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Journal of the European Ceramic Society 26 (2006) 817–823

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Extrusion of alumina and cordierite-based tubes containing Al-rich anodising sludge

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Available online 18 August 2005

Abstract

An Al-rich anodising sludge has been used as the feedstock to produce alumina and cordierite-based tubes produced by extrusion. The extrudability is strongly dependent on the materials composition and on the resultant plasticity of the pastes. For the process to be successful, the design and operating conditions need to be considered in detail.

In this work, the effect of die design, ram speed and pressure was evaluated using the Benbow–Bridgwater model of paste extrusion. In general, predicted and measured values were in good agreement. This approach revealed differences in the flow between the two ceramic formulations and it was possible to relate the rheological observations during extrusion to the quality of the final product.

Keywords: Alumina; Extrusion

1. Introduction

Alumina (Al_2O_3) and cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) ceramic materials show interesting thermomechanical properties.[1,2] Alumina is renowned for its high refractoriness and mechanical strength,[1] while cordierite is very resistant to thermal shock[3] due to its very low thermal expansion coefficient. Accordingly, cordierite-based materials have found favour as honeycomb supports for catalytic converters in automobiles, as furniture for self-cleaning ovens and in industrial heat exchangers for gas turbines. Many processing routes including slip casting and dry processing[3–6] can make devices based on these two materials. Extrusion[6] has long been used to shape ceramic objects, mostly for traditional applications such as bricks, tiles and pipes. Additionally, extrusion is frequently used as an auxiliary pre-shaping technique to improve compositional and microstructural homogeneity of pastes that are subsiquently processed by other means. The technique is commonly used in other industrial sectors, including food, agricultural, chemical, and pharmaceutical industries.[7]

Benbow and Bridgwater demonstrated that the extrusion of particulate pastes, comprising fine particles suspended in a liquid continuous phase, through dies with circular cross section and having a square entry (see Fig. 1), can be described by Eq. (1):[7,8]

$$P = P_e + P_l = 2(\sigma_0 + \alpha V^n)\ln\left(\frac{D_0}{D}\right) + (\tau_0 + \beta V^m)4\left(\frac{L}{D}\right) \quad (1)$$

where α is a velocity-dependent factor for the convergent flow, β is the velocity-dependent factor for parallel flow, n and m are exponents, σ_0 is the paste bulk yield value, τ_0 is the paste characteristic initial wall shear stress, D_0 and D are the diameters of the barrel and of the die respectively, L is the die-land length and V is the extrudate velocity. In this equation, die-entry (P_e) and die-land (P_l) pressures are separated.

A coefficient of static friction for the extrudate (μ) can be calculated by the relationship:

$$\mu = \frac{\tau_0}{\sigma_0} \quad (2)$$

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doi:10.1016/j.jeurceramsoc.2005.07.040

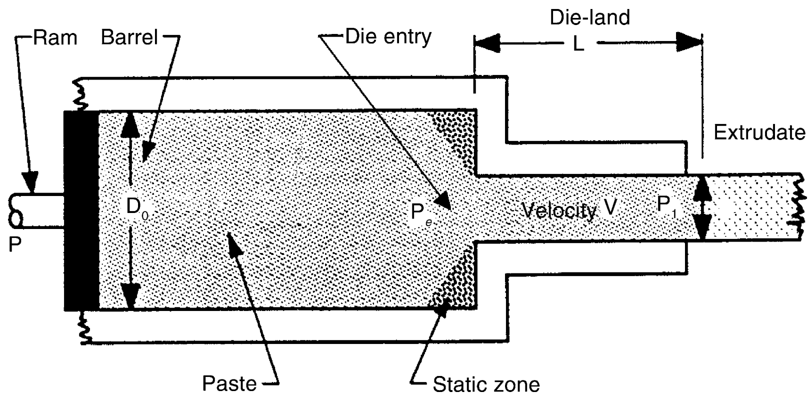

Fig. 1. Schematic view of the extrusion through a square die in a ram extruder. P: total extrusion pressure; P_e: die entry pressure and P_l: die land pressure of paste.

and can be considered a key parameter for controlled extrusion.[9]

In this work cordierite and alumina-based tubes were extruded using two different ceramic pastes containing Al-sludge (waste from the aluminium anodising process), diatomite, and talc. In order to adjust the plasticity level to allow defect free extrusion, plasticizing and lubricating agents were added. Plastic behaviour was characterised by stress-deformation curves and compared with that of standard industrially-prepared pastes.[10] The applicability of the Benbow–Bridgwater model was tested in the extrusion of tubes, using sludge-based formulations and dies of different die-land dimensions.

2. Experimental

The cordierite paste (CP) was prepared from a premixed powder containing 25 wt.% of pre-calcined (at 1400 °C) Al-anodising sludge (Extrusal, S.A., Aveiro, PT), 43 wt.% talc (Luzenac, FR) and 32 wt.% diatomite (Anglo-Portuguese Society of Diatomite, Óbidos, PT). The alumina paste (AP) was formulated from a 50 to 50 wt.% mixture of Al-anodising sludge and 1400 °C pre-calcined material. Details of preparation and characterisation of the sludge are given elsewhere.[10–12] In order to adjust the plasticity level, commercial additives were used: two plasticizers, Zusoplast PS1 and C28, and a lubricant (Zusoplast O59), all from Zschimmer & Schwarz, *D*, were incorporated in the test formulations, details are given in Table 1.

The yield value and plasticity level of each paste was obtained from stress/deformation tests carried out by plastic compression (Lloyd Instruments LR 30 K) in metal moulds. The formulations (Table 1) were pre-extruded through a cylindrical die (33.0 mm in diameter) to improve mixing and homogeneity. These rods were then cut into test billets (33 mm diameter and approximately 43.0 mm length). A minimum of three specimens per composition were tested. Compression tests were conducted at a constant loading rate of 2.0 mm/min until a maximum deformation of, approximately 70% or the ultimate limit of the load cell (500 N) was reached.[10]

Extrusion tests were performed in a ram extruder using two dies of different die-land length. The dies used in this work are referenced as 30*L* and 120*L*, according to their die length (30 and 120 mm, respectively). Tested ram velocities were: 1, 2, 5, 10, 20, 30, 60, 100 and 200 mm/min. Fig. 2 shows a general view of the apparatus, while Fig. 3 details the die region and illustrates all the contributing pressure drops. Values of total pressure (P) applied through the ram and pressure at the die entry were measured through digital sensors. We should note that P_e now measured and the value in the Eqs. (1) and (3) are not exactly equal.

3. Results and discussion

3.1. Stress-deformation behaviour

The plastic deformation of CP and AP pastes, with or without lubrication and plasticizer additions were obtained by plastic compression. The resulting curves are presented in Fig. 4. Pastes without additives exhibited low levels of plasticity, as defined in previous research.[10] The plastic defor-

Table 1
Tested CP and AP batch formulations (wt.%) containing or not different amounts of additives

Composition	Zusoplast C28 (wt.%)	Zusoplast PS1 (wt.%)	Zusoplast O59 (wt.%)	Moisture content (%)
CP/withoutad45.8H	–	–	–	45.8
CP/6P4L45.8H	–	6	4	45.8
AP/withoutad47.1H	–	–	–	47.1
AP/6P4L40.2H	6	–	2	40.2

P: plasticizer; L: lubricant; H: moisture level.

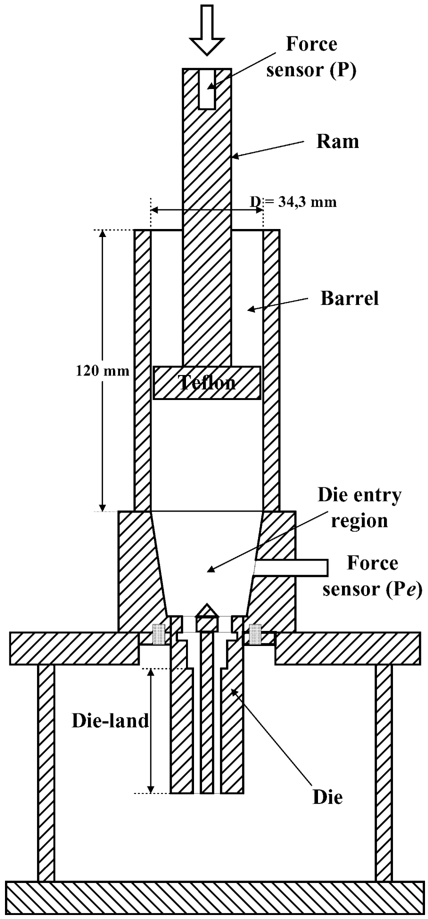

Fig. 2. Ram extruder apparatus used in the extrusion tests.

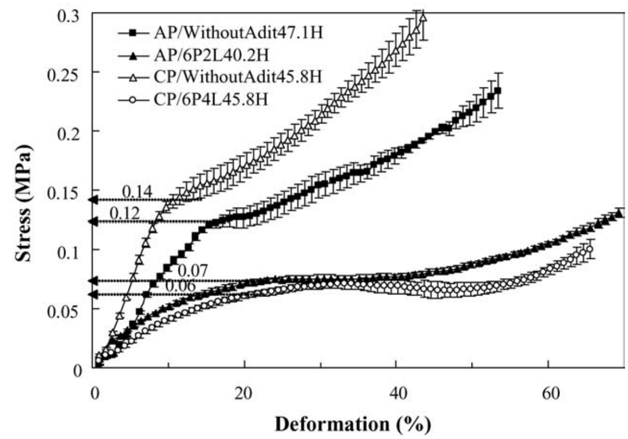

Fig. 4. Stress-deformation curves of tested formulations, obtained by plastic compression.

mation region was very narrow and yield stress values were rather high. Paste formulations exhibiting this curve form were predicted to fail in extrusion and this proved to be the case with several failed attempts to obtain simple rods even when applying relatively high pressures. The CP pastes were less plastic when compared to the AP materials, despite the presence of talc and a lower sludge content. The amount of water required is slightly higher for the AP pastes, due to the use of non-calcined sludge,[4] which is highly hygroscopic. This might explain the difference between the two pastes, since previous work[10] showed water to be a major contributor to the level of plastic behaviour. Where lubricant and/or plasticizer is added the level of water required was reversed, such that the CP formulations required more water and lubricant when compared to the AP material, this can be attributed to the presence of diatomite. The water sequestration effect induced by diatomite particles is well documented.[13] Due to the higher moisture content of the CP formulation (with additives) greater problems were predicted to occur in subsequent drying and firing operations.

Yield stress values shown in Fig. 4 were then used as a comparative parameter for extrusion modelling.

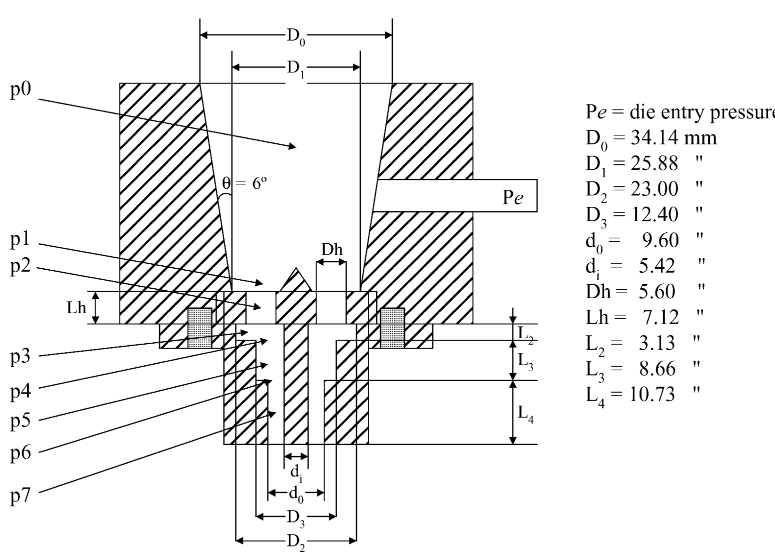

Fig. 3. Detailed representation of the die 30*L* used for ram extrusion of hole-tubes. The design of 120*L* die is the same but with $L_4 = 99.0$ mm.

3.2. Extrusion characterisation

Extrusion was characterised by application of the Benbow–Bridgwater equations used for modelling the flow of pastes through dies with complex geometry.[7,8,14] The total pressure drop for the current die-design comprised several definable contributions, p_0–p_7, as indicated in Eq. (3) and shown in Fig. 3:

$$\begin{aligned} P_L &= P_e + P_l = p_0 + \ldots + p_7 \\ &= \left[2(\sigma_0 + \alpha V^n + \tau_0 \cot\theta)\ln\left(\frac{D_0}{D_1}\right) + \beta V^m \cot\theta\right] \\ &\quad + \left[2\left(\sigma_0 + \alpha\left(\frac{4Q}{\pi Dh^2 N}\right)^n\right)\ln\left(\frac{D_1}{Dh\sqrt{N}}\right)\right] \\ &\quad + \left[4\left(\tau_0 + \beta\left(\frac{4Q}{\pi Dh^2 N}\right)^m\right)\left(\frac{Lh}{Dh}\right)\right] \\ &\quad + \left[(\tau_0 + \beta V^m)\left(\frac{L_2 M_2}{A_2}\right)\right] + \left[\ln\left(\frac{A_2}{A_3}\right)(\sigma_0 + \alpha V^n)\right] \\ &\quad + \left[(\tau_0 + \beta V^m)\left(\frac{4L_3}{D_3 - d_i}\right)\right] \\ &\quad + \left[\ln\left(\frac{A_3}{A_4}\right)(\sigma_0 + \alpha V^n)\right] + \left[(\tau_0 + \beta V^m)\left(\frac{4L_4}{d_0 - d_i}\right)\right] \end{aligned} \quad (3)$$

where N is the number of internal holes with diameter Dh, Q is the volumetric flow rate, A_x is the area at location x, M_x is the perimeter length at the location x, L_x is the die-land length at location x and θ is the angle of die-entry region.

As a result of the geometrical similarity between both dies, the differential pressure drop between them is given by:

$$P_{120L} - P_{30L} = (\tau_0 + \beta V^m)\frac{4(L_{120L} - L_{30L})}{d_0 - d_i} \quad (4)$$

where $L_{120L} - L_{30L} = 79.27$ mm. Eq. (4) includes only three fitting parameters: τ_0, β and m and can be resolved from extrusion data collected at different speeds. Two further parameters (α and n) were obtained from Eq. (3) once τ_0, β and m were known. The yield value (σ_0) was assumed to equate to the yield stress determined from stress-deformation curves of Fig. 4.

Fig. 5 shows the differential pressure drop differences between the 120L and 30L dies for both pastes determined experimentally and calculated from least squares fitting of Eq. (4). To investigate the differences (%) obtained between predicted and experimental work, values were estimated from the quotient: predicted-experimental/experimental. There are significant differences at low extrusion rates (over the first two points) and these differences reached 22 and 9% for AP and CP formulations, respectively. These differences appear to arise from the poor control of experimental conditions at slow flow rates (1 and 2 mm/min ram velocity).

Results of the full fitting procedure, obtained from Eq. (3), are shown in Fig. 6. In general, results predicted by the model (Eq. (3)) and measured values are in good agreement. The total pressure drop is higher for the 120L-die due to its longer length. Despite some differences in the curve evolution, the general behaviour AP and CP pastes with additives was similar. The differences are related to different plastic flow mechanisms, which are discussed later.

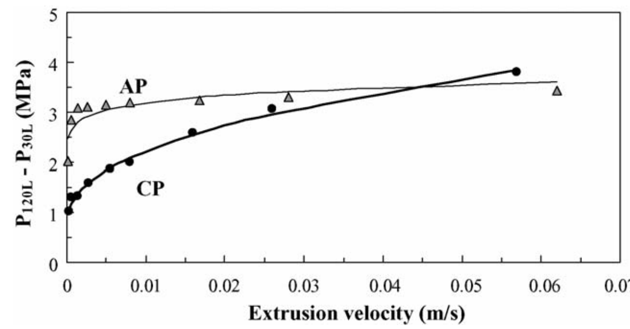

Fig. 5. Pressure drop differences between 120L and 30L dies, developed during the extrusion of CP/6P4L45.8H and AL/6P2L40.2H pastes. Measured (points) and fitted (lines) results are given.

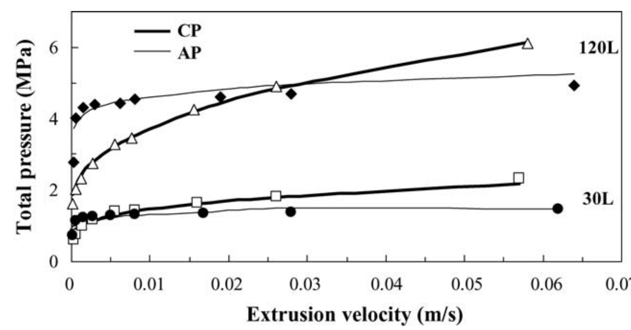

Fig. 6. Total pressure drop developed upon the extrusion of hole-tubes of CP/6P4L45.8H and AP/6P2L40.2H pastes through 120L and 30L-dies. Measured (points) and fitted (lines) results are given.

Table 2 shows derived parameters estimated from the first and the second mathematical fitting of Eqs. (3) and (4), respectively. It is interesting to observe that values estimated for the AP paste are similar to those referred to by Benbow et al.[7] for α-alumina-based pastes. This suggests that the final waste-based formulation was satisfactory and the extruded bodies showed good shape retention and physical properties. The only drawback relating to the final formulation was the relatively high water content, which led to a requirement for special care during drying and firing to prevent failure at this stage.

Table 2
Benbow's extrusion parameters for AP and CP-pastes

Parameter	AP/6P2L40.2H	CP/6P4L45.8H
α [MPa (s m^{-1})^n]	0.061	0.462
n	0.687	0.284
β [MPa (s m^{-1})^m]	0.043	0.126
m	0.088	0.433
τ_0 (MPa)	0.00859	0.00909
σ_0 (MPa)	0.07	0.06
μ	0.123	0.152

σ_0 was obtained through the stress-deformation curves[10].

According to Das et al.[3] n values in the range 0.2–0.6 correspond to predominantly pseudo-plastic behaviour, but for the extrusion of bodies with intricate shapes such as honeycomb structures values under 0.4 are recommended. In fact, the apparent viscosity should be low in the region of the die, to aid distribution of the paste across the die face, but should then reach higher values when the body emerges from the die, to help retain the desired shape. In this study, the derived n values for the AP formulation are out of this specified range ($n = 0.687$), while those for CP are well within the range ($n = 0.284$). By considering this single indicator, it seems that current cordierite-based material is better suited for complex extrusion, while alumina-based formulations would require further optimisation.

Some authors[7,8] have argued that is sufficient to interpret extrusion results by using the α and β parameters alone, since they reflect dimensional effects. By fixing the extrusion velocity ($V = 0.005$ m/s) Das et al.[3] alternatively suggested the use of dynamic stress components (αV^n and βV^m). Applying this concept to the formulations gives:

αV^n (CP/6P4L45.8H) = 0.1047 (MPa)	βV^m (CP/6P4L45.8H) = 0.0129 (MPa)
αV^n (AP/6P4L40.2H) = 0.0016 (MPa)	βV^m (AP/6P4L40.2H) = 0.0269 (MPa)

Despite the apparent similarity of the general behaviour between both formulations (Fig. 5) the analysis of dynamic stress components suggests different plastic flow contributions from each material. βV^m is dominant in AP-formulations, suggesting that parallel plastic flow is the main contributor to the pressure drop. At the same time, the pressure drop caused by the convergent flow plays a relatively minor role during the extrusion of tubes (n is higher but α is much lower). CP-formulations exhibit the opposite trend with the convergent flow contribution dominant (αV^n is higher than βV^m). When compared with AP, αV^n is almost two orders of magnitude higher, representing a major difference between the two formulations. Table 2 also shows the estimated values of the static friction coefficient (μ) of the extrudates. The CP materials exhibited higher values than the AP formulations, which would suggest greater resistance to extrusion through the tube die for CP pastes. This is in apparent contradiction with indications that resulted from the comparative analysis of n values only. The use of higher working pressures might partially overcome this difficulty.

The differences between the two formulations are difficult to explain, since the compositions are very different. One possible contribution to this might be found by considering the typical particle shape of major components. In CP, the talc particles have plate-like morphology, while the alumina grains (the dominant phase of AP formulations) are nearly spherical and much finer.[4] Interactions between particles are strongly dependent on these morphological aspects. Moreover, re-orientation of the talc platelets during flow might also contribute to the observed rheological differences.[15]

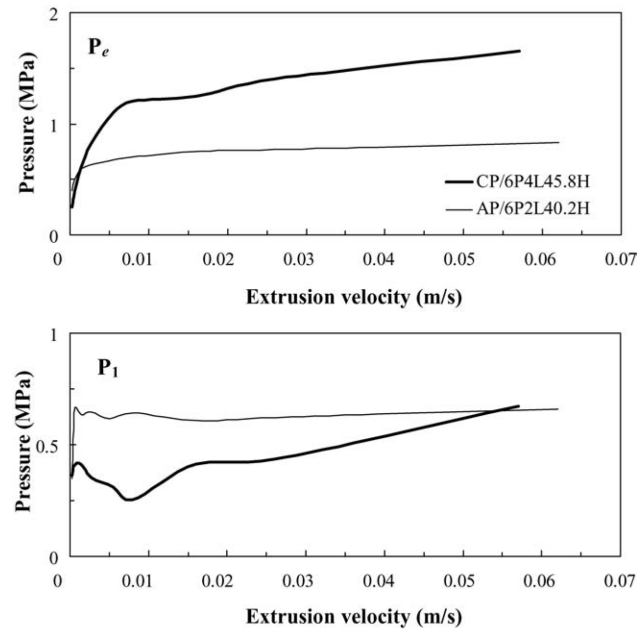

Fig. 7. Experimental values of partial pressure drops in the die-entry (P_e) and in the die-land (P_l) regions of the 30L-die for CP/6P4L45.8H and AP/6P2L40.2H pastes. Fitted values (lines) are also indicated.

The evolution of die-entry (P_e) and die-land (P_l) pressure drops is shown in Fig. 7. As expected from the previous discussion of dynamic stress components, P_e is higher for CP-materials, while the P_l contribution dominates the extrusion of AP-materials. Inside the die parallel plastic flows are dominant. The rearrangement of plate-like particles will increase the resistance to bulk deformation. In the converging flow the plate-like particles will align and this may in fact ease flow in the die land. In contrast, the near spherical particles of alumina are more readily re-ordered in the convergent region and yet may interact more strongly at the die walls in parallel flow. For production, the entry region governing convergent flow might easily changed to accommodate the extrudates behaviour, while die-land regions are fixed and confined by the desired product specifications. In that sense the plastic behaviour of extrudates in the die-land region is critical and should be carefully controlled.

Fig. 8 shows the total pressure drops developed during the extrusion of CP and AP through the 30L-die. As expected from the plastic behaviour shown in Fig. 4, formulations containing no additives require very high pressures to develop flow, even at low extrusion speeds. Moreover, the resultant bodies show high surface roughness due to poor lubrication.

With the use of additives, both materials exhibit similar working pressure drops for any given extrusion rate. Fig. 9 shows extruded tubes after freezing (24 h at −18 °C) followed by drying and firing (at 1000 °C). This procedure attempts to amplify the development of stresses to open defects and, in a very sensitive way, shows the nature of the flow pattern. Fig. 9A illustrates the situation where the convergent flow term is dominant (CP formulations), while in 9B shows the

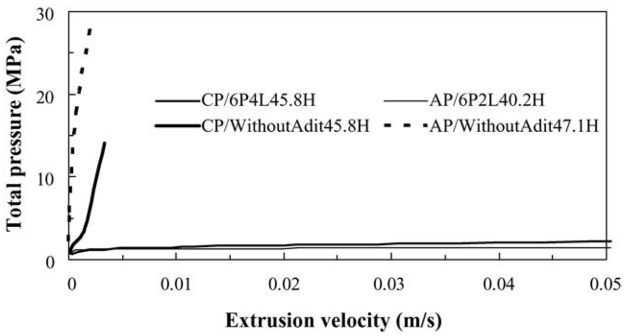

Fig. 8. Total pressure drop developed upon extrusion of CP and AP formulations through a 30*L*-die.

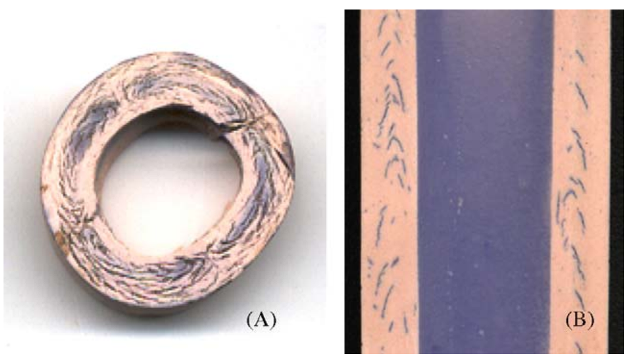

Fig. 9. View of extruded bodies properly treated (freezed at −18 °C before drying and firing) to amplify the formed falls: (A) dominance of convergent flow—CP material and (B) prevalence of differential laminar flow—AP formulations.

failures that are developed in a paste where the differential laminar flow term dominates (AP formulations).

Fig. 10 shows the bending strength evolution of dried tubes of AP and CP materials with the total amount of additives. Since processing conditions are optimised by the proper use of plasticizer and lubricant agents, the bending strength tends to increase. This effect seems more pronounced in CP formulations, probably due to the extremely poor initial paste quality before the inclusion of additives. The better intrinsic fluidity/extrudability of AP formulations justify the

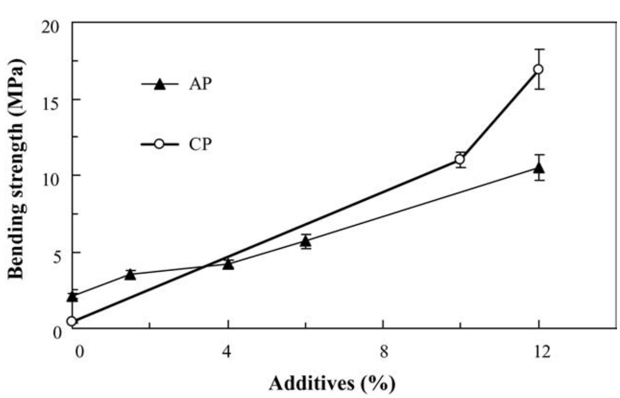

Fig. 10. Bending strength evolution of extruded and dried bodies of both formulations as a function of the total amount of additives.

higher mechanical resistance with null or low amounts of additives. In general, values are similar to those of alumina and cordierite materials processed from natural or chemical reagents. Since the water content is very high, drying and firing steps should be carefully controlled. The use of higher amounts of organic additives impose extra control needs. However, this practice is currently common in the production of such artefacts.[16]

4. Conclusions

Stress-deformation testing of pastes under compression is shown to be a reliable tool for the determination of the paste yield value (σ_0) of plastic ceramic pastes. It gives very sensitive information on the plasticity level and reduces the number of parameters to be fitted when applying the Benbow–Bridgwater equations to paste analysis. This is particularly important when only tube dies are available for experimentation. Thus for tube dies, a mathematical routine comprising two steps has been developed, firstly three parameters τ_0, β and m are calculated from the differential pressure between a long and a short die. Secondly the calculated parameters and σ_0 derived from the stress deformation test are used to resolve the final two parameters form the total pressure drop. This methodology was found to be useful in predicting and optimising the extrusion behaviour of cordierite (CP) and alumina (AP) pastes containing Al-anodising sludge.

The analysis of dynamic stress components (αV^n and βV^m) revealed that the extrusion of CP materials is dominated by the convergent contribution, while total pressure drop upon extrusion of AP pastes is dominated by the parallel plastic flow contribution.

Finally, it was demonstrated that the static friction coefficient (μ) of extrudates is another relevant parameter in defining extrusion issues and the ultimate surface quality of samples.

Acknowledgement

Financial support from PRODEP III, Medida 5/Acção 5.3 is greatly appreciated. The work was also supported by FCT (Project CTA/42448/2001).

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