Processing of Highly Concentrated Aqueous α-Alumina Suspensions Stabilized with Polyelectrolytes

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Stability and rheology of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) and poly(acrylic acid) polyelectrolytes were studied as a function of pH, solids loading, and molecular weight. Past work has found polyelectrolyte-stabilized suspensions to be fairly pH independent at low (e.g., 20 vol%) solids loadings. However, we now show that the effective pH range to provide dispersed and fluid suspensions narrows as the concentration of solids increases as related to interparticle forces. At high solids levels, the presence of excess polymer in solution has detrimental effects on stability, which increases as the molecular weight increases. Finally, with knowledge of these concepts, highly concentrated fluid suspensions of 60 vol% Al_2O_3 (>85 wt%) with submicrometer-size particles have been processed. Higher consolidated densities and reduced sintering temperatures are attained when compared with more conventional processing techniques.

I. Introduction

POLYELECTROLYTES are widely used in industrial applications to prepare highly concentrated (>50 vol%) ceramic suspensions which are subsequently fabricated into dense components by sintering. Although a variety of polyelectrolytes are commercially available and are used effectively in the preparation of suspensions, their role in colloidal stabilization has not been clearly understood.

In this paper, we intend to provide a clearer understanding of particle dispersion with adsorbed polyelectrolytes and relate it to the chemistries of the suspended-particle surfaces and polyelectrolytes and interparticle forces. Aqueous oxide suspensions will be considered as a general example. The particular emphasis will be on the dispersion of α-Al_2O_3 suspensions with poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA).

It is also an objective of this paper to describe the methodology of using polyelectrolyte stabilization for the processing of very highly concentrated (>60 vol%) aqueous ceramic suspensions. This was studied in model experiments with submicrometer-sized alumina which determined the guidelines for the selection of a proper pH range and related rheological behavior to molecular weight. Finally, the sintering behavior of compacts prepared by these techniques is compared with more conventional methods of processing.

II. Background Information

For detailed information concerning polyelectrolytes, surface charging of oxides, and related adsorption behavior of polyelectrolytes on oxides, the reader is referred to Ref. 1. The following brief discussion pertains to the particular aqueous system of aluminum oxide particles and PMAA.[1]

The structure of PMAA is shown in Fig. 1. For PMAA alone, each molecule has many carboxylic acid sites or functional groups, and, depending on the solvent conditions (i.e., pH and ionic strength), the fraction of functional groups that are dissociated (i.e., COO^-) and those that are nondissociated (i.e., COOH) will vary. As the fraction dissociated (α) increases from ≈0 to ≈1.0, the polymer surface charge varies from relatively neutral to highly negative. In general, for PMAA and other polyelectrolytes which have carboxylic acid groups as the functional groups, the dissociation and negative charge characteristics of the polymer increases as the pH increases.[2,3] For PMAA at pH ≥8.5, the molecules are effectively negative with α ≈1. In this condition, experimental evidence shows that the PMAA molecules are in the form of relatively large, expanded, random coils in solution.[4] This results from electrostatic repulsion between the negatively charged surface sites. As pH is decreased, the number of negatively charged sites is continually decreased until the PMAA is effectively neutral near pH 3.4 and α → 0. In this condition, the PMAA chains approach insolubility and form relatively small coils or clumps.[4]

In general, for oxides, the relative charge density (σ) on the surface of the particles also varies with pH, but in a different manner from the charging of anionic polyelectrolytes. For oxides, at every pH, there are large numbers of negative, neutral, and positive surface sites. The σ value gives the overall net charge density. At low pH values, positive sites are in the vast majority, and, therefore, σ is positive. At high pH values, negative sites are in the majority, and σ is negative. At the zero point of charge (zpc), which occurs when the number of positive sites equals the number of negative sites, σ = 0. For the relatively pure α-Al_2O_3 powders used in this study, the zpc is at pH ≈8.7.[1]

The comparison of the charging behavior of PMAA and Al_2O_3 with pH leads to an obvious conclusion that the saturation limit of PMAA adsorption on Al_2O_3 should be significantly affected by pH. Figure 2 is a plot of the amount of PMAA adsorbed at the saturation levels versus pH and simultaneously the amount of PMAA necessary for suspension stability. The amount of PMAA which must be adsorbed to achieve a stable suspension increases with decreasing pH. Regions above the solid curve are stable and dispersed. Regions below the curve are unstable and show an onset of flocculation. The regions below pH 4 are discussed in Ref. 1 and thus will not be discussed in this paper.

Figure 2 was developed for 20 vol% Al_2O_3 suspensions; therefore, in order to expand the concepts for different solids concentrations, pH, and polyelectrolyte molecular weight and to use these concepts for the processing of these suspensions, more experiments were conducted using polyelectrolytes and colloidal α-Al_2O_3.

III. Experimental Procedure

(1) Materials and Chemicals

The ceramics used in this study were of very-high-purity (>99.995%), submicrometer-size, and relatively monodisperse (0.2 to 1.0 μm) α-Al_2O_3 powders (AKP 20 and AKP 30).* The average diameter measured by an X-ray absorption/sedimentation technique† was 0.52 μm for AKP 20 and 0.41 μm for AKP 30.

PMAA   PAA

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     CH₃                      H
      |                       |
  —C —CH₂ —              —C —CH₂ —
      |                       |
     COOH      n             COOH      n
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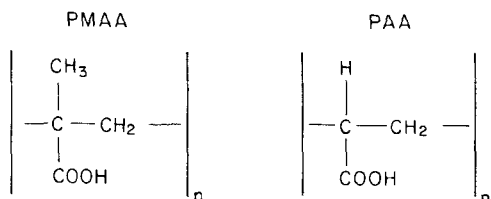
Fig. 1.   Schematic of PMAA and PAA polymer segments.

The average surface area as measured by standard BET N_2 adsorption[‡] was 4.5 m²/g for AKP 20 and 6.8 m²/g for AKP 30.

The polyelectrolytes used were the Na⁺ salt of poly(methacrylic acid) (PMAA-Na) with an average molecular weight (MW) of 15 000 and PAA of various molecular weights (1800, 5000, and 50 000).[§] These polyelectrolyte structures are shown in Fig. 1.

The water used was distilled and deionized. The pH was adjusted with standardized analytical-grade HCl and NaOH solutions (1.0N and 0.1N). Analytical-grade NaCl was used to adjust the ionic strength as desired.

(2) Experimental Methods

(A) Viscosity Measurements: Viscosity measurements were conducted with a rotary viscometer[¶] with a small sample chamber. To determine the relative magnitude of viscosity and whether the suspensions were flocculating or stabilized, the following rheological measurement method was used:

(i)   Each suspension was initially sheared at a relatively high shear rate of 93 s⁻¹. This ensured that permanent particle clusters (if any) were dispersed.

(ii)   The shear rate was then decreased every 30 s in eight increments to 0.46 s⁻¹ and the viscosities recorded at each shear rate.

(iii)   The suspensions were then undisturbed for 10 min so that nucleation and growth of particle clusters could occur.

(iv)   The shear rate was then increased every 30 s in eight increments to 93 s⁻¹ and the viscosities recorded again at each shear rate.

Large differences between the initial decreasing-rate sweep and the later increasing-rate sweep were assumed to be due to flocculation (i.e., the nucleation and growth of particle clusters). The magnitude of the viscosities was taken as a relative measure of the fluidity of the suspensions as related to the particle interaction energy and the degree of particle clustering.

(B) Zeta Potential and Interparticle Repulsive Potential Calculations: Zeta potential (ζ) was calculated by using the measured electrophoretic mobility[**] and Henry's equation[5] with Overbeek's correction, if necessary.[6] This correction takes into account electrophoretic retardation due to ions in the mobile part of the double layer. This effect is dependent on the value of κa, where κ is the inverse screening length and a is the particle diameter. In general, as the ionic strength of a suspension increases, κa increases. For the purpose of this paper, the actual polymer chains were not included in the calculation of κa; however, their associated ions were included in the κa determination. This is based on the assumption that the relatively large bulk anionic polymer molecules do not appreciably contribute to specific conductivity in such low concentrations. These measurements can only be completed on very dilute suspensions. Therefore, it was very important that the suspensions were centrifuged and the equilibrium supernatant carefully decanted into a beaker. Then a portion of the sediment was removed and readded to the equi-

‡Quantisorb, Quantachrome Co., Syosset, NY.
§Polysciences, Inc., Pittsburgh, PA.
¶Model RVTD Digital Viscometer, Brookfield Engineering Laboratories, Inc., Stoughton, MA.
**Micro-Particle Electrophoresis Apparatus Mark II, Rank Brothers, Bottisham, Cambridge, England.
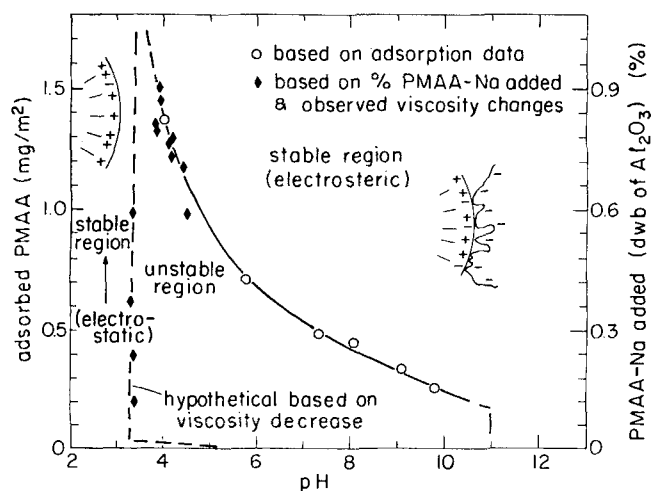††R. T. Vanderbilt Co., Norwalk, CT.

Fig. 2.   Stability map showing the amount of adsorbed PMAA required to form stable suspensions of 20 vol% AKP 30 α-Al₂O₃ as a function of pH.

librium supernatant to keep polymer adsorption constant. Prior to taking the measurements, the new dilute suspensions were very briefly ultrasonicated and magnetically stirred to ensure that only singlet particles were measured. At least 10 measurements were completed for each sample to ensure accuracy.

Interparticle repulsive potentials (V_r) were calculated from Deryagin–Landau and Verwey–Overbeek (DLVO) theory[7] according to

$$V_r = -2\pi\varepsilon a\Psi_d^2 \ln\left[1 - \exp(-\kappa H)\right] \qquad (1)$$

where ε and a are constant, H is the particle separation distance, and Ψ_d can be approximated by ζ to yield

$$cV_r = \zeta^2 \ln\left[1 - \exp(-\kappa H)\right] \qquad (2)$$

where c is a constant. For every sample studied, the van der Waals attractive potentials can be assumed to be equivalent; therefore, it is only necessary to compare the values of V_r for qualitative arguments concerning interparticle potentials since at any distance a higher V_r indicates a relatively larger electrostatic repulsion between particles. For 40 vol% dispersed suspensions of 0.41-μm particles, the average separation distance is ≈70 nm (700 Å). Therefore, in order to only examine the effects of V_r when interparticle interactions become important, comparisons of V_r are made at a particle separation distance of 10 nm (100 Å).

(C) Processing of Suspensions for Sintering: AKP 30 α-Al₂O₃ powder was dry-pressed, slip cast, and simply air cast (dried) in plastic molds. The dry-pressed pellets were approximately 2.54 cm in diameter and pressed biaxially at 51.8 MPa. All suspensions were prepared with commercially available PAA-NH₄⁺ (MW of 5000)[††] (0.22% (dry-weight basis (dwb))) and the pH adjusted to ≈8.8 with small amounts of citric acid (0.065% (dwb)). The slip-cast samples were prepared from 50 vol% suspensions cast between two slabs of plaster. The air-cast samples were made by pouring 5 mL of 40 vol% and highly concentrated (≈60 vol%) suspensions into plastic molds and allowing them to dry. All of the samples were then sintered in air at 990° to 1500°C. The samples were held at the maximum temperature for 1 h. The heating and cooling rates were 300°C/h. The sintered densities were measured by a standard alcohol immersion method.

IV.   Results and Discussion

(1) Viscosity versus pH

Figure 3 shows the effect of pH on viscosity for stabilized suspensions at various solids loading. Using Fig. 2 for representa-
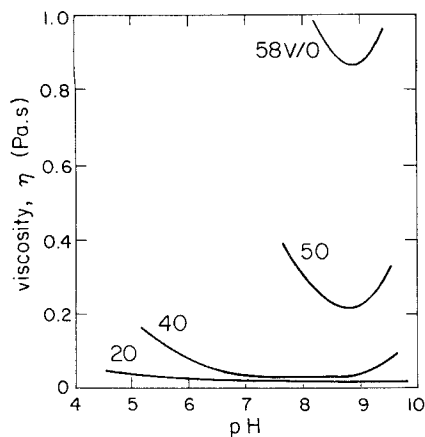
Fig. 3. Viscosity at 9.3 s^{-1} versus pH for PMAA-stabilized AKP 30 α-Al_2O_3 suspensions from 20 to 58 vol% solids concentrations. The amounts of PMAA added were enough to provide complete surface adsorption.

tion, all of these suspensions are in the stable region, but still relatively close to the stability boundary.

In 20 vol% Al_2O_3 suspensions, all of the stabilized systems have very low viscosities and the difference between suspensions stabilized at pH 4.5 and pH 10 is minimal. As the volume percent of solids increases, the magnitude of the viscosity also increases, whereas the effective pH range gets smaller (Fig. 3). In all cases, the minimum viscosity occurs at pH ≈ 8.8 with viscosity increasing for both increases and decreases in pH. Curiously, this pH coincides with the zpc of this Al_2O_3, where one might expect maximum viscosities. However, upon introduction of polyelectrolytes, the surface chemistry is governed by the adsorbed polyelectrolytes and not the bare Al_2O_3 surfaces.

For pH >9.0, the viscosity increase is due to the presence of excess polymer in solution which is not adsorbed on the Al_2O_3 particles. The presence of this excess polyelectrolyte is inevitable because of the adsorption behavior of the polyelectrolytes above pH 9.[1] Above pH 9, "high-affinity-type" adsorption does not occur; therefore, in order to reach the saturation adsorption limit (and complete stabilization), there has to be an equilibrium amount of polyelectrolyte in solution. This leads to high viscosities in concentrated suspensions where the amount of water is small and the concentration of excess polyelectrolyte in solution becomes appreciable. The effects of excess polymer in solution will be discussed in a following section.

For pH <8, the problems related to excess polyelectrolyte in solution can be avoided because of the high-affinity-type adsorption behavior.[1] However, the viscosity increases shown in Fig. 3 occur because of two other related phenomena: as the pH decreases, the amount of polyelectrolyte necessary to provide stabilization increases (Fig. 2), while at the same time the polyelectrolyte chains become less dissociated and behave more like neutral polymers.[1] This results in the Al_2O_3 particles being covered with increasing amounts of less negatively charged polyelectrolytes and leads to two problems. First, with less dissociation, the negative charge characteristics of the polyelectrolyte decrease and the relative solubility of the polymer also decreases.[1] This leads to a situation where the adsorbed polyelectrolyte has a smaller number of negatively charged functional groups extending into solution and, therefore, decreases the magnitude of the electrosteric repulsive barrier between particles.[1,8] Second, as the amount of polyelectrolyte increases, the concentration of ions associated with the polyelectrolyte and ions due to pH adjustment also increases and, therefore, reduces the electrostatic portion of particle repulsion due to high ionic strengths. These results are summarized in Table I.

These destabilizing effects become more appreciable at higher solids concentrations since the particle repulsion necessary to provide stability increases with increasing solids concentrations (e.g., Fig. 3).[9,10] For a stable 20 vol% suspension at pH 5.5, the volume percent solids is relatively low, and under these conditions of polyelectrolyte dissociation and ionic strength, the binding energy between particles is low enough to prevent the nucleation and growth of particle clusters and the resultant viscosity remains low. In contrast, for a stable 40 vol% suspension at pH 5.5, the binding energy between particles is low enough to prevent permanent clusters, but high enough to induce a large increase in viscosity. To have more fluid and stable suspensions at higher solids concentrations requires adjustment to a more optimum pH where the adsorbed polyelectrolyte is more fully dissociated and ionic strengths lowered so that a more effective electrosteric repulsion can exist between particles.

These concepts will be revealed in more detail in the following section; however, it should be noted that for this system the optimum seems to be pH ≈ 8.8. This pH is where the minimum viscosity occurs (Fig. 3) and coincides with the point at which the polyelectrolyte is fully charged and maintains maximum solubility while high-affinity-type adsorption still occurs and the ionic strength is relatively low. Under these conditions, the amount of polyelectrolyte in solution is low and the binding energy between particles is small.

Although the shapes of the viscosity curves shown in Fig. 3 are primarily due to polyelectrolyte chemistry and interparticle forces (discussed in detail below) there is undoubtedly a sec-

Table I. Relation between Interparticle Force and Rheological Behavior*

pH	Polymer ratio[†]		κa[‡]	ζ (mV)[§]	cV_r (J)[¶]	η_0 to η_{10}**[**] (mPa·s)	Stability[††]
8.1	B	0.76	139	−35	1.4	220–405	F
	B	0.95	152	−41	1.0	60–205	F
		1.2	164	−37	0.5	37–37	S
		1.9	198	−33	0.1	50–70	S
8.1[‡‡]		0.95	265	−26	0.0	415–645	F
	C	1.2	271	−27	0.0	55–82	SF
	C	1.4	279	−22	0.0	50–60	S
9.5	B	0.55	100	−31	7.3	55–115	F
		1.2	135	−32	1.4	85–87	S
		1.7	163	−32	0.4	205–215	S
9.0		1.3	143	−34	1.1	20–20	S
8.8	A	1.37	152	−32	0.6	20–20	S
6.5	A,C	1.2	213	−24	0.0	45–50	S
5.3	A	1.1	265	−17	0.0	205–230	SF
4.6	A	1.3	325	−13	0.0	1300–1700	F

*40 vol% AKP-30 α-Al_2O_3 suspensions with PMAA. [†]Polymer ratio is the actual amount of polymer added to the amount needed for complete surface coverage (from Fig. 2). Refer to text for meaning of A, B, and C. [‡]κa is the inverse Debye–Huckel length times the particle diameter. [§]ζ is the zeta potential. [¶]cV_r is the relative measure of the electrostatic repulsion between two particles. **η_0 to η_{10} is the initial viscosity and viscosity after ≈ 10 min at a shear rate of 9.3 s^{-1}. [††]S, F, SF mean stable, flocced, slightly flocced. [‡‡]With 0.1M NaCl.

ondary effect due to changes in the adsorbed polyelectrolyte configuration as a function of pH. With changes in polyelectrolyte configurations come associated changes in the effective hydrodynamic radii of the particles. These effects may also show minima in viscosity and become more appreciable as the particle concentration and the adsorbed polymer molecular weight increase. However, changes in hydrodynamic radii will not be discussed in this paper.

(2) Relating Interparticle Forces to Rheological Behavior

Table I shows a summary of data relating interparticle forces to rheological behavior for 40 vol% AKP 30 suspensions stabilized with PMAA. The polymer ratio is a measure of the amount of polymer added in relation to that necessary for adsorption saturation according to Fig. 2. The value of κa is a relative measure of the ionic strength of the solution. As κa increases, the ionic strength increases, and, as a reference for this system, a κa value of 213 is equivalent to a $0.1M$ NaCl solution. The cV_r values are a relative measure of the repulsive potential between particles due solely to calculated electrostatic repulsion at a separation distance of 10 nm (100 Å). The η_0 to η_{10} values are a measure of the change in viscosity over a period of ≈ 10 min at a shear rate of 9.3 s^{-1}, and the comments S, F, and SF are qualitative observations meaning stable, flocced, and slightly flocced, respectively.

The information in Table I can be used to provide some preliminary conclusions relating to interparticle forces. First, from pH 8.8 to pH 4.6, a decrease in the magnitude of the negative charge characteristics of the adsorbed polyelectrolyte causes less repulsion between particles and induces an increase in viscosity. This is shown in Table I by the data points labeled A. It is shown that as pH is decreased from 8.8 to 4.6, the zeta potential decreases as the polyelectrolyte begins to behave more like a neutral polymer.[1] Also, the ionic strength (κa values) increases because of the presence of counterions. These two effects result in a decrease in repulsion between particles and a corresponding increase in viscosity with the eventual loss of stability.

Second, the data points labeled B in Table I indicate that the most dominant cause for flocculation in polyelectrolyte-stabilized suspensions is incomplete adsorption, which provides a driving force for particles to cluster together in an effort to form saturated monolayers. This is clearly shown in Table I in that, in all cases where the polymer ratio is <1.0, flocculation resulted even though the zeta potential and electrostatic repulsive forces are relatively high. This is especially true for pH <8.8, where high-affinity-type adsorption occurs.[1] However, as expected, at pH >8.8, where high-affinity-type adsorption does not occur, the driving force for flocculation due to incomplete adsorption is not as strong as at lower pH. This is particularly evident for the sample at pH 9.5, which has a high cV_r value due to low ionic strength. Even though this sample has a polymer ratio of only 0.55, it exhibits a lower viscosity than the sample at pH 8.1 with a polymer ratio of 0.76.

It may also be concluded that, once enough polymer has been adsorbed, there is a stabilization effect due solely to the polyelectrolyte, even in the absence of appreciable repulsion due to electrostatics. This is especially apparent for the data labeled C for pH 8.1 with NaCl and pH 6.5 where $V_r \approx 0$, but stable fluid suspensions resulted. Further evidence for the stabilizing effects due to the polyelectrolyte is that, for the same 40 vol% system in the absence of polymer, an electrostatic value of $cV_r \approx 3$ is necessary to induce comparable levels of stability and viscosity as those found for PMAA-stabilized suspensions at pH 8.8 with a cV_r value of 0.7.[11]

Finally, even though Table I shows that, for 40 vol% suspensions, polyelectrolyte stabilization can exist, even under conditions of high ionic strength and low electrostatic repulsion, it is still necessary to have a $|\zeta|$ of >20 mV. This value indicates that the polyelectrolyte is still charged and has negative soluble functional groups extending into the solvent so that an enthalpic steric stabilization mechanism can be functional with an electrostatic stabilization mechanism.[8]

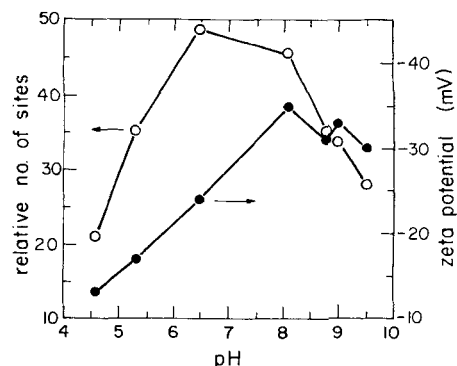Another important aspect of polyelectrolyte stabilization is that

Fig. 4. Relative number of COO$^-$ polyelectrolyte sites and zeta potential versus pH for 40 vol% AKP 30 α-Al$_2$O$_3$ suspensions with enough PMAA for complete surface adsorption.

the resulting zeta potential of stabilized suspensions tabulated in Table I can be directly correlated to the charge on the Al$_2$O$_3$ particles, amount of polyelectrolyte dissociation, and the amount of polyelectrolyte adsorbed on the surface. This concept is represented in Fig. 4, which shows the zeta potential (ζ) and relative number of dissociated COO$^-$ polymer sites (RNS) versus pH. The RNS was calculated by multiplying the amount of adsorbed PMAA (Fig. 2) times the percent of COOH groups dissociated (measured in Ref. 1). This quantity effectively represents the number of negative sites which are available to charge a particle surface once adsorbed. If there is no electrical interaction between the charged polymer and the particle surface, then ζ should ideally correspond directly with RNS; i.e., as the amount of adsorbed charged polymer increases ζ increases. However, in this system, the polymer has electrical interactions with the particle surface; therefore, Fig. 4 shows that the combination of RNS and the influence of particle surface charge determines the resulting zeta potential.

Figure 4 was constructed so that RNS and ζ cross over at pH ≈ 8.7 since this pH is very close to the zpc of the Al$_2$O$_3$, and, therefore, the overall net charge of the Al$_2$O$_3$ will have a minimal contribution to the observed ζ. As pH decreases to 8.1, RNS increases and ζ becomes more negative, as expected. However, at pH 6.5, RNS is at a maximum whereas ζ decreases in magnitude appreciably. From this it may be concluded that, below the zpc, the excess positive surface sites on the Al$_2$O$_3$ begin to neutralize excesss negative sites on the polyelectrolyte and the effective ζ is lower than expected. This behavior is shown to continue to lower pH values; however, it is expected that for pH <3, the ζ will be determined only by the Al$_2$O$_3$ surface since RNS approaches 0. However, for pH <3, the ζ will probably still be lower than expected because of the physical presence of an adsorbed neutral polymer layer.

At pH values above the zpc, ζ is slightly more negative than expected from the RNS values. This suggests that, above the zpc, the excess negative surface sites on the Al$_2$O$_3$ become additive to the negative sites on the polymer. It is emphasized that, for this system, ζ is a strong contributing factor to the overall suspension viscosity, but not the sole determining factor. Maximum ζ is at pH 8.1; however, the best suspensions in terms of stability and viscosity are observed at pH 8.6 to pH 9.0.

(3) Viscosity versus Amount of Polyelectrolyte

Figure 5 shows the viscosity of 50 vol% AKP 20 Al$_2$O$_3$ suspensions (pH 9) versus the amount of PAA added for various molecular weights. For each sample, the viscosity was recorded at 0 and 10 min at a shear rate of 9.3 s^{-1}. Increases in viscosity (connected by tie lines) show that flocculation is occurring in the suspensions. For each molecular weight, there is a critical amount of polymer that must be added before stabilization and low viscosities result. This corresponds to the saturation adsorp-
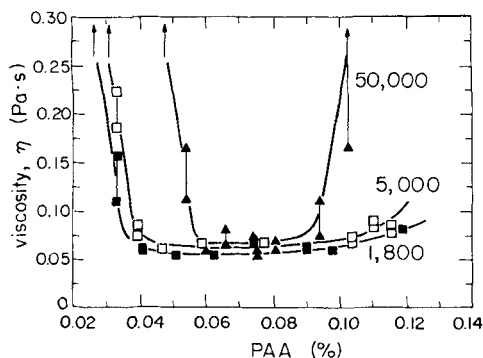
Fig. 5. Viscosity versus the amount of PAA added (dwb of Al_2O_3) for various molecular weights for 50 vol% AKP 20 α-Al_2O_3 suspensions at pH 9. ($\Diamond$), ($\Box$), and ($\triangle$) values are at 0 min and ($\blacklozenge$), ($\blacksquare$), and ($\blacktriangle$) are at 10 min.

Fig. 6. Sintering behavior of AKP 30 α-Al_2O_3 for various processing techniques.

tion limit of the polyelectrolytes on Al_2O_3 and is in agreement with the previous discussion concerning the stability map in Fig. 2.

Further additions of polymer past the adsorption saturation limit only serve to provide excess polymer in solution. As shown in Fig. 5, the rheological effects due to excess polymer are much more drastic as the molecular weight increases. This is probably due to two reasons. First, the viscosity of polymer solutions is proportional to the size of the individual polymer coils.[4] Therefore, as the molecular weight increases, the viscosity of the aqueous solution drastically increases. Second, it is observed that, as the molecular weight increases, a more pronounced thixotropic effect occurs due to the excess polymer. This is the result of a destabilization mechanism called depletion flocculation.[8,12] Basically, depletion flocculation is the result of an osmotic pressure increase due to the polymer in solution, thereby forcing particles together. This effect increases with increasing molecular weight.

Therefore, for processing concerns, the use of lower molecular weight polyelectrolytes (i.e., MW of 1000 to 10 000) seems to produce more "forgiving" dispersed suspensions with a wider range of stability. The amount of polyelectrolyte necessary for stabilization increases as the molecular weight increases; this is an indication that the adsorbed layer thickness may also be increasing with molecular weight. This may have substantial effects in highly concentrated suspensions.

(4) Processing with Polyelectrolyte-Stabilized Suspensions

To show the advantage of increasing the solids concentration in suspension, some samples were air cast in plastic molds from 40 to 60 vol% suspensions and then sintered at 1400°C for 45 min. The suspensions were fabricated at pH $\approx$8.8 for optimum dispersion properties. Because of the reduced volume fraction of solids and longer casting times for the 40 vol% suspensions, it is expected that long-range particle segregation took place.[13] This resulted in slightly lower green densities for the 40 vol% suspensions. This also became apparent after sintering, when all of the samples made from the 40 vol% suspensions consistently resulted in 3% to 6% lower sintered densities.

To more clearly show the possible benefits of processing with highly concentrated suspensions, two powder systems of high-purity α-Al_2O_3 were processed by pressing, slip-casting 50 vol% suspensions, and casting $\approx$60 vol% suspensions in plastic molds. The sintering behaviors and the results for AKP 30 Al_2O_3 are shown in Fig. 6. Figure 6 shows clearly that processing from highly concentrated polyelectrolyte-stabilized suspensions leads to higher consolidated densities and that these benefits carry over in the form of reduced sintering temperatures. The samples processed from 60 vol% suspensions had a consolidated density of 65.8% of theoretical and sintered to 99% of theoretical at 1350°C. For an Al_2O_3 powder with a relatively low surface area
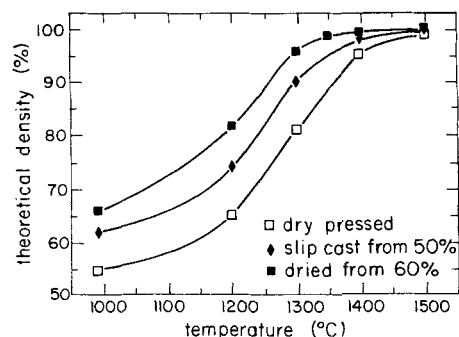
of 6.8 m^2/g, this is a very low sintering temperature. In contrast, filtration channels cause the development of excess voids in slip-cast microstructures and yield a consolidated density of 62.1% of theoretical, and higher sintering temperatures are required for the elimination of these voids.[14] As expected, the local density variations and the inefficient particle packing caused by dry-pressing yield a consolidated density of 55.0% of theoretical and even higher temperatures for complete void elimination.

V. Conclusions

In highly concentrated ($>$50 vol%) Al_2O_3 suspensions stabilized with PMAA, a viscosity minimum is observed at pH $\approx$8.8. This conicides with the pH at which the polyelectrolyte is fully charged and maintains maximum solubility, whereas high-affinity-type adsorption still occurs and the ionic strength is relatively low.

Below pH $\approx$8.8, the viscosity increases because of a decrease in the negative charge characteristics of the adsorbed polyelectrolyte and a decrease in the electrosteric repulsive barrier between particles. Above pH $\approx$8.8, viscosity increases because high-affinity-type adsorption behavior is lost and excess polymer in solution becomes appreciable. Excess polymer can also lead to depletion flocculation and this effect becomes greater as molecular weight increases.

Polyelectrolyte stabilization can exist even in the absence of appreciable electrostatic repulsive forces due to conditions of relatively high ionic strength. However, even though polyelectrolyte stabilization can exist with low levels of electrostatic repulsion, it is necessary that an appreciable zeta potential be present on the particles. The actual zeta potential built up on particles due to polyelectrolyte adsorption is a function of the amount of polyelectrolyte adsorbed, the fraction of polyelectrolyte dissociation, and the surface charge of the bare particle. For anionic PMAA and Al_2O_3 at pH values below the zpc of Al_2O_3, the actual zeta potential is less than expected from the adsorbed PMAA because of the cancellation effect between the negative PMAA and positive Al_2O_3 surfaces. At pH values above the zpc, there is an additive effect between the negative PMAA and the negative surface which yields a larger zeta potential than expected from the amount of PMAA adsorbed.

In general, by understanding the chemistries of the polyelectrolyte and particle surface, polyelectrolyte adsorption behavior, and polyelectrolyte rheological effects, one may control the viscosity and rheology for all solids levels. If it is desired to work at low solids, but still prevent problems due to segregation, then the proper polyelectrolyte conditions can be tailored for a high-viscosity thixotropic suspension. If dispersion and high solids are desired, then the polyelectrolyte conditions can again be tailored. To date, 62 vol% ($>$86 wt%) AKP 30 α-Al_2O_3 suspensions have been fabricated with viscosities of $<$500 mPa·s at 93 s^{-1}. These are very low viscosities for such highly concentrated suspensions of 0.41-μm-size particles.

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Reactions of Silicon-Based Ceramics in Mixed Oxidation Chlorination Environments

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The reaction of silicon-based ceramics with 2% Cl$_2$/Ar and 1% Cl$_2$/1% to 20% O$_2$/Ar at 950°C was studied with thermogravimetric analysis and high-pressure mass spectrometry. Pure Si, SiO$_2$, several types of SiC, and Si$_3$N$_4$ were examined. The primary corrosion products were SiCl$_4$(g) and SiO$_2$(s) with smaller amounts of volatile silicon oxychlorides. The reactions appear to occur by chlorine penetration of the SiO$_2$ layer, and gas-phase diffusion of the silicon chlorides away from the sample appears to be rate limiting. Pure SiO$_2$ shows very little reaction with Cl$_2$. SiC with excess Si is more reactive than the other materials with Cl$_2$, whereas SiC with excess carbon is more reactive than the other materials with Cl$_2$/O$_2$. Si$_3$N$_4$ shows very little reaction with Cl$_2$. These differences are explained on the basis of thermodynamic and microstructural factors.

I.   Introduction

THE recent developments in advanced ceramic materials have made these materials candidates for applications previously restricted to metals and superalloys. In particular, Si-based ceramics are prime candidates for use in advanced heat engines and heat exchangers because of their excellent high-temperature strength and oxidation resistance.

During the operation of these systems, the materials are often exposed to severe oxidative and/or corrosive gases. Marine-based turbine engines ingest sodium chloride from sea salt spray, making the mixed oxidation/chloride reactions of these materials important. Similarly, Si-based ceramics used in heat exchanger technology are exposed to a variety of halide gases (typically fluorine and chlorine) when used in the refining of Ti and Zr and the remelting of aluminum.[1] Silicon-based ceramics are inherently unstable in oxidizing atmospheres, but obtain their oxidation resistance by the formation of a protective silica layer at the gas–solid interface. The mixed oxidation/chlorination behavior of these materials is further complicated by the volatility of the silicon chloride compounds.

The mixed oxidation/chlorination behavior of metals and superalloys at high temperatures has been studied by various researchers.[2–8] Jacobson et al.[5–8] have made use of a high-pressure mass spectrometer sampling system and conventional thermogravimetric analysis to study these reactions. The former analytical technique allows the volatile corrosion products to be unambiguously identified. This identification, coupled with kinetic information, leads to a further understanding of the mechanisms of the corrosion process.

Although the behavior of metals in high-temperature environments containing both chlorine and oxygen has been examined, little work has been done to investigate the behavior of silicon-based materials in these environments. Chlorine, however, is widely used in the thermal oxidation of high-purity silicon for the production of gate oxide devices. The chlorine acts to limit the amount of sodium impurities present in the growing oxide and thereby increases the performance characteristics of the device. As a result of this practice, the role of chlorine in the thermal oxidation of silicon has been widely studied;[9–12] however, the majority of the previous work has focused on the characteristics of the oxide film and more specifically on chlorine incorporation