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Plastic forming of alumina from coagulated suspensions

J. Davies [1], J.G.P. Binner *,[2]

Division of Materials, School of Mechanical, Materials, Manufacturing Engineering and Management, The University of Nottingham, Nottingham NG7 2RD, UK

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Abstract

A processing system has been investigated in which alumina suspensions are initially dispersed at very high solids loadings and then subsequently coagulated by the introduction of salt to the system creating a plastic paste with rheological properties suitable for extrusion. Such coagulated pastes containing an alumina content of 81 wt% (50.7 vol%) have been extruded to produce sintered components possessing an average three point bend strength of 445 MPa. This corresponds to an improvement of 35–45% over samples prepared by a flocculated processing route at the solids loading required for extrusion. This increase in strength is attributed to the initial dispersion of samples at the high solids loading, which serves to maximise suspension homogeneity and leads to a smaller critical flaw size in the final sintered extrudate even though the microstructures and densities are very similar. At present the coagulated pastes produce relatively soft extrudates which can be subsequently moulded into more intricate shapes. Further work is required to formulate stiffer pastes resulting from higher alumina contents.

Keywords: Al_2O_3; Extrusion; Microstructure-final; Strength; Suspensions

1. Introduction

Plastic forming processes such as extrusion demand that the green ceramic body exhibits a degree of plasticity to enable it to be deformed and subsequently maintain that shape. Unlike clays, however, advanced ceramic powders do not inherently possess such plasticity and so large quantities of polymers are necessary to confer the necessary rheological flow characteristics onto the ceramic. After forming, the polymeric material must be removed from the ceramic component and this is commonly achieved by thermal degradation. This process can introduce defects into the component such as cracks and voids, which act to reduce its final sintered strength severely. There is therefore a need, and indeed an increasing trend, to formulate deformable plastic bodies that have a much lower polymer content, without causing detriment to the flow properties.

Research such as that of Sarker et al.[1] has focused on the use of water-soluble polymers such as methylcellulose and associated derivatives. These are required in relatively low concentrations to impart the required flow characteristics. For example, Schuetz[2] found that a concentration of 2wt% methylcellulose was adequate to extrude 51 vol% (80 wt%) alumina, although an increase to 5 wt% improved the green strength of the formed body.

One of the most important properties of a paste is the viscosity of the liquid phase. If the viscosity is too low, water will migrate or seep ahead of the solids phase, Benbow et al.[3] This causes the paste to stiffen and may, in severe instances, lead to the cessation of extrusion.

To avoid this effect a high liquid phase viscosity and/or a yield value are a necessity. This is often achieved by the addition of an aqueous clay suspension (e.g. Benbow et al.[4]), but in instances where high purity components are desired, a high molecular weight, pseudoplastic polymer solution of sufficiently high viscosity is used.

At present, plastic bodies or pastes prepared with water soluble polymers are commonly mixed at the solids loading required for processing using a high shear mixer. However, this often requires prolonged mixing times to produce a uniform body and disperse agglomerates.

* Corresponding author.
E-mail address: j.binner@lboro.ac.uk (J.G.P. Binner).
[1] Now with Blue Circle Industries plc, London, UK.
[2] Now with IPTME, Loughborough University, Leicestershire, UK.

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Those systems that do not use high shear mixing require diluted conditions for mixing followed by consolidation to the desired solids loading, Salamone et al.[5] This can be difficult to control and is again time consuming.

The use of colloidal powder processing can result in the rapid formation of highly homogeneous, de-agglomerated and hence dispersed suspensions if the inter-particle potentials are carefully controlled. The degree of de-agglomeration using this route is often greater than that achieved using high shear mixing and so upon drying, more uniform components result. Such uniformity is of benefit to the final component strength and hence it is for this reason that colloidal processing has become the focus of recent research in ceramic processing. Unfortunately dispersed systems without significant polymer addition do not have the rheological characteristics necessary for plastic forming, tending to be fluid and not possessing a yield value. Modification of the dispersed suspension is, therefore, required before it can be used for plastic forming processes. This modification transforms the suspension into a cohesive, viscous paste, with a yield point.

Recent research has examined, (i) the role of ammonium polyacrylate, NHPA, as a dispersant for high solids content alumina suspensions at high pH, Davies and Binner[6] and (ii) the role of salts in the coagulation of the resulting electrosterically dispersed, concentrated alumina suspensions, Davies and Binner.[7] The ultimate objective has been the achievement of a viscous, pseudoplastic paste possessing a yield point. The rationale is that the initial dispersion of powder and subsequent coagulation at a sufficiently high solids loading will produce more uniformly mixed and de-agglomerated pastes. These should give rise to components of higher strength compared to those produced by existing processing routes, where high shear mixing or initial diluted conditions are necessary. Furthermore, the concentration of polymer required to confer the necessary rheology for processing should be at an absolute minimum in order to avoid the problems associated with post-forming polymer burnout. This paper presents the results of research into the extrusion behaviour of these coagulated pastes.

2. Experimental

2.1. Paste preparation

A series of coagulated suspensions were prepared with alumina contents in the range 80–82 wt% (50–52 vol%), measured as weight percent of the total sample mass. For each sample, appropriate quantities of de-ionised water, weighed to ± 0.02 g, and an ammonium polyacrylate, NHPA, dispersant solution, weighed to ± 0.003 g, were added together. The water associated with the dispersant solution was accounted for in the calculations. The solution was mixed until the dispersant was uniformly distributed. A16SG alumina powder[3], weighed to ± 0.02 g, was added to the mixture and the blend stirred until an homogeneous body formed. This was then left for 1 h to allow adsorption of the dispersant onto the alumina. The dispersant used was Dispex A40,[4] a 37.6 ± 0.5 wt% solution of ammonium polyacrylate (NHPA). It is important to note that the masses quoted refer to the actual amount of NHPA used, not the Dispex A40 solution. The mass of NHPA used was measured in milligrams per gram of alumina powder and hence is denoted as mg g^{-1}. As a result of previous work,[6] the level of NHPA used was in the range 0.7– 2.1 mg g^{-1}.

The suspension was subjected to ultrasonic agitation[5] for 45 s, a time previously determined to be optimum, Davies and Binner.[6] To prevent water evaporation the beaker was sealed and left for 1 h to cool and attain equilibrium. Subsequently, each suspension was coagulated using ammonium chloride, NH_4Cl, powder. A concentration of 0.8 M NH_4Cl had been found sufficient to achieve full coagulation within the range of NHPA used, Davies and Binner.[6] The powder was weighed to ± 0.02 g, added to the suspension and mixed thoroughly and vigorously. Each sample was then exposed to a 60 mm Hg vacuum for 1 h for de-airing.

In tests that included the use of a methylcellulose binder,[6] the powder was mixed into the suspension and left for 24 h before the addition of salt. It was used to increase the viscosity of the liquid phase in order to prevent migration of water during the extrusion process. Methylcellulose was primarily chosen because of its non-ionic water soluble nature, so that it should not interfere electrostatically with the adsorbed NHPA. Furthermore, methylcellulose solutions are pseudoplastic, possess the ability to retain water and provide strength to extruded components in the green state, Sarker et al.[1] and Schuetz.[2] It should be noted that the thermal gelling properties of the methylcellulose were not utilised. To study the effects of different methylcellulose concentrations on sample extrusion behaviour, concentrations from 0.10 to 0.38 wt% of the total sample mass were used. A concentration of 0.38 wt% corresponds to a concentration of 2.0 wt% with respect to the water present, which is the quoted maximum solubility of methylcellulose in water. Flocculated pastes were also prepared to provide control samples for comparison with the coagulated pastes. These essentially consisted of a suspension of alumina powder and de-ionised

[3] Alcoa Manufacturing (GB) Ltd, Worcester, UK.
[4] Allied Colloids, Bradford, UK.
[5] Kerry ultrasound unit; output power 150 W, frequency 20 kHz. Kerry Ultrasonics Ltd., Hitchin, UK.
[6] Tylose, Fluka Chemicals, Glossop, Derbyshire, UK.

water adjusted to pH 8.0, the measured PZC of the alumina powder used. For these samples ultrasonic agitation was found to be ineffective. In some control experiments methylcellulose and/or ammonium chloride were added to the suspension prior to the addition of the powder.

2.2. Extrusion

The extrusion system used is illustrated in Fig. 1. Essentially, paste was forced through a high chromium stainless steel cylindrical die by a mild steel plunger with a polytetrafluroethene (PTFE) piston coated in silicone grease. The extrusion force was produced by a M30K Lloyd[7] testing machine and measured by a 10 kN load cell. Fitting into a base housing recess, the dies used were 3 mm in diameter, with the die land length varying from 3 to 35 mm. A 25 mm barrel down which the paste was extruded was positioned on top, with vertical alignment ensured by screw threads which firmly secured the barrel and die to the base.

The standard test procedure adopted was to extrude at a speed of 5 mm min^{-1} through the die of diameter 3.0 mm and length 3.0 mm, with a piston-force verses distance graph plotted to assess the flow behaviour. Paste was loaded into the barrel in a manner that ensured there was no trapped air between it and the piston, which in early test runs affected the extrusion trace produced. If the extrusion force continually increased with distance, water was assumed to be migrating from the paste and the degree of seepage, S_d, calculated as the gradient of the extrusion trace. When a flat or decreasing extrusion trace was produced the paste was seen to form an acceptable extrudate and the force required for extrusion, F, was noted and the corresponding extrusion pressure, P, calculated. In later tests the standard die was replaced with one with a much longer, 35 mm, die-land. Furthermore, also in later experiments the speed of extrusion was increased up to 100 mm min^{-1}.

2.3. Sintering and characterisation

Samples were dried at 85°C for 1 week to ensure they were completely dry and then sintered using ramp rate of 3°C min^{-1} up to 400°C, followed by 30 min dwell time. Temperature then increased at 3°C min^{-1} up to 1540°C and held for 2 h before cooling to ambient.

The density of both green and sintered extruded samples was measured by mercury densimetry. Quoted values are based on an average of at least three samples.

The mechanical properties of sintered components were measured using the three point bend strength technique and the appropriate equation for cylindrical

[7] Lloyd Instruments PLC, Fareham, Hampshire, UK.

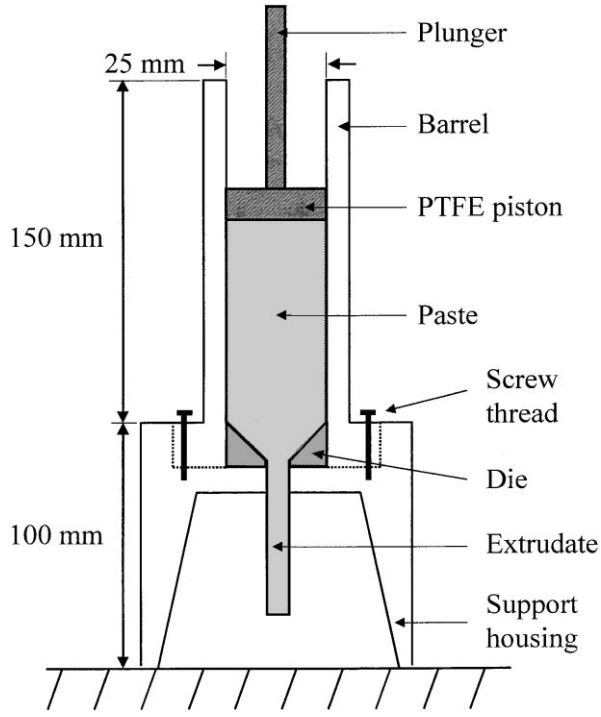

Fig. 1. Extruder design used in the research, adapted from Ref. 3 and 4.

samples (Eq. 1), from which a critical flaw size calculated using the Griffith crack equation Eq. (2). A minimum of 50 valid tests were used to calculate average values, with any samples that did not break at the point of maximum load being discarded.

$$\sigma_{3pt} = \frac{FL}{\pi r^3} \tag{1}$$

where,

σ_{3pt} = Average three point bend strength/Pa
F = Maximum load before failure/N
L = Span length of bend test pivots/m
r = Radius of sample/m

$$\sigma_{3pt} = \sqrt{\frac{G_c E}{\pi c}} \tag{2}$$

where,

c = Half largest flaw size/m
G_c = Critical strain energy release rate/J m^{-2}
E = Young's modulus/Pa

G_c was taken to be 60 J m^{-2} (Anderson et al.[8]). E was selected to be 350 GPa, a typical value for 98% dense sintered alumina components (Lee[9]). Sintered specimens were prepared for analysis by scanning electron microscopy by diamond polishing first with a 25 μm diamond

wheel for 10 min, followed by 9, 6 and 3 μm polishing wheels sequentially for 20 min each. The samples were thermally etched at 1540°C for 10 min using a rapid ramp rate of 10°C min^{-1} prior to being coated in gold for analysis.

3. Results

3.1. Extrusion of pastes without methylcellulose addition

These pastes did not extrude in an acceptable manner, Fig. 2. That is, virtually all samples, both flocculated and coagulated, suffered water migration. Furthermore an increase in surface roughness and warpage was observed with increasing NHPA content. Evidence for the water migration is clearly seen from the positive gradient of each line in Fig. 2. The calculated gradient, i.e. degree of seepage, S_d, is given in Table 1 for pastes containing 81 wt% alumina along with the other measured parameters. It can be seen that the degree of seepage of the coagulated pastes was significantly smaller than that of the flocculated pastes and that the amount of seepage decreased with increasing NHPA concentration. A similar trend can also be noted in the measured bend strength values. Samples prepared with NHPA concentrations below 1.4 mg g^{-1} had approximately 50% higher bend strength than flocculated samples and as the NHPA concentration increased the strengths fell to flocculated sample levels. Apart from these differences, the samples were of comparable density and possessed a similar microstructure, with an average grain size of 1.3 μm. The results of the experiments performed with varying alumina content, Table 2, indicate that, as expected, water seepage increases significantly with solids content. Even when the NHPA was increased from 1.40 to 2.10 mg g^{-1} the pastes remained unextrudable, although the degree of seepage did reduce substantially.

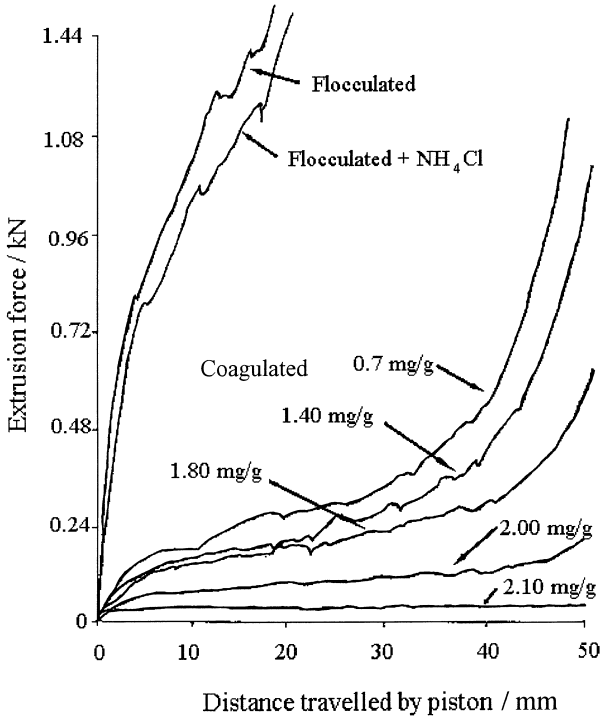

Fig. 2. Extrusion plots for coagulated and flocculated pastes prepared with different concentrations of NHPA. 0.8 M NH_4Cl was used as the coagulant.

3.2. Extrusion of pastes containing methylcellulose

From Table 3 it can be seen that the degree of seepage decreased with increasing methylcellulose levels, reaching zero seepage at a concentration of 0.29 wt%. Results of viscosity measurements confirmed that the role of the additive was to increase the viscosity of the liquid phase. It was also noted that the concentration of 0.38 wt% increased the green strength of the extruded body, allowing easier handling. This concentration of methylcellulose became the standard for the remainder of the work. Thus a *standard coagulated paste* is defined as containing 1.40 mg g^{-1} NHPA, 0.8 M NH_4Cl and 0.38 wt% methylcellulose. The alumina content will always be stated and the balance is deionised water.

An extrusion trace for the standard coagulated paste containing 81 wt% alumina is compared to those of flocculated bodies containing an identical concentration of 0.38 wt% methylcellulose in Fig. 3. The methylcellulose not only cured water migration in the coagulated pastes, but also significantly reduced it in the flocculated samples. However, the coagulated paste trace was much smoother than the flocculated counterparts and in addition the pressure required to extrude the coagulated sample was significantly lower. The measured extrusion pressures are summarised in Table 4, along with the other measured parameters.

In the green state the measured densities of the coagulated pastes were comparable to those of the flocculated pastes, all the values being slightly higher than corresponding extrudates prepared without methylcellulose. Despite the coagulated sintered components being of slightly lower density, they were marginally stronger than those prepared from flocculated pastes. The calculated Weibull modulus was significantly higher for the rods prepared by the standard coagulated processing route, however. Sintered SEM microstructures of standard coagulated pastes and flocculated pastes are shown in Figs. 4 and 5 respectively. The microstructures were taken from samples exhibiting the average bend strength of their respective paste type. All samples exhibited a similar grain structure with an average grain size of 1.3 μm, however, the standard coagulated pastes possessed small amounts of very fine porosity at some of the grain boundaries.

Table 1
Properties of coagulated and flocculated pastes prepared at 81.0 wt% alumina as a function of NHPA concentration and without methylcellulose

Concentration of NHPA (mg g^{-1})	Degree of seepage, S_d(kN m^{-1})	Green density, ρ_g (g cm^{-3}) ± 0.04	Sintered density, ρ_g(g cm^{-3}) ± 0.02	Diametral shrinkage (%) ± 1	Average 3pt. bend strength σ_{3pt} (MPa)	Approx. flaw size causing failure 2c (μm)
0.70	6.0 ± 0.9	2.14	3.83	18	402 ± 56	82
1.40	4.8 ± 0.2	2.17	3.83	19	349 ± 31	109
1.80	4.2 ± 0.4	2.15	3.83	19	238 ± 24	236
2.00	1.5 ± 0.3	2.14	3.81	18	239 ± 27	248
2.10	–	2.17	3.80	20	232 ± 25	224
Flocculated	40 ± 10	2.13	3.84	18	244 ± 23	224
Flocculated + 0.8 M NH_4Cl	40 ± 10	2.15	3.84	17	244 ± 27	224

Table 2
Degree of seepage at various alumina solids loadings

Alumina content (wt%)	Concentration of NHPA (mg g^{-1})	Degree of seepage, S_d, without methylcellulose (kN m^{-1})	Degree of seepage, S_d, with 0.38 wt% methylcellulose (kN m^{-1})
80.0	1.40	1.5 ± 0.4	–
80.5	1.40	3.6 ± 0.9	–
81.0	1.40	4.8 ± 0.2	0
81.5	1.40	25 ± 10	0
82.0	1.40	40 ± 10	5.5 ± 0.5
82.0	2.10	7 ± 1	0
83.0	2.10	66 ± 10	–

Table 3
Effect of methylcellulose concentration on the extrusion characteristics of standard coagulated pastes prepared at 81.0 wt% alumina

Concentration of methylcellulose (wt%)	Degree of seepage, S_d (kN m^{-1})	Extrusion force (F/kN)
0	4.8 ± 0.5	–
0.10	3.0 ± 0.6	–
0.19	1.2 ± 0.6	–
0.29	0	0.33 ± 0.04
0.38	0	0.34 ± 0.04

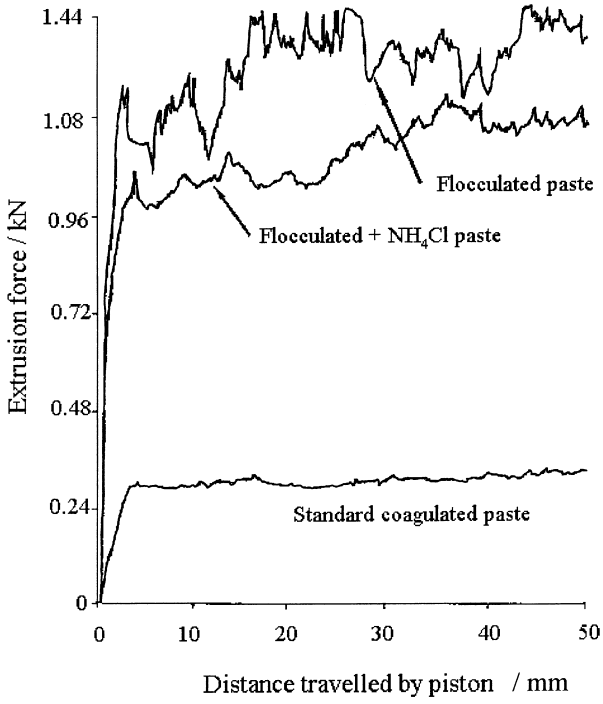

Fig. 3. Extrusion behaviour of standard coagulated and flocculated pastes containing 0.38 wt% methylcellulose and 0.8 M NH_4Cl.

3.2.1. Effect of solids loading

See page results for coagulated pastes prepared from suspensions containing 81.5 and 82 wt% alumina are presented in Table 2. These results indicate that a solids loading of 81.5 wt% alumina was the maximum solids loading that could be extruded before water seepage became a problem for a standard coagulated paste. However, if the dispersant level was increased to 2.10 mg g^{-1} NHPA then a solids content of 82 wt% alumina could be extruded acceptably. Density, diametric shrinkage and sintered strength values for these pastes may be seen in Table 5. The results show that processing at higher alumina contents did not result in an increased density, all values being within error of pastes prepared at 81 wt% alumina, although there was an indication that shrinkage decreased as the alumina content in the paste increased. The strength of the sintered rods increased with solids content, although the increase in dispersant level to 2.10 mg g^{-1} NHPA resulted in an

Table 4
Properties of coagulated and flocculated pastes prepared at 81.0 wt% alumina and with 0.38 wt% methylcellulose

Paste type	Extrusion force, F (kN)	Green density, ρ_g (g cm^{-3}) ± 0.04	Sintered density, ρ_g (g cm^{-3}) ± 0.02	Diametral shrinkage (%) ± 0.7	Average 3pt. bend strength σ_{3pt} (MPa)	Approx. flaw size causing failure (μ m)	Weibull modulus, m ± 0.1
Standard coagulated	0.35 ± 0.04	2.19	3.83	18.4	355 ± 19	106	6.0
Flocculated	1.45 ± 0.1	2.19	3.86	17.1	308 ± 20	140	3.8
Flocculated + 0.8 M NH_4Cl	1.10 ± 0.1	2.22	3.87	18.4	330 ± 28	122	3.6

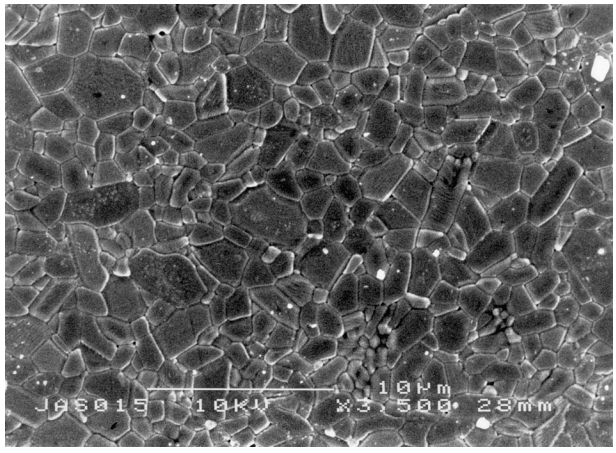

Fig. 4. Microstructure of sintered flocculated pastes prepared at 81 wt% alumina with 0.38 wt% methylcellulose.

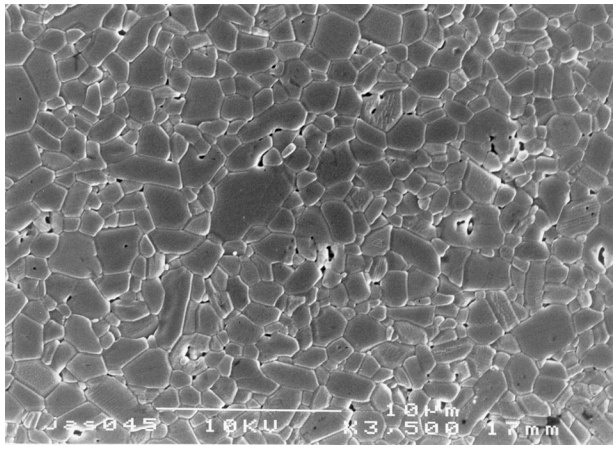

Fig. 5. Microstructure of sintered standard coagulated paste bodies prepared with 81 wt% alumina.

unexpectedly low bend strength and Weibull modulus. The Weibull modulus for standard coagulated bodies was independent of solids loading over the range tested, ranging between 5.6 and 6.0.

3.2.2. Effect of extrusion conditions

Fig. 6 shows the effect of both extrudate velocity and die length on the force required to extrude standard coagulated pastes containing 81 wt% alumina. The effect of using the longer die length of 35.1 mm was to increase the force required for extrusion to 1.1 kN. This was comparable to that required by flocculated bodies when extruded through the normal die of length 3.2 mm. Increasing the extrudate velocity to 100 mm min^{-1} and extruding the paste twice with the standard die length of 3.2 mm resulted in a paste which also initially required the higher extrusion force of approximately 1.1 kN. However, this gradually decreased to about 0.7 kN, a value approximately double that required for the same paste extruded under the 'standard' extrusion test conditions (5 mm min^{-1} and a die length of 3.2 mm).

Sample characteristics are recorded in Table 6. When compared to Table 4, the most notable observation was the increase in bend strength. For example, samples extruded using the 35 mm die-land exhibited bend strengths of 445 MPa, an improvement of 35% over comparable flocculated pastes (330 MPa) and 25% over standard coagulated pastes extruded under standard conditions (355 MPa). The sintered microstructures of the pastes produced under the higher extrusion pressures both exhibited a similar average grain size of 1.2 μm, Fig. 7, similar to all other test conditions.

4. Discussion

4.1. Extrusion of coagulated pastes without methylcellulose

The problem of water seepage for these pastes can be attributed to the difference in viscosity between the paste itself and the fluid phase contained within it. The viscosity of the paste is, in turn, a function of the type of interparticle force dominating between the particles. The much lower degree of seepage, S_d, values calculated for the coagulated bodies given in Table 1 compared to the flocculated bodies is attributed to the lubricating nature of the adsorbed NHPA. This conclusion is drawn from both the progressive decrease in S_d with increasing concentrations of NHPA and the corresponding decrease in paste viscosity found when developing the pastes, Davies and Binner.[7] Although seepage was not a problem for samples prepared with 2.10 mg g^{-1} NHPA, these pastes were really too fluid to be extruded and in all cases the dried extrudates were very brittle indeed and required very careful handling.

Table 5
Properties of coagulated and flocculated pastes prepared at 81.0 wt% alumina and with 0.38 wt% methylcellulose

Coagulated paste NHPA content (mg g^{-1})	Alumina content (wt%)	Extrusion force, F (kN)	Degree of seepage, S_d (kN m^{-1})	Green density, ρ_g (g cm^{-3}) ± 0.04	Sintered density, ρ_s (g cm^{-3}) ± 0.02	Diametral shrinkage (%) ± 0.7	Average 3pt. bend strength σ_{3pt} (MPa)	Approx. flaw size causing failure 2c (μm)	Weibull modulus, m ± 0.2
1.40	81.5	0.50 ± 0.04	0	2.17	3.84	18.3	341 ± 22	115	5.6
1.40	82.0	–	5.5 ± 0.5	2.19	3.86	17.0	381 ± 28	92	5.8
2.10	82.0	1.30 ± 0.1	0	2.18	3.83	16.0	318 ± 22	132	4.4

With respect to the bend strength values of the sintered components, two features are notable:

1. the higher values of the coagulated samples containing 0.70 and 1.40 mg g^{-1} NHPA compared to the flocculated samples, and
2. the decrease in bend strength with increasing NHPA content.

With respect to the former, since the use of scanning electron microscopy failed to reveal any substantial differences in the samples' sintered microstructure it is believed that the higher strengths of the coagulated pastes result from a small reduction in the degree of agglomeration present. This is attributed to the initial preparation of a high solids content, dispersed suspension, which results in a very fluid, de-agglomerated suspension in which the dispersed particles tend to be very closely packed. Although the addition of the NH_4Cl appears to re-induce a degree of particle agglomeration, the attractive network of closely packed particles formed on coagulation is clearly preferable to the loose, low-density flocs formed on conventional flocculation.

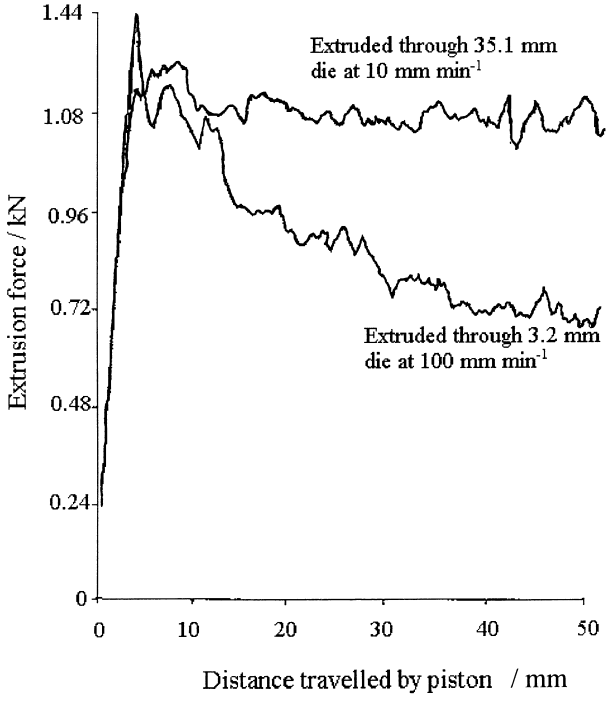

Fig. 6. Effect of speed and die length on the pressure required to extrude standard coagulated pastes at 81 wt% alumina.

The decrease in bend strength with increasing NHPA content may be explained by an increase in warpage during drying and the progressive roughening of the extrudate surface with increasing NHPA content. A greater number of surface tears and fine striations perpendicular to the extrudate flow were observed. This can again be linked to the lubricating nature of the NHPA.

4.2. Extrusion of coagulated pastes containing methylcellulose

The addition of methylcellulose transformed pastes from being rather sticky to a much more plastic, mouldable paste with the presence of 0.38 wt% methylcellulose eliminating the problem of water seepage in the coagulated pastes and substantially reducing it for the flocculated pastes. The most noticeable difference between flocculated and coagulated pastes was the much smaller force required for extrusion by coagulated pastes, Fig. 3. This is again attributed to the lubricating nature of the adsorbed NHPA. The slightly lower extrusion force associated with flocculated pastes containing salt compared to their non-salted counterparts is consistent with their lower viscosity, Table 4.

The addition of methylcellulose to flocculated pastes increased the bend strength to levels comparable to coagulated pastes. In contrast, addition of methylcellulose to coagulated pastes had no effect. This contributes further evidence of the lower degree of agglomeration caused by coagulation, since in the absence of a dispersant the methylcellulose not only acts to increase the liquid phase viscosity, but also as a dispersant breaking up agglomerates. Whilst in both flocculated and coagulated systems the average grain size was identical (1.3 μm), one notable feature of the coagulated pastes was the presence of very fine porosity at the grain boundaries, Fig. 5. This is believed to be a consequence of air entrapment during methylcellulose addition and perhaps also during ultrasonic agitation. The air was subsequently not expelled upon extrusion due to the lower pressures required and hence will have limited the strength of the coagulated pastes to little better than the flocculated pastes containing methylcellulose.

Table 6
Effect of extrusion speed and die length on properties of extruded standard coagulated pastes containing 81.0 wt.% alumina

Extrusion conditions	Extrusion force, F (kN)	Green density, ρ_g (g cm^{-3}) ± 0.04	Sintered density, ρ_s (g cm^{-3}) ± 0.02	Diametral shrinkage (%) ± 0.7	Average 3pt. bend strength σ_{3pt} (MPa)	Approx. flaw size causing failure (μm)	Weibull modulus, m ± 0.1
Extruded twice through 3.2 mm die at 100 mm min^{-1}	1.4 ± 0.7	2.18	3.82	17.6	397 ± 20	85	6.5
Extruded through 35 mm die at 10 mm min^{-1}	1.1 ± 0.1	2.18	3.83	17.9	445 ± 22	68	5.9

4.2.1. Effect of solids loading

As expected the extrusion pressure increased with increasing alumina content, Table 5. At 82 wt% alumina water seepage again became a problem for the standard coagulation paste as a result of an excessive increase in paste viscosity. An increase in NHPA content to 2.10 mg g^{-1} eliminated this problem, but again the resultant extrudate was too soft. From Table 5 it would appear that neither the shrinkage values nor the green or sintered densities were affected by very small increases in solids content above 81 wt%. The strengths of the rods containing 1.40 mg g^{-1} of NHPA were also similar to each other and to the value obtained at 81 wt% alumina, Table 4. The unexpectedly low strengths and Weibull modulus recorded for rods prepared from 2.10 mg g^{-1} NHPA pastes may be a result of the softer nature of the extrudate resulting in a greater number of surface flaws.

Suitable pastes could not be prepared for solids contents above 81 wt% using 1.40 mg g^{-1} NHPA due to water seepage problems. However, it is expected that the use of a higher molecular weight methylcellulose would overcome this problem. This will form part of the next stage of the research that will develop the theory of reduced agglomeration upon coagulation, since at higher solids contents the particles should be in an even closer packed arrangement in the initial, dispersed phase.

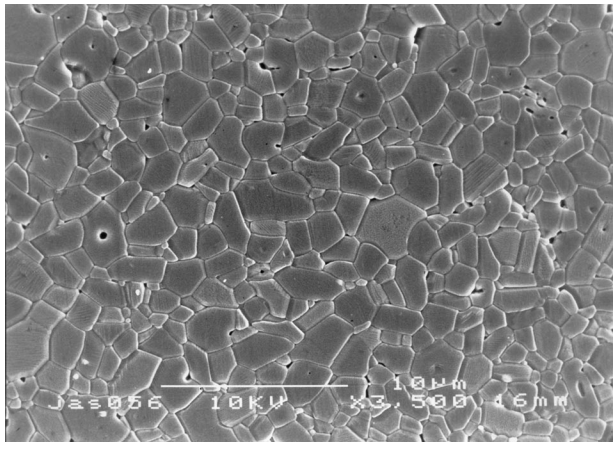

Fig. 7. Microstructure of sintered standard coagulated paste containing 81 wt% alumina and extruded through 35.1 mm die at a pressure of 2.2 MPa.

4.2.2. Effect of extrusion conditions

The rougher extrusion traces, Fig. 6, produced whilst extruding at both a higher speed and force are indicative of an increased level of expulsion of entrapped air within the paste. As a result significant improvements in bend strength and an increase in Weibull modulus were noted, Table 6. The highest average bend strengths, 445 MPa, were recorded whilst extruding at the high extrusion force of 1.1 kN. This compares favourably with the average strength of 355 MPa obtained with the same material extruded at 0.35 kN and of 330 MPa for the flocculated pastes containing methylcellulose that were also extruded at 1.1 kN.

4.3. Comparison to existing systems

Several processing systems using methylcellulose as a processing aid for alumina have been developed, including Chen and Cawley[10,11] and Schuetz.[2] However, the results of this research may be more directly compared to the work of Salamone and Reed[5] who examined the extrusion of A16SG alumina powder using 0.6 wt% methylcellulose at a water content of 21.5 wt%. They found that direct blending using a high shear mixer at the required water content produced components with a three point bend strength of 368 MPa. This is comparable to the maximum values recorded for flocculated pastes containing 0.38 wt% methylcellulose in this research indicating that the flocculated pastes produced in this research are typical. Salamone and Reed[5] reported that if samples were prepared under much more dilute conditions and ball milled to break up agglomerates before being filter pressed to the required water content for extrusion, sintered components exhibited a much improved strength of 449 MPa. This value is almost identical to that recorded in this research for rods prepared from coagulated pastes extruded at an elevated pressure. This supports the proposed theory that salt induced coagulation of a highly loaded dispersion gives rise to an attractive network of closely packed particles/agglomerates rather than the formation of low density flocs as in conventional flocculation.

The advantage of using this newly developed system over existing systems is that pastes may be prepared at the given solids loading required for extrusion without the need for high shear mixing and initial dilute conditions, both of which would entail more prolonged processing and extra equipment cost.

5. Conclusions

A new processing system has been developed based on initially dispersing a suspension at a very high solid loading and subsequently coagulating the system by adding salt to form a body with a rheology suitable for plastic forming techniques such as extrusion. This processing route has yielded components with three point bend strengths up to 445 MPa, an improvement of ~40% over flocculated bodies mixed in a similar manner. The system has the added advantage of using only 0.5 wt% polymeric additive, which virtually eliminates any problems associated with post-forming polymer burn out. It is proposed that the improved mechanical properties arise from the initial dispersion at very high solids loadings which upon coagulation form relatively dense attractive particle networks or agglomerates that give rise to smaller flaws in the sintered state compared to flocculated samples.

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