Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 1227–1232

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microwave-assisted sol–gel synthesis of alpha alumina nanopowder and study of the rheological behavior

Leyla Sharifi[a,b,*], Maryam Beyhaghi[c,d], Touradj Ebadzadeh[b], Ebrahim Ghasemi[e]

[a]*Academic Center for Education, Culture and Research, Yazd Branch, Iran*

[b]*Ceramics Department, Materials and Energy Research Center, PO Box 14155-4777, Alborz, Iran*

[c]*Department of Materials Science and Metallurgical Engineering, Engineering Faculty, Ferdowsi University of Mashhad, P O Box 91775-1111, Mashhad, Iran*

[d]*Department of Metallurgical Engineering, Faculty of Engineering, Mashhad Branch, Islamic Azad University, Mashhad, Iran*

[e]*Institute for Color Science and Technology, PO Box 16765-654, Tehran, Iran*

Received 9 June 2012; received in revised form 12 July 2012; accepted 15 July 2012
Available online 10 August 2012

Abstract

In the present work, alpha alumina nanopowder was synthesized via a sol–gel route. After preparation of bohemite (AlOOH) sol, carbon black was added and the resultant sol was dried and calcined in microwave furnace for 10 min. XRD results showed that alpha alumina was the only crystalline phase with specific surface area, mean diameter and crystallite size of 51 $m^2 g^{-1}$, 100 and 25 nm, respectively. Rheological measurements revealed that the optimal content of Tiron at pH = 10 is 1 and 0.1 g per 100 g nano- and micron-alumina (1.5 $m^2 g^{-1}$), respectively. Furthermore, the optimum solid content of the slips was determined as 35–45 and 70 wt.% for nano- and micron-alumina, respectively.

Keywords: A. Microwave processing; A. Sol–gel processes; D. Alumina; D. Carbon

1. Introduction

Although alumina has been used in different industries for different applications since a long time ago, yet improving its specific surface area is a challenging research area [1,2]. Besides, nowadays nanostructured materials are considered one of the most attractive fields in science and technology [3]. Synthesis processes of nano alpha Al_2O_3 involve mechanical milling, vapor phase reaction, precipitation, sol–gel, hydrothermal and combustion methods. Mechanical synthesis of alpha Al_2O_3 needs extensive mechanical ball milling which easily introduces impurities. Vapor phase reaction method for production of fine alpha Al_2O_3 powder from a gas phase precursor requires high temperature above 1200 °C. The precipitation method has the obstacle of complexity and time consuming [4]. High temperature and pressure are needed for the direct formation of alpha Al_2O_3 via the hydrothermal method. The powder obtained from the combustion process is usually hard aggregated but contains nano-sized primary particles [5,6]. Sol–gel as a commonly used technique, involves the formation of an amorphous gel from a precursor solution. This method based on molecular precursors usually makes use of metal alkoxides as raw material [6]. Fabrication of high quality nanopowders is possible via this method. For complex powders, it achieves ultra-homogeneity of the several components on a molecular scale with lower preparation temperature which saves energy, cost and the ability to form unique composition [7]. Mirjalili et al. [6] synthesized nano alpha alumina particles with the finest particle size (20–30 nm) by the sol–gel method. They found that introduction of surfactant stabilizing agents and different stirring times would affect the size and shape of particles and the degree of aggregation. Sharbatdaran et al. [8] investigated the effects of utilization an aluminum alkoxide with a donor functionalized group, as a new precursor for the preparation of alumina by the sol–gel

*Corresponding author at: Academic Center for Education, Culture and Research, Yazd Branch, Iran. Tel.: +98 351 6292960; fax: +98 351 6292961.
E-mail address: sharifi.leila.jd@gmail.com (L. Sharifi).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.07.050

method. They achieved a novel morphology for the alumina prepared from aluminum alkoxide with donor-functionalized group. Among other methods for processing advance materials, microwave has found a new station [9]. If the material system is properly chosen, microwave processing has many advantages over conventional techniques [10]. Due to its different heating mechanism, microwave processing of materials is fundamentally different from the conventional processing. In a microwave oven, the heat is generated within the sample itself due to the interaction of micro-waves with the material [11]. In conventional heating, the heat is generated by heating elements and then it is transferred to the sample surface [9]. In spite of intense attractions towards nanotechnology, there is a basic limitation to gain new markets for nanometric-sized ceramic particles due to the effects of nanoparticle agglomeration during production or work. Powder agglomeration does not allow getting near-net-shape and crack-free green bodies with high green density. Most of the previous works have concentrated on the increase of the stability of slips in micrometer-sized ceramic powder during the development of short-range repulsive inter-particle forces by one of three methods: electrostatic, steric and electrosteric stabilization [3,12].

In this work, alpha alumina nano powders were synthesized via sol–gel route using microwave energy. The rheological behavior of slips prepared from synthesized nano powder was compared with a micron-sized alpha alumina powder.

2. Experimental procedure

2.1. Materials

Materials used in this work were aluminum nitrate ($Al(NO_3)\cdot 9H_2O$, Merck no. 595463, 99.9% purity), a micron-sized alumina powder (ZN-2O3, MARTOXID, 99.3% purity and with specific surface area of 1.5 $m^2\,g^{-1}$), Tiron ($C_6H_4Na_2O_8S_2$, BDH) used as a dispersant and carbon black (specific surface area of 106 $m^2\,g^{-1}$).

2.2. Synthesis of alumina nanopowder and characterization

Aluminum nitrate was dissolved in distilled water in the ratio 1:20 on a hot plate at 80 °C. The pH was fixed at 8 with ammonia and measured using a Metrohm pH meter instrument, model 691, Switzerland. Hydrolyzed aluminum nitrate aged for 24 h was separated from solution with a paper filter and washed with distilled water three times. Afterwards, nitric acid was added and condensation was fulfilled. A colloidal sol was achieved at pH 4. Then, 20 g carbon black was added to the sol containing 100 g primary aluminum nitrate. The mixture was heated at 100 °C to prepare a gel. Then, the gel was dried in oven at 120 °C. The calcination of dried gel was performed in a microwave furnace (2.45 GHz and 900 W) [13]. Finally, the residual carbon was removed by heating the resultant powder at 650 °C in a furnace. Phase identification of the synthesized products was examined using XRD. The microstructure and particle size of synthesized alumina nanopowder were evaluated using a TEM (FEG Philips CM 200) and Zeta Sizer (Malvern HSC1330–3000), respectively.

2.3. Slip preparation and rheological tests

In the first stage, some slips were prepared from the synthesized alumina nanopowders. The effect of pH on stability of the slips in different dispersant (Tiron) contents was investigated. For this purpose, the same slips were prepared in pH = 3, 7 and 10. Tiron content was in the range of 0–2 g per 100 g alumina. Alumina powder was added to the dissolved Tiron and the resultant was milled for 15 min.

In the second stage, two types of slips were prepared: N-slips prepared from alumina nanopowder synthesized in the current study, and M-slips prepared from micron-size alumina powder (ZN-203) and the rheological behavior of these two slips was investigated. There were two main purposes in this stage; first: optimization of the content of Tiron in M- and N-slips. For this purpose, the sedimentation tests were performed on M- and N-slips containing 50 and 35 wt.% solid, respectively, with different amounts of Tiron. Second: the investigation of the effect of solid content on the rheological behavior of slips. N- and M-slips were prepared using 25, 35, 45 and 50 wt.%, and 30, 50 and 80 wt.% nano- and micron-size alumina powder, respectively. Rheological studies were carried out on alumina slips containing 0.1 and 1 g Tiron per 100 g alumina for M- and N-slips at pH = 10 in which the best results of stabilization were observed and in a range of shear rates from 0.1 to 1000 s^{-1}. Sedimentation tests were performed using test tubes filled with 5 cm^3 of the slips and sedimentation height measurements were carried out after 24 h. The viscosity was measured using a rotational viscometer filled with 20 cm^3 of the slips in a range of shear rates from 0.1 to 1000 s^{-1}.

3. Results and discussion

3.1. Synthesis of alumina nanopowder

The product of hydrolysis of aluminum nitrate at pH = 8 up to 80 °C was aged for 24 h. The XRD pattern of sedimentation product in Fig. 1 shows the presence of bohemite (AlOOH). Fig. 2 demonstrates the variation of zeta potential of bohemite versus pH in aqueous media. As it can be seen, the zeta potential and repulsive force between bohemite particles are maximum at pH = 4, then sols were prepared at this pH. Fig. 3 shows the effect of microwave heating times on the formation of different phases. After 4 min of heating, the nucleation of γ-alumina occurred and with increasing heating time to 6 min, the growth of γ-alumina proceeded. The combination of α- and γ-alumina was detected in powder calcined for

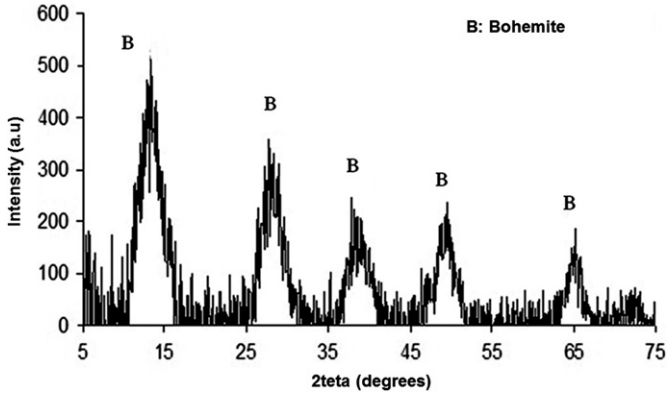

Fig. 1. XRD pattern of the white sediment produced by hydrolysis of aluminum nitrate in pH = 8 and 80 °C.

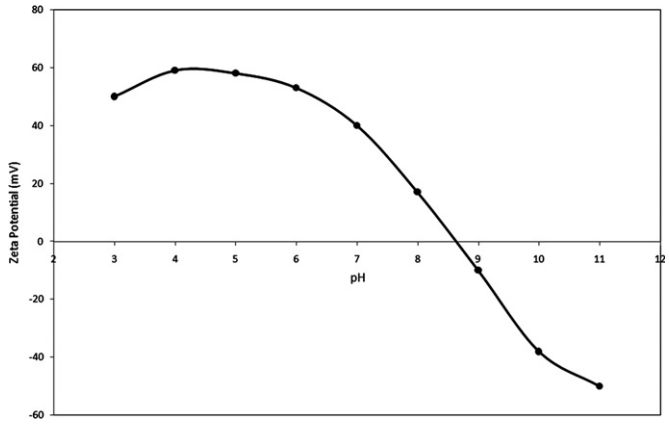

Fig. 2. Variation of zeta potential of Bohemite versus pH in aqueous media.

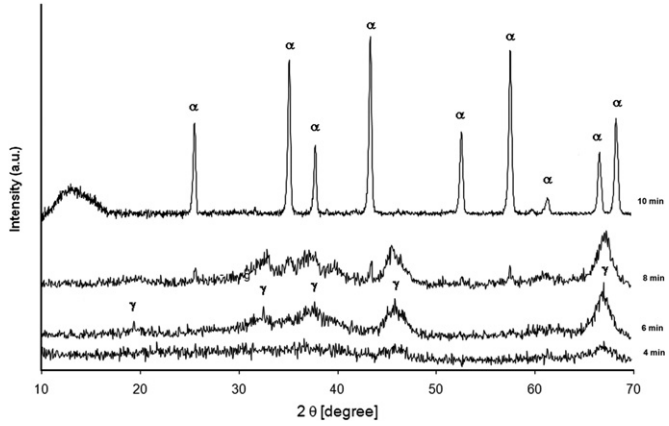

Fig. 3. XRD patterns of formed phases in different microwave heating times.

8 min. After 10 min of heating, α-alumina was the only crystalline phase with crystallite size of about 25 nm (according to Scherrer equation). The size distribution of alumina powder calcined in microwave for 10 min was measured by zeta sizer and the results are shown in Fig. 4. From this figure, alumina powder has the mean particle

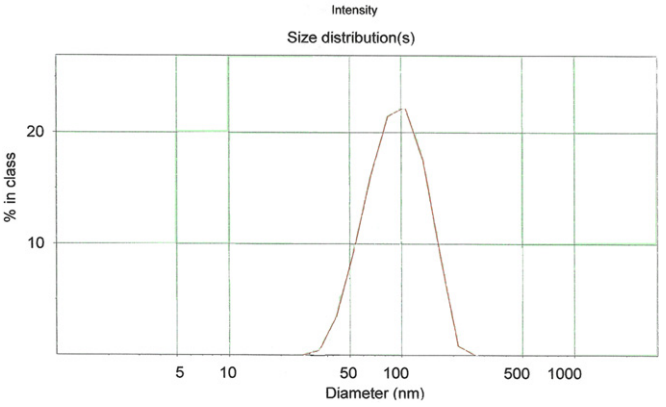

Fig. 4. Size distribution of alumina particles calcined in microwave for 10 min.

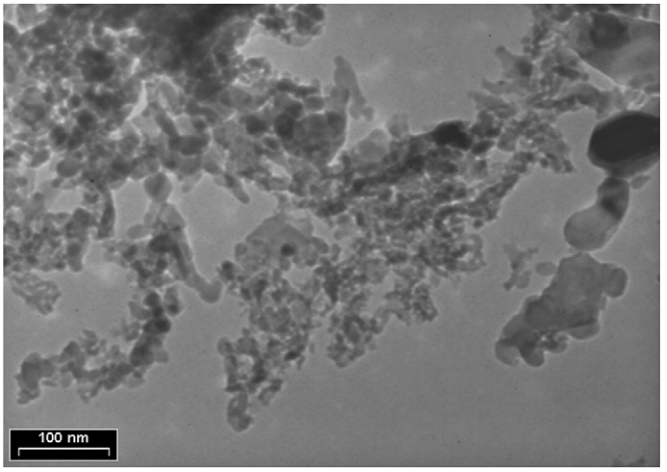

Fig. 5. TEM image of α-alumina formed by heating for 10 min in microwave.

size about 100 nm confirmed by TEM studies which is shown in Fig. 5.

3.2. Slip characterization

The surface electrical charge of alumina particles in water is positive. Dissociation of surface groups of Tiron in water increases the negative charges. When Tiron is added, it is adsorbed on the alumina particle surface in slips and the magnitude and sign of surface charge is changed [12].

To investigate the effect of dispersant and pH on slip stability, slips containing 35 wt.% of nano alumina with different amounts of Tiron at pH = 3, 7 and 10 were prepared. A well-dispersed slip can be obtained with a high surface charge density to generate strong repulsive forces [13]. Refer to Fig. 6, the slip containing 1–1.2 g Tiron per 100 g alumina at pH = 10 has a minimum height of sediment and shows the maximum stability. The above results clearly show that the alumina slip creates a good dispersion at alkaline pH due to the negatively charged groups of Tiron adsorbed on surface of alumina particles.

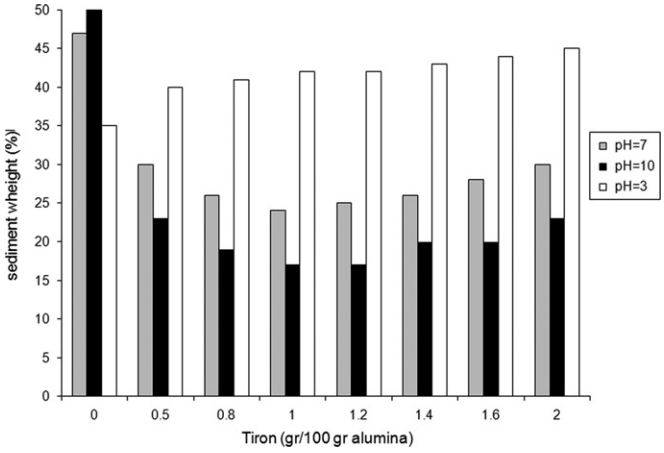

Fig. 6. Sediment height of synthesized alumina slips versus Tiron content in different pHs.

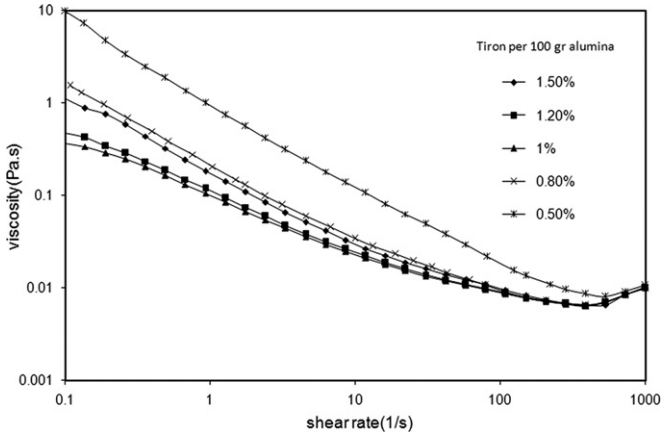

Fig. 7. The effect of Tiron g per 100 g alumina on viscosity of N-slips.

The sedimentation height increased by reducing the Tiron content less than optimal. This is because the dispersant could not cover the surface of alumina particles when it is less than optimal and due to the predominant van der Waals attraction, flocculation occurred. If the amount of Tiron is more than 1.2 g per 100 g alumina, the excess dispersant is not absorbed on the surface of particles and so entered in the liquid media. The increase of the ionic strength will tend to contract the electrical double layer around alumina particles. In these cases, the amount of Tiron is not in optimal range and the stability of slips decreases, and subsequently increases the sedimentation height.

As it can be observed in Fig. 6, the stability of slips prepared from nano alumina containing Tiron in acidic conditions decreases and the sediment height increases. In acidic conditions, Tiron negative charged groups were adsorbed on the surface of alumina particles and decreased the resultant zeta potential. Furthermore, it can be observed that in basic conditions the stability of alumina slips containing Tiron improves. The active surface groups of Tiron are dissociated completely at alkaline pH and adsorbed on the surface of alumina particles. In this case, the zeta potential increases and subsequently the sediment height decreases.

3.2.1. Effect of Tiron content on rheological behavior

The viscosity of the slips as a function of shear rate and added Tiron at pH = 10 is shown in Figs. 7 and 8 for N- and M-slips. It is obvious that the optimal Tiron content is 1 and 0.1 g per 100 g alumina for N- and M-slips, respectively. The viscosity results of N-slips are in good agreement with sedimentation test results shown in Fig. 6. In both M- and N-slips the sediment height increased as the optimum Tiron content was changed. The optimum Tiron content was different in M-and N-slips due to the differences in specific surface area of alumina powders. The requisite amount of Tiron increased with increasing the specific surface area, since more Tiron is absorbed at the surface of particles. There is a

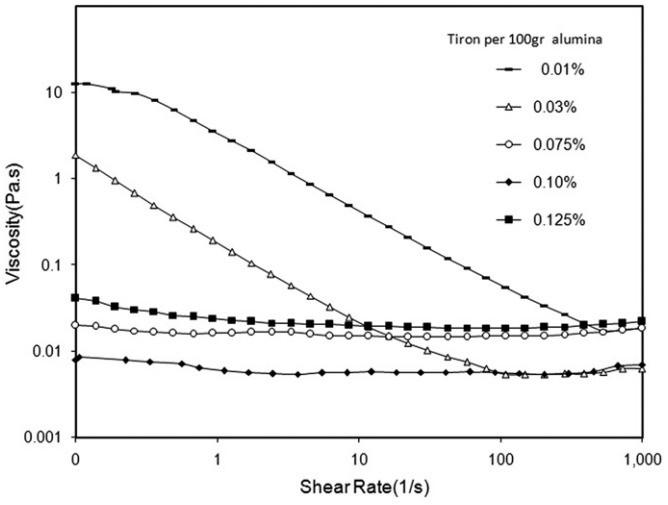

Fig. 8. The effect of Tiron g per 100 g alumina on viscosity of M-slips.

good agreement between viscometry and sedimentation test results and so in the optimum Tiron content.

3.2.2. Effect of solid content on rheological behavior

Results of rheological tests on M- and N-slips containing different amounts of alumina are shown in Figs. 9 and 10. M-slips containing 30 wt.% alumina show Newtonian behavior because of low solid concentration. In this case, since the distance between particles increases, the van der Waals bonds weaken and therefore, the viscosity does not change significantly with changing shear rate. As expected, the viscosity of slips increases with the increase of solid concentration. Also, the pseudoplastic behavior is observed at low shear rates. With increasing shear rate, Newtonian behavior dominates. The rheological behavior of M-slip containing 80 wt.% alumina in high shear rates is dilatancy, since in these shear rates, the slip layer movements are impossible and so the particle interactions cause perturbations [14]. To have a good quality slip casting, the viscosity should be in the

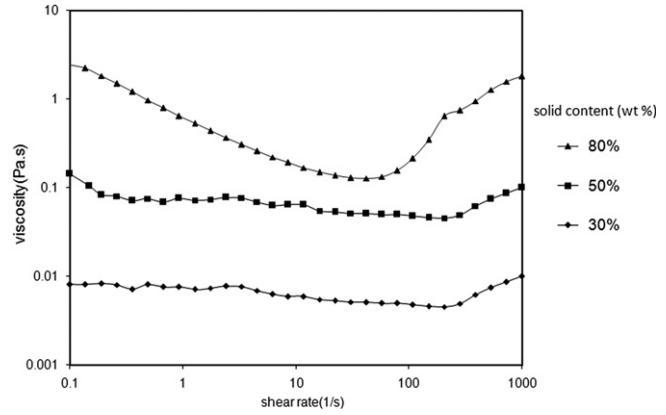

Fig. 9. The effect of shear rate on viscosity of M-slips on different solid contents.

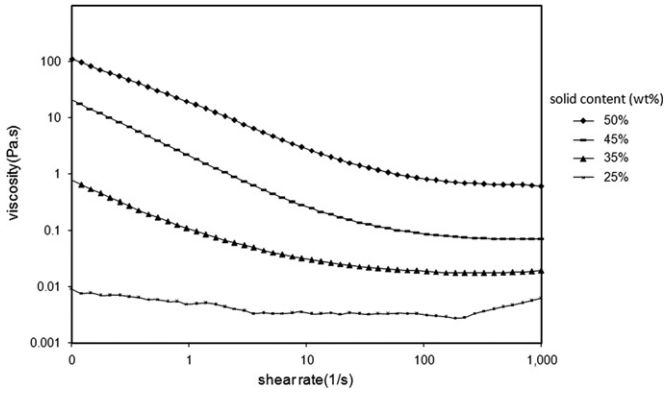

Fig. 10. The effect of shear rate on viscosity of N-slips on different solid contents.

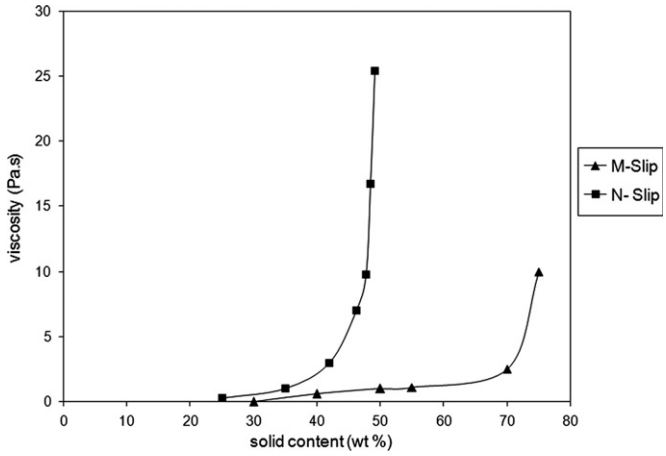

Fig. 11. The variation of viscosity of M- and N-slips versus solid content in shear rate of 1 S^{-1}.

range of 1–10 Pa S at shear rate of 1 S^{-1} [15]. The variation of viscosity of both M- and N-slips versus solid content is represented in Fig. 11. On the basis of this statement, the optimum solid content is 35–45 wt.% for N-slips and 70 wt.% for M-slips. The viscosity of slips increases by increasing the concentration of solids. In this case, the electrical double layers overlap due to the increase of particle interactions and the domination of van der Waals attraction. At the same concentration of solids, N-slip has more viscosity than M-slip, because nano particles in N-slip have more specific area than micron particles in M-slip.

4. Conclusions

In this work, alpha alumina nanopowder was synthesized via sol–gel route. The heat treatment of dried gel was performed with microwave energy. The specifications of alpha alumina achieved in this study were as follows: specific surface area of 51 $m^2 g^{-1}$, mean diameter of 100 nm and crystallite size of 25 nm. The dispersability of Tiron ($C_6H_4O_8S_2Na_2 \cdot H_2O$) in slips containing nanopowder of alumina at different pHs was studied. It was shown that the optimum Tiron content was 1 g per 100 g nano alumina in basic conditions. For comparison, some slips were also prepared with a micron size alumina. In order to obtain a successful slip casting, the optimum Tiron and solid content for micron-size alumina were found to be less and more than those for nano-size alumina, respectively, due to differences in specific surface area of alumina particles in slips.

References

[1] Q. Sun, Y. Zheng, Y. Zheng, Y. Xiao, Guohui Cai, K. Wei, Synthesis of highly thermally stable lanthanum-doped ordered mesoporous alumina, Scripta Materialia 65 (2011) 1026–1029.
[2] H. Barzegar-Bafrooei, T. Ebadzadeh, Synthesis of nanocomposite powders of gamma-alumina-carbon nanotube by sol–gel method, Advanced Powder Technology 22 (2011) 366–369.
[3] C.H. Schilling, M. Sikora, P. Tomasik, C. Li, V. Garcia, Rheology of alumina–nanoparticle suspensions: effects of lower saccharides and sugar alcohols, Journal of the European Ceramic Society 22 (2002) 917–921.
[4] S.A. Hassanzadeh-Tabrizi, E. Taheri-Nassaj, Sol–gel synthesis and characterization of Al_2O_3–CeO_2 composite nanopowder, Journal of Alloys and Compounds 494 (2010) 289–294.
[5] M.G. Ma, Y.J. Zhu, Z.L. Xu, A new route to synthesis of gamma alumina nanorods, Materials Letters 61 (2007) 1812–1815.
[6] F. Mirjalili, M. Hasmaliza, L.C. Abdullah, Size-controlled synthesis of nano a-alumina particles through the sol–gel method, Ceramics International 36 (2010) 1253–1257.
[7] Y.K. Park, Z.E.H. Tadd, Melissa, R. Tannenbaum, Size-controlled synthesis of alumina nanoparticles from aluminum alkoxides, Materials Research Bulletin 40 (2005) 1506–1512.
[8] M. Sharbatdaran, M.M. Amini, A. Majdabadi, Effect of aluminium alkoxide with donor-functionalized group on texture and morphology of the alumina prepared by sol–gel processing, Materials Letters 64 (2010) 503–505.
[9] K. Tahmasebi, M.H. Paydar, Microwave assisted solution combustion synthesis of alumina–zirconia, ZTA, nanocomposite powder, Journal of Alloys and Compounds 509 (2011) 1192–1196.
[10] C.Y. Fang, C. Wang, A.V. Polotai, D.K. Agrawal, M.T. Lanagan, Microwave synthesis of nano-sized barium titanate, Materials Letters 62 (2008) 2551–2553.
[11] T. Ebadzadeh, M.H. Sarrafi, E. Salahi, Microwave-assisted synthesis and sintering of mullite, Ceramics International 35 (2009) 3175–3179.

[12] C. Falamaki, M. Beyhaghi, A thorough study of the slip casting process for the manufacture of tubular alumina microfiltration membranes, J. Mater. Sci.—Poland 27 (2009) 427–441.
[13] T. Ebadzadeh, L. Sharifi, Synthesis of τ-Al_2O_3 from a mixture of aluminum nitrate and carboxymethyl cellulose, Journal of the American Ceramic Society 91 (10) (2008) 3408–3409.
[14] A.G. Dobrovolskiy, Development of slip molding methods, Ceramurgia Int. 3–4 (1977) 159–163.
[15] L. Sharifi, Investigation of Rheological Behavior for Nano Alumina Slips, M.Sc. Thesis, Under Supervision of Dr. T. Ebadzadeh and Dr. B. Raisi Dehkordi, Ceramics Department, Materials and Energy Research Center (MERC), 2008.