TAILORING SUSPENSION FLOW FOR THE GELCASTING OF OXIDE AND NONOXIDE CERAMICS

Conf-940411--55

O. O. OMATETE AND A. BLEIER
Oak Ridge National Laboratory, Oak Ridge, TN 37831.

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ABSTRACT

The rheology of gelcasting slurries of concentrated (30 - 60 vol%) alumina, zirconia, silicon nitride, and sialon powders with isoelectric points varying between pH 5 and 9, was studied by measuring the viscosity and yield stress as functions of pH. Typically, the rheology is non-Newtonian. The lowest values of viscosity and yield stress that permit the highest solids loading were obtained at high and low pH values, where the powders are colloidally stable, far from the isoelectric points. This relationship applies whether or not a polymer dispersant is present. The acrylamide monomer which is used in gelcasting slurries, lowers these non-Newtonian properties permitting the preparation of more concentrated slurries. Fluid and pourable gelcasting slurries of each powder had apparent viscosities and yield stresses less than 2.0 Pa·s and 50 Pa, respectively.

INTRODUCTION

Gelcasting is a forming process in which a concentrated slurry of ceramic powders suspended in a solution of organic monomers is polymerized to form a green body of the powder held in a polymeric gel [1,2]. The process is suited to the production of near-net-shape complex parts. The slurry should contain high solids loading (~50 vol %) in order to minimize shrinkage and distortion during drying and, thus, to produce a relatively dense green body that facilitates sintering of the green part to full density. To produce complex-shaped bodies, however, the slurry has to be fluid at the high solids loading, to flow, and to fill complex-shaped molds. Consequently, there is the need to study the rheology of the gelcasting slurries of typical ceramic powders in order to understand the factors that govern the flow and pourability of these slurries. A wide range of ceramic powders, oxide and nonoxide with typical isoelectric points varying between pH = 5 and 9, has been selected to address this need.

The colloidal stability (the tendency of particles not to settle from suspensions) of aqueous gelcasting slurries has been examined [3,4,5]. Typically, the slurries are stable at pH values below (Region I) and above (Region III) the isoelectric point (pH_{iep}) of the powder, and they are unstable around the isoelectric point (Region II). At the high, basic pH values (Region III), dispersants enhanced the stability of the slurries with high solids concentration. In this work, however, the primary objective was to study the rheology of gelcasting slurries by measuring the shear stress versus the shear rate of these suspensions as a function of pH and colloidal stability in these three regions.

In order to increase the solids concentration of the slurry, dispersants are added and the slurry is milled. The effect of the dispersant addition and the milling on the rheology was also examined. In addition, the influence of the gelcasting monomer, acrylamide, on the rheology of the slurries was studied. Fluidity and pourability are desirable qualities of gelcasting slurries because they flow under gravity and fill the mold being used. Therefore, a further objective of this study was to establish some criteria for defining the flowable state of gelcasting slurries.

EXPERIMENTAL MATERIALS AND METHODS

The particle size distribution of alumina (Al_2O_3), zirconia (ZrO_2), silicon nitride (Si_3N_4), and sialon (SiAlON) was measured using a particle size analyzer (CAPA 500, Horiba Instruments, Irvine, CA) and a mean diameter was determined for each powder. The electrophoretic mobilities of the powders were measured (System 3000, Pen Kem Inc., Bedford Hills, NY) as a function of pH. The background electrolyte was either potassium chloride or potassium nitrate solution at 0.01 mol/dm³ concentration. Table I, summarizes the results of these measurements, and, in addition, gives the sources of the powders.

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Table I: Suppliers and properties of the powders used.

POWDER	MEAN DIAMETER (μm)	IEP (pH)
Silicon Nitride SN-E10, Ube Industries, Japan	0.56	5.8
Zirconia TZ-3YS, Tosoh Corp., Atlanta, GA	0.39	7.5
Alumina RCHP-DBM, Malakoff Inc, Malakoff, TX	0.55	8.7
SiAlON AA, Vesuvius Research, Pittsburgh, PA	0.44	7.2

The slurries were prepared by mixing the powder either in demineralized water or in a 15 wt % aqueous solution of the gelcasting monomer, acrylamide. The mixing was accomplished by hand stirring and then agitating the slurry with a mechanical shaker for two hours. The pH of the slurries were varied by using nitric acid, tetramethylammonium hydroxide or by the addition of the basic dispersant, Darvan C, ammonium polymethacrylate (R. T. Vanderbilt Co. Inc., Norwalk, CT). A few samples were ball-milled. The rheological measurements were obtained (RFS 8400, Rheometrics Inc., Piscataway, NJ) in a thixotropic loop mode. The shear rate was varied from 0 - 100 s^{-1} in 60 s, held at 100 s^{-1} for 60 s, reduced to 0 s^{-1} in 60 s, and increased to 100 s^{-1} in 60 s. The data from the last step of the thixotropic loop were used in the study.

These measurements were carried out for Al_2O_3 at low and high solids loading in Region I (Regions are shown in Fig. 1) and at high solids loading only, in Region III with the aid of the dispersant, Darvan C. Similar measurements were made for ZrO_2 . For Si_3N_4 , measurements were made in all the three stability regions; furthermore, the effects of the addition of a dispersant to the slurry and of milling the slurry, were examined. Measurements were made for SiAlON at high pH-values (Region III) in water, in the acrylamide solution, and in the acrylamide solution plus dispersant.

In this study the non-Newtonian properties of the slurries were best represented by the Bingham plastic model, with a yield stress and an apparent viscosity for each slurry [6]. At a shear rate of 38.5 s^{-1} and above, the data points were adequately approximated by a linear relationship.

Figure 1: Mobility vs pH for Al_2O_3 , ZrO_2 , SiAlON, & Si_3N_4

RESULTS AND DISCUSSIONS

As Table I indicates, the mean particle sizes of all the ceramic powders were about 0.5 μm . Figure 1 shows the variation of the electrophoretic mobility with pH for each powder. The pH_{iep}

obtained from the figure is tabulated in Table I. The isoelectric point of Si_3N_4 , $\text{pH}_{\text{iep}} = 5.8$, is acidic and those for the other three powders SiAlON , $\text{pH}_{\text{iep}} = 7.2$, ZrO_2 , $\text{pH}_{\text{iep}} = 7.5$ and Al_2O_3 , $\text{pH}_{\text{iep}} = 8.7$ are neutral to basic.

For each powder in Figure 1, there are three regions of colloidal stability corresponding to (a) the low pH values far below the pH_{iep} (Region I), (b) the high pH values far above the pH_{iep} (Region III), and (c) the pH values around the pH_{iep} (Region II). These regions, based on the absolute electrophoretic mobility or zeta potential, have been discussed in detail elsewhere for Al_2O_3 and ZrO_2 [3,4,5]. For each powder in this study, the surface is highly charged at electrophoretic mobility values greater than $\pm 2.5 \times 10^{-8} \text{ m}^2/\text{Vs}$, equivalent to a zeta potential of $\pm \sim 30 \text{ mV}$. The lines drawn at these values are shown in Figure 1, and they demarcate the regions of stability. The pH values that define these regions are different for each powder; Region II for each powder, where slurries are colloiddally unstable, is essentially symmetric about the pH_{iep} .

Alumina Slurries. Figure 2 shows the data of the shear stress versus shear rate for selected alumina slurries. Table II summarizes, the Bingham constants, the yield stress and the apparent viscosity, for the Al_2O_3 and ZrO_2 slurries.

In Table II-1, the slurries contain neither the gelcasting monomer, acrylamide, nor the dispersant, Darvan C. The slurries whose pH is 4.2 ± 0.2 are in the low pH range (Region I) where they are stable. Consequently, their flow is nearly Newtonian, even at 50 vol % solids loading; the corresponding yield stresses and apparent viscosities are low. These Bingham constants are seen to remain low but to increase slightly as the solids concentration increases. This behavior indicates that the non-Newtonian behavior in this stable region is controlled by particle crowding.

In gelcasting, we are interested in the highest solids loading of the acrylamide solution in order to produce high green density which facilitates sintering. Table II-2 shows the Bingham constants of the slurries in acrylamide solution at solids loading $\geq 50 \text{ vol } \%$ in Region I. Table II-3 shows similar data for slurries in the acrylamide solution containing the basic dispersant, Darvan C which adjusts the pH to 9.3 ± 0.6 in the stable Region III. The Bingham constants for slurries in Tables II-2 and II-3 increase with solids concentration, again indicating that in the stable region the non-Newtonian behavior is due to particle crowding.

Figure 2: Shear Stress vs Shear Rate for Al_2O_3

In Figure 2, only the data for Al_2O_3 slurries with high solids loading ($\geq 50 \text{ vol } \%$) are presented. The three slurries at 50 vol % (in water, in acrylamide solution, and in acrylamide solution plus the dispersant) can be compared. They are in different stability regions; that is, those in water and in acrylamide are in the stable Region I and that in acrylamide plus dispersant is in the

Table II: Summary of Bingham constants for Al_2O_3 and ZrO_2 slurries¹

Loading(vol %)	pH	Yield Stress(Pa)	Apparent Viscosity (Pa.s)
<u>1. Al_2O_3 in water (Stable Region I)</u>			
30.0	4.2	0.01	0.006
40.0	4.2	0.06	0.11
50.0*	4.0	7.73	0.40
<u>2. Al_2O_3 in acrylamide solution (Stable Region I)</u>			
50.0*	4.9	3.75	0.22
55.0	4.3	28.24	1.14
60.0*	3.7	64.04	2.37
<u>3. Al_2O_3 in acrylamide solution + dispersant (Stable Region III)</u>			
50.0*	9.6	4.87	0.31
52.0	9.3	11.7	0.66
57.0*	8.9	49.0	1.89
<u>4. ZrO_2 in water (Stable Region I)</u>			
30.0	4.0	6.6	0.23
40.0	3.9	16.1	0.63

*Data for these slurries are plotted in Figure 2

¹The sequence of the slurries is based on the Bingham constants.

stable Region III. Nevertheless, the lowest line (smallest viscosity) is found for the slurry in the acrylamide solution and the highest (largest viscosity) is found for that in the acrylamide plus dispersant. Thus, the acrylamide reduces the viscosity of the slurry. The data in Table II also confirm this effect; the non-Newtonian parameters are lowest for the slurry in the acrylamide solution. This behavior implies that, at a given rheological condition, higher solids loading are attainable with slurries in acrylamide solution than in either water only or in acrylamide solution plus dispersant. Similar results were seen in previous work [2]. The remaining data in Figure 2 clearly show that, in the two stable regions, the slurries become more non-Newtonian (increased Bingham constants) as the solids loading increases due to particle crowding.

In Table II, two slurries, 60 vol % Al_2O_3 in acrylamide solution and 57 vol % Al_2O_3 in acrylamide solution plus dispersants, give the highest Bingham constants. The 57 vol % slurry was barely pourable and its constants, therefore, define the limit of flowable gelcasting slurries. Consequently, the yield stress and apparent viscosity of a fluid and pourable gelcasting slurry should be less than 50 Pa and 1.9 Pa.s, respectively.

Zirconia Slurries. Earlier studies [3,5] showed that both oxides, Al_2O_3 and ZrO_2 , behave similarly in their corresponding stability regions. The main difference is that ZrO_2 , because of its lower surface charge, attains a much lower solids loading than Al_2O_3 . The data in Table II demonstrate this. The Bingham constants for the ZrO_2 slurry at 30 vol % are comparable to those for Al_2O_3 slurries at 50 vol %. The constants for ZrO_2 at 40 vol % are much higher than those for Al_2O_3 slurries at 50 vol %.

Silicon Nitride Slurries. Figure 3 shows the shear stress versus shear rate for selected Si_3N_4 slurries. The constants corresponding to the Bingham model for all the Si_3N_4 slurries are summarized in Table III. Table III-1 shows the Bingham constants for the slurries at high pH (12.8 ± 0.3) corresponding to the stable Region III. For the Si_3N_4 powder, 40 vol % was the highest concentration of fluid and pourable slurry attained by hand mixing. The increase in the Bingham constants with solids concentration indicates that the non-Newtonian behavior is controlled by particle crowding as the solids loading increases. The two lowest lines of Fig. 3 demonstrate this.

Table III-2 shows the Bingham constants for three slurries (~25 vol %) in water at three different pH values corresponding to the three regions of stability for Si_3N_4 . At high pH (12.6) in the stable Region III, the slurry is virtually Newtonian as is evidenced by the low viscosity and yield stress. At low pH (1.1) in the stable Region I, the slurry is slightly non-Newtonian with greater Bingham constants. At the intermediate pH (6.9) near the isoelectric point of 5.8 (Region II), the slurry is highly non-Newtonian with large Bingham constants. The data for these three slurries are shown by the open data points and solid lines in Figure 3. Because the solids loading is relatively low, the highly non-Newtonian behavior in Region II is due to particle flocculation and

Figure 3: Shear Stress vs Shear Rate for Si₃N₄

not particle crowding. Also, these data indicate that the highest solids loading for Si₃N₄ slurries are possible in the stable Region III where Si₃N₄ particle surfaces are more highly charged at the basic pH than at the acidic pH in Region I.

Table III: Summary of Bingham constants for Si₃N₄ slurries¹

Loading(vol %)	pH	Yield Stress(Pa)	Apparent Viscosity (Pa.s)
<u>1. In water (Stable Region III)</u>			
25.0*	13.1	3.0	0.10
35.0	13.2	7.8	0.40
40.0*	12.8	16.2	0.74
<u>2. In water (Regions I, II & III)</u>			
25.0*	13.1 (III)	3.0	0.10
25.0*	1.1 (I)	40.0	1.19
24.0*	6.9 (II)	119.0	3.52
<u>3. In acrylamide with and without dispersant.</u>			
35.0	13.1	7.5	0.40 (No disp.)
39.6*	7.8	20.5	0.67 (Milled + disp.)
32.6*	8.0	26.5	1.29 (With disp.)

*Data for these slurries are plotted in Figure 3.

¹The sequence of the slurries is based on the Bingham constants.

Table III-3 shows the Bingham constants for the slurries in the acrylamide solution. These are also indicated by the filled data points in Figure 3. In Table III-3, the effects of the presence of the dispersant only and of the dispersant plus milling are shown compared to the slurry at high pH (13.1) obtained by the addition of tetramethylammonium hydroxide. The addition of the dispersant gives the slurries a slightly basic pH (~8.0) and they are located just within Region III. The slurry with the dispersant is highly non-Newtonian although it is at the lowest solids loading (32.4 vol %) of those shown. Milling a similar slurry reduces the Bingham constants even though the solids loading is higher, 39.6 vol %. The milling breaks up the agglomerates thereby lowering the viscosity of the slurry.

The summary in Table III shows that for this Si₃N₄ powder, fluid and pourable slurries

obtained by hand mixing, have yield stresses and apparent viscosities less than 50 Pa and 1.5 Pa·s, respectively. The 25 vol % slurry in Region II, pH 6.9, is not fluid and pourable.

SiAlON Slurries. Table IV shows the Bingham constants for SiAlON slurries. Figure 4 shows the data for concentrated slurries (≥ 50 vol %) of SiAlON, in water, in acrylamide solution, and in acrylamide plus water. The data points for slurries at 50 vol %

Table IV: Summary of Bingham constants for SiAlON slurries (Region III)¹

Loading(vol %)	pH	Yield Stress(Pa)	Apparent Viscosity (Pa.s)
<u>1. In water</u>			
45.0	9.7	1.9	0.11
50.0*	9.8	5.81	0.29
<u>2. In acrylamide solution</u>			
45.0	10.1	1.26	0.10
50.0*	9.7	3.46	0.20
55.0*	10.4	5.54	0.36
<u>3. In acrylamide solution + dispersant</u>			
50.0*	10.1	5.78	0.31
55.0*	9.8	10.2	0.68

*Data for these slurries are plotted in Figure 4

¹The sequence of the slurries is based on the Bingham constants.

are open while those at 55 vol % are closed. All the slurries are in the pH range of 9.7 to 10.6 which is the stable Region III. As in the stable region for the other powders, the Bingham constants increase with solids concentration showing that the non-Newtonian behavior is due to particle crowding.

Figure 4: Shear Stress vs Shear Rate for SiAlON in Region III

A comparison of the data at 50 vol % solids loading for the three types of slurries shows that the acrylamide slurry is least non-Newtonian (lowest Bingham constants) resembling the behavior of Al₂O₃ discussed earlier. Even at 55 vol % loading the data for the slurry in acrylamide almost matches that for the slurry in acrylamide plus dispersant at 50 vol % as evident in both Figure 3 and in Table IV. All the slurries in Table IV are fluid and pourable as demonstrated by the low Bingham constants. The yield stress and apparent viscosity are less than 11.0 Pa and 0.70 Pa·s, respectively.

CONCLUSIONS

Three regions of colloidal stability were defined for the four powders, Al_2O_3 , ZrO_2 , Si_3N_4 , and SiALON, by recognizing that their surfaces were highly charged at electrophoretic mobility $\geq \pm 2.5 \times 10^{-8} \text{ m}^2/\text{Vs}$. The three regions of colloidal stability exhibited by each powder correspond to pH values far below, far above, and around the isoelectric point. The measurement of the shear stress versus shear rate of the slurries, as functions of the pH, show that they are non-Newtonian and that the three regions of colloidal stability control the rheology of the gelcasting slurries.

The non-Newtonian behavior of the slurries was obtained under different pH conditions for each powder, reflecting the range of isoelectric points (pH 5 to pH 9). The Bingham plastic model approximates the yield stress and apparent viscosity of the data obtained. The magnitude of the Bingham constants indicates that the mechanism of the non-Newtonian behavior of each powder is different in the three regions of stability. In the two stable regions, the non-Newtonian behavior is controlled by particle crowding; the Bingham constants are relatively low and increase with solids concentration. However, in the unstable region, only low solid loadings are achievable; the behavior is highly non-Newtonian (large Bingham constants) and is controlled by particle flocculation. This range of rheological properties was obtained with each powder, and the pH dependence of these properties is clearly linked to the isoelectric point.

At the same solids concentration, the Bingham constants of the slurries in acrylamide solution were lower than those for slurries in water or in acrylamide solution plus dispersant. Hence the presence of the acrylamide increases the solids loading of the gelcasting slurry prepared by hand mixing.

Milling of the slurry also reduced the Bingham constants by breaking up agglomerates. This implies that milling should be done to maximize the solids concentration of gelcasting slurries. The addition of the basic dispersant, Darvan C, forced the slurries to the stable Region III at the high pH value. But for comparable solids concentration, the Bingham constants were higher in the presence of dispersants in the stable Region III than without dispersants in the stable Region I.

Finally, based on the yield stresses and the apparent viscosities listed for each slurry in Tables II - IV, flowable and pourable gelcasting slurries at high solids loading may be defined to a first approximation as those that possess yield stresses and apparent viscosities less than 50 Pa and 2.0 Pa-s, respectively.

ACKNOWLEDGEMENT

Research is sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency, Office of Transportation Technologies, as part of the Ceramic Technology Project of the Materials Development Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The authors are grateful to Drs. M. A. Janney, S. D. Nunn, and R. J. Lauf for reviewing the manuscript and for their comments, and also to C. G. Westmoreland and S. D. Knowles for experimental assistance.

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