J Electroceram (2007) 18:1–7
DOI 10.1007/s10832-007-9000-2

Synthesis of fine Ca-doped $BaTiO_3$ powders by solid-state reaction method—Part II: Rheological study on milling

Sang-Kyun Lee · Sung-Soo Ryu · Dang-Hyok Yoon

Received: 26 May 2006 / Accepted: 10 January 2007 /

Abstract The observations and explanations for the rheological behavior associated with the slurry processing for Ca-doped $BaTiO_3$ synthesis are included in this second part of our report. The optimum slurry conditions containing three ceramic constituents were decided by using a mixture rule after the determination of each constituent's optimum condition. This approach was quite applicable based on the reproducibility test in determining the parameters such as water to ceramic ratio and dispersant content. In addition, a small amount of NH_4OH addition without any further addition of liquid medium or dispersant was very effective in lowering the slurry viscosity when it was too high to operate the mill in our system. The optimum slurry pH range of 8.5–10.0 was suggested for high energy milling based on the experimental results. Possible models to explain this rheological behavior are also presented in terms of electrosteric mechanism and ionic exchange of dispersant molecule.

Keywords Milling · Mixing · Suspensions · Powder-solid state reaction

S.-K. Lee
Samsung Electro-Mechanics Co., Suwon 442-743, South Korea

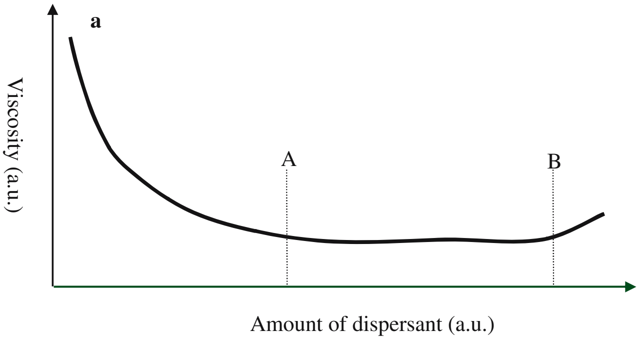
S.-S. Ryu
Korea Institute of Ceramic Engineering and Technology,
Seoul 153-801, South Korea

D.-H. Yoon (✉)
School of Materials Science and Engineering,
Yeungnam University, Gyeongsan 712-749, South Korea
e-mail: dhyoon@ynu.ac.kr

1 Introduction

The purpose of wet milling is to obtain fine and well-dispersed particles with long-term stability in a suspension form. Flocculated and coarse particles are typically broken down by applying shear force but will form again when the shear is removed in the absence of long-term stability. Dispersant is usually added to liquid medium to increase the stability by keeping particles apart and to increase the solid loading by decreasing the viscosity of slurry. Considering that dispersant covers the surface of ceramic particles and that new surface is created during the milling process, the amount of adequate dispersant needs to be increased proportionally to the whole surface area of the particles. However, fixed amount of dispersant is added just once in the beginning of the milling process in general without any further consideration. In practice, industrial milling tends to operate near rheological limits by increasing the solid loading in order to maximize the unit capacity per equipment. Since milling is a dynamic process creating a new particle surface, operators frequently confront problems such as low milling efficiency caused by operation far from the optimum condition or usage of slurries beyond the operational limit. Therefore, research on milling efficiency related with the rheological properties of slurry and counterplans for confronting problems are very important.

A well-dispersed slurry displays lower viscosity due to the particle mobility offered by the fluid interparticulate layer [1]. Slurries with insufficient or excessive dispersant show relatively higher viscosity than those with an adequate amount, as shown in Fig. 1a [2, 3]. Since the ceramic particle is the only portion of the batch left while others are simple facilitators for easy processing, minimum amounts of dispersant and liquid medium are desirable.



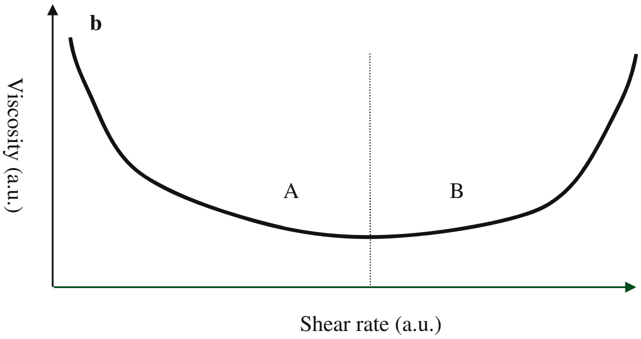


Fig. 1 Rheological behavior of general slurries as a function of **a** dispersant content and **b** shear rate [2, 3]

Therefore, the amount of A in Fig. 1a is the optimum dispersant content for mixing purpose, while the amount of B is reasonable for milling purpose because new surface is created on milling. Most ceramic slurries or slips containing polymeric species show pseudo-plastic behavior at low or moderate shear rate, as shown with the region A of Fig. 1b, while the rheology is changed to dilatancy at high shear rate, as shown in the region B of the same figure [4]. The shear rate of conventional ball milling does not reach the dilatancy region due to its relatively low rotational speed. However, the shear rate of a high energy mill working at a few thousand rpm is enough to reach the dilatancy region. Therefore, the ceramic slurry may show extremely high viscosity in the milling chamber which may be beyond the operating limit even though it shows a moderate viscosity under low shear rate.

The long-term slurry stability depends on the sign and magnitude of the total energy of interaction between particles [5, 6]. Stabilization is achieved by electrostatic and steric mechanisms, both of which prevent particles from approaching close by using electrostatic repulsive force and hindrance by the adsorption of polymeric molecules on the particle surface, respectively [5–8]. When the slurry stability is not guaranteed, the segregation of compositions due to differences in their densities and/or agglomeration among particles is expected, which results in an inhomogeneous distribution of starting materials during further processing such as drying and heat treatment.

The present study was therefore conducted to define the determination method of an appropriate dispersant content of slurry and to demonstrate how to decrease the viscosity when confronting excessive viscosity due to the increased surface area during milling. Explanations are also provided in terms of electrostatic and steric mechanism for the peculiar observation that we made during the synthesis of Ca-doped $BaTiO_3$.

2 Experimental procedure

The details of the starting materials used in this experiment are described in Part I. The relative ratio of formulated powder on a weight-base was approximately TiO_2:$BaCO_3$:$CaCO_3$=28.60:70.70:0.70 in order to obtain the stoichiometry of $(Ba_{0.98}Ca_{0.02})_{1.002}TiO_3$. Since each starting material has different characteristics such as particle size and specific surface area, the slurry composition, including the ceramic to water ratio and dispersant content, was approached for each material first. After selecting the optimum condition for each starting material, slurries containing the formulated A- and R-powders were prepared and characterized further based on each starting material's optimum condition using a mixture rule. The water/ceramic powder was 3/1 only for the fine, anatase-rich TiO_2 due to its large surface area, while others were fixed at 1/1.

In order to determine the adequate amount of dispersant for each starting material, the following pre-tests were performed. Fifty grams of each starting material containing deionized water according to the above ratio were ball-milled for 24 hours with various amounts of ammonium salt of polycarboxylic acid dispersant (Cerasperse 5468CF, San Nopco, Korea). The viscosity of each slurry at 20°C was measured using a computer-controlled viscometer (DV-II+ Pro, Brookfield, MA, USA) using a small sample adapter with SC4-18 spindle at various shear rates. The amount of

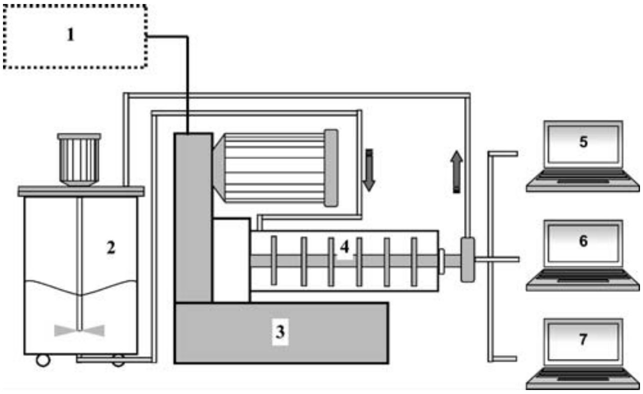


Fig. 2 Schematic of experimental system. 1: Controller, 2: Mixing tank, 3: High energy mill, 4: Milling chamber with agitator shaft and beads, 5: Viscometer, 6: Zeta potential analyzer, 7: Particle size analyzer

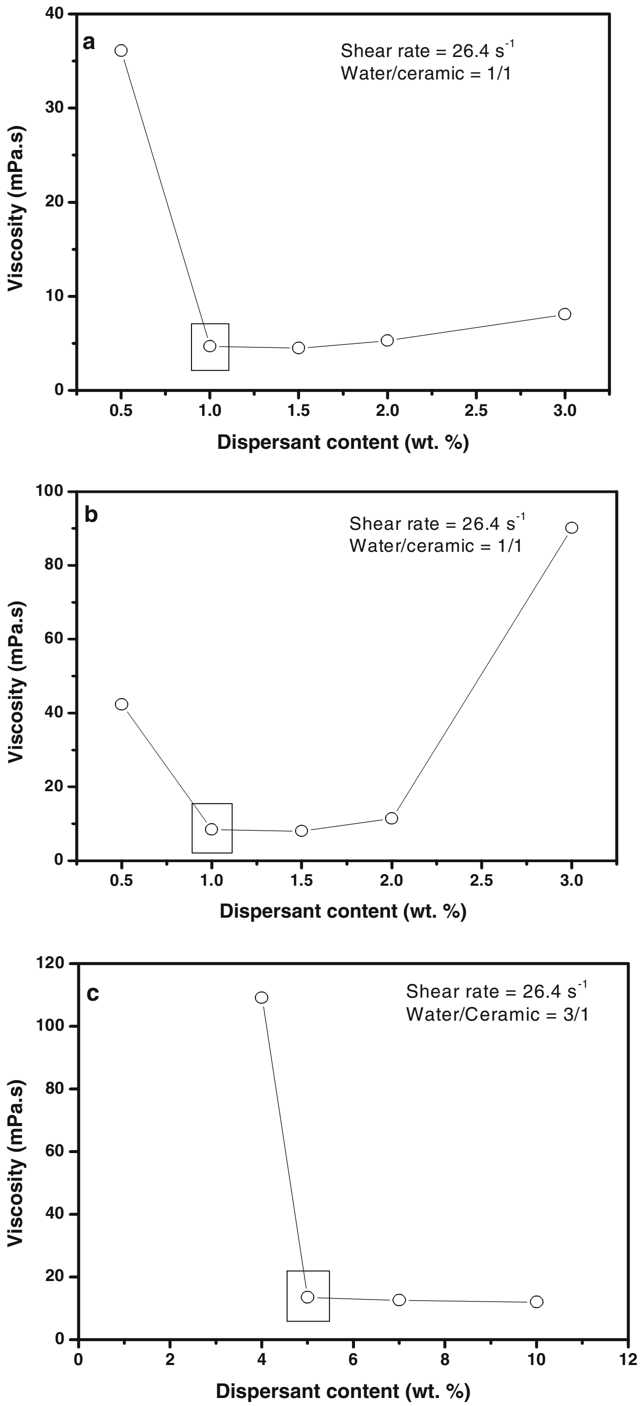


Fig. 3 Viscosity of starting materials at a fixed shear rate of 26.4 s^{-1} as a function of dispersant content containing **a** $BaCO_3$, **b** coarse TiO_2 and **c** fine TiO_2

dispersant which showed the initial low value was determined to be the optimum content. Based on the pre-test results, the reproducibility of the slurry viscosity containing the formulated R- and A-powders was confirmed by following the same experimental step.

Figure 2 presents a schematic of mill system for the treatment of large batch sizes. The horizontal stirred beads mill (LME 4, Netzsch, Germany) had an alumina lining with a 2.4-l of milling chamber which was filled with 80 vol.% of 0.65 mm ZrO_2 beads. A simple circulation method was adopted for milling as shown in the figure. The slurry properties were characterized using a Brookfield viscometer, an electrophoretic-type [9] zeta potential analyzer (ELS-8000, Otsuka Electronics Co., Japan), and a laser scattering particle size analyzer (LA-920, Horiba, Japan). Using this system, the viscosity of the $BaCO_3$ slurry was monitored during milling for 20 hours. In order to cope with the abrupt increase in viscosity that stopped the high energy mill during the milling process, 0.2 wt.% of NH_4OH with respect to the amount of deionized water in the slurry was added. Since NH_4OH addition was successful in decreasing the viscosity of the $BaCO_3$ slurry, this effect was further confirmed using the slurries containing a fine, anatase-rich TiO_2 and a formulated A-powder. In order to explain these phenomena, zeta potentials of each starting material and formulated A-powder were measured after extreme dilution. Since further testing confirmed that the effect of ionic strength was insignificant on the zeta

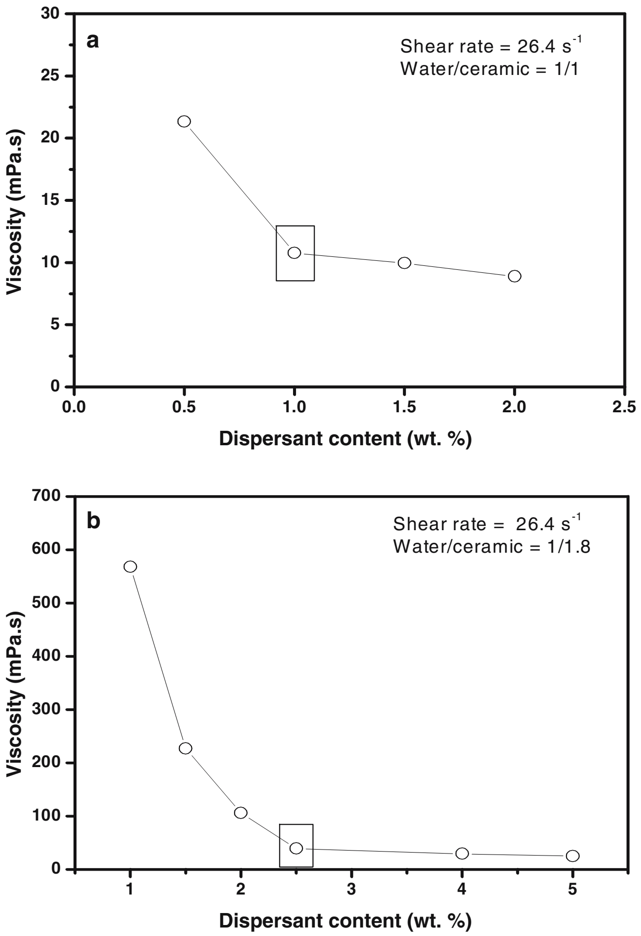


Fig. 4 Viscosity of two types of formulated powder at a fixed shear rate of 26.4 s^{-1} as a function of dispersion content for **a** R- and **b** A-powders

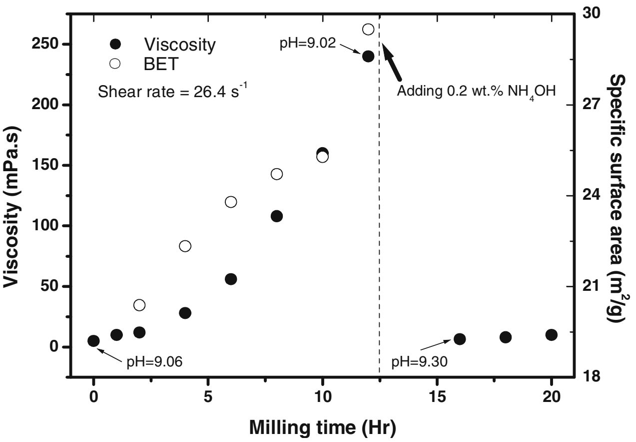


Fig. 5 Effects of milling time and NH_4OH addition on $BaCO_3$ slurry viscosity. Changes of the specific surface area are also shown for milling time up to 12 h

potential for our system, it was not considered any more. Finally, the morphological difference of dried powder was compared between spray and vat drying.

3 Results and discussion

Figure 3 shows the rheological behavior of the starting materials at a fixed shear rate of 26.4 s^{-1} as a function of dispersant content. The optimum dispersant contents which showed an initial low viscosity were 1.0, 1.0, and 5.0 wt.% with respect to the ceramic weight for the slurries with $BaCO_3$, coarse, rutile-rich TiO_2 and fine, anatase-rich TiO_2 powders, respectively. The viscosity of the three slurry types with the optimum dispersant content was below 15 mPa.s. The high viscosity at low dispersant concentration was due to the incomplete adsorption on the particle surface, while the gradual increase of viscosity above the optimum content, especially with the slurry containing coarse, rutile-rich TiO_2 in Fig. 3b, was attributed to the polymeric bridging effect as has already been observed by other researchers [2, 3]. Due to the high surface area of the fine anatase-rich TiO_2, this slurry required much more dispersant to show the minimum viscosity, as shown in Fig. 3c.

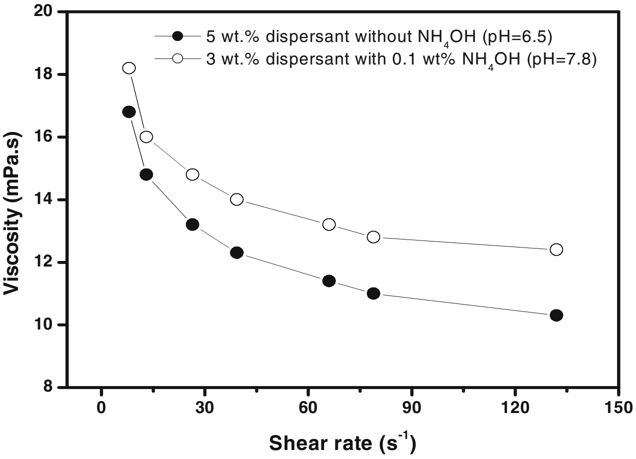


Fig. 6 Effect of NH_4OH addition on fine anatase-rich TiO_2 slurry with two different dispersant contents

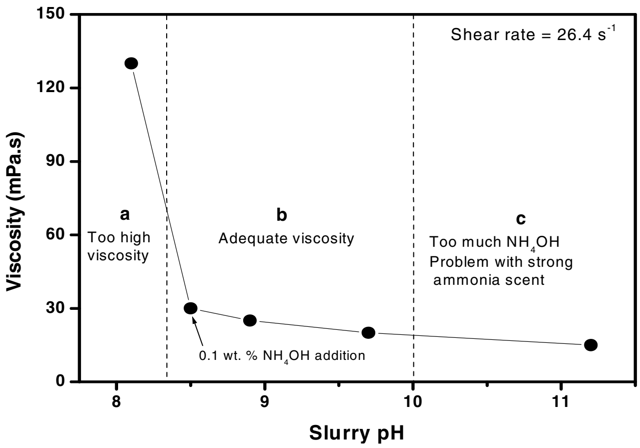


Fig. 7 Viscosity behavior of the slurry containing A-powder at different pH

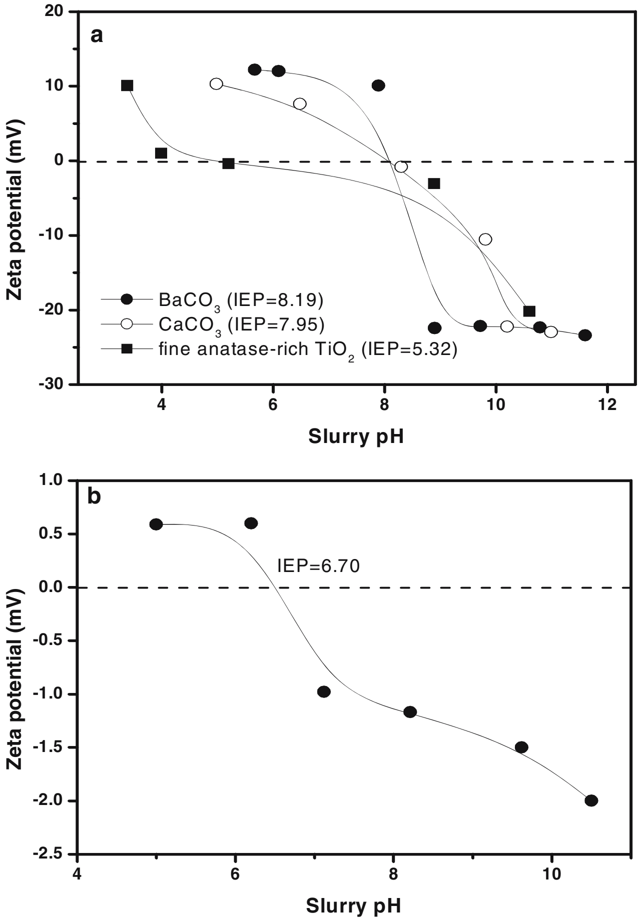


Fig. 8 Behavior of zeta potential on slurry pH for **a** starting materials and **b** slurry containing A-powder

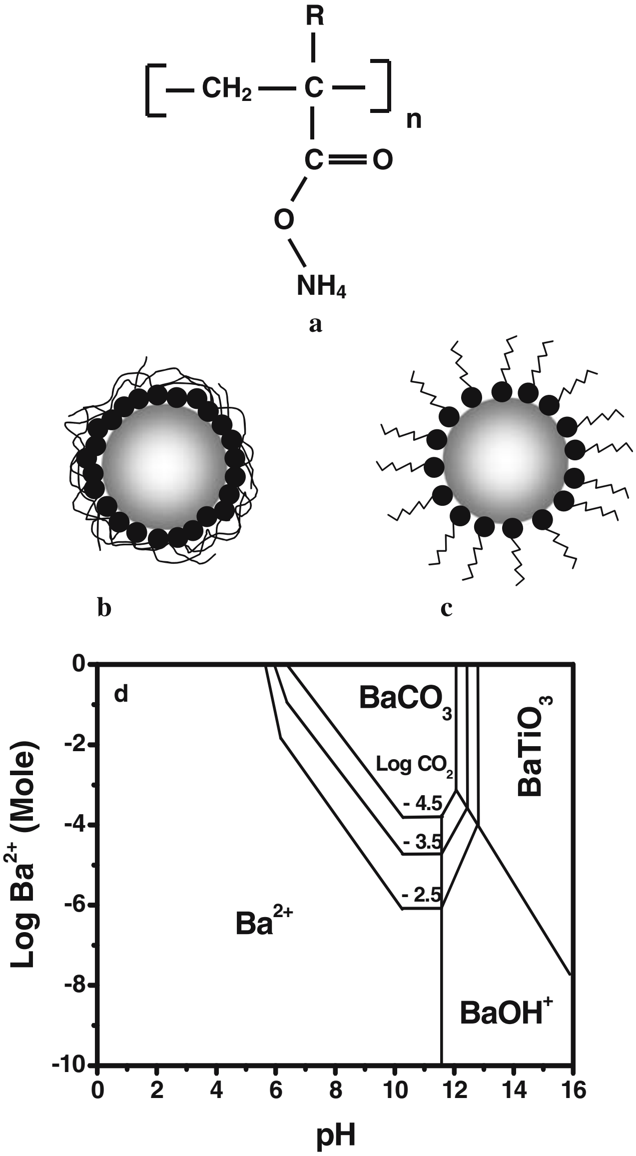


Fig. 9 **a** Molecular structure of dispersant, **b** schematic conformation of dispersant at low and **c** high pH, and **d** the theoretical phase stability diagram of the Ba-Ti-CO_2-H_2O system [16]

The results of reproducibility test with the slurries containing formulated R- and A-powders are shown in Fig. 4. The dispersant content marked with a rectangle in the figure corresponds to the average optimum dispersant content determined for each material based on the mixing rule. Both slurries showed reasonable low viscosity, although they did not reach the minimum value, indicating that this method is applicable for the determination of optimum dispersant content for a mixture.

LME 4 mill is not allowed to operate a $BaCO_3$ slurry with a viscosity higher than 300 mPa.s at 26.4 s^{-1} shear rate, since the viscosity in the mill chamber must be very high due to the extreme shear rate, according to Fig. 1b. The changes in viscosity of the $BaCO_3$ slurry at a fixed shear rate of 26.4 s^{-1} during high energy milling are shown in Fig. 5 with the resultant specific surface area of the particles. The viscosity was proportionally increased with increasing specific surface area up to 12 h of milling. Therefore, the slurry viscosity needs to be lowered at this point for continued mill operation. More dispersant or liquid medium can be added for this purpose, although any such additives need to be eliminated later during the drying and binder burn-out process. However, the slurry viscosity of 240 mPa.s was decreased to less than 20 mPa.s by adding 0.2 wt.% of NH_4OH with respect to the weight of water without any further addition of dispersant or water. The slurry pH was 9.06 initially, decreased to 9.02 after 12 h milling, and then increased to 9.30 after adding 0.2 wt. % of NH_4OH. This simple treatment enabled continuous mill operation. The viscosity of the slurry with fine, anatase-rich TiO_2 was also lowered by adding a small amount of NH_4OH, as shown in Fig. 6, as was the slurry with formulated A-powder, as shown in Fig. 7. Excessive NH_4OH addition, i.e., with a pH higher than 10, generated a problem with the working condition due to the strong ammonia scent, as shown in Fig. 7. Therefore, the pH needs

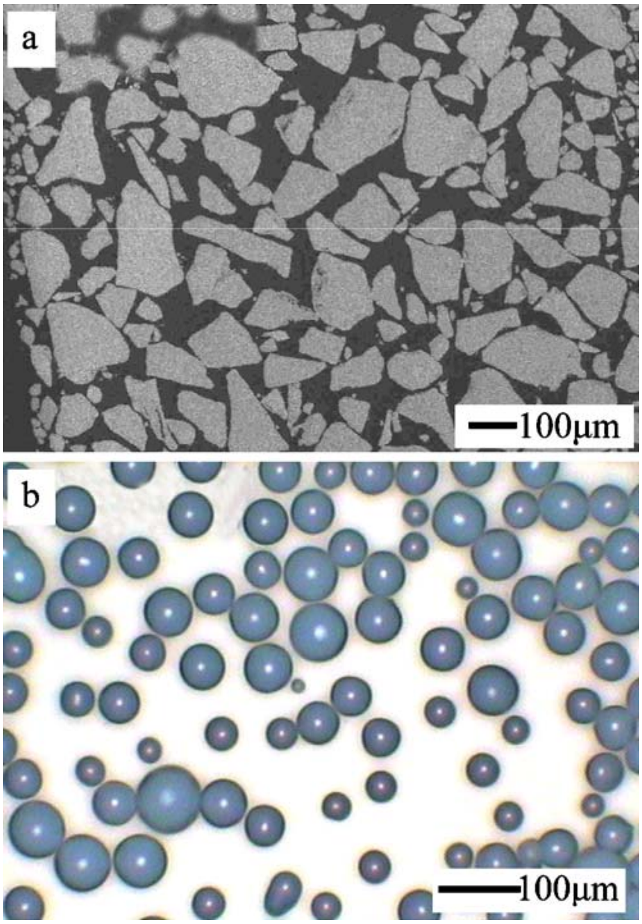


Fig. 10 Morphological comparison of dried powders: **a** SEM image of a vat-dried and atomized, and **b** optical microscope image of a spray-dried A-powder

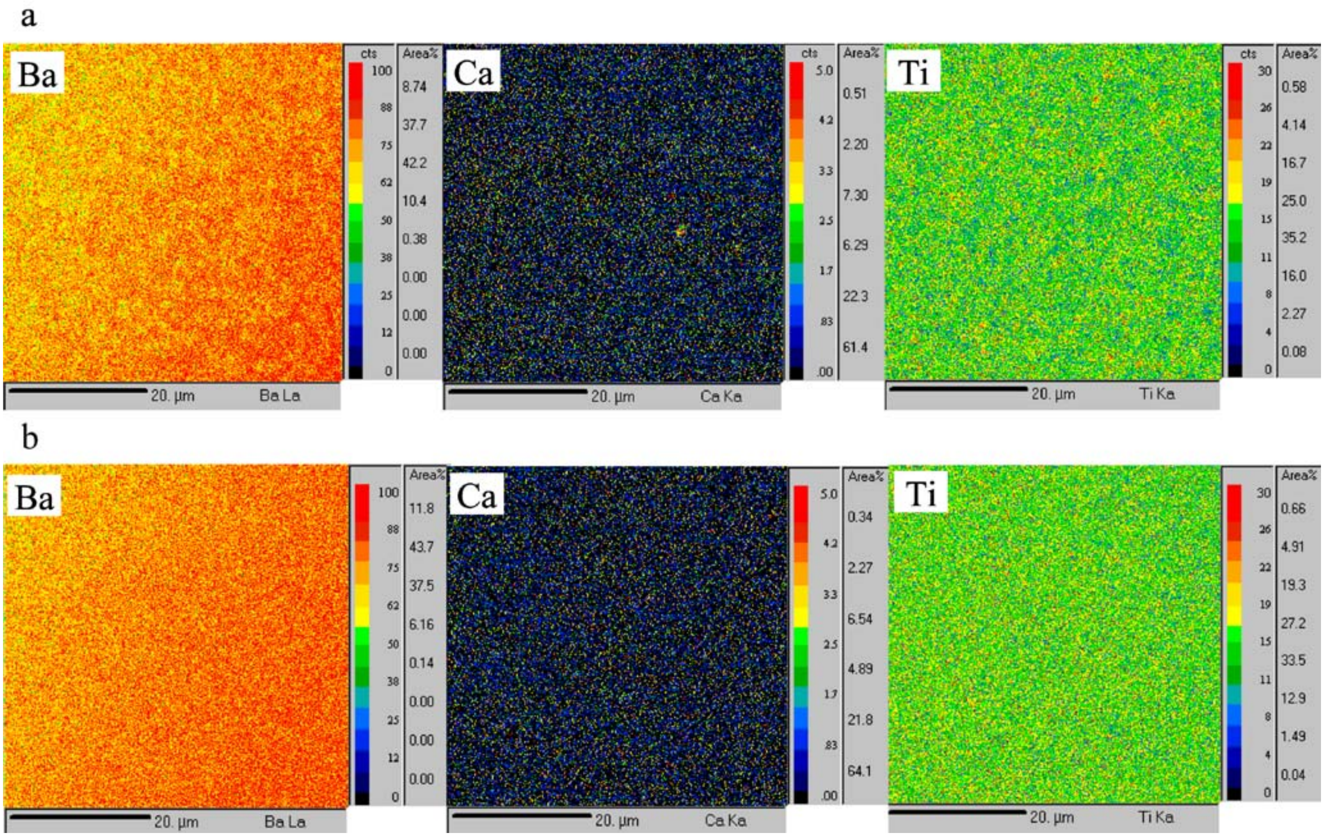


Fig. 11 Results of the electron probe microanalysis (EPMA) for **a** vat-dried powder and **b** spray-dried one, showing the more inhomogeneous distribution of the Ba, Ca and Ti elements with the vat-dried powder

to be adjusted between 8.5 and 10 to decrease the viscosity in this system with formulated A-powder.

In order to explain this phenomenon, the zeta potential of each starting material was measured using an electrophoretic-type zetameter after extreme dilution of the slurry, with the results being shown in Fig. 8a. Both $BaCO_3$ and $CaCO_3$ particles showed an iso-electric point (IEP) of approximately pH=8, while the fine, anatase-rich TiO_2 showed at pH=5.3, which is consistent with the previously reported values [10]. The pH values of $BaCO_3$ and TiO_2 slurries were 9.06 and 6.50, respectively, both of which were slightly higher than their IEPs. It is difficult to measure an exact IEP for each starting material in a dense slurry form by utilizing an electrophoretic method because the extreme dilution is essential with this method [9, 11]. Dilution usually induces changes of electrical double-layer thickness and dispersant concentration which result in the variation of zeta potential [11, 12]. Even though an electroacoustic method is reported to be capable of measuring the zeta potential for dense slurries [13, 14], mismatch between the two types of measurement has been reported [11]. If we consider the effect of dispersant only on the zeta potential associated with the dilution, IEP before dilution should be lower than the observed value because Cerasperse 5468CF is an anionic dispersant. Therefore, it is estimated that the actual difference between IEP and slurry pH will be greater than the observed one. The IEP of the slurry containing A-powder was located near pH=6.70, as shown in Fig. 8b, and the magnitude of the zeta potential was quite small, indicating that the electrostatic mechanism was not significant for this system, even though it may have had a slight effect. Based on the above results, therefore, the electrostatic mechanism along cannot explain the drastic decrease in viscosity with small NH_4OH addition.

Figure 9a shows the molecular structure of the ammonium salt of polycarboxylic acid in which the hydrogen ion of carboxylic acid is replaced by ammonium ion (NH_4^+) that acts as an anchoring group on the particle surface since the particle surface charge is negative. Based on our experience, this anchoring group seems to be easily dissociated from the dispersant during the milling process because an ammonia smell comes from the slurry. The decreased number of the anchoring group indicates the reduced dispersing efficiency of the dispersant. However, it seems that the number of anchoring groups can be increased by adding a small amount of NH_4OH due to its very effective viscosity reduction. One further possible explanation for the effect of NH_4OH addition is the change of polymeric molecular structure with slurry pH. According to Jean and Wang [15], an anionic dispersant has a shrunken and coiled conformation at low pH but a more stretched conformation at high pH due to the electrostatic repulsion between the side groups on the particle surface, as shown in Fig. 9b and c, respectively. The more stretched conformation of the dispersant at high pH, achieved by adding NH_4OH, results in high dispersing efficiency due to the large hydrodynamic radius of dispersant and the resultant high steric hindrance effect. The processing of $BaCO_3$ at relatively high pH is desirable in order to minimize the dissolution of barium ions which tend to leach out from $BaCO_3$ and even from $BaTiO_3$ at low pH in water, as shown in Fig. 9d [16].

Figure 10 presents a morphological comparison between vat-dried and spray-dried powders with their irregular and spherical shapes, respectively. The more important problem associated with the vat-drying method is the microscopically inhomogeneous distribution of the constituents, which is caused by the segregation of the starting materials due to their density difference during the relatively slow drying process, according to the electron probe microanalysis (EPMA) results shown in Fig. 11. On the contrary, spray drying is initiated by spraying the well-dispersed suspensions into tiny droplets and then rapidly drying them to give a more uniform distribution of constituent distribution than achieved with the vat-dried method.

4 Conclusion

The present study was performed to determine the optimum slurry condition containing a ceramic mixture for high energy milling and to overcome the abrupt increase in viscosity that stopped the mill during processing. Based on the experimental results, the following conclusions were drawn:

1. The determination of optimum slurry conditions containing multi-components based on the optimum conditions of each constituent was confirmed to be applicable by the reproducibility test.
2. The slurry viscosity, which was excessively high for mill operation, was effectively lowered by small amount of NH_4OH additions for many slurry systems containing an ammonium salt of polycarboxylic acid dispersant.
3. The effect of NH_4OH addition in decreasing slurry viscosity was explained by using the ionic exchange of dispersant molecules, and the combination of electrostatic and steric mechanisms based on the viscosity and zeta potential data. The slurry pH range of 8.5–10 was recommended for the processing of the Ca-doped $BaTiO_3$ system used in this experiment.

Acknowledgements The authors thank Dr. K. H. Hur, Mr. H. S. Jung and Mr. D. S. Lee at Samsung Electro-Mechanics Co. for their considerable cooperation.

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