

Boehmite modification of nano grade α -alumina and the rheological properties of the modified slurry

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Abstract

The boehmite effect on the modification of the surface of a nano grade α -alumina was studied. The pre-aging process was performed by adding boehmite to a nano grade α -alumina (N α -A) slurry and adjusting the pH value of the mixed slurry to less than 4. After the pre-aging process, boehmite was coated onto the surface of N α -A particles to change its zero charged point (PZC) from pH = 6–7 to 9–10, similar to that of the boehmite slurry. Mixed and boehmite slurries show thixotropic behavior if the pre-aging process is adjusted to pH = 1. However, there is no thixotropic behavior if the pre-aging process is adjusted to pH = \sim 2. Boehmite degrades to a nano grade sol as the pH of the pre-aging process decreases, especially at pH = \sim 1. The rheology and the thixotropic properties of the mixed slurry at different pre-aging conditions are discussed in this article.

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1. Introduction

Nano size ceramic powders have excellent properties for use in many fields, such as structural, optical, and electrical material, etc. Aluminum oxide is an important ceramic oxide in modern industry because it is inexpensive and possesses good mechanical and optical properties. Alumina slurry settles easily under the action of gravity, which restricts alumina slurry applications. Several patents were registered for alumina and boehmite composites. Wassermann and Meyer [1] discussed a process for making dispersible aluminum hydroxide. Water dispersible aluminum hydroxide is prepared by treating an acid dispersible aluminum hydroxide with 1–9 wt.% of gaseous acid. Meyer et al. [2] discussed a process for producing boehmite alumina. This preparation was carried out by obtaining an alumina suspension from a neutral aluminum alkoxide hydrolysis and then aging the alumina suspension in an autoclave at 1–30 bar at 100–235 °C. Hurlburt and Plummer [3] proposed a method for making boehmite alumina where alumina powder was modified by boehmite with a compound X

(SO₃M)_n (X is an organic moiety, M is a monovalent cation) at elevated temperature. The rheological properties of the ceramic slurry have been reported in the literature [4–7]. Moreno et al. [4] and Schilling et al. [5] studied the effect of additives on the rheology of alumina slurry. They indicated that surfactants can reduce the viscosity and thixotropic effect of a high solid content slurry. Rao et al. [6,7] studied the suspension properties of SiC slurry by measuring the zeta potential and the sedimentary height of SiC slurry at various pH values. They indicated that pH has a great influence on the zeta potential and slurry suspension properties.

A very simple way to modify N α -A with boehmite was developed in this study. N α -A slurry is modified with boehmite by pre-aging at a pH less than 4. The sedimentary heights, the rheological properties and the zeta potential of the slurries are discussed to understand the properties of mixed slurry.

2. Experimental

2.1. Sedimentary height measurement

A 30 wt.% slurry of nano grade α phase alumina (N α -A) (Design & Quality Enterprise Co., Ltd, Taipei) was the raw material in this study, which was modified with ammonium

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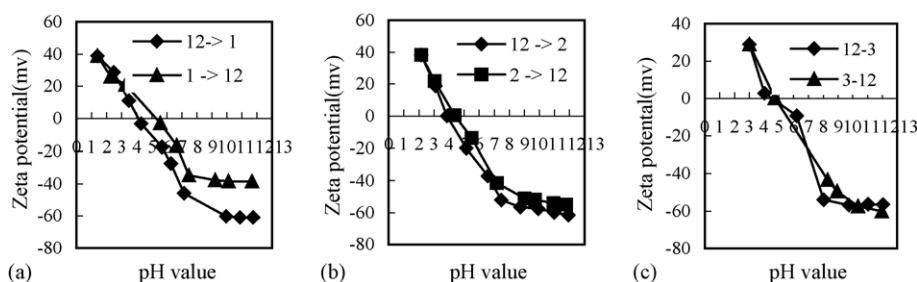


Fig. 1. The zeta potential of pure α -alumina slurry at different pre-aged processes: (a) pH = 12 \rightarrow 1 \rightarrow 12, (b) pH = 12 \rightarrow 2 \rightarrow 12, and (c) pH = 12 \rightarrow 3 \rightarrow 12.

polymath acrylate. The commercial slurry was filtered and subsequently dried in a microwave furnace. Five grams of the dried nano grade α - Al_2O_3 powder was then weighted with 100 g de-ionized (DI) water to form a slurry for the sedimentary height measurement. The mixed powder slurry consisted of 5 g nano grade α - Al_2O_3 , 5 g boehmite (Condea, trade name: dispersal) and 100 g DI water. These slurries were divided into 10 parts that were pH adjusted to the desired values from 1 to 10, respectively, and then introduced into cylinders that were placed on a flat, vibration free plate for 2 weeks. The sedimentary heights of the slurries were recorded.

2.2. Zeta potential measurement

The diluted pure N α -A and pure boehmite slurries were adjusted to pH = \sim 12 using aqueous potassium hydroxide. The sample was injected into a cell for measuring the zeta potential. The diluted slurry was then titrated by adding diluted hydrogen nitrate continuously to adjust the pH into the acid range. During titration, the diluted slurry was sampled to measure the zeta potential. After titrating to the desired pH, the diluted slurry was reverse titrated using potassium hydroxide to adjust the pH into the basic range. The zeta potential of this diluted slurry was also measured. The point of zero charge (PZC) at each process of pure alumina slurry, pure boehmite slurry and mixed powder slurry, respectively, were identified by these measurements.

2.3. Rheology measurement

The slurries consisting of 5 wt.% of N α -A, 5 wt.% pure boehmite and 5 wt.% mixed powders were prepared for rheological property measurements. The thixotropic measurement was performed by recording the slurry viscosity at 25 rpm

shear rate for 200 s. If the slurry has no thixotropic behavior, the viscosity will not change with time. If the viscosity decreases with increasing time at constant shear rate, the thixotropic effect is present. The slurry rheology was studied at different pH pre-aging processes pH = 1, pH = 1 \rightarrow 4 (i.e., pH pre-aging at pH = 1 and then adjusting to pH = 4), pH = 1 \rightarrow 9, pH = 2, pH = 2 \rightarrow 4, and pH = 2 \rightarrow 9.

3. Results and discussions

Fig. 1 shows the zeta potential of pure alumina slurry. In general, regardless of the slurry crystalline structure, pure alumina slurry will have a PZC in pH = 9–10. However, the PZC of the commercial N α -A in this study was at pH = 4–5. This may be due to the addition of ammonium polymath acrylate in the commercial product. The zeta potentials of the particles did not change with the titration process to pH = 12 \rightarrow 1 \rightarrow 12, pH = 12 \rightarrow 2 \rightarrow 12, and pH = 12 \rightarrow 3 \rightarrow 12, as shown in Fig. 1. Fig. 2(a)–(c) show the zeta potential of the boehmite at different titrating processes for the pH values. The PZC of the boehmite slurry in the pH = 12 \rightarrow 1 \rightarrow 12 process was at pH = 9–10, which is quite similar to that for the pH = 12 \rightarrow 2 \rightarrow 12 and pH = 12 \rightarrow 3 \rightarrow 12 process. This means that the surface property of the boehmite did not change with the pH adjustment. The zeta potentials of the mixed slurries are shown in Fig. 3. The PZC of the mixed slurries were at pH = 6–7 in the pH = 12 \rightarrow pH = 1, 2, 3, and 4 processes, respectively. However, they changed to pH = 9–10 during the pH = 1, 2, 3, and 4 processes, respectively, \rightarrow pH = 12, as shown in Fig. 3(a)–(d). In the pH = 12 \rightarrow 5–6 \rightarrow 12 processes, the PZC of the mixed slurry did not change during the entire process. The PZC of the mixture of N α -A and boehmite may be at pH = 5–6. As the pH = $<$ 4 \rightarrow 12 was adjusted, the PZC of the mixed slurry in this

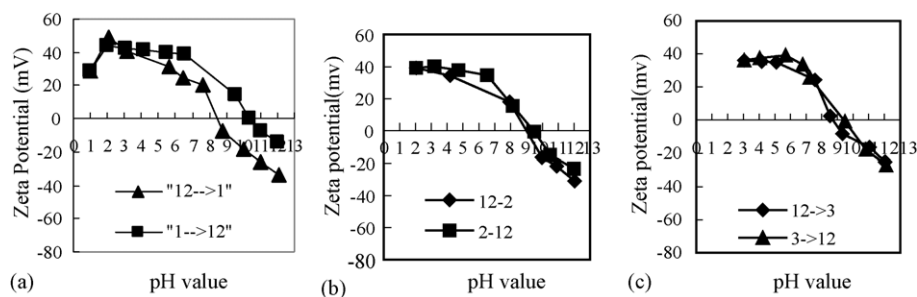


Fig. 2. The zeta potential of pure boehmite slurry at different pre-aged processes: (a) pH = 12 \rightarrow 1 \rightarrow 12, (b) pH = 12 \rightarrow 2 \rightarrow 12, and (c) pH = 12 \rightarrow 3 \rightarrow 12.

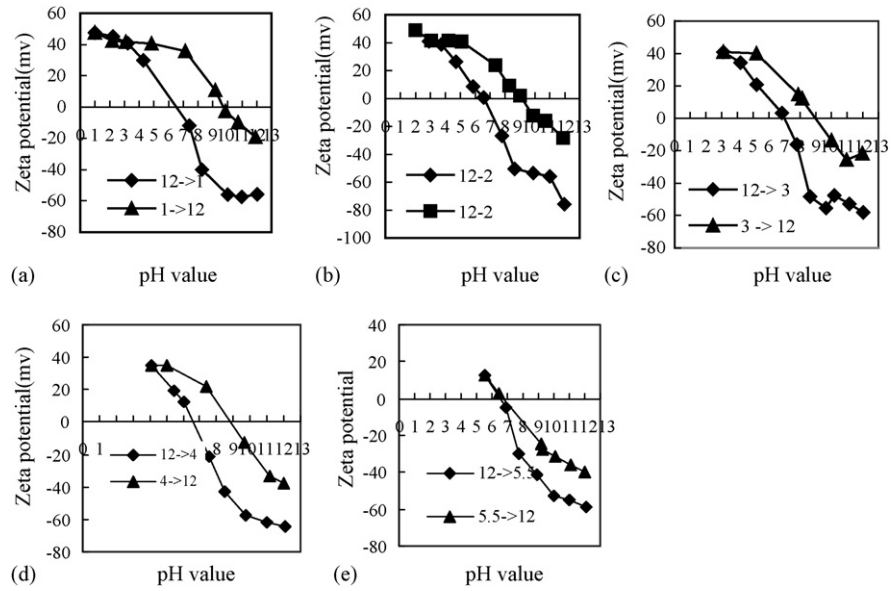


Fig. 3. The zeta potential of the mixed slurry at different pre-aged processes: (a) pH = 12 → 1 → 12, (b) pH = 12 → 2 → 12, (c) pH = 12 → 3 → 12, (d) pH = 12 → 4 → 12, and (e) pH = 12 → 5.5 → 12.

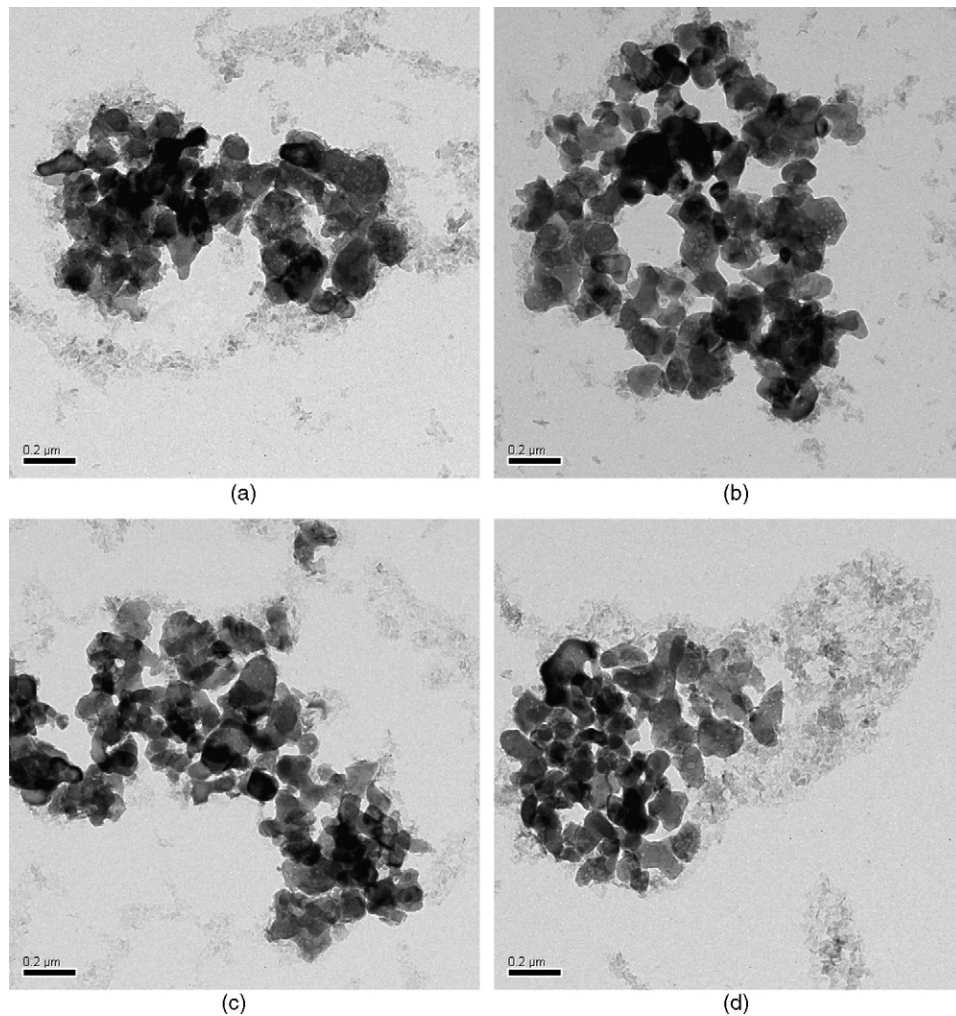


Fig. 4. The morphologies of the powder: (a) pure alumina and the mixed powder pre-aged at (b) pH = 1, (c) pH = 2, (d) pH = 3, (e) pH = 4, (f) pH = 5, and (g) pH = 6.

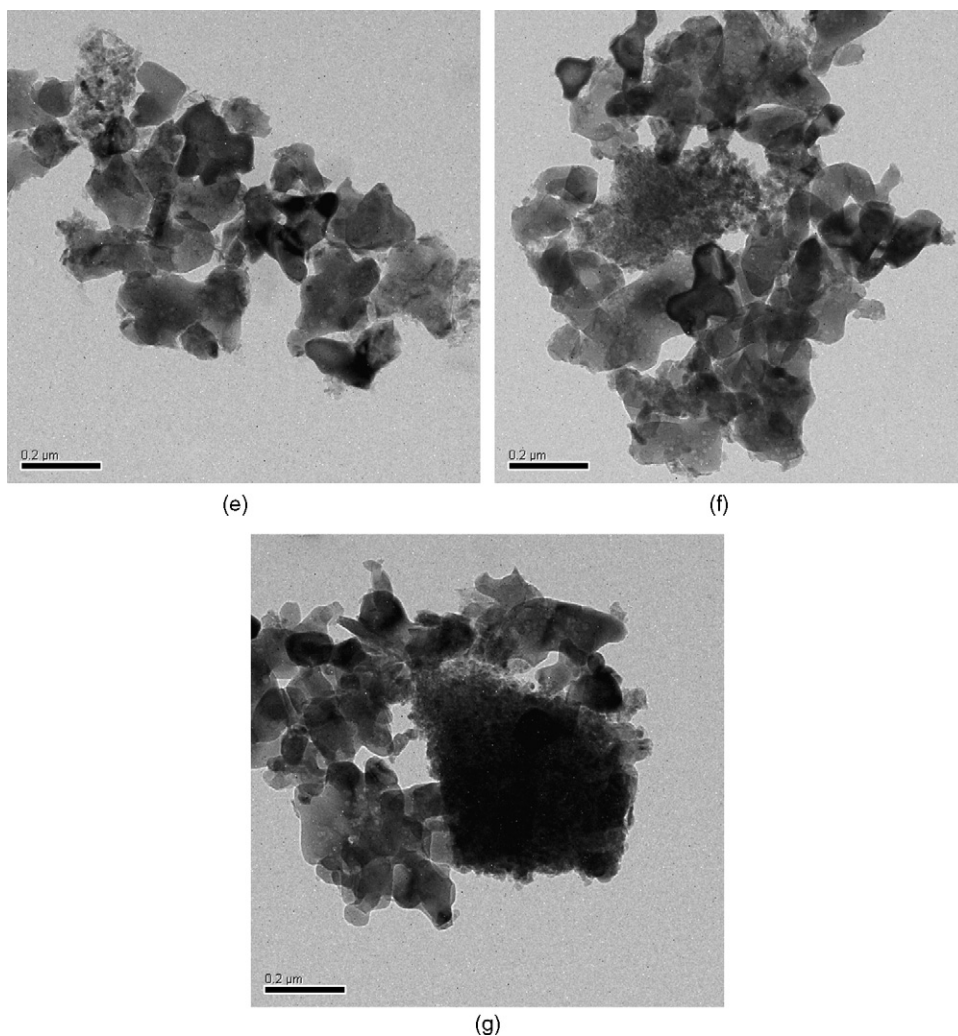


Fig. 4. (Continued).

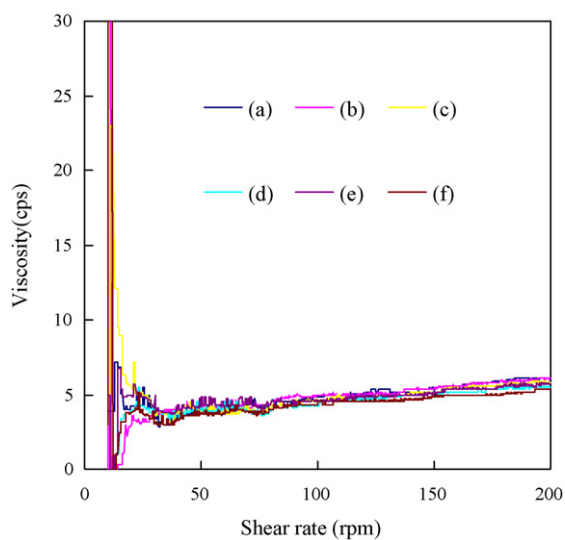


Fig. 5. The rheological properties of pure alumina slurry at different pre-aged processes: (a) pH = ~ 1 , (b) pH = $1 \rightarrow 4$, (c) pH = $1 \rightarrow 9$, (d) pH = ~ 2 , (e) pH = $2 \rightarrow 4$, and (f) pH = $2 \rightarrow 9$.

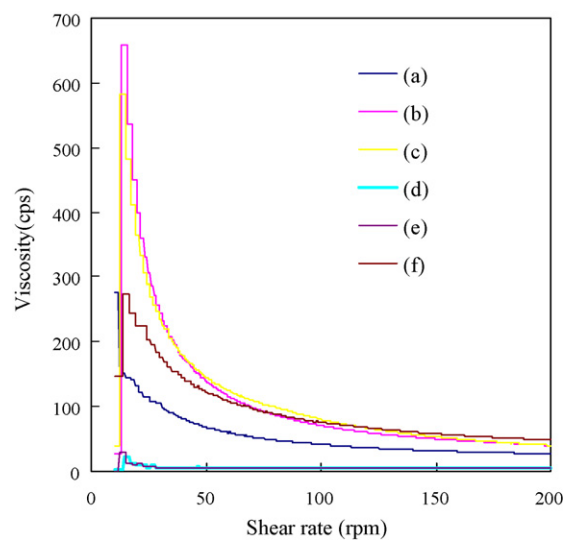


Fig. 6. The rheological properties of pure boehmite slurry at different pre-aged processes: (a) pH = ~ 1 , (b) pH = $1 \rightarrow 4$, (c) pH = $1 \rightarrow 9$, (d) pH = ~ 2 , (e) pH = $2 \rightarrow 4$, and (f) pH = $2 \rightarrow 9$.

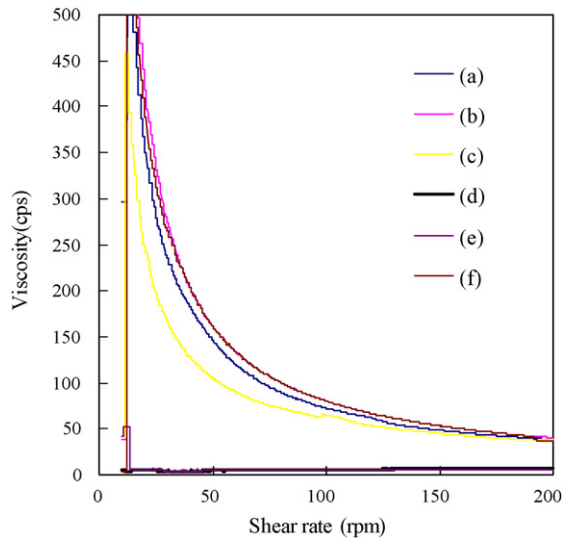


Fig. 7. The rheological properties of the mixed slurry at different pre-aged processes: (a) pH = ~ 1 , (b) pH = 1 \rightarrow 4, (c) pH = 1 \rightarrow 9, (d) pH = ~ 2 , (e) pH = 2 \rightarrow 4, and (f) pH = 2 \rightarrow 9.

process was at pH = 9–10, which is similar to the PZC of the boehmite slurry in the same process. From the results in Figs. 1–3, we can conclude that the boehmite was coated onto the alumina powder surface by adjusting the pre-aging pH value to less than 4.

The modified boehmite/N α -A slurry has the same PZC as the boehmite slurry. To understand the boehmite coating behavior on the alumina surface, the morphologies of the mixed slurry at different pre-aging pH values were observed, as shown in Fig. 4. The morphology of N α -A is shown in Fig. 4(a). The shape of the particles is irregular and the primary particle size is about 100–200 nm. Fig. 4(a) shows that the edges of the particles are clear. Fig. 4(b)–(g) are the morphologies of the

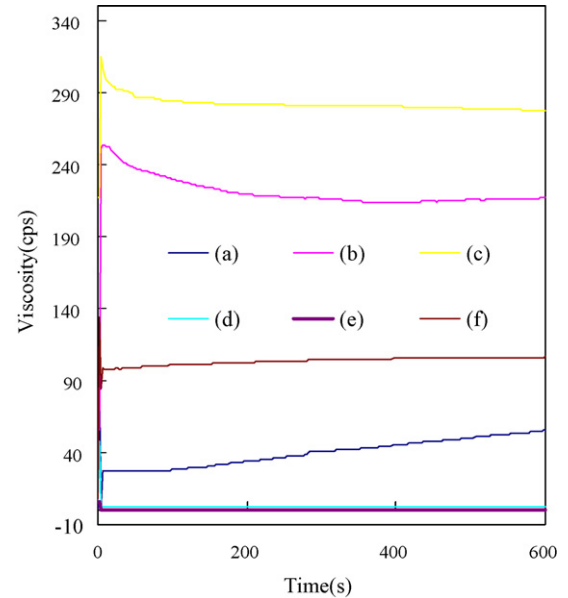


Fig. 9. The thixotropic properties of pure boehmite slurry at different pre-aged processes: (a) pH = ~ 1 , (b) pH = 1 \rightarrow 4, (c) pH = 1 \rightarrow 9, (d) pH = ~ 2 , (e) pH = 2 \rightarrow 4, and (f) pH = 2 \rightarrow 9.

mixed powder at pre-aged pH values: of 1–6, respectively. The smaller primary particles in Fig. 4(b)–(d) are boehmite. As the pre-aged pH value becomes less than 3, the alumina surface becomes coated with small particles of boehmite. This result agrees with the result of zeta potential measurement. The agglomerated boehmite particles mixed with the agglomerated alumina particles, but the boehmite cannot be validated as coating the alumina particle surfaces, as shown in Fig. 4(e)–(g). The boehmite is degraded to the final particle by decreasing the pH value of the mixed slurry. Modifying the mixed particles by pre-aging at pH = 1 produced a more complete and uniform mix than pre-aging at pH greater than 1 (i.e., the pre-aging

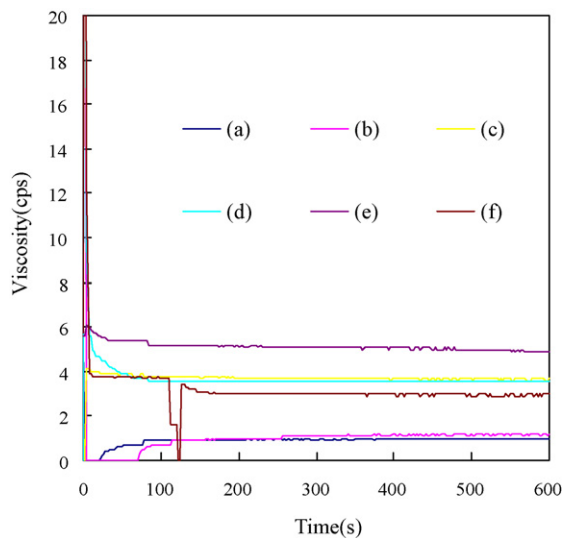


Fig. 8. The thixotropic properties of pure alumina slurry at different pre-aged processes: (a) pH = ~ 1 , (b) pH = 1 \rightarrow 4, (c) pH = 1 \rightarrow 9, (d) pH = ~ 2 , (e) pH = 2 \rightarrow 4, and (f) pH = 2 \rightarrow 9.

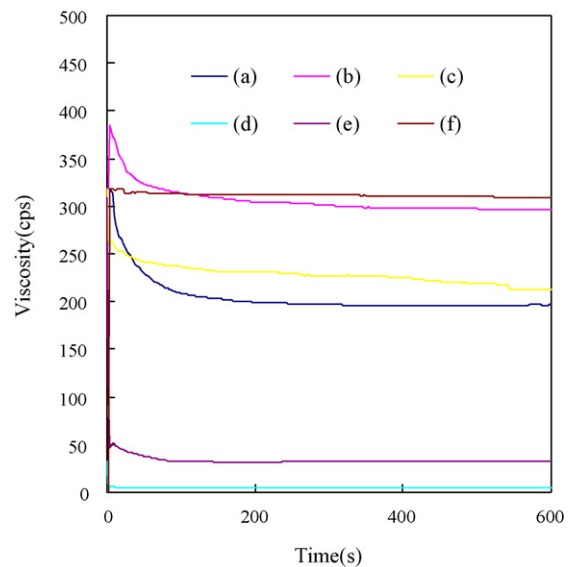


Fig. 10. The thixotropic property of the mixed slurry at different pre-aged processes: (a) pH = ~ 1 , (b) pH = 1 \rightarrow 4, (c) pH = 1 \rightarrow 9, (d) pH = ~ 2 , (e) pH = 2 \rightarrow 4, and (f) pH = 2 \rightarrow 9.

Table 1
Time dependent property of aged slurry

Aged condition	pH = ~ 1	pH = $1 \rightarrow 4$	pH = $1 \rightarrow 9$	pH = ~ 2	pH = $2 \rightarrow 4$	pH = $2 \rightarrow 9$
Alumina slurry	N	N	N	N	N	N
Boehmite slurry	A	T	S	N	N	S
Alumina with boehmite slurry	T	T	S	N	N	S

N: no thixotropic property (time independent); S: slight thixotropic property (slight time dependent); A: anti-thixotropic property (time dependent); T: thixotropic property (time dependent).

pH = 2, 3, 4, ..., respectively). Fig. 5 shows the rheological property of the $N\alpha$ -A slurry. The shear rate does not affect the viscosity of the $N\alpha$ -A slurry. Regardless of the pre-aging process used, the rheology of the slurry is near the Newtonian fluid property. The rheology of the pure boehmite slurries at different pre-aging processes are shown in Fig. 6. The slurry in the pH = 1, pH = $1 \rightarrow 4$, pH = $1 \rightarrow 9$, and pH = $2 \rightarrow 9$ processes exhibit shear thinner properties in which the viscosity decreases with increasing the shear rate. However, the pH = 2 and pH = $2 \rightarrow 4$ slurry processes were near the Newtonian fluid. The rheological properties of the mixed slurry are shown in Fig. 7. This result is similar to that of the boehmite slurry. After modification treatment, the mixed slurry exhibited the a-

like rheology of the boehmite slurry. This is evidence that the boehmite particles are coated onto the surface of the $N\alpha$ -A particles.

For further understanding the behavior of the boehmite slurry and the mixed slurry, the time dependence of the viscosity of these slurries were measured at a constant shear rate. Figs. 8–10 show the time dependent properties of the $N\alpha$ -A slurry, the boehmite and the mixed powder slurry, respectively, subjected to different aging processes. The results of Figs. 8–10 are summarized in Table 1. The $N\alpha$ -A slurries showed no significant thixotropy in all the aging processes, since the viscosity of the pure $N\alpha$ -A slurries does not change with time. The viscosity of boehmite slurries showed a slight

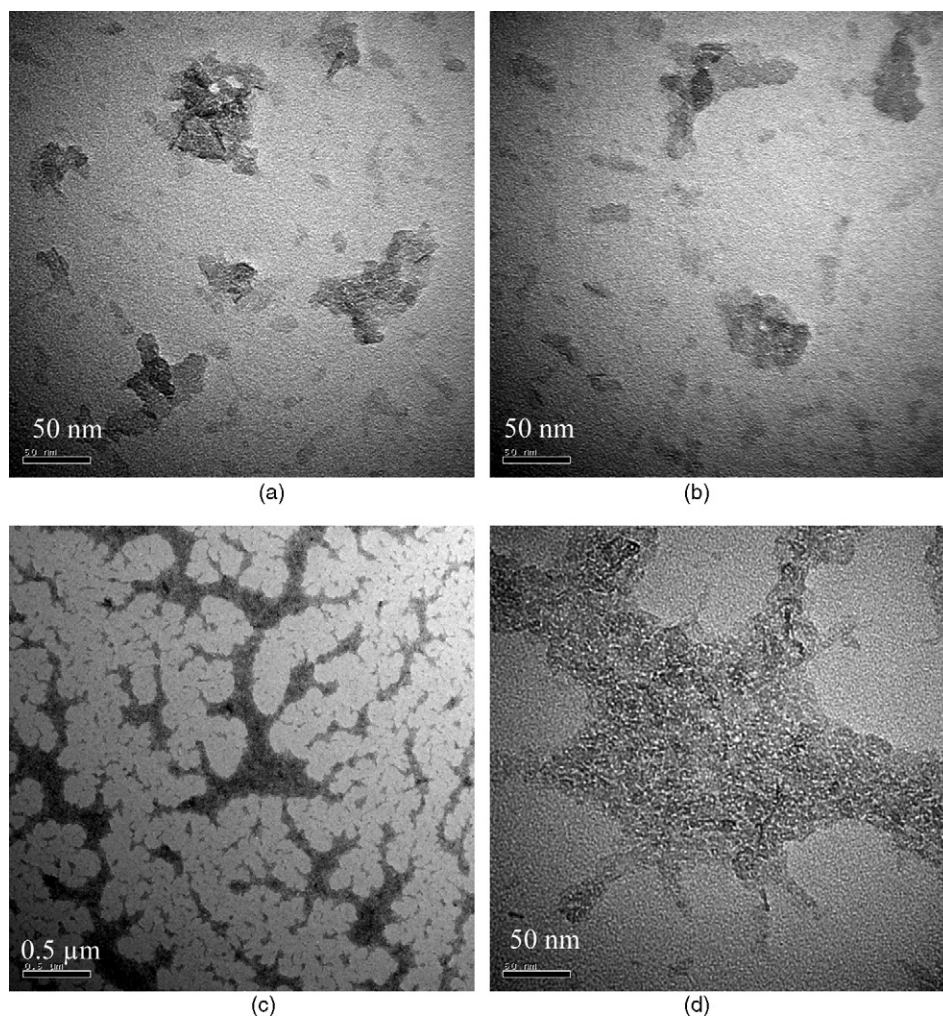


Fig. 11. The morphologies of boehmite: (a) pH = 3, (b) pH = 2, (c) pH = 1, and (d) magnified (c).

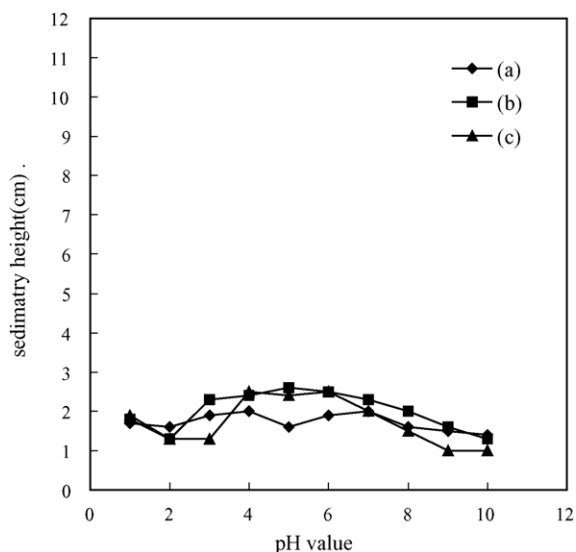


Fig. 12. The sedimentary height of the pure alumina slurry, pre-aged at: (a) pH = 1, (b) pH = 2, and (c) pH = 3.

increase with time as pre-aged at pH = 1; however, viscosity decreased with time when the slurry was pre-aged at pH = 1 → 4 and pH = 1 → 9. On the other hand, when pre-aged at pH = 2, the viscosity of the boehmite slurry shows a slight thixotropy as shown in Fig. 8(d)–(f).

The time dependence of viscosity of the N α -A with boehmite slurries is shown in Table 1. In addition, when comparing Figs. 9 and 10 with Figs. 6 and 7, the slurries (after a final adjustment to pH = 9) present only a slight thixotropy. The thixotropy of the Boehmite slurry and the mixed oxide slurry decreases as pH increases. The particles in these conditions are aggregates with small thixotropy. The suspension of the slurries aged at pH = 9 is poor. SEM of the boehmite particles at pH = 1, 2, and 3 (Fig. 11) show a decreasing Boehmite agglomerate size with decreasing pH. When decreasing the pH value, the agglomerate size of boehmite decreases. The primary boehmite particle becomes gel like, small and spherical at pH = 1. This is a very different morphology from the pH = 3 and 2 particles, as shown in Fig. 11.

Regardless of the pre-aging pH process used, the N α -A slurries settled throughout the pH range, as shown in Fig. 12. The sedimentary heights of the mixed powder slurry were higher than that for the N α -A slurry in the entire pH range, as shown in Fig. 13. The boehmite-modified slurry could disperse well in aqueous solutions. In addition, the slurry pre-aged at pH = 1 exhibited better suspension properties than the one pre-aged at pH = 2 and 3, as shown in Fig. 13. The slight sedimentation at pH > 9 is consistent with the results of the above discussion.

4. Conclusions

The modification process was performed by adding boehmite to N α -A slurry and adjusting the pH of the mixed

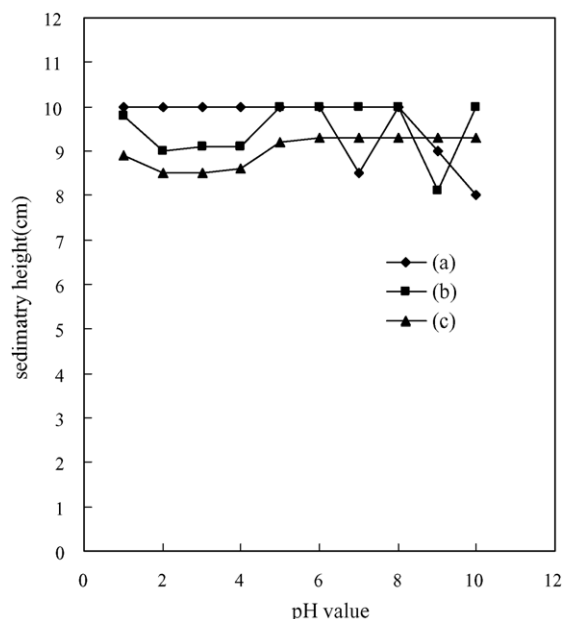


Fig. 13. The sedimentary height of the mixed powder slurry, pre-aged at: (a) pH = 1, (b) pH = 2, and (c) pH = 3.

slurry to less than 4. The rheological properties of the mixed slurry were also quite similar to those of the boehmite slurry after the coating process. The rheological properties of the mixed slurry and boehmite slurry were thixotropic if the pre-aging process was adjusted to pH = ~1. However, no thixotropy was exhibited if the pre-aging process was adjusted to pH = ~2. Boehmite degrades to a nano grade sol when the aging pH value decreased to pH = ~1. The N α -A slurry could be successfully suspended in aqueous solutions by adding boehmite and pre-aging at pH = 1.

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References

- [1] M.W. Wassermann, A.W. Meyer, Method for making water dispersible aluminum hydroxide, US patent 4010247, 1977.
- [2] A. Meyer, K. Noweck, A. Reichenauer, Process for the production of boehmite aluminas, US patent 5055019, 1991.
- [3] P.K. Hurlburt, D.T. Plummer, Method for making modified boehmite alumina, US patent 6224846, 2001.
- [4] R. Moreno, A. Salomoni, I. Stamenkovic, J. Eur. Ceram. Soc. 17 (1997) 327–331.
- [5] C.H. Schilling, C. Li, P. Tomasik, J.C. Kim, J. Eur. Ceram. Soc. 22 (2002) 923–931.
- [6] R.R. Rao, H.N. Roopa, T.S. Kammam, J. Eur. Ceram. Soc. 19 (1999) 2763–2771.
- [7] R.R. Rao, H.N. Roopa, T.S. Kannan, Ceram. Int. 25 (1999) 223–230.