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Influence of the Debinding Method on the Mechanical Properties of Plastic Formed Ceramics

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Abstract

A new method of extraction of organic additives, by a supercritical fluid, is presented. Flexural strengths and Weibull moduli of extrusion molded alumina, debinded by classical pyrolysis and by supercritical CO_2 extraction are compared. Better mechanical properties are obtained after a short time (3 h) of supercritical treatment (σ = 277 MPa, m = 13·7) than after 18 h of pyrolysis (σ = 253 MPa, m = 12·4). The binder extraction from green pieces by supercritical fluids is limited by two factors, solubility and diffusivity of organic compounds. The major factors causing defects in the pyrolytic binder removal, such as binder redistribution in the liquid phase and the outward diffusion of degradation products, do not take place in the supercritical debinding method.

1 Introduction

Ceramic components are made by applying ceramic processing techniques to ceramic materials. One of the main difficulties that structural engineering ceramics have to overcome to find industrial applications lies on the fabrication of shapes from powders. The forming of green pieces is critical, because it affects both final properties of materials, for example because it introduces cracks, and the characteristics of components, for example because it alters the size accuracy of the shapes.

Most high technology ceramic processings require the use of transitory, organic compounds, which are eliminated by subsequent treatments before sintering. A compromise must be found between the ease of shape forming and the necessity of removing the binders. Therefore, the optimization of ceramic processing techniques must take not only the forming method, but also the removal of the organic additives into account.

Plastic forming methods as injection and extrusion-molding are attractive for producing complex shapes of high dimensional accuracy and high uniformity at a rather low cost. These techniques require the use of a large amount of organic compounds in order to confer properties as cohesion, flexibility and workability in the green state.[1] Amounts as large as 50 vol.% of organic are sometimes added to the ceramic powder. A major drawback of these processing methods remains the removal of these organics.

Although thermal decomposition is the method currently used, studies of pyrolytic removal of organic additives in a green ceramic body, are very recent.[2–8] In the last few years, an effort was made to understand the many physico-chemical processes that occur during binder removal. Binder removal by thermal treatment involves: (i) chemical mechanisms with the thermal degradation of organic compounds into volatile species and, (ii) physical mechanisms as the diffusion of these species to the surface as well as the changes in the binder distribution within the green body. Changes in the binder distribution, governed by diffusion and capillary migration, and the magnitude of the mass- and heat-transfer limitations are critical parameters for the design of the efficient heating cycle to prevent stresses and the formation of defects in ceramic parts.[6]

Thermal debinding remains one of the most critical steps of ceramic processing, especially in the case of large size parts for three main reasons: (i) defects are generated which affect properties of the sintered pieces, (ii) it is very time-consuming, the binder removal time being directly proportional to square of the section thickness[2] and (iii) residues of pyrolytic degradation can be detrimental during the subsequent sintering stage.

Alternative techniques are needed to produce defect-free green bodies and to reduce debinding time. In this respect, approaches including chemical degradation, evaporation or sublimation, solvent extraction and capillary action can be beneficial. In the present work, we have used an original method of extraction of organic compounds based on the unique dissolving characteristics and transport properties of fluids at temperatures and pressures beyond the critical point, i.e. supercritical fluids. While the densities of liquids and supercritical fluids are more or less similar, the diffusion coefficients are expected to be much larger in the later media. The binder extraction by the supercritical fluid is controlled by the solubility and the diffusivity of the polymeric compounds. The largest solubility of a binder in the supercritical fluid can be estimated using solubility parameters and the diffusivity of dissolved organic species in green samples has been modelled.[9]

The purpose of this paper is to compare mechanical properties (flexural strength and Weibull modulus) of extrusion-molded ceramics debinded by classic pyrolysis and by supercritical extraction of organics.

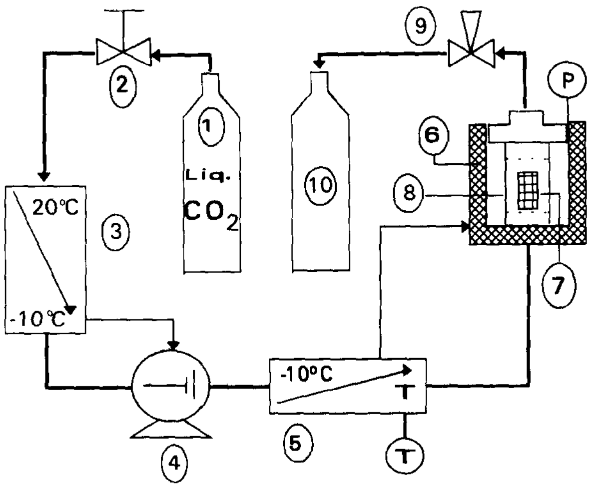


Fig. 1. Schematics of the equipment: (1) CO_2 storage cylinder; (2) shutoff valve; (3) cooling circulator; (4) high pressure pump; (5) thermostated oil bath; (6) extraction vessel; (7) ceramic sample; (8) cylindrical basket; (9) micrometering valve; (10) collector cylinder.

2 Experimental

2.1 Preparation of green samples

Samples with a square section (4×4 mm^2) were prepared by extrusion-molding of a mixture containing 86 wt.% alumina, 2 wt.% polystyrene and 12 wt.% paraffin oil (Prolabo, France). The alumina (P172SB, Péchiney, France) was 99·7 wt% purity, 0·6 μm mean particle size and 10 m^2.g^{-1} specific surface area. The molecular weight of the polystyrene (Lacqrene 4801, Elf Atochem, France) was 150 000. The green density was 56% of theoretical density.

2.2 Removal of organic compounds

Two routes were used to remove organic compounds: pyrolysis and treatment with a supercritical fluid.

The pyrolysis was carried out with four heating rates up to 550°C; 0·5, 1, 2 and 4·5°C.mn^{-1} without dwell.

Extraction of binders was performed by using carbon dioxide in a supercritical state. Carbon dioxide, which is extensively used in the food or perfume industry, has shown promising possibilities for the extraction of light organic compounds in ceramic forming processes.[10] The main advantages of carbon dioxide lie in a low cost, low critical temperature and pressure ($Tc = 31$°C, $Pc = 7{\cdot}37$ MPa) as well as in absence of toxicity and flammability.

The schematics of the equipment used during the present work are shown in Fig. 1. Green samples to be debinded (7) are introduced in a cylindrical basket (8) fitted with sintered metallic parts at both ends. This basket, located into the extractor (6), acts as a sample holder for the polymer-containing materials, and remains quite permeable to the fluids. Carbon dioxide, taken from a storage tank (1), is cooled down to −10°C by means of a heat exchanger (3). The resultant liquid carbon dioxide is pressurized up to the working pressure, by means of the pump (4). Then, the pressurized liquid is heated up to the working temperature (15–120°C) with a second heat exchanger (5), leading to supercritical carbon dioxide. The carbon dioxide, in the supercritical state, is flowing through the extractor, dissolving binders from the green sample. The dissolved binders are recovered in a collector cylinder (10). The process temperature of the extractor (6) and the temperatures of the two heat exchangers (3 and 5) are regulated by thermostated baths.

2.3 Sintering

The two series of samples, e.g. those submitted to supercritical treatment, thus still containing a low amount of non-soluble binder, and those debinded by pyrolysis, were sintered in an electric furnace with $MoSi_2$ heating elements, with the same heating cycle, i.e. 5°C.mn^{-1} up to 1600°C with a dwell time of 3 h.

2.4 Characterization

The density of sintered samples was measured by the Archimedes method in distilled water.

The room temperature strength was measured by the classical four-point bend test (outer span: 40 mm, inner: 20 mm) at a cross head speed of 0·5 mm.min^{-1}. The tensile face was polished and the edges were bevelled.

The fracture of a homogeneous brittle material depends on the stress necessary to propagate an existing critical flaw or crack present in it. Variable sizes and shapes of flaws in ceramic materials are responsible of the scatter of failure strengths observed when 'identical' specimens are tested under identical loading conditions. The Weibull statistics[11,12] were commonly used in the analysis of strength of brittle materials. This method, based on the 'weakest link of a chain', assumes that the most critical flaw under a given stress distribution leads to failure.

The major defects included in injected molded ceramics, in particular in the case of thick parts with submicrometer particle sizes, can be associated with removal of organic compounds[13,14] The Weibull statistics were used to provide a means of comparison of strength distribution, and then of flaw size distribution, between the two series of samples.

The strength data (N = 20 samples) was analysed using the usual two-parameter empirical formula relating the probability of failure, P_f, to the stress, σ_f:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma_f}{\sigma_0}\right)^m\right] \qquad (1)$$

where m is the Weibull modulus and σ_0 a normalizing factor. Flexural strengths were ranked in order and assigned a probability of failure according to the formula:

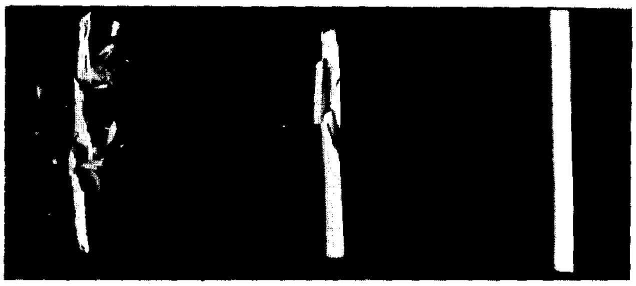
$$P_f = (i\text{–}0{\cdot}5)/\mathrm{N} \qquad (2)$$

where i is the i^{th} specimen. The Weibull modulus is the slope of a plot of LnLn $(1/P_f)$ versus Ln σ_f.

3 Results and Discussion

The supercritical treatment of the green pieces was carried out at 88°C under 28 MPa for 3 h. Under these conditions, supercritical CO_2 is a relatively good solvent for paraffin oil, but the high molecular weight polystyrene was not dissolved. The molecular weight distribution of the paraffin used is large, and only 67% of the paraffin introduced, probably corresponding to the lighter backbone, was dissolved. It is noteworthy that a small amount of undissolved polystyrene presents the advantage of maintaining a cohesion of ceramic green bodies, and that it does not seem to affect properties of sintered parts.

Extruded samples pyrolyzed with a heating rate higher than 1°C.mn^{-1} exhibit macro-defects as blistering, bloating and cracking (Fig. 2). Hence, the strength analysis was performed on samples pyrolyzed at rates of 0·5 and 1°C.mn^{-1}.



(a) (b) (c)

Fig. 2. Samples (4 × 4 mm^2) after removal of the organic compounds by heating at a rate of (a) 4·5°C.min^{-1}, (b) 2°C.min^{-1} and (c) 1°C.min^{-1}.

Weibull diagrams of sintered samples previously debinded by pyrolysis and by supercritical treatment are given in Fig. 3. The relative density of the sintered samples was 97%. Taking into account that testing bars were polished, it can be assumed that critical defects are volumic ones. Samples submitted to thermal and supercritical treatments were prepared using the same forming technique. Hence, differences in strength-controlling defects can be associated with the removal of organic compounds and not with the forming method. The mean failure strengths, in the four-point bend test, were 219, 253 and 277 MPa for samples pyrolysed at rates of 1 and 0·5°C.mn^{-1}, and for samples submitted to supercritical treatment, respectively. The Weibull modulus was low, i.e. 5·4, for samples thermally debinded at a rate of 1°C.mn^{-1}, whereas samples thermally debinded at a rate of 0·5°C.mn^{-1} and those supercritically treated exhibited a larger and similar value of the Weibull modulus, i.e. 12·4 and 13·7, respectively.

A first comment concerns the higher strength of samples debinded by supercritical treatment. This

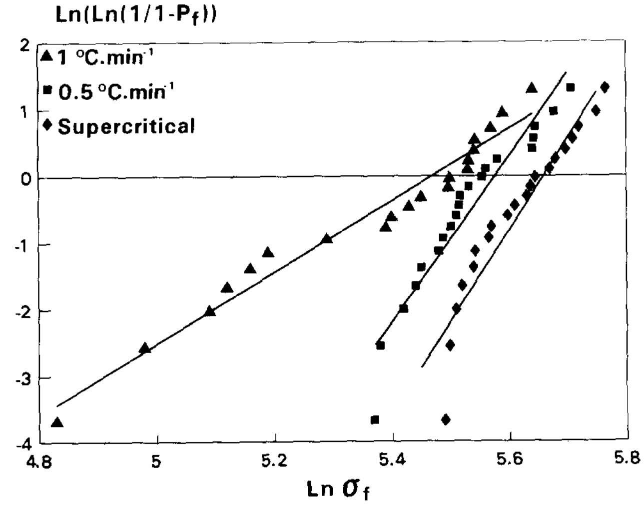


Fig. 3. Weibull diagrams of sintered samples previously debinded by pyrolysis with heating rates of 0·5°C.mn^{-1} (σ = 253 MPa, m = 12·4) and 1°C.mn^{-1} (σ = 219 MPa, m = 5·4), and by supercritical treatment (σ = 277 MPa, m = 13·7).

suggests that this method of binder removal leads to a more homogeneous green state before firing, with smaller critical defects than after classical thermal debinding.

A second comment concerns the higher Weibull modulus of samples debinded with a very slow heating rate and for samples debinded by supercritical treatment. The scatter of failure strengths, hence the scatter of defect sizes and/or shapes, was lower for samples debinded by a supercritical fluid.

As far as the treatment duration is concerned, better mechanical properties were achieved after 3 h of supercritical treatment than after about 18 h of thermal treatment on similar extruded samples. The time parameter then becomes critical for large ceramic parts.

Mutsuddy[15] reported a three-point flexural strength of 260 MPa and Fanelli *et al.*[16] a four-point flexural strength of 309 MPa for injection molded alumina (A16SG, AlCoA, Pittsburgh, PA) after thermal debinding and sintering. This alumina has similar characteristics to the one used in this study. Three-point bend tests generally lead to higher values of flexural strength than four-point bend tests, due to the Weibull effect. Concerning the Weibull modulus, G. D. Quinn[17] reported values ranging between 7 and 13 for nearly fully densified alumina. The values of four-point flexural strength (277 MPa) and of Weibull modulus (13.4), obtained after 3 h of supercritical debinding, are slightly higher than those generally quoted in the literature.

Pyrolytic binder removal is controlled by two main phenomena,[2,18] namely capillary migration in the liquid phase and diffusion in the gas phase. These two mechanisms lead to a redistribution of the binder in the green body, which determines the path length over which molten binder or volatile species must migrate or diffuse.[8,19] Due to capillary forces, molten binder, in the early stage of removal, segregates to the smallest pores of the green body, leading to the apparition of stress gradients. The magnitude of capillary forces depends on the surface tension and of the viscosity of the organic liquid. At higher temperature, cracking occurs if the generation of volatile species produced by thermal decomposition of organics is in excess of the amount removed by outward diffusion and evaporation at the surface.[20] The major factor causing defects was attributed to the diffusion of degradation products in solution in the binder.[3,4] Then, the formation of defects is dependent on balancing the rates of diffusion and degradation/evaporation. The thermogravimetric analysis of extruded samples (Fig. 4) shows that about 10 wt% of organics are removed over a very narrow temperature range during pyrolysis, making kinetics control difficult. To summarize, chemical kinetics, liquid diffusivity, vapour phase transport and binder redistribution are critical parameters of the pyrolytic binder removal process. These parameters can hardly fulfil requirements together in order to avoid the formation of defects in the green body.

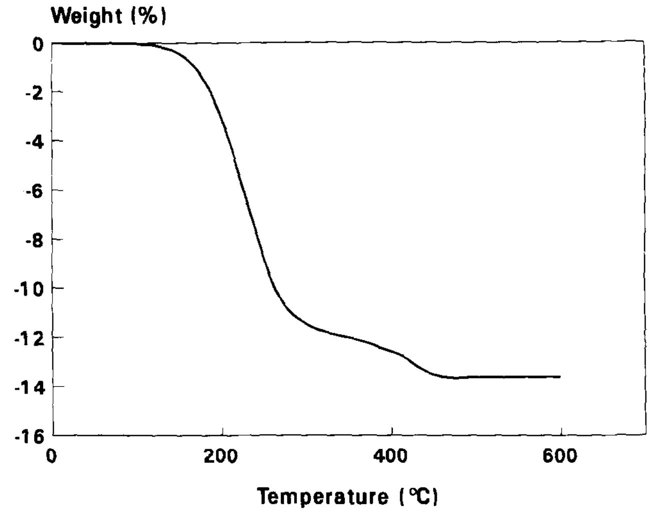


Fig. 4. Thermal gravimetric analysis for alumina–polystyrene–paraffin extruded samples (in air with a heating rate of 5°C.min^{-1}). The total amount of organic compounds is 14 wt%.

The supercritical debinding method was performed at a rather low temperature, (i.e. lower than 120°C), at which no redistribution of the binder in the green body, due to capillary forces, takes place and at which no degradation of organic compounds occurs. For example, in the case of the polypropylene-based binder system studied by Pinwill,[5] defects occur at temperatures higher than 160°C.

Extraction by the supercritical fluid acts through two steps, namely solubilization of organics without degradation and diffusion of dissolved species through the porous medium. On one hand, the density of the supercritical fluid, which depends on pressure and temperature, leading to the largest solubility of a binder can be estimated using solubility parameters. On the other hand, a model based on diffusion equations was recently developed to estimate diffusivity of dissolved organic species in green samples.[9] Solubility and diffusivity control the binder extraction with opposite pressure and temperature dependencies. The limiting mechanism of supercritical debinding is the diffusion of dissolved species, here soluble paraffin, through the space available between ceramic particles, keeping in mind that a large portion of this space (about 50 vol.%) is still occupied by undissolved binder (non-soluble paraffin and polystyrene). The diffusion coefficient is also reduced by the tortuosity factor.

The small amount of undissolved polystyrene by the supercritical CO_2 maintains the cohesion of the ceramic green body. Organic bridges between ceramic particles are preserved, avoiding the deformation of the green part during and after the extraction of the largest amount of organics. According to calculations based on a diffusion model,[9] the amount of organics which have to be removed, by supercritical treatment, to reach an open and interconnected porosity over the whole sample was evaluated at 42% of the initial organic content. Then volatile species produced during the subsequent pyrolysis can diffuse more freely between ceramic particles and escape to the gas phase without causing large stresses. The supercritical treatment, by itself, allows the extraction of 50 vol.% of binders under the present conditions. Then, it remains possible that the unavoidable pyrolysis of residual organics at a heating rate of 5°C min^{-1} could affect mechanical properties of sintered specimens through the mechanisms involved earlier in this section, and thus a reduced heating rate during the presintering stage could possibly improve the strength to failure and the Weibull modulus to some extent. This is presently under investigation, but nevertheless it is noteworthy that interesting benefits can be expected from a 'soft' technique of binder removal such as supercritical extraction.

4 Conclusions

Organic removal from green ceramic parts is a crucial stage in ceramic processing, especially when large pieces are produced. This work has demonstrated that organic removal by supercritical carbon dioxide leads to plastic formed materials with higher mechanical properties than thermally treated ones. Higher values of strength to failure and Weibull modulus were obtained after 3 h of supercritical treatment ($\sigma = 277$ MPa, $m = 13{\cdot}7$) than after 18 h of thermal treatment ($\sigma = 253$ MPa, $m \simeq 12{\cdot}4$).

This original method offers the great advantage of removing binders from ceramic green pieces without melting and without degradation of these organic compounds. Binder redistribution due to capillary forces and outward diffusion of degradation products, which are the major factors causing defects in the pyrolytic binder removal, does not take place during the supercritical extraction. Supercritical debinding involves two mechanisms, namely solubility of organics and diffusion of dissolved species through the porosity created.

The selective solvent properties of supercritical carbon dioxide allow a small amount of high molecular weight binder to be kept in order to maintain the cohesion of the ceramic green bodies after the extraction treatment.

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