, 24 (1931); D. W. Clelland, W. M. Cumming and P. D. Ritchie, *J. Appl. Chem.*, **2**, 31 (1952).

[3] H. Takahashi, *Nendo-Kagaku no Shimpo (Advances in Clay Sci.)*, **4**, 25 (1962).

[4] For example, G. E. Bacon, *Acta Cryst.*, **5**, 392 (1952); H. Takahashi, This Bulletin, **32**, 235, 245, 252, 381 (1959); T. Kubo, M. Kato, M. Mitarai, J. Takahashi and K. Okura, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 318 (1963).

[5] For example, M. A. Bredig, *J. Phys. Chem.*, **46**, 801 (1942); J. H. Burns and M. A. Bredig, *J. Chem. Phys.*, **25**, 1281 (1956); F. Dachille and R. Roy, *Nature*, **186**, 34 (1960); Y. Banshô, S. Suzuki, I. Saitô and T. Sekiguchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 168 (1964).

[6] G. L. Clark and R. Rowan, *J. Am. Chem. Soc.*, **63**, 1302 (1941); T. Kubo, M. Katô, M. Mitarai and K. Uchida, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 403 (1963); H. Akamatu and H. Takahashi, *Nendo Kagaku no Shimpo (Advances in Clay Sci.)*, **5**, 197 (1965).

surface area.

Zinc oxide is a material useful as a pigment, filler, and other things. Furthermore, its physical properties such as photoconduction are well known. Accordingly, it is of interest to establish the correlation between the structure and the physicochemical properties of zinc oxide.

Experimental

The samples of zinc oxide were prepared by the pyrolysis of zinc oxalate (extra-pure-quality) in the air at 400, at 800 and at 1000°C for five hours. X-Ray diffraction analysis showed that these samples had been completely converted into zinc oxide. For the sake of convenience, the samples thus prepared will be referred to ZnO(400), ZnO(800) and ZnO(1000) respectively. The sample was dry-ground by a ball mill at 90 rpm in association with a porcelain pot the inner capacity of which was about 0.9 *l*. For each run, 70 g of the zinc oxide sample was charged in. Specimens were taken out at various intervals of grinding and examined.

X-Ray diffraction diagrams were recorded by a X-ray diffractometer (Geigerflex). As a X-ray radiation source, nickel-filtered copper radiation at 35 kV and 15 mA was used, with a scanning speed of 1/4° per min, a time constant of 4 sec, a divergence slit of 1°, and a receiving slit of 0.2 mm.

Generally, the line broadening of the X-ray diffraction diagram for a powder crystal is affected by two factors. One is the effect of the crystallite size; the line broadening due to this effect (B_s) is expressed by Scherrer's formula:⁷⁾

$$B_s = K\lambda/D\cos\theta, \tag{1}$$

where λ is the wavelength; θ, the diffraction angle; D, the crystallite size, and K, a shape factor. The value of a shape factor is 0.9. The other is the effect of lattice distortion; the line broadening based on this effect (B_d) is expressed by Stokes' formula:⁸⁾

$$B_d = \eta\sin\theta/\cos\theta, \tag{2}$$

where η is the effective lattice distortion.

When neither factor can be neglected, the observed half-value of the breadth (B) can be expressed, as has been empirically proved by Hall,⁹⁾ as follows:

$$B = B_s + B_d, \tag{3}$$

or

$$B\cos\theta = K\lambda/D + \eta\sin\theta. \tag{4}$$

The crystallite size and the lattice distortion were estimated from the plot of $B\cos\theta$ against $\sin\theta$, in association with Eq. (4), for about 10 diffraction lines in the scope of the value for 2θ, from 30 to 130°.

The instrumental broadening was corrected¹⁰⁾ using silicon with a good crystallinity as the internal standard. K_{α_1} and K_{α_2} doublets in the diffraction lines were separated by Brill¹¹⁾ and Rachinger¹²⁾ methods. The crystallinity was estimated from the average value of the integral intensity of the (100), (101) and (002) diffraction lines. In this case, calcium fluoride was used as the internal standard.

The electronmicrographs were taken by a Hitachi HU-11A-type electronmicroscope.

The specific surface area was measured by the BET method, from the nitrogen gas adsorption at the temperature of liquid nitrogen. The specimens was pretreated under a pressure of 10^{-4} mmHg at 150°C for about three hours. This temperature was selected because the structural disorder due to mechanical treatment began to disappear when the specimens were heat-treated at above 200°C.

The densities of the specimens were measured by a pycnometer in butanol after they had been dried at 110°C.

Results and Discussion

X-Ray diffraction diagrams of the zinc oxide at various stages of the mechanical treatment are

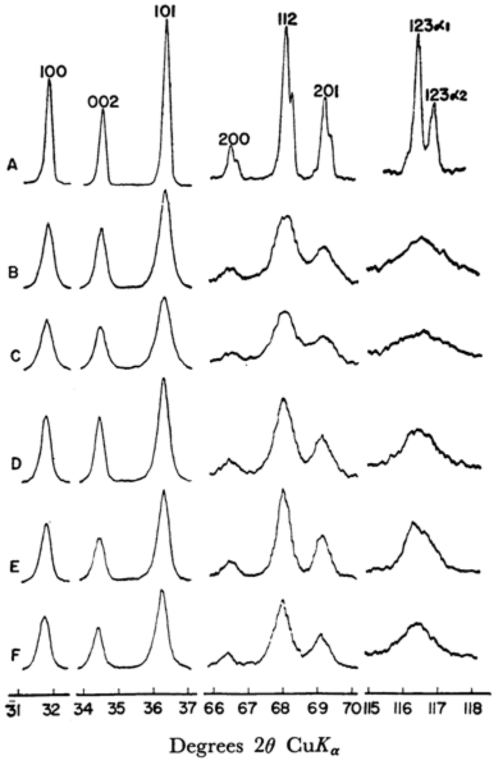

Fig. 1. X-Ray diffractometer traces of mechanically treated and heat-treated zinc oxide.

A. ZnO(1000) original
B. ZnO(1000) ground for 48 hr
C. ZnO(1000) ground for 384 hr
D. C. heat-treated at 600°C for 1 hr
E. ZnO(400) original
F. ZnO(400) ground for 384 hr

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7) P. Scherrer, *Göttingen Nachrichten*, **2**, 98 (1918).

8) A. R. Stokes and A. J. C. Wilson, *Proc. Phys. Soc.*, **56**, 174 (1944).

9) W. H. Hall, *ibid.*, **A62**, 741 (1949).

10) H. R. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," John Wiley & Sons, New York (1954), p. 509.

11) R. Brill, *Z. Krist.*, **68**, 387 (1928).

12) W. A. Rachinger, *J. Sci. Inst.*, **25**, 254 (1948).

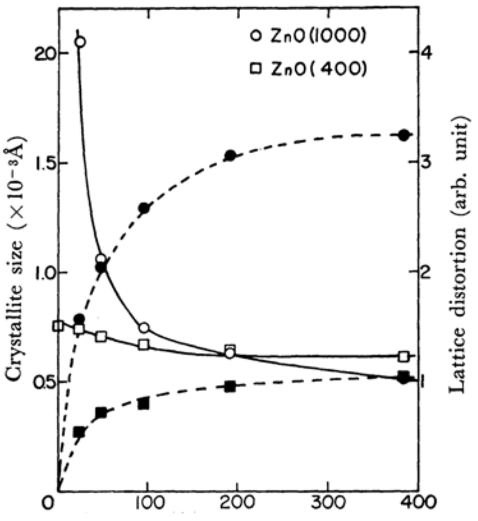

Fig. 2. Changes of the crystallite size and the lattice distortion of zinc oxide with the time of mechanical treatment.
Open symbol : crystallite size
Closed symbol : lattice distortion

given in Fig. 1. It can be seen from this figure that, with the progress of the treatment, the peak intensity is reduced and the line-width is broadened for all diffraction lines, while the intensity of the background increases. This indicates that, as a result of the mechanical treatment, the crystalline part in a particle decreases and the structure becomes disordered. The values of the lattice constants were kept nearly constant throughout the process of mechanical treatment.

The crystallite size and the lattice distortion were obtained by Hall's method. Their changes with respect to the grinding time are shown in Fig. 2. In the case of ZnO(1000), the crystallite size of the original specimen is too large to be measured by X-ray analysis, but it decreases rapidly in the early stage of grinding. In the case of ZnO(400), the crystallite size slowly decreases with grinding. For both samples, however, the crystallite size attains nearly the same value after they have been ground for about 100 hr. On the other hand, the lattice distortion rapidly increases in ZnO(1000), but not so remarkable in ZnO(400). ZnO(800) shows an intermediate behavior, as is to be expected. These results indicate that the zinc oxide which has been prepared at a higher temperature is more sensitive to the mechanical treatment than the one prepared at a low temperature. This is also shown in the color change of the zinc oxide during the process of the mechanical treatment. The original samples are white. The ZnO(1000) becomes yellowish after several hours of grinding and dark yellow after grinding for 100 hr, while ZnO(400) became only slightly yellowish even after a long period of grinding; this probably shows a lesser effect on the structural defect. Such a color change, unlike the thermochromism[13] of zinc oxide, is not reversible to the original white color without heat treatment.

A study was made of the annealing effect to observe the recovery of crystallite size and lattice distortion. The specimens ground for 384 hours were heat-treated for one hour. The specimen of ZnO(1000) rapidly recovered its crystallite size by heat treatment above 400°C. For the ZnO(400) its crystallite growth took place above 300°C. The lattice distrotion in both specimens slowly recovered above 200°C. The ZnO(1000) remained only slightly yellowish even after heat treatment at 1000°C, but the ZnO(400) again became completly white after heat treatment at 800°C for one hour.

The crystallinity obtained from the integral intensity of the X-ray diffraction lines is shown in Fig. 3. After 24 hr of grinding, the crystalline part of ZnO(1000) was 89.0% and that of ZnO(400) was 92.0%. These values were reduced to 53.5% for ZnO(1000) and 61.7% for ZnO(400) after 384 hr of treatment. The density also changed with grinding, as is shown in Table 1. As the grinding progresses, the density gradually decreases. These facts agree with the fact that the crystallinity of zinc oxide is reduced by the mechanical treatment.

The electronmicrographs of ZnO(1000) and ZnO(400) before and after grinding are shown in Fig. 4. The photographs for ZnO(1000) show that the destruction of its particle shape due to

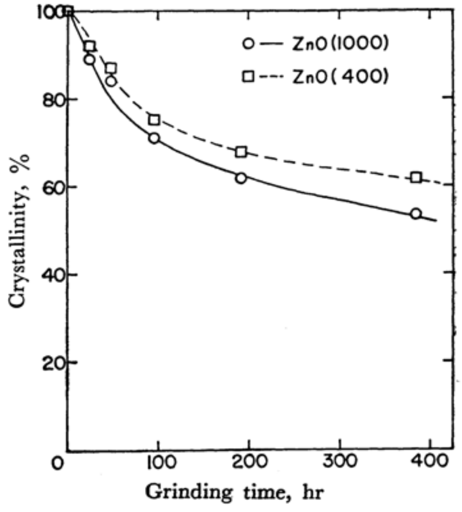

Fig. 3. Change of the crystallinity of zinc oxide with the time of mechanical treatment.

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[13] C. K. Coogan and A. L. G. Rees, *J. Chem. Phys.*, **20**, 1650 (1952).

TABLE 1. CHANGE OF THE DENSITY OF ZINC OXIDE BY THE MECHANICAL TREATMENT

Species		Density g/cm^3
ZnO(1000)	original	5.572
ZnO(1000)	ground for 48 hr	5.447
ZnO(1000)	96	5.320
ZnO(1000)	192	5.267
ZnO(1000)	384	5.275
ZnO(400)	original	5.112
ZnO(400)	ground for 384 hr	4.898

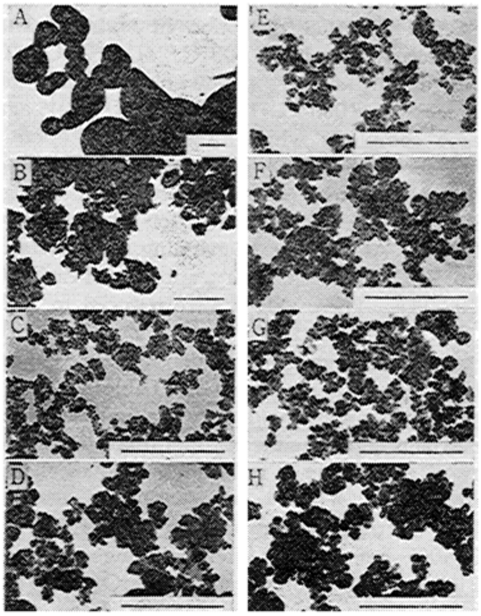

Fig. 4. Electronmicrographs of mechanically treated and heat-treated zinc oxide. The linear dimension on electronmicrograph represents one micron.

A. ZnO(1000) original
B. ZnO(1000) ground for 48 hr
C. ZnO(1000) ground for 384 hr
D. C. heat-treated at 600°C for 1 hr
E. ZnO(400) original
F. ZnO(400) ground for 48 hr
G. ZnO(400) ground for 384 hr
H. G. heat-treated at 600°C for 1 hr

grinding is remarkable and that its structural disorder is large. It is also seen that as the grinding progresses, its primary particles aggregate with each other and the growth of secondary particles takes place. The particle size attains nearly a constant value after 200 hr of grinding; this agrees with the results of the X-ray diffraction analysis.

The specific surface area of the zinc oxide is plotted against the time of grinding in Fig. 5. It is interesting to see that the surface area of ZnO(1000) gradually increases with the treatment, while that of ZnO(400) decreases. No periodical change in the specific surface area such as that observed in the case of NaCl is seen.[14] As the causes of the change in the specific surface area which takes place in the process of grinding, two factors are considerable. One is associated with changes in the crystallite or particle size, the shape of particles, and the growth of cracks, that is, with the primary structural changes. The other factor is related to the formation of secondary particles which grow due to the aggregation or agglomeration of primary particles.

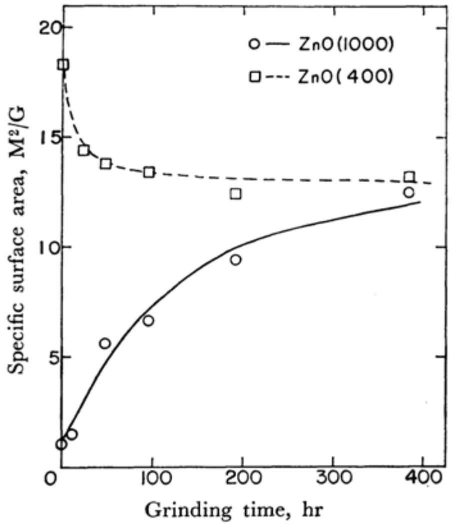

Fig. 5. Change of the BET specific surface area of zinc oxide with the time of mechanical treatment.

In the case of ZnO(400), as has been mentioned above, the grinding is not very effective for the reduction in the crystallite size or an increase in the lattice distortion. Thus, the primary structural changes will not greatly contribute to an increase in the specific surface area. On the other hand, a growth of the secondary particles is observed, as is shown in the electronmicrographs; this could compensate for the primary structural effects and results even in the decrease in the specific surface area. A similar situation has been found for kaolinite and quartz.[15,16] In the case of ZnO (1000), compared with that of ZnO(400), a remarkable decrease in the crystallite size and a remarkable increase in the lattice distortion due to grinding have been observed. Thus, in its ground state, particles should have many diverse structural distortions as well as new surfaces,

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[14] G. Naeser, W. Scholz and A. Fiedler, *Kolloid-Z.*, **188**, 147 (1963).

[15] S. J. Gregg, K. J. Hill and T. W. Parker, *J. Appl. Chem.*, **4**, 631 (1954); S. J. Gregg, T. W. Parker and M. J. Stephens, *ibid.*, **4**, 666 (1954).

[16] V. F. Kiselev, K. G. Krasilnikov and G. S. Khodakov, *Doklady Akad. Nauk S. S. S. R.*, **130**, 1273 (1960).

these will contribute to an increase in the specific surface area much more than the opposed effect of the formation of secondary particles. The specific surface area approaches a constant value, not showing any maximum point, as has been discovered by Gregg for graphite and Kaolinite.(17)

The above results show that the changes measured by an X-ray diffraction method, electronmicroscopy, BET specific surface area and density correspond to the primary structural change in zinc oxide. In the process of the mechanical treatment of zinc oxide, the following effects are observable:

1) a diversification of the crystallinity of the particles;
2) a structural disordering on the surface and in the interior;
3) a color change, and
4) an aggregation or agglomeration of particles.

These primary structural changes show a gradual increase, a gradual decrease, or a change in linearity with respect to the treatment time. Such changes depend upon the nature of the materials before treatment, that is, on the conditions of the preparation; the interior and surface structures, such as the rigidity, shape, size and adhesive property of the particles, are closely related. Essentially, it is considered that the viscosity or viscoelasticity of the zinc oxide itself may affect the susceptivity to treatment.

Summary

The structural characteristics of zinc oxide, with mechanical energy added, change in the following ways. With the progress of treatment, the crystallite size decreases and the lattice disorder increases. The crystalline part decreases and the amorphous part appears. These changes depend upon the preparing temperature of the zinc oxide; they are more remarkable with specimens prepared at a higher temperature. The changes in the particle size and structure observed by electronmicroscopy correspond with the above observations. The BET specific surface area also changes. The change includes a gradual reduction or a gradual increase with the progress of treatment, according to the method used to prepare the original material.

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17) S. J. Gregg, *Kolloid-Z.*, **169**, 5 (1960).