G Model
JASCER-283; No. of Pages 5
ARTICLE IN PRESS
Journal of Asian Ceramic Societies xxx (2017) xxx–xxx
Contents lists available at ScienceDirect
Journal of Asian Ceramic Societies
journal homepage: www.elsevier.com/locate/jascer

Effect of TMAH on the rheological behavior of alumina slurries for gelcasting

Jian Zhang[a], Yi Sun[a,b,*], Shunzo Shimai[a,c], Xiang Peng[a,b], Jin Zhao[a,b], Guohong Zhou[a], Shiwei Wang[a,*]

[a] *The State Key Laboratory on High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Tokyo University of Agriculture and Technology, Tokyo 183-8538, Japan*

ARTICLE INFO

Article history:
Received 25 January 2017
Received in revised form 28 April 2017
Accepted 11 May 2017
Available online xxx

Keywords:
Gelcasting
Slurry
Hydrolysis enhancement
Hydrophobic modification
Shear-thickening behavior delay

ABSTRACT

Tetramethyl ammonium hydroxide (TMAH) has been demonstrated to increase solids loading effectively and to accelerate gelling rate of alumina slurries gelled by Isobam (a copolymer of isobutylene and maleic anhydride) system. With 0.5 vol% addition of TMAH, solids loading of alumina slurry was increased from 56 vol% to 58 vol%. Meanwhile, storage modulus (G') of the slurry with 56 vol% solids loading was increased from 964 Pa to 2850 Pa at a testing time of 30 min. The enhanced dispersing and gelling behavior was ascribed to the hydrolysis and hydrophobic modification of Isobam by TMAH. Flexural strength of the final alumina ceramics from 58 vol% solids loading was 543 ± 10 MPa, higher than that of the ceramics from 56 vol% solids loading (531 ± 13 MPa).

1. Introduction

Gelcasting as a near-net shaping method is suitable for fabricating large-sized or complex-shaped ceramic green bodies with homogeneous microstructure and sufficient strength for machining [1,2]. Up to now, many gelcasting systems have been developed to manufacture ceramics [3–6]. The prerequisite of gelcasting is to prepare a stable slurry with as high solids loading as possible by less organic addition, which results in high density of green bodies, low organic-burning exhaust, and excellent properties of ceramics. Generally, solids loading of a slurry is influenced by gelling system [7,8], dispersant [9], and pH [10,11].

Recently, Yang et al. reported a new gelling system that it can spontaneously gel at room temperature in air via a copolymer of isobutylene and maleic anhydride with a molecular weight of 55,000–65,000 (commercial name Isobam104) [12]. The copolymer contains three functional groups, i.e. –$COONH_4$, –$CONH_2$, and maleic anhydride in a structural unit. With one tenth molecular weight of Isobam104 and two –$COONH_4$ groups, one maleic anhydride group in a structural unit, Isobam600AF was found effectively to improve solids loading of alumina slurry from 50 vol% up to 56 vol% by partially replacing Isobam104 [13]. Actually, polyacrylate with carboxylic acid groups (–COO^- and/or —COOH) has been demonstrated to be an effective dispersant for alumina slurries [8,9,14]. Here under the same content addition, if a high proportion of –COO^- and/or –$COO^-NH_4^+$ group can be obtained by enhancing the hydrolysis of anhydride and/or $CONH_2$ groups of Isobam104 and Isobam600AF through alkali addition, solids loading and rheological properties of alumina slurries are hopeful to be further improved.

From another aspect, a large number of publications on hydrophobic modification have appeared in polymer area [15,16]. Hydrophobically modified alkali-soluble associative polymer is able to destruct associative junctions resulting in a continuous decrease of viscosity at high shear rates. Therefore, tetramethyl ammonium hydroxide (TMAH), a strong alkali with hydrophobic group, is selected to interact with Isobam. Dispersing and gelling behavior of alumina slurries should be modified by the interaction between hydrophobic groups of TMAH attached on the backbone of Isobam copolymer or alumina particles.

In the present study, the effect of TMAH content on the rheological behavior of alumina slurries was evaluated. A comparative study

* Corresponding authors at: The State Key Laboratory on High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, China. Fax: +86 21 52415263.
E-mail addresses: siyecaosy@163.com (Y. Sun), swwang51@mail.sic.ac.cn (S. Wang).

http://dx.doi.org/10.1016/j.jascer.2017.05.002

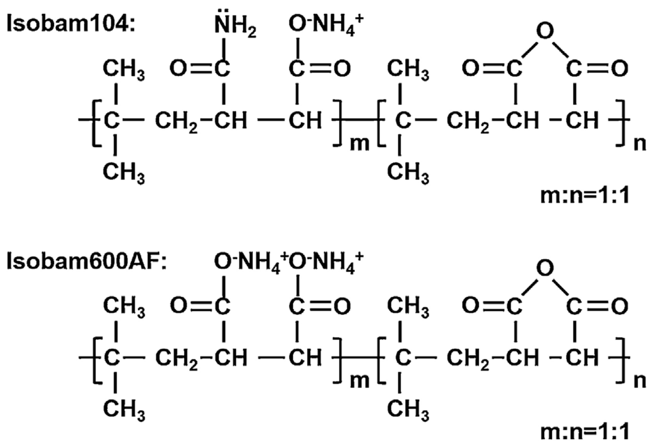

Fig. 1. Molecular structures of Isobam104 and Isobam600AF.

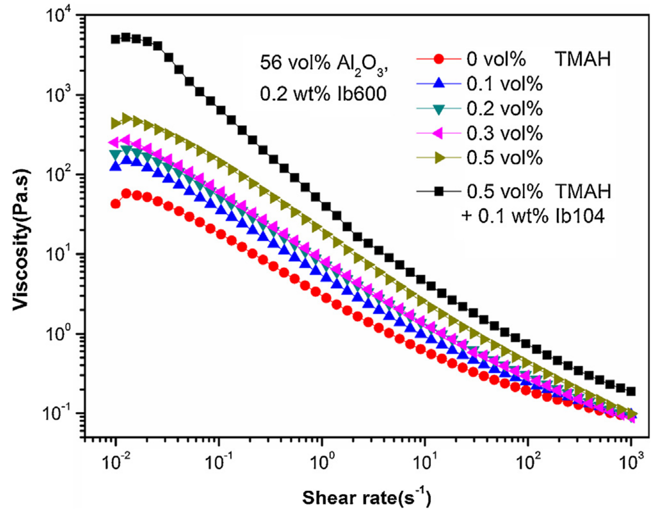

Fig. 2. Rheological behavior of the slurries with 56 vol% solids loading and 0.2 wt% Ib600 or/and 0.1 wt% Ib104 versus TMAH content.

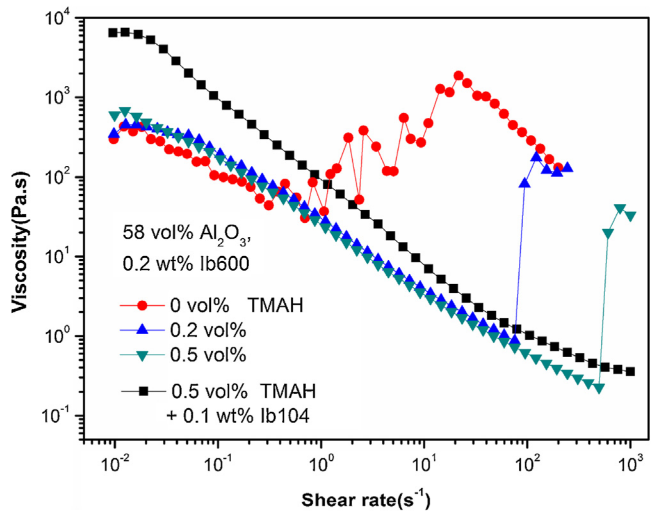

Fig. 3. Rheological behavior of the slurries with 58 vol% solids loading and 0.2 wt% Ib600 or/and 0.1 wt% Ib104 versus TMAH content.

using strong alkali sodium hydroxide (NaOH) without hydrophobic group was carried out to demonstrate the effect of TMAH. Further, the influence of solids loading on resultant density of pre-sintered bodies and flexural strength of ceramics were investigated.

2. Experimental procedure

Commercial alumina powder (AES-11, Sumitomo Chemical Co., Ltd., Japan, $D_{50} = 0.45\ \mu m$, BET = 6.4 m^2/g) was used as raw material. Isobam104 and Isobam600AF with a molecular weight of 55,000–65,000 and 5500–5600, respectively (Kuraray, Osaka, Japan) were used as both dispersant and gelling agent. The molecular structures of Isobam104 and Isobam600AF are shown in Fig. 1. TMAH ($(CH_3)_4N{\cdot}OH$, Sinopharm Chemical Reagent Co., Ltd) as a 25 vol% aqueous solution and NaOH (Sinopharm Chemical Reagent Co., Ltd, AR) were respectively added to adjust the slurry performance.

Alumina slurries containing 56 vol%, 58 vol% and 60 vol% solids loading were prepared by ball-milling the mixture of alumina powder, deionized water, 0.2 wt% Isobam 600AF and/or 0.1 wt% Isobam104 (simply noted as Ib600 and Ib104, hereafter), and 0–0.5 vol% TMAH or 0.1 wt% NaOH (Here, the TMAH content is calculated by excluding water from the TMAH aqueous solution. And solids loading is compared to the slurry volume including water and powder volume, volume of additives such as Isobam and alkali is negligible in this study.). Then, the slurries were degassed, gelled at room temperature in air, demolded, dried, and pre-sintered with heating rate of 1 °C/min at 1000 °C for 2 h to burn out organic additives. Final sintering was carried out in air at 1550 °C for 3 h.

Rheological behavior was characterized using a stress-controlled rheometer (Physica MCR301, Anton Paar, Graz, Austria) with a parallel plate (25 mm in diameter). Viscosity of the slurries was measured with the continuous shear mode increasing from 1 s^{-1} to 1000 s^{-1} at a constant temperature of 25 °C. Gelation behavior of the alumina slurries was studied in an oscillatory mode, under a frequency of 1.0 Hz and a constant strain of 0.5%. Zeta potentials of the dilute alumina slurries (powder/water: 0.2 g/L) were measured using electrophoretic mobility (Zeta Plus, Brookhaven, NY), pH values were adjusted by HCl and TMAH solutions. Pore size distribution of the pre-sintered bodies was measured using mercury porosimetry using a poremaster (PoreMaster-33, Quantachrome Corporation, Boynton Beach, FL, U.S.). Flexural strength (three samples for each point) of the sintered ceramics was measured using three-point bending on bars of 36 mm × 4 mm × 3 mm with a crosshead speed of 0.5 mm/min (Instron-5566, Norwood, MA).

3. Results and discussion

3.1. Influence of TMAH on rheological behavior

In our previous study [13], a 56 vol% solids loading slurry with the same alumina powder (AES-11) was prepared with good fluidity. To evaluate the effect of TMAH on the dispersing behavior of alumina slurries, viscosity of the slurries with 56 vol% solids loading and 0.2 wt% Ib600 was examined on the basis of TMAH content. All slurries showed a similar shear-thinning behavior with increasing shear rate (Fig. 2). Viscosity of the slurries increased slightly from 0.20 Pa·s to 0.45 Pa·s at 100 s^{-1} when the TMAH content was increased from 0 vol% to 0.5 vol%. Meanwhile, the slurry with 56 vol% solids loading, 0.2 wt% Ib600 and 0.1 wt% Ib104 was included. The maximum viscosity of this slurry was 0.7 Pa·s at 100 s^{-1} when TMAH addition was 0.5 vol%, slightly higher than those of the slurries without 0.1 wt% Ib104. Further, solids loading of the alumina slurry was increased to 58 vol%. Fig. 3 shows the rheological behavior of the slurries composed of 58 vol% solids loading and 0.2 wt% Ib600. Without TMAH, there were shear-thinning behavior at low shear rates and a sharp shear-thickening (dilatancy) behavior at a shear rate of 1 s^{-1}. Shear-thickening behavior is a com-