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Reaction Process of Mechanochemically Assisted Synthesis of Barium Titanate Powders

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Reaction mechanism for the synthesis of barium titanate from TiO_2 and $Ba(OH)_2 \cdot 8H_2O$ under grinding has been estimated by a conventional fitting method to kinetic functions. The formation of $BaTiO_3$ progressed through a boundary-reaction controlled interface contracting kinetics, while amorphization of TiO_2, which takes place previously to the formation of titanate, indicates varied reaction indices depending on the grinding stress and the progress in reactions. At low grinding stresses, the stress-induced amorphization at the early stage grinding is successively replaced by the reaction-controlled one. The later process suggests the amorphization promoted by kneading the constituents in micro-agglomerates functioning as micro-reaction fields. Over a threshold grinding stress, the reaction index shows a contraction kinetics assuming a gradually decreasing crystallinity from the crystalline core to the amorphous surface inside TiO_2 particles. These observations agree with the previously proposed mechanism, where the surface acid generated on the hydrated TiO_2 particles with a certain progress in amorphization reacts with $Ba(OH)_2 \cdot H_2O$ formed by a partial dehydration of $Ba(OH)_2 \cdot 8H_2O$ in the agglomerates.

key words: barium titanate, planetary mill, mechanochemistry, reaction mechanism

1. INTRODUCTION

Recently available high-energy grinding equipments enable the application of mechanochemical reactions to syntheses of ceramic powders[1-7]. The authors have demonstrated its application to the preparation of titanate ($MTiO_3$, M: Ba, Sr, Ca)[3-5] and hexaferrite ($BaFe_{12}O_{19}$)[6, 7] powders. In the previous work using a planetary ball mill, the high shear stress and high-frequency swaying motion of grinding media induce (1) size reduction and surface modification of primary particles, (2) agglomeration by inverse grinding due to the increased polarity of the modified surface, (3) size reduction of the agglomerates, and (4) complete mixing of the constituents inside the agglomerates. Controlled inverse grinding generates agglomerates functioning as "reaction fields" with controlled size and morphology to lead reduced calcination temperatures, the controlled morphology of synthesized powders, and the resulting microstructural control of sintered materials.[4, 6, 7].

The fine grinding of the starting powders and the suitable surface modification induce chemical reactions during grinding. Planetary milling of TiO_2 and alkaline-earth hydroxides ($M(OH)_2 \cdot 8H_2O$, M: Ba, Sr) in acetone is one of the examples for this "mechanochemical reactions", where sinterable $BaTiO_3$ powders can be synthesized directly by the grinding operation. Acid-base reactions between acid sites on TiO_2 and $Ba(OH)_2 \cdot H_2O$ inside their co-agglomerates ($<1\ \mu m$) is proposed for the reaction process[4, 6]. The co-agglomerates functioning as "micro-reaction fields" are provided by the increased surface polarity of TiO_2 hydrated by the dissociated water from $Ba(OH)_2 \cdot 8H_2O$ in the less hydrophilic organic dispersant. The hydrated water is converted into Brϕnstead acid site under the kneading process of the co-agglomerates. However, few studies on the reaction mechanisms and kinetics have been conducted. In the present work, reaction mechanism and kinetics of the mechanochemical synthesis of $BaTiO_3$ has been studied by a conventional fitting method to kinetic functions.

2. EXPERIMENTAL

The starting TiO_2 powder was prepared by a heat-treatment of $TiO(OH)_2$ derived from $Ti(C_3H_7O)_4$ at 450°C. This powder had anatase phase with the specific surface area, $91.9\ m^2 \cdot g^{-1}$. Reagent-grade $Ba(OH)_2 \cdot 8H_2O$ (Wako Pure Chem.) was mortar-ground to 100 mesh in a glove chamber filled with a dry N_2 gas. A stoichiometric mixture of these materials (10g) was encapsulated into a silicon nitride vessel ($480\ cm^3$) with acetone and grinding media (ϕ3 silicon nitride balls) for grinding operation using a planetary ball mill (Kurimoto-Tekko-Sho). The grinding conditions are summarized in Table I. The ground powders were filtered through a 0.2 μm Teflon membrane, washed by acetone, and dried under vacuum at 150°C.

The reaction products were identified by X-ray diffractometry (XRD) with CuKα radiation. The phase contents were determined from the integrated peak intensities of the overlapped (101) and (110) reflections for $BaTiO_3$ and the (101) reflection for TiO_2 as the ratio to the completely crystallized $BaTiO_3$ powder and anatase in the starting mixture. The reaction mechanism was estimated upon the indices in the kinetic plots proposed by Hancock and Sharp[8]. The specific surface area (*SSA*) was determined by a N_2 adsorption BET method. The morphology of the ground powders was observed by SEM.

Table I Grinding conditions of the mixtures

revolution frequency / Hz	acceleration / $m \cdot s^{-2}$ max.	min.
3.00	118.0	9.9
4.00	209.7	17.7
5.00	327.7	27.6

Grinding time: (10), 30, 60, 180, 360 min
Fractional filling of the grinding media: 0.40
Fractional filling of the starting slurry
to the vacancy of media: 1.00

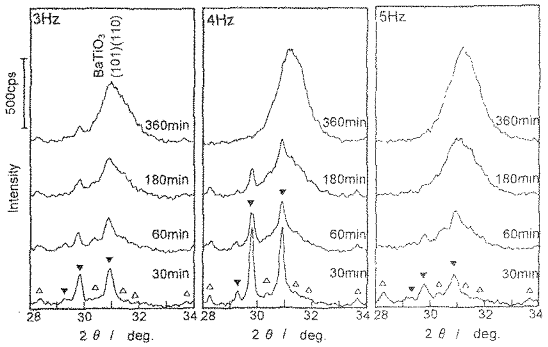

Fig. 1 XRD profiles of the ground products.
△: $Ba(OH)_2 \cdot 3H_2O$, ▼: $Ba(OH)_2 \cdot H_2O$

3. RESULTS AND DISCUSSION

3.1 Formation of $BaTiO_3$ and amorphization of TiO_2 under grinding

Figure 1 shows the X-ray diffraction profiles of the ground products. The starting $Ba(OH)_2 \cdot 8H_2O$ was immediately dehydrated to $Ba(OH)_2 \cdot 3H_2O$ and $Ba(OH)_2 \cdot H_2O$. As described previously[4, 6], the dissolved water hydrates the TiO_2 particles to induce inverse grinding providing agglomerates. The *SSA* of the ground products in Table II was reduced with the progress in grinding. However, the size of agglomerates observed in Fig. 2 was quite small; 0.2-0.8 μm after grinding for 360 min at 4 Hz. The fibrous particles observed in Fig. 2 were $Ba(OH)_2 \cdot H_2O$ formed by recrystallization during vacuum drying at 150°C. This high drying temperature was adopted so as to identify the intermediates by XRD. The ground powders dried at 70°C did not show the fibrous particles. Large rod-like $Ba(OH)_2 \cdot H_2O$ particles observed at the early stage grinding (30 and 60 min) changed to smaller ones after grinding for 180 min due to the reduced amount of $Ba(OH)_2 \cdot H_2O$. After grinding for 360 min, no fibrous particles were observed and almost single phase $BaTiO_3$ was synthesized at 4 Hz. Rod-like $Ba(OH)_2 \cdot H_2O$ particles remained after grinding for 360 min at 3Hz but disappeared for 180 min at 5Hz.

Figure 3 shows the phase content obtained from the XRD intensities as a function of grinding time. The formation of $BaTiO_3$ and the amorphization of TiO_2 progressed after induction periods due to the deflocculation of the starting TiO_2 aggregated during the calcination. The higher revolution frequency resulted in the shorter induction period. The formation of $BaTiO_3$ was promoted by the increase in revolution frequency, that is, the increased grinding stress. The 56.5 % conversion of TiO_2 into $BaTiO_3$ at 3Hz (360 min) increased to 83.3 % at 4Hz, and 96.5 % at 5Hz, where the synthesizing reaction had almost completed.

In contrast to the uniquely progressing $BaTiO_3$ formation, the amorphization of anatase-TiO_2 showed two step processes of the rapid reduction of crystalline TiO_2 at the early stage within 30-60 min and the following gradual amorphization. The transition grinding time between these two processes became shorter at the higher revolution frequency. At the lowest grinding stress examined (3Hz), the amorphization once terminated at 180 min and then progressed gradually at 360 min. The formation process of $BaTiO_3$ and the amorphization progressed congruously at the later stage of grinding at 3Hz.

Table II Specific surface area ($m^2 \cdot g^{-1}$) of ground products

revolution frequency / Hz	grinding time / min 30	60	180	360
3.00			16.3	13.8
4.00	19.4	18.8	16.1	11.4
5.00			12.5	11.5

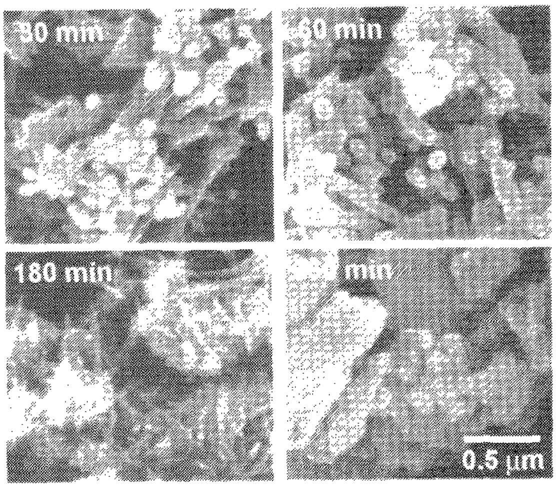

Fig. 2 Morphology of ground powders at 4Hz.

The amorphization of TiO_2 was promoted by the coexistence of barium hydroxide as presented in Fig. 3, where the amorphization without $Ba(OH)_2 \cdot 8H_2O$ (line **a** at 4Hz) was not attained to those for the mixing-grinding process below 180 min. The amorphization of TiO_2 without $Ba(OH)_2 \cdot 8H_2O$ takes place through the kneading process of the agglomerates consisting of nano-crystalline TiO_2 adhered by the titania-sol ($TiO_2 \cdot xH_2O$) after a certain amorphization accompanied by

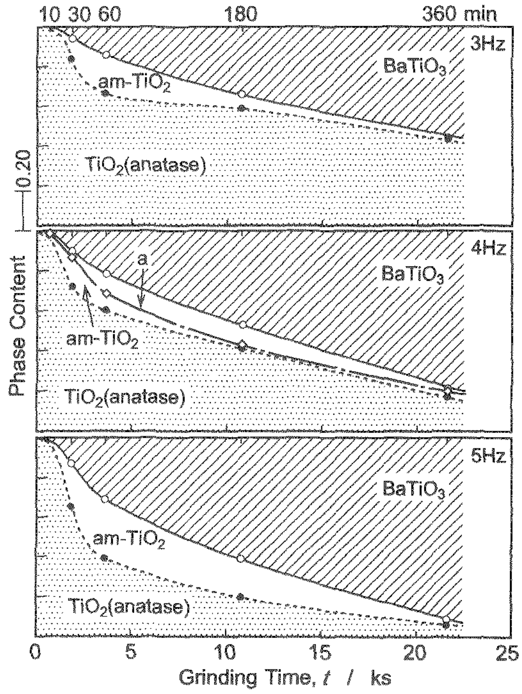

Fig. 3 Phase content of ground products.

Line **a** (◇) shows the amorphization of TiO_2 without coexistence of $Ba(OH)_2 \cdot 8H_2O$.

Table III Reaction mechanism and suggested index, *m* [8)]

Boundary-reaction-controlled contracting mechanism	
three dimensional	1.07
two dimensional	1.11
Nucleation growth mechanism	
three dimensional	3.00
two dimensional	2.00
Diffusion-controlled contracting mechanism	
three dimensional	0.54
two dimensional	0.57

palverization[9, 10)]. The termination and the congruent amorphization observed at 3Hz strongly indicated the immediate consumption of acidic titania-sol by the formation reaction of $BaTiO_3$ at the later stage of grinding. This consumption of titania-sol contributing agglomeration suggests the formation kinetics of $BaTiO_3$ controlled by the amorphization rate and a threshold grinding stress to form excess titania-sol (and amorphous TiO_2) for the $BaTiO_3$ formation *via* the acid-base kinetics.

3.2 Formation kinetics of $BaTiO_3$

The formation mechanism of $BaTiO_3$ was estimated from the reaction index, *m*, obtained by fitting the concentration data into the following function[8)]:

$$\ln[-\ln(1-\alpha)] = m\cdot\ln t_c \qquad (1)$$

where α was the $BaTiO_3$ content and t_c was the grinding time after the correction on the time required to the deflocculation. The gradient, *m*, in Eq. (1) showed the reaction index suggesting the reaction mechanisms listed in Table III.

The obtained $\ln[-\ln(1-\alpha)]$ *versus* $\ln t_c$ plots, Hankock-Sharp plots, is shown in Fig. 4. The boundary-reaction-controlled contracting mechanism was estimated from the gradient 1.05-1.07 for the plots at 4Hz and 5Hz. This mechanism agreed with "unreacted core model" for gas-solid and liquid-solid reactions. The swift removal of the synthesized $BaTiO_3$ from the contact zone of the reactants could be easily assumed for the reactions under grinding. This should provide the reaction according to unreacted core model.

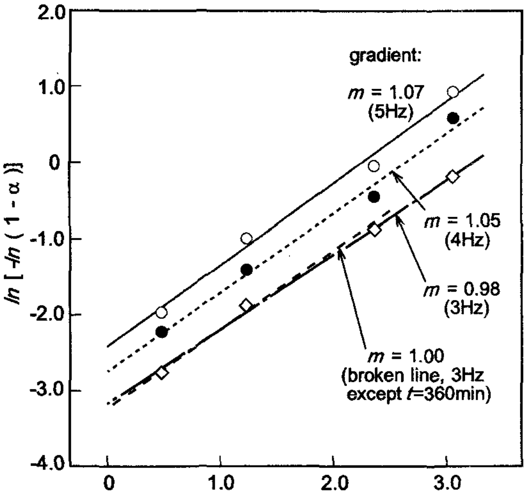

Fig. 4 Hankock-Sharp plots to estimate the formation mechanism of $BaTiO_3$.

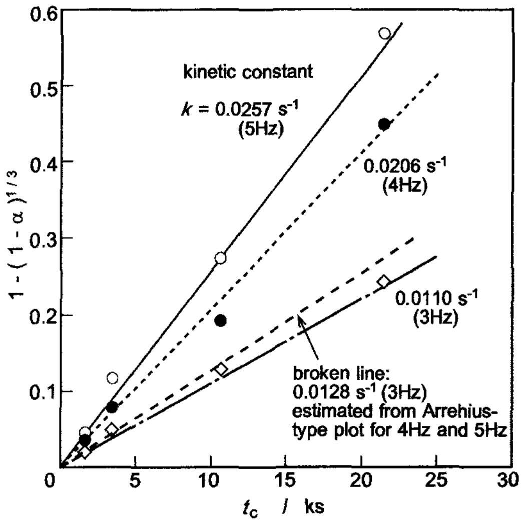

Fig. 5 Fitting of the concentration of $BaTiO_3$ to kinetics for unreacted core model.

However, the gradient, 0.98, for the reaction at 3Hz meant the deviation from the unreacted core model. This deviation should be caused by the transition of the reaction mechanism from the boundary-reaction-controlled process to amorphization-rate-controlled process, because the formation of $BaTiO_3$ progressed congruously with the amorphization of TiO_2 at the later grinding stage (>180min) and the gradient for reaction at the early grinding stage (<180min) increased to close 1.07.

The kinetic constant, *k*, was obtained according to Eq. (2) for the unreacted core model.

$$1-(1-\alpha)^{1/3} = k\cdot t_c \qquad (2)$$

The kinetic plots shown in Fig. 5 indicated almost linear relations for 4 and 5Hz. However, the deviation for 3Hz suggested a threshold grinding stress for the boundary-reaction-controlled process. To certify the threshold grinding stress, the left term in Eq. (2) was plotted against the number of swaying motion, n_c, that was the product of rotation frequency and grinding time. As shown in Fig. 6, the relation between $1-(1-\alpha)^{1/3}$ and n_c indicated one linear relation for 4Hz and

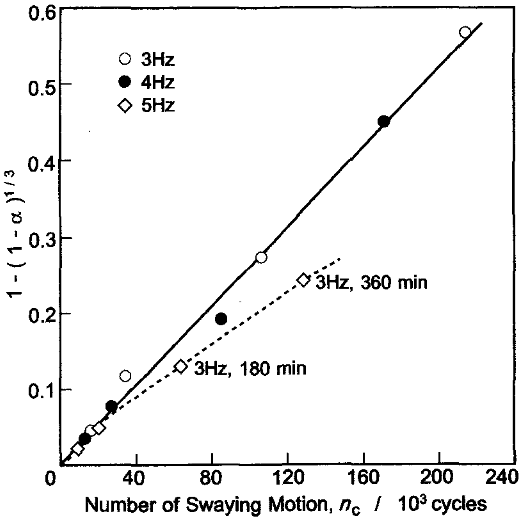

Fig. 6 Kinetic plots for the formation of $BaTiO_3$ against number of swaying motion.

5Hz and for the early stage grinding at 3Hz. This relation, irrespective of the grinding stress, meant the quite small threshold stress for the acid-base reactions of the hydrated TiO_2 with barium hydroxide when enough (excess) amounts of acidic site on TiO_2 could be provided. However, at 3Hz, the plots negatively deviated from the linear relation at the later grinding stage for the congruously progressing amorphization and formation reaction of $BaTiO_3$ at 180 and 360 min. It was considered that a threshold grinding stress between 3 and 4Hz was required to satisfy the excess concentration of the acidic sites beyond the consumption rate of them by the formation reaction of $BaTiO_3$. The agglomeration providing "reaction field" for the contracting mechanism would also be degraded by the reduced concentration of the acidic sites having high polarity.

3.3 Amorphization kinetics of TiO_2

The amorphization mechanism and kinetics influencing the formation reaction of $BaTiO_3$ was estimated from the gradient in Eq. (1) using the content of remained anatase-TiO_2, β, instead of $1 - \alpha$. The obtained fitting plots are presented in Fig. 7. The gradient for the mixing-grinding process at 5 Hz agreed with the index supposed for diffusion-controlled contracting reaction mechanism. It is difficult to assume the diffusion-induced amorphization, but this kinetics can be recognized by assuming the gradient of crystallinity from the crystalline core to amorphous surface inside the TiO_2 particles. Although the error function on diffusion processes can not be applied to this crystallinity-gradient theoretically, it would provide an approximately linear relation within the accuracy in Fig. 7.

The plot for the amorphization of TiO_2 without coexistence of $Ba(OH)_2 \cdot 8H_2O$ also indicated a linear relation. But, the gradient, 0.845, did not agree with the reaction indices listed in Table III as well as those for the other possible mechanisms; ordered reactions and branching reactions. The intermediate value of the gradient between the indices suggesting the reaction-controlled and "diffusion-controlled" mechanisms would indicate one of the possibilities in the combination of concurrently progressing amorphization and acid-base reaction with the gradual change in rate-determining process, gradual transition of the amorphization mechanism, or the gradual change in the crystallinity profile inside the particles.

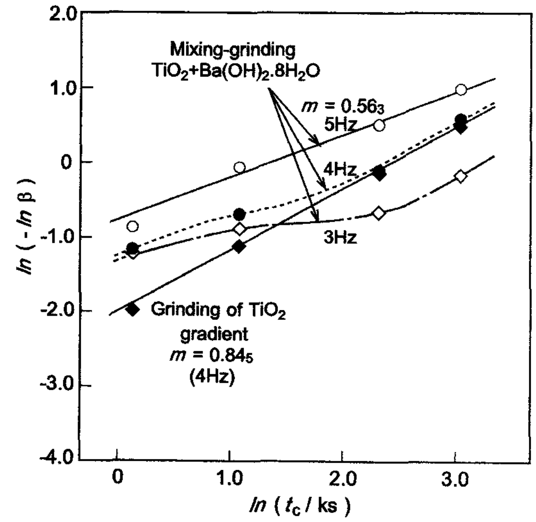

Fig. 7 Hancock-Sharp plots to estimate the amorphization mechanism of TiO_2.

The Hancock-Sharp plot for 3Hz and 4Hz initially showed the gradients similar to that for 5Hz, but the reduction of the amorphization rate caused the negative deviation of the plots at 60-180 min, and the gradients increased again by the prolonged grinding (>180 min). The negative deviation was not marked for 4 Hz , but the gradient evidently increased at 360 min. The increment of the gradients at the later stage grinding suggested the progress in amorphization accompanying to the consumption of acidic sites by the formation reaction of $BaTiO_3$. The gradient for the later stage (> 180 min) for 3Hz and 4Hz was higher than 0.57 for 5Hz, supposing the congruent progress in the amorphization and the formation reaction. Under the grinding stresses over a threshold one corresponding to about 4Hz for the grinding conditions listed in Table I, the amorphization providing enough amounts of acid site on ground TiO_2 particles in agglomerates should result in the boundary-reaction-controlled kinetics.

4. CONCLUSION

Reaction mechanism for the synthesis of $BaTiO_3$ from TiO_2 and $Ba(OH)_2 \cdot 8H_2O$ under grinding has been studied by a conventional kinetic analysis. A boundary-reaction-controlled interface contracting kinetics and a contraction kinetics with a crystallinity gradient inside TiO_2 particles are proposed for the formation of $BaTiO_3$ and amorphization of TiO_2, respectively. At low grinding stresses, the stress-induced amorphization at the early stage grinding is successively replaced by the reaction-controlled one. The reaction index for the later process suggests the congruent progress in amorphization and formation of $BaTiO_3$ under kneading the constituents in micro-agglomerates functioning as micro-reaction fields. Over a threshold grinding stress, the amorphization providing enough amounts of acid site on ground TiO_2 results in the boundary-reaction-controlled formation of $BaTiO_3$.

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