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RHEOLOGY AND MICROSTRUCTURE OF CONCENTRATED ZIRCONIA-ALUMINA SUSPENSIONS FOR
GELCASTING COMPOSITES

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ABSTRACT

The relationships among colloidal stability, suspension rheology, and solids loading are elucidated for zirconia-alumina mixtures containing 20 vol% ZrO_2 , based on solids. The lower colloidal stability of ZrO_2 limits the rheological properties of this system. If the zeta potential of ZrO_2 is less than 49 mV, high degrees of pseudoplasticity, high yield stress, high viscosity, and long relaxation times characterize the binary suspensions. These effects occur, despite the fact that ZrO_2 is the minor ceramic constituent. If the zeta potential of ZrO_2 is maintained above 49 mV, suspensions with high solids loading (55 vol%) can be prepared which behave as Newtonian fluids over the 0-to-200 s^{-1} shear rate range and as an elastic solid at higher rates. As the solids loading of a highly stable binary suspension is increased, the rheological properties change. They evolve from those of a near Newtonian-like fluid with nearly independent particles (40 vol%) to those of a pseudoplastic fluid with a weakly interacting particle network (50 vol%) to those of an elastic-like solid composed of crowded, strongly repulsive particles (55 vol%). Low-shear conditions for suspension-transport and mold-filling operations that ensure a homogeneous arrangement of ZrO_2 and Al_2O_3 particles in a gelcast ceramic seem promising.

INTRODUCTION

Many ceramic composites are fabricated using concentrated suspensions. Yet, the dependence of rheology on the adjustable processing variables, such as the pH, zeta potentials of ceramic powders, and presence of polymeric dispersants, are typically understood for only dilute unary suspensions. Often, this status results in unreliable control of the microstructures in composites and the physical properties of the final components. The controlled processing of suspensions that contain more than one type of solid can be complicated, ultimately relying on the empirical tailoring of the colloidal properties that govern the rheology of suspensions. Hence, a refined view of the relationships between colloidal properties and rheological behavior is desirable for the full exploitation of gelcasting methods in ceramic composite processing [1].

This study addresses this need, in part, by examining the colloidal stability and rheological behavior that underpins the network-like concentrated suspensions. Suspensions that represent those used to gelcast zirconia-alumina composites were examined, recognizing that agglomeration must be avoided in useful systems. [2] Moreover, the interactions among similar and dissimilar particles need to be regulated in order to ensure that promising suspensions have sufficiently low viscosity and low yield stress. [3] Lastly, these constraints must be met while maintaining a homogeneous geometric array of dispersed zirconia and alumina particles that do not exhibit differential sedimentation. [4]

COLLOIDAL PROPERTIES AND MAXIMUM SOLIDS LOADING

Powders and Their Colloidal Stability. Pertinent properties of the zirconia (ZrO_2) and alumina (Al_2O_3) powders used are listed in Table I. The methodologies and procedures by which the data in this table were obtained are described elsewhere. [2,3] Recent sedimentation studies of the colloidal stability of each oxide reveal that three pH regimes, each characterized by unique colloidal features, exist for each solid. [2,3] These regimes relate to the isoelectric points (pH_{iep}) given in Table I. At low pH, far from the pH_{iep} -value of either

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powder, the particles have a high positive zeta potential and are colloiddally stable. In the vicinity of the pH_{iep} , the particles have a low ζ -potential which may be either positive ($\text{pH} < \text{pH}_{\text{iep}}$) or negative ($\text{pH} > \text{pH}_{\text{iep}}$); suspensions prepared within this region are colloiddally unstable and consist of large agglomerates that are likely to lead to porous gelcast ceramics. Lastly, at high pH, far from the pH_{iep} -value of either powder, the particles have a high negative ζ -potential and are colloiddally stable. Although the low and high pH regimes are similar, the profiles in Figure 1 show that the saturation ζ -potentials and the breadth of the pH range over which the potential is nearly maximized provide better colloiddal stability at low pH.

Maximum Loading for Gelcasting. The suitability of unary and binary suspensions for gelcasting the powders in Table I has recently been assessed by evaluating the maximum solids loading under various pH conditions. [2,3] For unary systems, this property is the maximum dispersible concentration of a solid, such that the suspension remains pourable. This concentration has been determined for each oxide by incorporating increasing amounts of powder into a suspension until it has a prohibitively high viscosity and becomes pastelike. [2] Minimum shrinkage during the drying and sintering stages is desired, making 50 vol% the minimum acceptable concentration of solids for gelcasting. [1-3]

The pH-dependent maximum loadings for binary mixtures of the ZrO_2 and Al_2O_3 powders in Table I have been evaluated for compositions containing 20 and 80 vol% ZrO_2 , based on the total amount of solids. [3] The loading limits for the individual powders and the mixture containing 20 vol% ZrO_2 are given in Figure 2 as functions of pH. Each unary system has a pH-dependent profile with two regimes (Region I at low pH and a less-distinctive and virtually pH-insensitive Region III at high pH), within which the maximum loading is weakly pH-dependent. These regions of optimized loading are for positively and negatively charged particles, respectively (Figure 1). Region II separates these regimes and contains conditions that respectively minimize the loading at pH 7.0 and 8.2 for ZrO_2 and Al_2O_3 , near the appropriate pH_{iep} -value (Table I and Figure 1). A strong correspondence exists among the colloiddal stability of the particles, their surface charge, and the maximum loading. Namely, the loading and the colloiddal stability are both maximized by achieving the highest zeta potential. [3]

Similarly, the maximum loadings for the binary system with 20 vol% ZrO_2 , also shown in Figure 2, has a strong pH-dependence, resembling those of the constituent oxides and resides between them. The minimum pH values at the transitions between Regions I and II are given in Table II, along with the corresponding ζ -potential for each powder (Figure 1 and Table II). The range in the vicinity of ~ 50 mV is critical for these oxides; higher ζ -potentials lead to the highest loadings for either oxide, whereas lower potentials lead to greatly reduced loadings. The similarity of the pH-transition between Regions I and II for the mixture and that for ZrO_2 (Figure 2 and Table II), reveals that the lower potential of ZrO_2 sets the transitions between Regions I and II for the binary system. Similar results exist for the transition between Regions II and III. [3]

RHEOLOGICAL BEHAVIOR OF CONCENTRATED SUSPENSIONS

Procedures. The rheological properties of six binary suspensions, Systems A to F denoted in Figure 2, were examined; each contains 20 vol% ZrO_2 , but only D and F are outside Region I. The shear stress (τ) was measured at desired shear rates ($\dot{\gamma}$) with a parallel-plate viscometer (Rheometrics, Model 8400) in either a thixotropic loop mode set with five stages that resembles the loop used in a previous study [3] and a transient mode set with four stages. The five stages of the thixotropic loop were (1) 60 s to increase $\dot{\gamma}$ from 0 to 300 s^{-1} , (2) 60 s at 300 s^{-1} , (3) 60 s to reduce $\dot{\gamma}$ to 0 s^{-1} , (4) 60 s to increase $\dot{\gamma}$ again from 0 to 300 s^{-1} , and (5) 60 s to reduce it again to 0 s^{-1} . This strategy allowed the study of (i) apparent viscosity ($\eta^{\text{app}} \equiv \tau/\dot{\gamma}$), Bingham plastic flow with yield stress (τ_B) and constant differential viscosity ($\eta^{\text{dif}} \equiv d\tau/d\dot{\gamma}$) when $\tau \geq \tau_B$, (ii) pseudoplastic flow (η^{app} and η^{dif} differ regularly with increasing $\dot{\gamma}$), (iii) hysteresis ($\tau_4 \neq \tau_5$, subscripts specify stages), and (iv) thixotropy (time-dependent τ). [5] The four stages in the transient mode were (1) 60 s at 15 s^{-1} , (2) 60 s at 300 s^{-1} , (3) 60 s at 0.01 s^{-1} , (4) 240 s at 0.01 s^{-1} . This approach

permitted viscous relaxation (i.e., mechanical recovery after the cessation of shear at a constant rate) to be monitored as a function of time (t). [5,6] The transient-mode scan was conducted at the conclusion of the thixotropic loop scan. Stages (4) and (5) were then repeated to identify longer term effects.

For purposes of comparison, the six suspensions identified in Figure 2 are subdivided into two families. Group 1, consists of Systems A to D; these suspensions have solids loadings of 40 vol% but their pH conditions differ. Group 2, consists of Systems B (also in Group 1), E, and F, whose pH conditions are nearly identical but whose respective solids loading are 40, 50 and 55 vol%.

Thixotropic Loop Mode. Systems A to F mostly exhibit Bingham-like flow, described by a yield stress, τ_B , and a constant differential viscosity, η^{dif} . Values for these properties are given in Table III. The yield stress and viscosity values for Systems A and B are essentially equal to those for similar 40-vol% suspensions within Region I of Figure 2 that are described elsewhere [3]. Each has a very low yield stress and its flow behavior is nearly Newtonian.

System C, which also lies within Region I for the binary systems has a higher τ_B -value, while its viscosity is of the same magnitude as those for A and B. Thus, although this suspension requires a higher yield stress to be overcome in order for it to flow, its resistance to flow is minimal once this condition is met. System D, on the other hand, exhibits a high viscosity, in addition to a high yield stress. Comparison of the data for Systems C and D reveals, after consideration of their locations in Figure 2, i.e., relative to the transitions between Regions I and II for each unary system and for the binary systems, that the high yield stresses of Systems C and D are induced by the colloidal properties of ZrO_2 . For instance, the ζ -potential of the ZrO_2 particles in System C is -32 mV, an insufficient value for this [3] and similar ZrO_2 powders [4,7,8] to be colloidally stable against the strong London-van der Waals forces that promote agglomeration; note the comparatively large Hamaker constant for this material in Table I. In comparison, the Al_2O_3 powder possesses a higher ζ -potential in System C (Figure 1), while having a lower Hamaker constant; thus, it is the more colloidally stable component and the less pH-sensitive one in the present system. Similar concepts explain the yield stress and viscosity for System D (Region II); here, the ζ -potential of ZrO_2 is even lower. Also, the flow behavior of D is better described as pseudoplastic rather than Bingham-like.

In summary, the trend of the Bingham yield stress, τ_B , can be portrayed for Group 1 as $A \approx B < C < D$, while the related trend of the differential viscosity, η^{dif} , is $A \approx B \approx C < D$. These sequences reflect the increasingly dominant role of the ζ -potential of ZrO_2 , which decreases rapidly from 49 mV at pH 5.5 (Figure 1), while the ζ -potential of Al_2O_3 remains above its critical value of 52 mV (Table II).

The data in Table III show that Systems E and F have higher yield stresses than do Systems A and B. Regarding viscosity, the η^{dif} -value for System E resembles the values for A and B, but the η^{dif} -value for System F (above Region I) is notably higher, residing between the η^{dif} -range established by Systems A to C and the value for System D. These yield stress and viscosity data further indicate that Systems E and F, which have 50 and 55 vol% solids, respectively, exhibit more Newtonian-like rheology than do the less concentrated suspensions, C and D. Thus, the trends for the Bingham yield stress and the differential viscosity within Group 2 are, respectively, $B < E < F$ and $B \approx E < F$.

Other data [9] demonstrate that System F is unique among the members of Group 2, regarding its shear stress-shear rate behavior. All three systems behaved similarly below 200 s^{-1} , the τ -value for F was on the order of 100 Pa when the $\dot{\gamma}$ -value approached 200 s^{-1} , as the τ_B and η^{dif} data in Table III would suggest. However, as this shear rate was exceeded, within the limits of the rheometer, an "infinite" shear stress was observed for shear rates greater than 200 s^{-1} in Stages (1), (2), and (4). When $\dot{\gamma}$ was reduced to 0 s^{-1} in Stages (3) and (5), a high degree of hysteresis was observed (τ remained "infinite") until $\dot{\gamma}$ approached 30 s^{-1} , at which point the shear stress plummeted; hysteresis was not observed between 30 and 0 s^{-1} . This behavior resembles that of an elastic, solid-like system. Together with the sequences for the Bingham yield stress, τ_B , and the differential viscosity, η^{dif} , it suggests that members of Group 2 experience an increased degree of particle crowding with increased solids loading. Systems B, E, and F, which have virtually identical pH conditions and,

therefore, nearly identical pairs of ζ -potentials, have very different microstructures. The microstructure evolves in Region I from one with virtually independent particles that provide Newtonian-like flow (B) to one with a weakly interacting particle network that shows Bingham-like flow (E) to a third for which the highly crowded stable particles act collectively to resemble an elastic-like solid (F) as the solids loading increases from 40 to 55 vol%.

Transient Mode. The two right-hand columns in Table III contain, respectively, the values of shear stress established at a constant shear rate of 15 s^{-1} (τ_{15}) for System A to F and the relaxation time of each after cessation of shear at constant rates of 15 and 300 s^{-1} . The lower shear rate depicts a state for which the flow is elastic-like and hysteresis was nil. The higher shear rate represents a state for which the shear stress greatly exceeds τ_B in each system and for which hysteresis was sometimes present. We do not explicitly report the τ_{300} -values here, owing to space limitations, but they can be estimated using the τ_B - and η^{dif} -values in Table III and the equation, $\tau_{300} = \tau_B + 300\eta^{\text{dif}}$.

The τ_{15} -values in Table III for Systems A to F are consistent with the rheological behavior already described. The data for the mechanical relaxation after shear at 15 s^{-1} (t_{15}) and 300 s^{-1} (t_{300}) reveal the time of recovery is essentially instantaneous in many cases, being less than or equal to 0.6 s. However, System C in Group 1 required 95 and 131 s to recover from the shear at 15 and 300 s^{-1} , respectively, and System D never recovered within the 240 s during which data were gathered after shear at either rate. In contrast, each member of Group 2 recovered instantaneously after shear at 15 s^{-1} , and only System F failed to do so after shear at the higher rate, 200 s^{-1} ; it required ~17 s to relax. Therefore, the arrangements of ZrO₂ and Al₂O₃ particles in Systems A and B in Group 1 and in each member of Group 2 are reversibly deformed or perturbed, recovering or relaxing quickly (Table III) without hysteresis [9]. The rapid recovery of System F reveals that this system again behaves as an elastic solid would. In contrast, System D never recovers within the time frame of the experiments and is plastically deformed by shear. These two systems exemplify extreme sets of rheological properties. One contains crowded, colloiddally stable ZrO₂ and Al₂O₃ particles (F), and the other has agglomerates of ZrO₂ and, probably, agglomerates of mixed (heterocoagulated) composition (D).

CONCLUSIONS

High colloidal stability is central to the preparation of concentrated, binary suspensions that are used to gelcast ZrO₂-Al₂O₃ composites. The suspension pH is a critical processing parameter because it governs the absolute and relative zeta potentials that ensure high colloidal stability. Each oxide component influences the rheology of the binary system, but the lower stability of ZrO₂ ultimately limits the useful pH range for gelcasting by increasing the pseudoplasticity and the Bingham yield stress of the suspension. As binary systems with equal solids loading (40 vol%) demonstrate, agglomeration increases the yield stress, viscosity, and the relaxation times following a period of either low or high shear, if the ζ -potential of ZrO₂ is below 49 mV. This state exists for our systems when the pH exceeds 5.5. Ultimately, the agglomeration induced by weakly charged ZrO₂ particles imparts a suspension microstructure that is irreversibly (plastically) deformed by both low or high shear.

If the ζ -potential of ZrO₂ is maintained above 49 mV, suspensions with high solids loading (55 vol%), that contain as much as 20 vol% ZrO₂, based on solids, can be prepared. These systems are reversibly affected by viscous shear and essentially behave as Newtonian fluids over the 0-to- 200 s^{-1} shear rate range and as elastic solids at higher rates. System F, whose microstructure consists of crowded, stable particles, typifies this case. Similar 50-vol% suspensions, represented here by System E, essentially behave as Newtonian fluids.

These findings imply that gelcast composites can be optimized, in part, by regulating the relationships among the surface properties of the powders, colloidal stability (including heterocoagulation interactions), rheology, and solids loading. They also suggest that the use of low-shear conditions for which relaxation times are very short can lead to advanced mold-filling and gelation. This approach would allow molds, especially complex ones with narrow

microstructure. Suitable drying and sintering can then yield composites of complex shape with tailored microstructures and controlled properties.

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Table I: Pertinent Properties of ZrO₂ and Al₂O₃ Powders. [2,3]

Property	Characterization	
Composition	t-ZrO ₂ ^a	α-Al ₂ O ₃ ^b
Surface Area, m ² g ⁻¹	6.98	6.37
Diameter, μm	0.39	0.55
Isoelectric Point, pH _{iep}	7.5	8.7
Hamaker Constant ^c , kT	34.5 ^d	11.2

^aTosoh, TZ-3Y; ^bReynolds, RCHP-DBM; ^cIn water [4]; ^dFor m-ZrO₂.

Table II: pH-Dependent Gelcasting Behavior of ZrO₂-Al₂O₃ Suspensions. [2]

Composition ^a (Vol% ZrO ₂)	Transitions ^{b,c} (I ↔ II)	Zeta Potential (mV)	
		ZrO ₂	Al ₂ O ₃
0	pH 6.2	-	52
20	pH 5.6	47	62
100	pH 5.5	49	-

Table III: Rheological Data for Systems A to F Identified in Figure 2.

System	pH	Loading (vol%)	Yield Stress ^a , (τ_B , Pa)	Viscosity ^a , (η^{dif} , mPa s)	Stress ^b , (τ_{15} , Pa)	Recovery ^c (t_i , s)
Group 1						
A	4.8	40	0.46	167	0.47	0, 0
B	5.5	40	0.66	139	0.38	0, 0
C	6.2	40	183	165	127.5	95, 131
D	6.5	40	>399	647	>4000	_d , _d
Group 2						
B	5.5	40	0.66	139	0.38	0, 0
E	5.4	50	7.7	95	52	0, 0
F	5.4	55	37	328*	266	0, 17.4*

^aStages (4) and (5); ^bTransient mode; ^cAfter shear at rate i , 15 and 300 s⁻¹, respectively; ^dGreatly exceeds 240 s; *Shear rate is 200 s⁻¹.

Figure 1: Zeta potential as a function of pH for ZrO₂ and Al₂O₃.

Figure 2: Maximum loadings for ZrO₂, Al₂O₃, and a mixture with 20 vol% ZrO₂, based on the solids, as functions of pH. Each type of suspension has its own Regions I, II, and III. Group 1 consists of A to D; each has 40 vol% solids. Group 2 consists of B, E, and F; they have 40, 50, and 55 vol% loading, respectively. The zeta potentials for ZrO₂ and Al₂O₃ (mV) for these systems are, in turn, A (63, 72), B (49, 63), C (33, 52), D (25, 46), E (52, 65), F (52, 65).

FIGURE 1

FIGURE 2

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