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THE EFFECT OF GRINDING ON POROSITY AND MECHANOCHEMICAL TRANSFORMATIONS IN AL_2O_3 POWDERS

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ABSTRACT

The thermal transformation of γ-Al_2O_3 to α-Al_2O_3 proceeds via intermediate forms κ and Θ, the transformation temperature exceeding 800°C. The mechanochemical transformation induced by grinding in a centrifugal-ball-mill at room temperature proceeds directly from Γ to α, when combined mechanochemical and thermal transformation is carried out namely: pregrinding followed by heating, the transformation also proceeds directly and the transformation temperature is lowered. It is suggested that the difference between the thermal and mechanochemical transformation is connected to the the structure of γ-Al_2O_3 which has the lowest cation ordering of all the spinel-like Al_2O_3 forms.

During grinding the total porosity decreased about 15%. This phenomenon is possibly connected with pores blocking by plastic deformation and welding.

INTRODUCTION

Alumina (Al_2O_3) exists in several crystallographic forms - polymorphs designated by Greek letters. The different forms are obtained one from another by thermal treatment which leads to irreversible polymorphic chain transformation, starting from γ-Al_2O_3 and ending with α-Al_2O_3. Except for α-Alumina all the other forms have spinel structure, oxygen ions are arranged in a framework of cubic close-packed structure (C.C.P.) while Al ions

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occupy some octahedral or tetrahedral position. The general formula is $Al^{[4]}[Al_{5/3} \ v_{1/3}]^{[6]}O_4$ where v stands for vacancy, [4] and [6] are cation coordinating numbers.

The spinel-like aluminas differ from each other in the degree of cation ordering in their occupation sites, being less ordered in the lower temperature forms γ, χ η and more ordered in higher temperature forms such as κ and Θ (1, 2,). α-Al_2O_3 has a rhombohedral structure, oxygen ions are arranged in hexagonal close packing (H.C.P.), with all cations in octahedral sites. This form is the final product of the thermal transformations.

"Mechanochemical process" is a general term used to define chemical changes which occur when materials are subjected to the action of unisotropic mechanical forces. Thesises changes occur without heating, or heating at lower temperatures which may be predicted from phase diagrams. For instance, a regime of unisotropic forces exists when particles are comminuted by grinding, and therefore an intensive grinding may cause mechanochemical process. Comprehensive reviews on the subject have been given by Lin et al (3,4).

In this work the effect of grinding on the mechanochemical transformation between alumina forms, was studied.

EXPERIMENTAL

Material: Merck 1077 alumina was used in all grinding experiments. It was identified as γ-Al_2O_3 by comparison of its X.R.D. pattern to those shown by Burleson (5).

Grinding: 10 grams of powder were ground in a centrifugal - ball - mill at 400 rpm. Unless otherwise stated seven tungsten - carbide (WC) balls, Ø=20mm, were used. The grinding time lasted from 15 to 105 min.

Instrumentation: X-ray powder diffractograms were taken with a Philips PW 1050/25 unit using CuKα radiation. The samples were scanned at 1° 2Θ/min for identification purposes and 0.25° 2Θ/min for determination of peak width. S E M pictures were taken with Joel T-200 model. Porosity was measured by an Amico Mercury Porosimeter which works up to a pressure of 60000 Psi. This pressure enables measurement of pore diameters which exceed 30 Å.

RESULTS AND DISCUSSION

Physical and morphological changes:

two distinct populations of pores exist in the original material, fig. 1, one with pores whose diameter exceeds 10μ, the other with less than 0.02μ diameter. These populations respectively hold about 60% and 30% of pore volume. Only about 10% of the total volume is contributed by pores in the range 0.02 - 10μ. This distribution is a result of the particle shape, fig. 2.

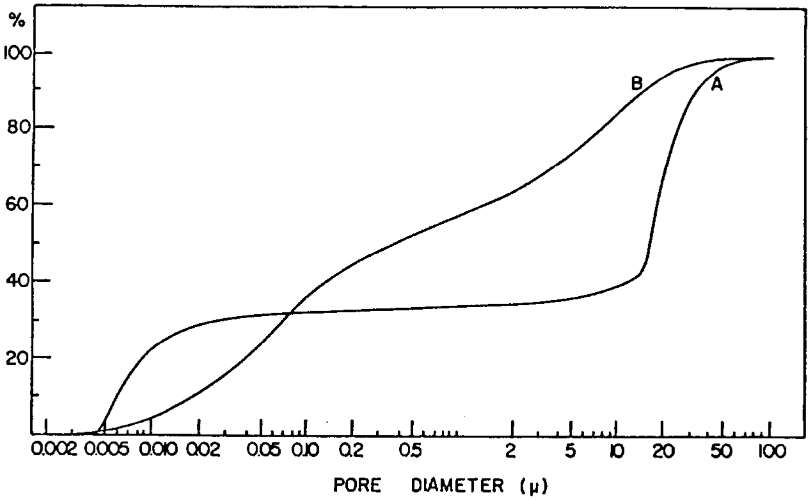

Fig. 1: Pore size alumina powder cummulative curve.
A - Initial material, total pore volume 1.12 Cm^3
B - After 90 min grinding, total pore volume 0.94 Cm^3

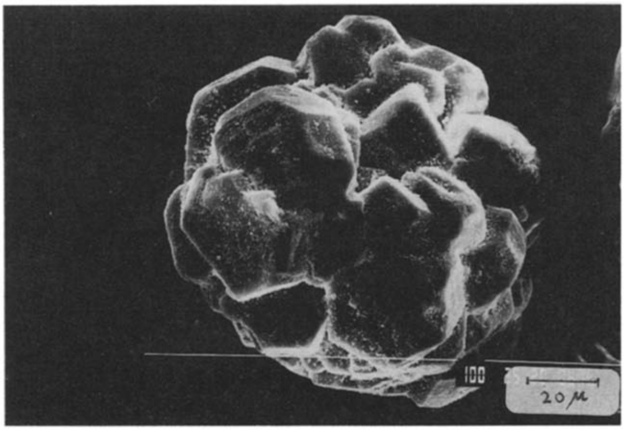

Fig. 2: Aggregate of unground gamma alumina

These particles are spherical aggregates of about 100μ diameter. They are built from polyhedron-like bodies, about 20μ size, which adhere to one another. The large pores are those which exist between the aggregates or the polyhedron bodies, the small pores are those within the bodies.

The grinding cause a breakdown of the polyhedron bodies to small spheres with average diameter less than 1μ - fig. 3.

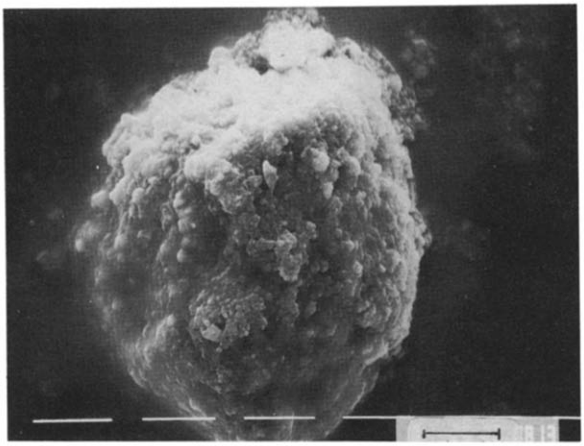

Fig. 3: Aggregate of ground alumina, grinding time 105 min.

These spheres are still adhered to one another and as a result there is only a slight diminution in the aggregate diameter, the total pore volume being reduced from 1.12 to 0.94 cm^3/g.

However, the distribution of pore size is remarkably changed, fig.1. The volume fraction in the range above 10μ and below 0.02μ decreased respectively from 60% to 15% and from 30% to 10% or less, while the intermediate range 0,02-10μ is increased from about 10% to 70-80%. As a result, a more uniform distribution is obtained. This means that grinding does not necessarily result in increasing the total porosity or even the fraction of small size pores.

The new distribution is probably a result of two opposite processes: propagation of cracks and fracturing which cause formation of new pores from one side, plastic deformation and welding which cause pore blocking from the other side. The occurence of the second process requires a non-brittle character which is unexpected in the case of alumina. It should be mentioned that definition of a material as being brittle or non brittle is not unequivocal. In some circumstances brittle material may show plastic character, while brittle fracture may occur in material which is considered to have plastic behavior. Actually brittle material tend to show plastic behavior when their particle diameter falls below 1μ. The phenomenon of plastic deformation and blocking of small pores was also detected in ground $CaCO_3$ (7).

Mechanochemical transformation:

X-ray examination of the grinding products, fig 4, shows that the transformation proceeds directly from γ to α alumina with no other forms as intermediates. The same results were obtained when the WC balls were replaced by steel balls, but the transformation rate decreased considerably. For example, it can be seen from fig. 4 that less α alumina was obtained by grinding 2 hours with steel balls than in 15 minutes with WC balls. In the latter case some, alumina could still be detected after 105 minutes, but the grinding was stopped in order to avoid accumulation of WC impurities in the powder.

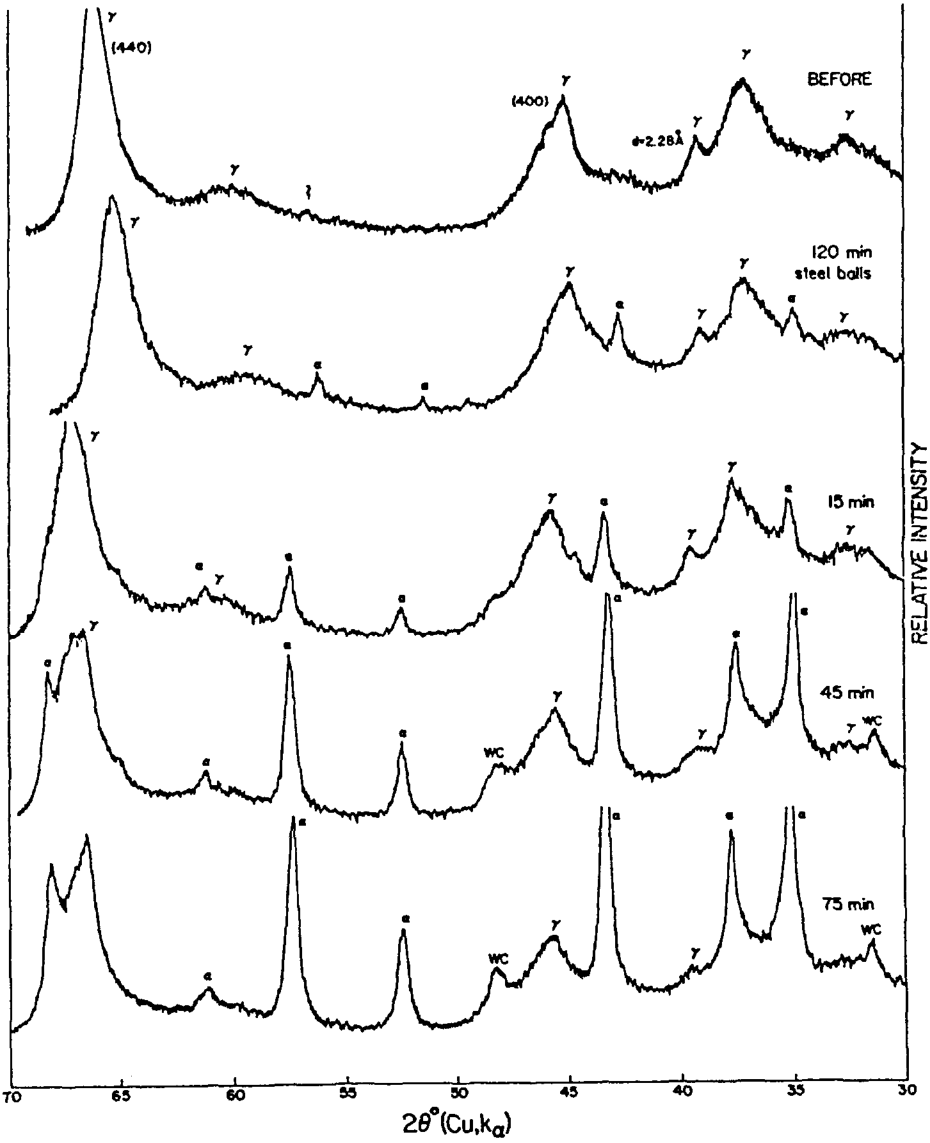

Fig 4: X.R.D. patterns of γ Al_2O_3 grinding products powder.

The degree of microstrains and crystallite size of the mechanochemical formed α-Al_2O_3, in direction perpendicular to (012) planes were calculated by X-ray line broadening method. Average values of about 0.3% and 200 Å were found for microstrain and crystallite size respectively, Table 1. The existence of 0.3% of microstrains gives some support to the idea of plasticity phenomena in alumina. Still this value is lower than the average of 0.6% found in calcite ground by steel balls (6). It seems that the structure of closely packed oxygen prevents accumulation of strain energy, which is released by fracture mechanism. The structure of calcite enables higher displacement of atoms from their original position and therefore higher strain energy can be accumulated. Indeed, the average crystallite size of the ground calcite was found to be somewhat higher, being 320 Å. It should be mentioned that in ground calcite some of the strain energy is also released by transformation to its polymorph aragonite.

The effect of pregrinding on thermal transformation was studied by grinding for 30 min followed by heating for 2 hours at various temperatures, and by X.R.D. examination, table 2.

For unground samples the transformation proceeds in the expected path, namely from γ to α via intermediate forms. The transformation temperature exceeds 800°C. Some difficulties arose in the study of preground samples due to formation of some mechanochemical alpha alumina at the grinding stage, however, the X.R.D. examinations led to two conclusions: (a) - the pregrinding caused the thermal transformation to occur in the same way as purely mechanochemical, namely directly from γ to α form; (b) - the transformation temperature is somewhat lowered. This phenomenon resembles that of the Fe_2O_3 system in which pregrinding (8) or preliminary pressing (9) of γ-Fe_2O_3 results in lowering of its transformation temperature to α-Fe_2O_3.

The unique structure of γ-Al_2O_3 is the main factor for the difference between thermal and mechanochemical transformation.

Table 1: Crystallite size and microstrains in alpha alumina obtained from gamma alumina by grinding.

Grinding time minutes	microstrains ε% (012)	crystallite size Å (012)
45	0.24	197
60	0.17	194
75	0.43	213
90	0.10	199
105	0.46	210

Table 2: Relative diffraction-peak intensities in aluminas obtained from gamma alumina after 2 hrs heating.

α	Θ	κ	γ	Heating Temp. °C	Grinding time(min.)
			++++	800	
++	+++	+++	+++	1000	0
+++	+++	+++	+++	1100	0
++++	+	+		1200	0
+++	+++	+++	+	1200(*)	0
++			++++	600	30
+++			+++	800	30

+ Very weak; ++ Weak-medium;
+++ Medium-strong; ++++ very strong;
(*) Heating for 17 minutes only.

Of all the spinel-like aluminas this form has the lowest ordering of cations at their occupation sites in the lattice. The γ form is therefore relatively more stable than other spinel-like aluminas in grinding process which acts against ordering. In addition, the vacancies permit some strain in the structure without loss of the crystallographic identity.

At a later stage, under conditions of high straining and shear forces in the mill, the cubic close-packed oxygen framework of the gamma form can easily rearrange itself into that of the hexagonal-close-packed framework of alpha form. This process is faster than that needed for the rearrangement of all cations in ordered position of other spinel-like aluminas.

In this work no estimation was carried out about the quantity of the strain energy. Using D.S.C. technique, Imai & Senna (10) estimated that in ground γ-Fe_2O_3 it is twice that of the enthalpy of the transformation to α-Fe_2O_3 and thus the transformation temperature is lowered. It is believed that similar phenomena occur in the Al_2O_3 system.

CONCLUSION

The difference between grinding induced mechanochemical and thermal transformation of γ to α Al_2O_3 is connected mainly with the unique structure of the former. The total porosity is reduced possibly due to pore blocking by plastic deformations and welding.

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