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Effects of the Ultrafine and Nano-sized Clay on Rheological Behavior of the Matrix of ρ-alumina Bonded Castable

Sungho Cheon and Byungsei Jun†

Division of Advanced Materials Engineering, Kyungnam University, Masan 631-701, Korea

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ABSTRACT

To prepare the alumina cement free vibrated alumina castable, ρ-alumina is employed as a binder material, and nano-sized clay is added to enhance the curing strength and give thixotropic behavior. The rheological behavior of matrix of castable is controlled by investigating the influences of ultrafines, ρ-alumina, and nano-sized clay on the viscosity of matrix. The microsilica and ultrafine alumina were added 3 wt% and 4 wt%, respectively to the matrix, which showed that the viscosities tends to be lowest values. The rheological property of the matrix is well estabilished by adding ρ-alumina as 8 wt% and clay as 4 wt%. The thixotropic behavior of the ρ-alumina bonded castable was appeared by introducing nano-sized clay into the matrix and adjusting the pH near to the PZC of the clay suspension.

Key words : ρ-alumina bonded castable, Nano-sized clay, Thixotropic behavior

1. Introduction

The advantages of refractory castables regarding ease of installation and thermomechanical behavior have made the replacement of conventional brick. Such advantages result from improvements of rheological behavior of the castable during working and from a significant reduction of liquid phase formation at high temperature.

The conventional castables typically contain 10 to 30% alumina cement as the binder for the curing strength. The curing strength of conventional castables is due to the gel formation of hydrated phases of alumina cement binder. Alumina cement permits a large amount of the water in the castables and a liquid phase at the low temperature formed by the reaction between CaO of the cement and aluminosilicate aggregates.1-4)

Therefore, low cement or cement free castables have been widely studied and fabricated to improve the high temperature properties.5) The clay, ultrafine particles or chemically bonded products have been used as the binder for these cement free castables. ρ-alumina is one of the promising binder materials for the cement free castables because the ρ-alumina forms the hydrated gel due to its high solubility in water.6) However, the problems with poor curing strength and poor explosion resistance have limited its use in actual practice.

Low apparent viscosity and yield stress of the matrix are essential requirement to obtain self-flow castables. The addition of an appropriate amount of fine particles can allow the production of high-flowability and easy-installation castables because the introduction of fine and superfine particles into the composition decreases the friction among large particles, and thus allow the flow behavior to be predominantly controlled by the fraction of particles under 100 micron. Fine and ultrafine particles that compose the castable matrix play also an essential role in enhancement of packing density. The introduction of microsilica, alumina or other oxide fine particles into the castable has markedly increased packing density, and enabled the reduction of binder materials.

Furthermore, the fine particles can be separated from large particles when the batch is strongly vibrated to enhance the packing density. To avoid this segregation between fine and large particles, thixotropic behavior of the suspension must be considered.

In this study, to prepare the alumina cement free vibrated alumina-based castable, ρ-alumina is employed as a binder material, and nano-sized clay is added to enhance a curing strength and give thixotropic behavior to avoid segregation during the vibrated casting.

The rheological behavior of matrix of castable will be also established by investigating the influences of ultrafines, ρ-alumina, and nanosized clay, on the viscosity of fines in slurry.

2. Experimental Procedure

To prepare the matrix of the vibrated alumina castable, andalusite was used as finer and ρ-alumina was added as a binder materials. Nano-sized clay was also added to enhance the drying strength and the plasticity of the ρ-alu-

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†Corresponding author : Byungsei Jun

E-mail : bsjun@kyungnam.ac.kr

Tel : +82-55-249-2694 Fax : +82-55-248-5033

mina bonded castable, and also permit a thixotropic behavior during vibration.

The nano-sized clay powder with 105 nm was prepared by comminution of kibushi-clay. The zeta potential of the clay suspension was kept maximum to enhance the milling efficiency. The particle size of the clay suspension was measured to seek for the suspension stability with changing pH from 2 to 11 by autotitrator.

The composition of matrix was essentially andalusite, but microsilica and ultrafine alpha alumina were added to the batches additionally for controlling rheology.

The raw materials were uniformly mixed according to the formulation, and then well blended with water and dispersant (Hexasodium metaphosphate, $(NaPO_3)_6$) additions to form slurries.

The effects of the contents of microsilica, ultrafine alumina, ρ-alumina, clay, water, and dispersant on the apparent viscosity and relationship between shear stress and shear rate of the suspensions were investigated by use of viscometer (DV-II, Brookfield).

The thixotropic behaviors of clay and matrix were also investigated by use of R/S rheometer (RHEO 2000 V2.6, Brookfield). The dispersion and coagulation behaviors of the clay suspension were investigated by zeta potentiometer (Zetasizer 3000HS, Malvern).

3. Results and Discussion

3.1. Effect of Ultra Fine Powders and Binders on the Rheological Behavior of Matrix

Most of the castable ceramics are produced from materials having a continuous distribution of particle sizes between some maximum and a finite minimum size. In the real particle system, the movement of particles into the minimum porosity configuration is hindered by the several factors. Coagulation, flocculation, and adhesion forces, which retard particle motion, may also hinder packing. Random arrangements of anisometric particles typically have a higher porosity and a wider range of pore sizes than for an ordered arrangement.[7)]

The parts of fine particles can allow the production of high-flowability and easy-installation castables if they are well dispersed in the matrix. Based on these considerations, this work should be focused on the rheological conditions necessary to minimize apparent viscosity of matrix part of the castable.

The microsilica has been normally used as an agent of improving of the flowability for the alumina cement bonded castables because of its surface character in aqueous slurry.[8)] Therefore the microsilica is also employed, in this study, for enhancing flowability of the ρ-alumina bonded alumina castable.

Alumina cement bonded castables with enhanced high temperature performance can be obtained either reducing the silica and calcia content in the matrix because they can make liquid phase at low temperature. There is no source of calcia in this work because ρ-alumina is used as a binder material. However microsilica has been still employed to improve the flowability in the any kinds of castables. Therefore effects of the microsilica content on the rheology must be first investigated to seek for the minimum requirement.

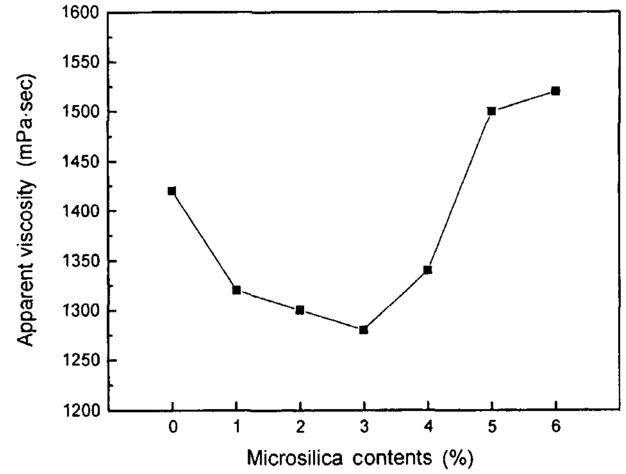

Fig. 1. Variation of viscosity with microsilica contents.

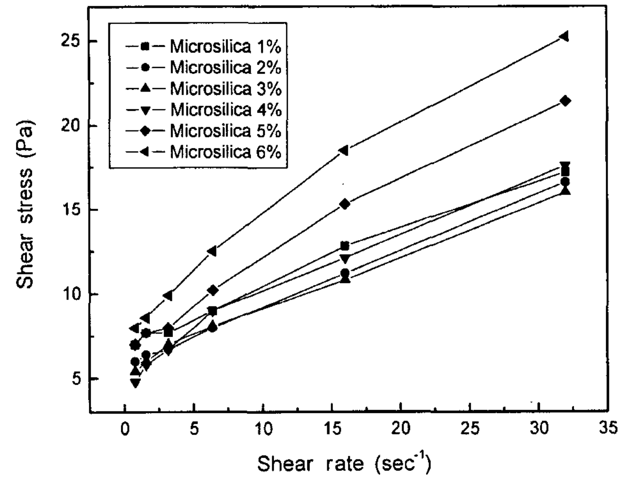

Fig. 2. Shear rate/shear stress curves for slurries with microsilica.

The effects of changes of microsilica content in andalusite fines with 16 wt% water and 0.1 wt% dispersant on viscosity show that the viscosity tends to be decreased by increasing of its content up to the 3 wt% in the slurries as shown in Fig. 1. But the viscosity tends to be highly increased at the above 3 wt%. The relationship between shear stress and shear rate at the condition of 3 wt% has also minimum value as shown in Fig. 2. Therefore 3 wt% addition of the microilica is introduced into the batches for this study. The result shows that microsilica may contribute significantly to the improvement of rheological properties.

Glassy phase at the grain boundary caused by the microsilica may give a weak thermal resistance, and therefore the microsilica must be reacted with any materials to form a high temperature material. The ultrafine alumina is intro-

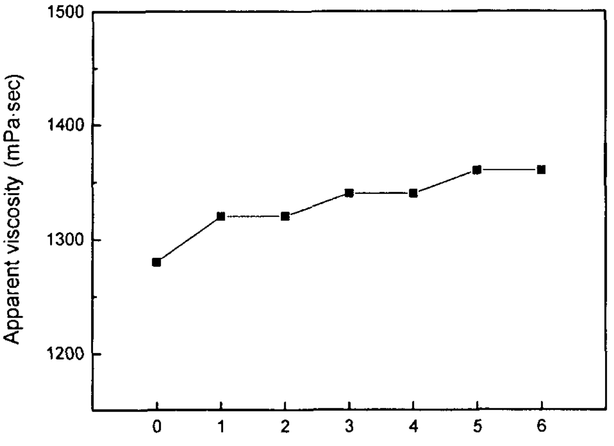

Fig. 3. Variation of viscosity with alumina contents.

Table 1. Batch Composition of Matrix and Binder Materials

Number	Materials	Contents (wt%)	Water (wt%)	Dispersion agent[4] (wt%)
# 1	Andalusite	93.5	16	0.1
	Microsilica	2.8		
	Ultra fine alumina	3.7		
# 2	Andalusite	86.6	19	0.1
	Microsilica[1]	2.6		
	Ultra fine alumina[2]	3.4		
	ρ-alumina[3]	7.4		

[1] Silica fume SF-98, Australian Fused Materials Pty Ltd., 0.5 μm.

[2] AM-21, Sumitomo Co., Japan, 4 μm.

[3] Showadenko, Japan, 30 μm.

[4] NaHMP, Hexasodium metaphosphate, $(NaPO_3)_6$.

duced into the matrix, because it is a candidate material to form a mullite phase.

The effects of the ultrafine alumina content on the viscosity may also be investigated to establish the rheological properties of the batch composition. The effects of changes of ultrafine alumina content in andalusite fines with 16 wt% water and 0.1 wt% dispersant on viscosity show that the viscosities have almost same values in the slurries as shown in Fig. 3. The fact drives that the ultrafine alumina is just added as much as 4 wt% to the composition of andalusite fines and microsilica to form a mullite phase at the high temperature. And thereafter a composition (#1) in Table 1 is prepared for finding out the effects of binder content on the viscosity. The apparent viscosity is gradually increased up to the 8 wt% of ρ-alumina addition, but highly increased at the above 8 wt% as shown in Fig. 4. Based on the pre-test results of the drying strength and viscosity of the alumina castable, 8 wt% addition may be regarded as a proper amount. However this amount may not be reached to the requirement for the drying strength of the alumina castables, and therefore nano-sized clay is added to the ρ-alumina bonded castable. So the batch composition (# 2) in

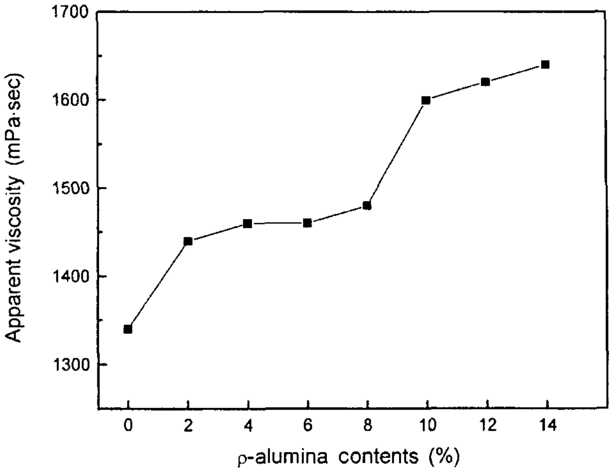

Fig. 4. Variation of viscosity with ρ-alumina contents.

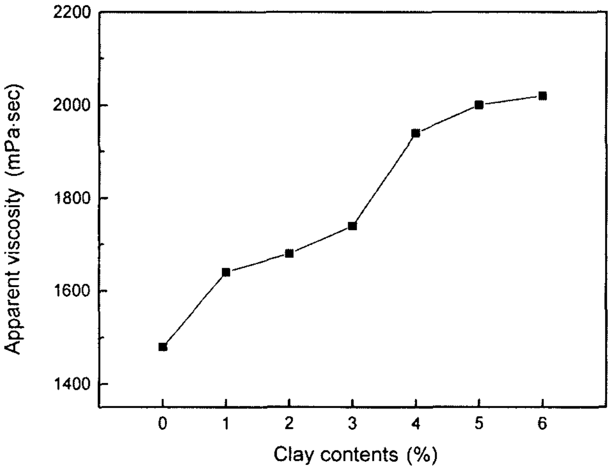

Fig. 5. Variation of viscosity with clay contents.

Table 1 is prepared to seek for the optimal viscosity by changing the amount of the clay. The apparent viscosity is gradually increased by adding of the clay, but highly increased at the above 3 wt% addition, and then saturated at the above 4 wt% addition as shown in Fig. 5. Therefore the 4 wt% addition is selected to establish binder system.

3.2. Effects of the Rheology of Nano-sized Clay on the Thixotropic Behavior of the Matrix

Vibration-casting techniques have been used with materials based on hydraulic cementing medium as the alumina cements. Relatively high water ratios are needed for these systems and the facts that may also drive the lower compaction and open pore results than other installation methods like ramming. Segregation between aggregate and fines, when the water is little more added than that of needs, may be caused by intensive vibration. It is not easy to control the rheological properties of the alumina cement binder system. Therefore the rheology of the batch composition must be controlled carefully by introducing a new binder system as ρ-alumina and clay. The ρ-alumina is, in this study, employed as a main binder material because ρ-alumina binder system permits relatively low water ratio compare to alumina cement. The ρ-alumina does not produce the thixotropic behavior to avoid segregation but the clay produce thixotropic properties. The strong thixotropic behavior may be expected by using nano-sized clay.

The clay minerals are distinguished from other colloidal materials by highly anisometric and often irregular particles shape, the broad particle size distribution, the flexibility of the layers, the different types of charges, the heterogeneity of the layer charges, the pronounced cation exchange capacity, and the different modes of aggregation.

Zetapotential of the clay suspension is measured to investigate the behavior of dispersion and coagulation at different pH as shown in Fig. 6. The Point of Zero Charge (PZC) of the suspension is shown at near pH 5 and maximum zeta potential is –43 mV at near pH 11. The zetapotential results of clay suspension is monitered to reduce the particle size of the clay into nano-scale. Fig. 7 shows that maximum particle size of the agglomerates was appeared at near to the PZC when changing pH from 11 to 5. When coagulating a clay suspension by changing of pH, heteropolar coagulation occurs at near to the PZC of the suspension. Heteropolar coagulation caused by contact edge and face, which may cause thixotropic behavior.

The viscosity is also rapidly increased by changing pH from 11 to PZC as shown in Fig. 8. This result may show that the rapid increasing of viscosity of the suspension must be caused by the coagulation forces and coagulation structure. The minimum viscosity of a clay suspension occurs when zeta potential is at maximum value and agglomerates are dispersed. Fig. 9 shows that the thixotropic behavior was appeared at the PZC of the clay suspension as the shear rate changes up to 50(1/s). After mixing the suspension, the yield stress and plastic viscosity decrease but will recover with time if left standing.[9] This occurs because the fragments of the network which are broken under shear, and then the time is needed for linking again to get a three-dimensional network. Therefore the clay suspensions show a time dependent flow behavior known as the thixotropy.

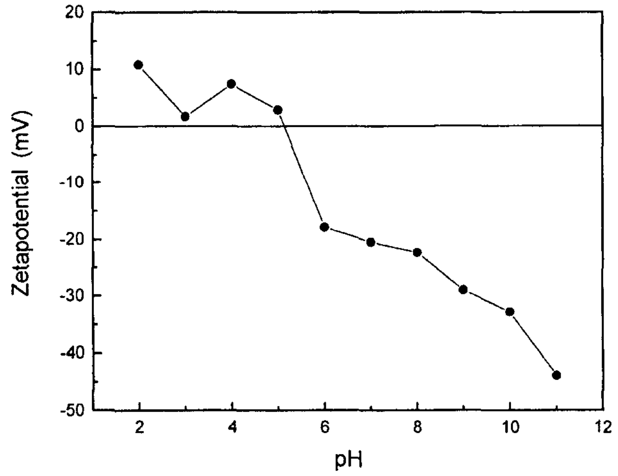

Fig. 6. Zeta potential of clay suspension varing with pH.

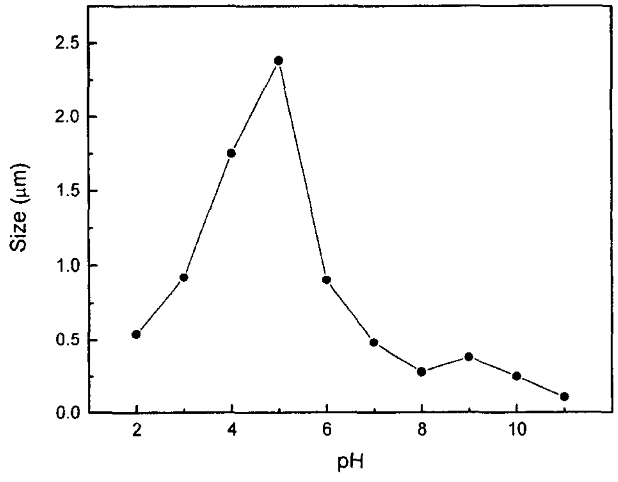

Fig. 7. Particle size of clay suspension varing with pH.

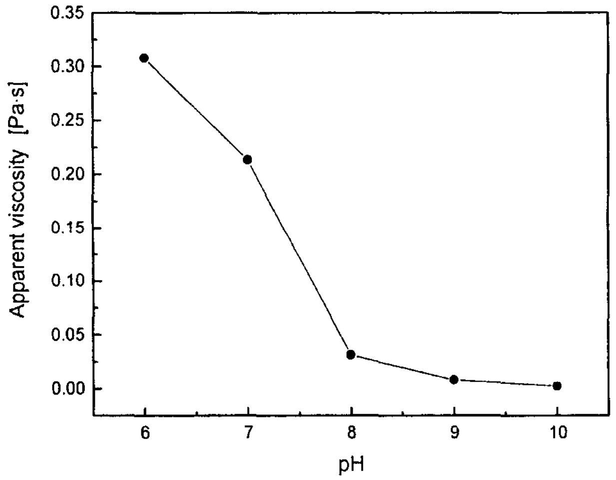

Fig. 8. Variation of viscosity of clay suspension varing with pH at shear rate 50(1/s) and solid loading 20 vol%.

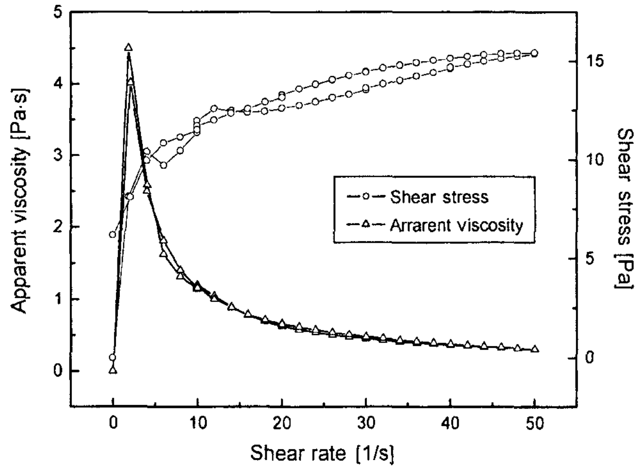

Fig. 9. Viscosity and shear rate/shear stress curves for clay suspension (solid loading 20 vol%) at PZC.

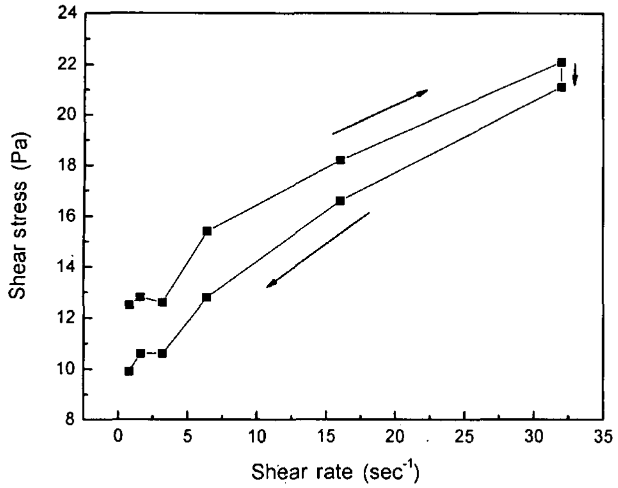

Fig. 10. Thixotropic behavior of the matrix slurry without clay.

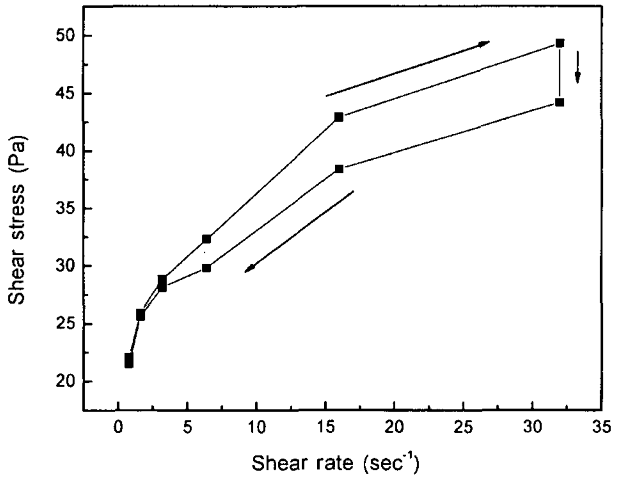

Fig. 11. Thixotropic behavior of the matrix slurry with clay.

The extent of the thixotropic property of the matrix without clay addition, in this study, is much smaller than that of expected value for working condition as shown in Fig. 10. This is because the viscosity of the suspension is mainly influenced by the gelation of hydrated phases of the ρ-alumina, and the thixotropic behavior will be time dependently disappeared as the gelation of ρ-alumina is gradually advanced. The $MgCl_2 \cdot 6H_2O$ as a coagulation agent is added to the matrix with clay, and then move the pH from 11 to 6. The thixotropic property is appeared at the pH 6 as shown in Fig. 11. The result shows the clay has heavily influenced rheological properties of the ρ-alumina bonded castable by introducing thixotropic behavior.

4. Conclusions

The rheological properties of matrix of castable were examined by investigating the influences of ultrafines, ρ-alumina, and nano-sized clay on the viscosity of matrix to establish the rheology of the vibrated alumina castable. The effects of changes of microsilica and ultrafine alumina contents in andalusite fines on viscosity show that the viscosities tends to be lowest value by adding 3 wt% and 4 wt% respectively. Based on the results of measurements of viscosities, addition of the ρ-alumina as 8 wt% and clay as 4 wt% to the matrix may be proper content as the binder materials for alumina cement free castable. The thixotropic behavior of the ρ-alumina bonded castable may be enhanced by introducing nano-sized clay in to the matrix and adjusting the pH near to the PZC of the clay suspension.

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