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Gelcasting of alumina using urea-formaldehyde

I. Preparation of concentrated aqueous slurries by particle treatment with hydrolysed aluminium

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Abstract

A treatment of α-alumina with hydrolysed aluminium (HA), generated in situ by homogenous hydrolysis of aqueous aluminium nitrate solution using hexamethylene tetramine (HMTA), has been evolved to enhance the surface activity of the powder towards complexation with H^+ and thus to promote dispersion of its aqueous concentrated (>50 vol%) slurries using a mineral acid (nitric acid) with a view to prepare slurries having high solids loading and low viscosity for gelcasting. Viscosity minimum of the slurries was obtained at HA minimum (Al^{3+} added in the system)$\sim 6\times10^{-6}$ mol/m^2 (BET surface area) of the powder. Slurries of solids loading >60 vol% having viscosity <1 Pa s at 93 s^{-1} could be prepared by HA treatment of α-aluminas of median particle size 0.3–0.8 μm to obtain green bodies with relative density of 65–71% by evaporational drying. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

The significant increase in demand for ceramic components during the last decade for applications such as heat engine technology has intensified research into fabrication of complex shapes from fine powder assemblies. ‘Gelcasting’ using aqueous/non-aqueous ceramic slurries is a recent development to this end which has shown several advantages over widely used injection moulding process using ceramic powder–polymer blends [1–4]. In this process strong, machinable near-net-shape green parts with binder loading <10 wt% are fabricated using aqueous/non-aqueous ceramic slurries by means of in-situ polymerisation of organic monomers and setting the slurry in a mold.

An aqueous gelcasting system is preferred to a non-aqueous system since use of water as solvent brings gelcasting closer to traditional ceramic processing, makes drying easier and avoids environmental problems associated with disposal of spent organic solvents. In the conventional process, aqueous systems are dispersed using polyacrylate dispersants at pH ∼9 and gelation is accomplished by free radical initiated polymerisation of certain acrylic monomers added in the system. Aqueous ceramic slurries in acidic medium, on the other hand, provide possibilities for using inexpensive monomers such as methylolureas (derived by reacting urea with formaldehyde) which undergo polymerisation and cross-linking under acidic conditions [5]. Also, mineral acids have been widely used for preparation of aqueous dispersions of alumina [6]. This has led us to probe into the possibility of developing an alternative aqueous gelcasting system for alumina ceramics.

Gelcasting system generally requires well dispersed concentrated (>55 vol%) ceramic slurries having viscosity less than 1 Pa s. However, dispersion using mineral acids often does not yield satisfactory and reliable results since the dispersion mechanism (electrostatic stabilization) is governed by the surface charge density which vary with the surface chemistry of the powders [7,8]. Moreover, development of high surface charge density should be assured to promote dispersion of concentrated slurries in contrast to dilute suspensions since particle repulsion necessary to provide stabilization of dispersions increases with solids loading [9].

In this paper we report a procedure for treatment of α-alumina surfaces using hydrolysed aluminium to enhance H^+ adsorption capacity of the powders and improve dispersion of concentrated (>50 vol%) aqueous slurries with an aim to use them for gelcasting.

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2. Experimental

Three α-Al_2O_3 powders (Table 1) were investigated in this study. Hydrolysed aluminium (HA) was generated by hydrolysis of aluminium nitrate [E. Merck (India) Ltd., India] using hexamethylenetetramine (HMTA) (Fluka AG, Switzerland) as base generator.

Treatment of alumina powders using HA generated in situ was carried out as following: a thick aqueous slurry (80 wt%) of the powders mixed with appropriate amount of the aluminium salt and stoichiometric amount of HMTA was tumbled along with zirconia balls in a polyethylene bottle for about 12 h. The resulting mix on attaining pH 5 (~36 h) was aged for another 24 h after adjusting the pH to 4 using nitric acid. The treated powder was separated centrifugally, washed several times with distilled water and dried in an air oven at temperatures below 80°C. As-received alumina powders used for comparison were also subjected to above operations without adding aluminium nitrate and HMTA.

A relative measure of surface activity towards complexation with H^+ of as-received and HA-treated alumina powders was carried out following a titration method described by Whitman and Feke [10] for Silicon carbide and nitride powders. Accordingly an aqueous suspension of alumina (5 wt%) at pH 3 was titrated with a base to pH 8 (near to pzc of alumina) and also taking equivalent volume of the suspension medium as reference solution. The difference between the amounts of titrant necessary to produce the same pH value in the suspension and the reference solution is attributed to desorption of protons complexed with surface sites of the particles.

Flow point of the powders was measured following the method described by Okomoto et al. [11]. Accordingly distilled water at pH 2 was added dropwise from a burette to the powder (20 g) while stirring the contents using a plastic rod. The minimum amount of water at which the slurry starts to flow was read as flow point.

Aqueous alumina slurries of desired concentrations were prepared by adding weighed amount of alumina in measured quantities of distilled water with stirring mechanically and adjusting the pH to 4 using nitric acid. Viscosity measurements of slurries were taken in a Brookfield Synchro-Lectic Viscometer (RVT/HBT model) using small sample adapter (SC4-21/13R) of coaxial cylinder geometry, employing a shear rate in the range 4.65 to 93 s^{-1}. Cylindrical green compacts (10 mm dia and 25 mm long) were prepared by casting concentrated slurries (~58 vol%) in PTFE molds and drying first at ambient conditions to enable ejection of the sample from the mold and then at 120°C for 2 h in an air oven. The density of the compacts were calculated from the volume measured by mercury displacement method.

3. Results and discussion

It has been established that homogenous hydrolysis of aluminium in aqueous solutions at low concentrations proceeds through generation of polynuclear cations of oligomeric nature [12]. These primary species, Al_{13} ions, $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$, and its subunits, possess high polyelectrolyte character or charge carrying capacity compared to their compact and condensed structures like boehmite sols. Their coatings onto alumina surfaces, therefore, is expected to provide uniform and enhanced surface activity to the powders and promote dispersion of their concentrated slurries.

The results of a relative measure of surface activity of alumina powders, untreated and HA treated, towards complexation with H^+ are given in Table 2. It can be seen that the untreated powders showed different H^+ adsorption values, lowest for MR-04 and highest for AKP-15, according to the purity of the powder. However, HA treatment enhanced the surface activity of all the powders to a close range suggesting that the treatment is effective to evolve uniform and enhanced surface activity to different grades of alumina powders by suppressing the effect of surface heterogeneity.

The effect of HA treatment on dispersion of alumina powders in aqueous medium is readily evident from their flow point values and density of green compacts prepared by evaporational drying of concentrated (~58 vol%) slurries (Table 2). Improvement in dispersion by the treatment resulted in increase of solids loading limit at flow point by 4.5–7.7 vol% and increase in the density of the green compacts by 4.4–5.6%.

The slurries of HA-treated powders showed viscosity minimum at pH 4–4.5 in the acidic range as for α-alumina

Table 1
Characteristics of alumina powders

Powder designation	Al_2O_3 content (%)	Median particle size (μm)	Surface area (BET) (m^2/g)	Density (g/cm^3)
MR-04[a]	98.9	0.79	6.23	3.83
AKP-15[b]	>99.9	0.63	3.70	3.94
A16SG[c]	99.8	0.34	10.80	3.91

[a] Indian Aluminium Company, Belgaum, India.
[b] Sumitomo Corporation, Tokyo, Japan.
[c] ACC, Alcoa Limited, Bombay, India.

powders, but showed significant reduction in the viscosity values compared to their untreated counterparts depending on the extent of treatment as shown in Fig. 1. The viscosity decreased with HA concentration and attained a minimum at concentrations of 3.7×10^{-5} and 2.2×10^{-5} mol/g, respectively, for MR-04 and AKP-15. These values were found related to the surface area (BET) of the powders that HA per unit surface area was more or less identical ($\sim6\times10^{-6}$ mol/m^2) for both the powders. It may be inferred that a continuous coating of HA onto the particles take place at this concentration level to impart more or less identical H^+ adsorption capacity to the powders as already seen.

In contrast to systems using polyacrylate dispersants, addition of HA in excess than required for observing viscosity minimum did not have any significant effect on viscosity. It appears that adsorption of HA onto alumina surfaces above a critical amount or thickness is not favoured in the present experimental conditions. Estimation of aluminum in the washings has shown that the amount of HA retained with the powder is only $\sim4\times10^{-6}$ mol/m^2.

Table 2
Effect of HA treatment of alumina on H^+ adsorption capacity, flow point value of powders and density of green compacts using concentrated slurries

Powder designation	H^+ adsorption capacity ($\times10^{-6}$ mol/m^2)	Solids loading at flow point (vol%)	Green body density (% T.D.)
MR-04	3.21 (2.12)[a]	60.5 (57.9)	66.1 (62.5)
AKP-15	3.24 (2.97)	62.1 (60.6)	71.1 (68.1)
Al6SG	3.37 (2.39)	62.2 (57.4)	65.3 (62.8)

[a] The values given in the parentheses are for the untreated powders.

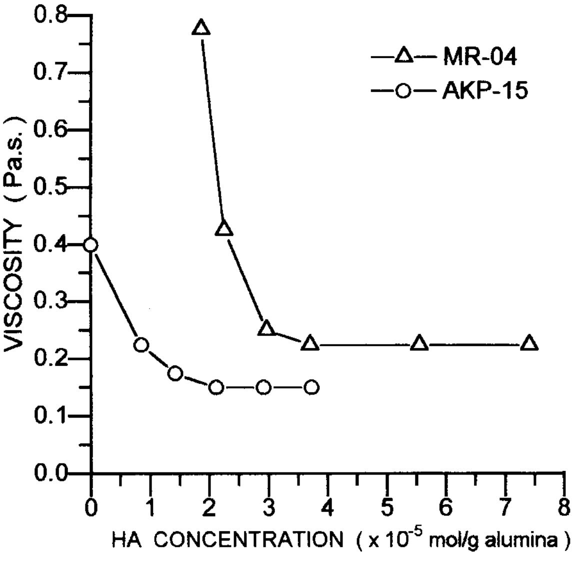

Fig. 1. Effect of HA concentration on viscosity of aqueous alumina slurries (pH 4, shear rate 9.3 s^{-1}).

Fig. 2 shows the change in viscosity with slurry concentration of untreated and HA-treated powders. Slurries of the treated aluminas showed lower viscosities than of its untreated counterparts which was found more pronounced with increase in solids loading, clearly suggesting that the enhanced surface activity of the powders obtained by the treatment provides higher particle repulsion necessary to promote dispersion of highly concentrated slurries.

The slurries in general exhibited shear thinning flow characteristics (Fig. 3) which became more pronounced at high solids loading. However, slurries of all the powders showed transition from shear thinning to dilatant

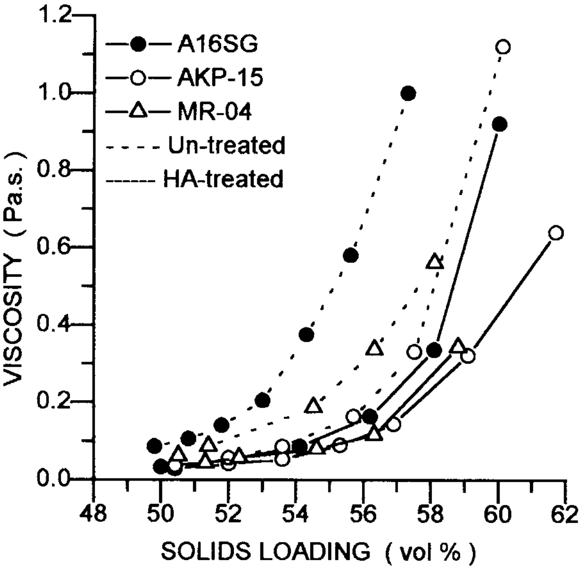

Fig. 2. Effect of solids loading on viscosity of untreated and HA-treated aqueous alumina slurries (pH 4, shear rate 93 s^{-1}).

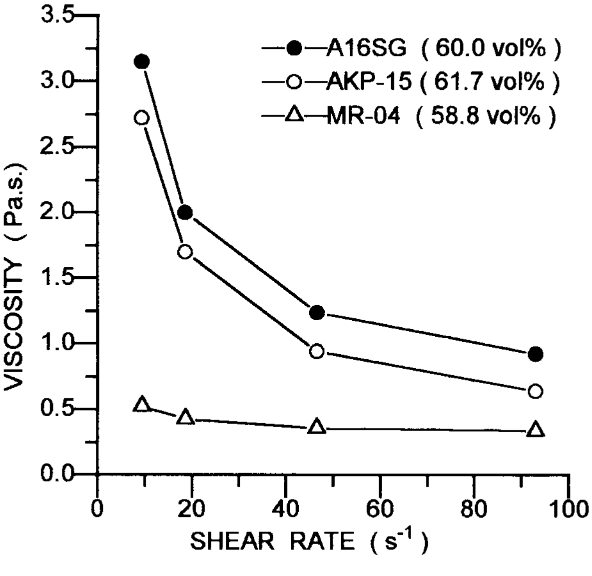

Fig. 3. Viscosity versus shear rate for HA-treated highly concentrated aqueous alumina slurries.

as solids loading nearing the flow point limit. The maximum solids loadings at which reproducible values of viscosities could be measured of MR-04, A16SG and AKP-15 were 58.8, 60 and 61.7 vol%, respectively, and the viscosities measured at 93 s^{-1} were 345, 920 and 640 mPa s, respectively, which are well within the requirement of slurries for gelcasting.

4. Conclusions

Treatment of α-alumina powders with hydrolysed aluminium (HA), generated in situ by homogenous hydrolysis of aluminium nitrate in aqueous medium using stoichiometric amount of hexamethylenetetramine (HMTA), not only enhanced the surface activity of the powders towards complexation with H^+ but also rendered uniform surface activity to powders which showed different surface activity in their as-received state. The enhanced surface activity of the powders promoted dispersion of their concentrated (> 50 vol%) aqueous slurries using nitric acid as evidenced by reduction in viscosity and enhanced density of green bodies. Optimum results were obtained at HA concentration minimum (in terms of Al^{3+} added in the reaction system) $\sim 6\times 10^{-6}$ mol/m^2 and at pH 4–4.5 of the slurries. As a result of the treatment, slurries having viscosities < 1 Pa s at 93 s^{-1} at solids loading > 58 vol% were possible using aluminas having median particle size 0.3–0.8 μm to prepare green bodies with relative density in the range 65–71%.

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