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Mechanisms of Binder Removal Involved in Supercritical Debinding of Injection Moulded Ceramics

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Abstract. — Extraction of organic additives from extrusion-moulded ceramic parts by supercritical carbon dioxide has proved to be an efficient method for debinding [1, 2]. A model of binder extraction based on diffusion equations was developed. This model was found to be in fair agreement with experimental results. Experimental kinetics of extraction of low melt point paraffins, by supercritical fluids, from injection-moulded samples are now established. A redistribution of the binder in the liquid state in the porosity of the sample, during supercritical debinding, is put in evidence. The importance of this mechanism and its influence on the validity of the model are discussed.

Résumé. — Des études précédentes [1, 2] ont montré l'intérêt de l'extraction, à l'aide de gaz carbonique dans l'état supercritique, des additifs organiques de mise en forme de pièces céramiques. Elles ont permis de développer un modèle, établi à partir des équations de diffusion, qui est en bon accord avec les résultats expérimentaux. Les cinétiques expérimentales d'extraction, par fluide supercritique, de paraffines à bas point de fusion utilisées comme liant pour des compositions d'injection sont maintenant étudiées. Une redistribution du liant à l'état liquide au sein de la porosité de l'échantillon pendant le déliantage supercritique est mise en évidence. L'importance de ce mécanisme et son influence sur la validité du modèle sont discutées.

1. Introduction

Most high technology ceramic processing like dry-pressing, tape-casting, injection or extrusion-moulding requires the use of organic compounds as dispersants, binders, plasticizers and so on, to confer such properties as cohesion, flexibility and workability in the green state. Amounts as large as 50 vol.% of organics are sometimes added to the ceramic powder during the forming step, and have to be removed prior to sintering. Thermal debinding, which is currently used, remains one of the most critical phases of ceramic processing, particularly for large size parts [3–6], and requires slow heating rates, thus being time consuming. It may also lead to defects which are detrimental to the properties of the sintered material [7].

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Table I. — *Typical values of the viscosity η , the density ρ and the self-diffusion coefficient D_s for some common gases, supercritical fluids and liquids.*

	ρ (g cm ⁻³)	η (mPa s)	D_s (m ² s ⁻¹)
gases, 1 atm, 15–30 °C	$(0.6\text{--}2) \times 10^{-3}$	$(1\text{--}3) \times 10^{-2}$	$(0.1\text{--}0.4) \times 10^{-4}$
supercritical fluids (*)			
T_c, P_c	0.2–0.5	$(1\text{--}3) \times 10^{-2}$	0.7×10^{-7}
$T_c, 4P_c$	0.4–0.9	$(3\text{--}9) \times 10^{-2}$	0.2×10^{-7}
liquids, 1 atm, 15–30 °C	0.6–1.6	0.2–3	$(0.2\text{--}2) \times 10^{-9}$

(*) T_c and P_c are the critical temperature and pressure of the fluid.

Extraction of binders by supercritical fluids, based on the dissolving characteristics and transport properties of fluids at temperatures and pressures beyond the critical point, thus appears to be an interesting alternative to reduce debinding time and to produce defect-free green bodies. Some typical features of supercritical fluids [8] are listed in Table I. While the densities of liquids and supercritical fluids are more or less similar, the self-diffusion coefficients are expected to be much larger in the latter media.

A first study dealing with supercritical debinding kinetics was performed on extrusion-moulded alumina cylinders [1]. It showed that two mechanisms were involved in the extraction process: solubilisation of soluble binder molecules and diffusion of these solubilised species (called solvato-complexes). A model based on diffusion equations was thus developed.

In the present work, we continue to investigate the different debinding mechanisms and to test the validity of this model. This time however, samples used are obtained by low pressure injection of a mixture of alumina and two paraffins. As the paraffins used melt at a low temperature, an additional mechanism of extraction by capillary migration can take place within the sample during the extraction process. Its influence on extraction rate and porosity development is thus studied in order to determine if the model can still be applied even when capillary flow is present.

2. Experimental Procedure

Carbon dioxide, extensively used in the food or perfume industry, has shown promising possibilities for extraction of light organic compounds in ceramic forming processes [9, 10]. Main advantages of carbon dioxide lie in a low cost as well as in the absence of toxicity and flammability. The equipment used for this study has already been described in reference [1] and [2]. The extraction can be operated up to 30 MPa, at temperatures ranging from 30 to 120 °C. The cell temperature is regulated within ± 1 °C and the pressure within ± 0.2 MPa. The high pressure membrane pump can supply up to 5 liters CO₂ (or 3 to 4.5 kg according to the pressure) per hour. The flow rate used during the experiments was set to 2.5 l h⁻¹, which avoids any problem of confinement.

The samples investigated here are injection-moulded bars made from an alumina powder consisting in a mixture of different granulometric distributions and two types of paraffin, one melting at 54 °C, the other at 64 °C.

These paraffins are introduced in equal quantities in a Duplex-Kneter mixer preheated at 100 °C. Once wax has melted, alumina is added and the batch is mixed for one hour under vacuum. The resulting mix is injected in a mould under a 0.6 MPa low pressure. Finally, a cold water circulation through the mould ensures solidification of the mix. Injected plates

Fig. 1 — Location of the parts cut in debinded samples and used for the thermogravimetric analysis.

($150 \times 150 \times 20 \text{ mm}^3$), in which paraffins fill the porosity of the ceramic bulk (porosity of 16.5 vol.% with a mean pore diameter of $1 \mu\text{m}$), are thus obtained.

Bars are cut in these plates to the desired dimensions, *i.e.* $10 \times 25 \times 40 \text{ mm}^3$ for porosity analysis or $20 \times 25 \times 40 \text{ mm}^3$ for the study of binder distribution that requires thicker samples.

Samples to be debinded are introduced in a cylindrical basket once weighted. This basket, fitted with sintered metallic parts at both ends, acts as a sample holder for the polymer-containing materials, and remains permeable to the fluids. It is put in position into the extractor and submitted to a flow of supercritical CO_2 .

The experimental extraction rate β , after a treatment time t , is estimated from the weight change $\Delta M(t)$ of the sample:

$$\beta = \frac{\Delta M(t)}{C_0 M_i} \quad (1)$$

where M_i is the initial weight of the sample and C_0 is the initial concentration of binder.

Samples were debinded under pressures of 16, 20, 24 and 28 MPa, at temperatures of 52, 62 and 72 °C, for one, two and three hours.

Pore size distributions were obtained by mercury porosimetry (Autopore II, Micromeritics, France) on the thinner samples.

The experimental binder distribution was determined by analysing the weight loss of small parts cut in the thicker bars already debinded as shown in Figure 1. Typical dimensions of these parts are $4 \times 4 \times 1 \text{ mm}^3$. Thermogravimetric analysis (L81, Linseis, Germany) were performed with an heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ up to 500 °C and an hold time of 5 minutes at this temperature.

3. Theoretical Background

When supercritical CO_2 is allowed to enter the basket, it immediately diffuses in the whole sample. CO_2 molecules form weak van der Waals type bonds with paraffin chains creating "solvato-complexes" which diffuse through the porosity of the sample to the surface. The solubility aspect will however be the topic of a further study. Solubilisation of wax and diffusion take place simultaneously. As binder is removed from the body, a non-planar diffusing front is created in the sample. According to the previous work [1], it has been shown that diffusion is the limiting step for the extraction of soluble paraffin.

Polymer diffusion through a parallelepipedic porous sample defined by its length L , width l and thickness e , is modelled in terms of the local polymer content $C(x, y, z, t)$ in the body, which is assumed to vary according to the classical diffusion equation:

$$\frac{\partial C(x, y, z, t)}{\partial t} = D \left(\frac{\partial^2 C(x, y, z, t)}{\partial x^2} + \frac{\partial^2 C(x, y, z, t)}{\partial y^2} + \frac{\partial^2 C(x, y, z, t)}{\partial z^2} \right), \quad (2)$$

D being the diffusivity of the polymer ($\text{m}^2 \text{s}^{-1}$).

The initial and boundary conditions are expressed as:

- concentration $C(x, y, z, 0) = C_0$;
- no binder at the surface during extraction (immediate evacuation): $C(L', l', h', t) = 0$ with $L' = L/2$, $l' = l/2$ and $e' = e/2$;
- $\partial C(x, y, z, t)/\partial x = 0$ for $x = 0$, $\partial C(x, y, z, t)/\partial y = 0$ for $y = 0$, $\partial C(x, y, z, t)/\partial z = 0$ for $z = 0$.

Integration of equation (2) gives the content of polymer which subsists in the green body after a given time t of extraction. Under the assumption that the diffusivity D is a constant, the problem is similar to that of heat conduction and the polymer content can be expressed by [11]:

$$\begin{aligned} \frac{\partial C(x, y, z, t)}{C_0} &= \frac{64}{\pi^3} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-1)^{i+j+k}}{(2i+1)(2j+1)(2k+1)} \\ &\times \cos \frac{(2i+1)\pi x}{2L'} \cos \frac{(2j+1)\pi y}{2l'} \cos \frac{(2k+1)\pi z}{2h'} \exp(-\alpha_{i,j,k} t) \end{aligned} \quad (3)$$

with:

$$\alpha_{i,j,k} = \frac{D\pi^2}{4} \left(\frac{(2i+1)^2}{L'^2} + \frac{(2j+1)^2}{l'^2} + \frac{(2k+1)^2}{h'^2} \right).$$

The mean concentration C_t at a given time t is obtained by: $C_t = \frac{\int C(x, y, z) dx dy dz}{\int dx dy dz}$

Thus:

$$\frac{C_t}{C_0} = \frac{512}{\pi^6} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{\exp(-\alpha_{i,j,k} t)}{((2i+1)(2j+1)(2k+1))^2}. \quad (4)$$

C_t/C_0 can also be expressed as a function of the extraction rate β .

$$\beta = 1 - \frac{C_t}{C_0}.$$

After long times of extraction (more than 2 hours) the first term of equation (4) ($i = j = k = 0$) prevails and the extraction rate is finally given by:

$$\ln \beta = \ln \left(1 - \frac{512}{\pi^6} \exp \left(-\frac{\pi^2}{4} \left(\frac{1}{L'^2} + \frac{1}{l'^2} + \frac{1}{h'^2} \right) D \times t \right) \right). \quad (5)$$

4. Results and Discussion

4.1. SOLUBILITY. — Supercritical CO_2 is a good solvent for polymers possessing non polar groups and/or a low molecular weight, such as alkanes and terpenes. It is fairly good for moderately polar species but becomes less efficient for compounds with polar groups and/or high molecular weight [12].

Fig. 2. — Phase diagram of carbon dioxide with experimentally determined solubility s of the paraffin mix (s : mass of paraffin dissolved in 100 g of CO_2).

An attempt was done to determine the solubility of both paraffins in supercritical CO_2 with our device for different temperature and pressure conditions. A given amount of paraffin was placed in the cylindrical basket and submitted to a flow of carbon dioxide. The solubility of paraffin is then evaluated by dividing the mass of paraffin removed during a 15 minutes treatment by the corresponding mass of flowing CO_2 . Values of solubility are reported in the phase diagram (Fig. 2).

Depending on pressure and temperature, supercritical CO_2 can prove to be a relatively good solvent for paraffin. Unfortunately, our results are not sufficiently accurate as the device does not include an equilibrium cell for phase diagram investigations. Nevertheless, their interest is to show the trends of paraffin solubility *versus* pressure and temperature. As clearly shown in Figure 2, the largest solubility corresponds to the largest density of CO_2 reached during the present work.

4.2. DIFFUSIVITY. — Using the value of the mass ΔM extracted after a debinding time of three hours, the extraction rate β has been determined with equation (1) for each experimental condition. The values of diffusivity D of dissolved organics, reported in Table II, are then calculated under different experimental conditions using equation (5). Pressure and temperature dependencies of D are plotted in Figures 3 and 4.

Equation (4) can then be used to calculate theoretical values of extraction for smaller times of treatment. An example of debinding kinetics is given in Figure 5 for the 52 °C case.

The paraffin content decreases progressively with time and reaches a plateau which does not correspond to a complete extraction even after prolonged experiments. The molecular weight distribution of paraffin is large, and probably the lighter backbones only can be dissolved. This is the reason why the following discussions will concern the soluble fraction of the binder mix only. The insoluble part remains present in the porosity of the ceramic green body.

Under constant pressure, the diffusivity is thermally activated in the range of temperature investigated. Under constant temperature, the diffusivity increases with pressure, excepted at 52 °C under 28 MPa (Fig. 3).

Fig. 3. — Evolution of diffusivity with pressure for different temperatures.

Fig. 4. — Evolution of diffusivity with temperature for different pressures

Fig. 5. — Kinetics of binder extraction obtained at 52 °C for different pressures (theoretical kinetics in dotted lines and experimental points).

Table II. — *Values of diffusivity D experimentally determined.*

P (MPa)	Diffusivity ($\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$)		
	$T(^{\circ}\text{C})$		
	52	62	72
16	2.0	3.0	3.0
20	3.1	5.0	5.0
24	4.2	7.0	7.2
28	2.4	8.8	9.5

The diffusivity depends on polymer solubility and diffusion of dissolved molecules, and both quantities are influenced by pressure and temperature. Diffusion as given by the Wilke and Chang equation [13], increases when temperature increases or pressure decreases, whereas solubility increases when temperature decreases or pressure increases.

Diffusivity variations with temperature and pressure are thus a balance between the variations of the amount of solubilised molecules and the diffusion of these species. The diffusivity increase with pressure can result from a solubility increase: more species are diffusing leading to an increase in the final extracted mass. The diffusivity decrease at 52 °C for pressures higher than 24 MPa may be the consequence of a too strong decrease in velocity. The diffusivity increase with temperature can be a consequence of a faster diffusion of dissolved wax molecules.

However, as temperature is raised above the melting point of the paraffins used in this study (54 °C and 64 °C), a liquid phase develops in the sample during binder removal. Then, liquid phase transport due to capillary migration is likely to occur leading to a redistribution of the binder within the sample.

4.3. DISTRIBUTION OF SOLUBLE BINDER AFTER DEBINDING. — This eventual redistribution of the organic phase during debinding has been experimentally verified by thermogravimetric analysis (TGA) on thicker bars debinded under 28 MPa, at 52, 62 and 72 °C, for two hours.

Using the values of diffusivity determined above, equation (3) allows to calculate the residual amount of soluble binder in the green body after a given time t of treatment as a function of the x , y , z coordinates. As the initial binder amount is known and supposed to be the same throughout the green body before the treatment, we can derive, from the above values, the loss of soluble binder after the same time t of treatment as a function of the x , y , z coordinates. These theoretical values can be compared to the experimental ones derived from the TGA measurements. As there is an evident central symmetry in binder distribution whatever the extraction time considered, we only consider values corresponding to the small parts located between 0 and $l/2$ (Fig. 1). Five values are thus obtained with x_c equal to 0.5 (centre), 3, 5.5, 8 and 10.5 (surface) mm.

Theoretical and experimental percentages of soluble binder removed are given in Table III. They agree very well at 52 °C, whereas they are quite different at 62 and 72 °C.

At 52 °C, the binder phase is solid and solubilised wax molecules can only be evacuated by diffusion in the porosity which develops as wax is removed from the green body. As diffusion is the only mechanism occurring at this temperature, equations (4) and (5) based on Fick's diffusion laws are particularly well suited to this case.

Table III. — *Theoretical and experimental percentages of soluble binder losses (28 MPa, 2 h).*

Debinding temperature	52 °C		62 °C		72 °C	
Part location: x_c	th. val.	exp. val.	th. val.	exp. val.	th. val.	exp. val.
0.5 mm (center)	0	0	0.9	7.6	1.8	51.1
3 mm	0	0	4.5	10.3	12.2	52.5
5.5 mm	1.6	2.8	17	31	27.6	51.3
8 mm	18.6	20	46.5	49	55	60.3
10.5 mm (surface)	50	50	85	43.5	90.1	49.5

Fig. 6. — Pore size distribution of a completely thermally debinded sample.

Fig. 7 — Porosity development of a sample debinded under 28 MPa, at 52 °C for a) 1 hour, b) 2 hours and c) 3 hours

Fig. 8. — Porosity development of a sample debinded under 28 MPa, at 62 °C for: a) 1 hour, b) 2 hours and c) 3 hours

Fig. 9 — Variation of the volume ratio of pores between 0.7 and 5 μm over pores between 0.1 and 0.7 μm as a function of time at 52 °C and 62 °C under 28 MPa

At 62 °C and 72 °C however, the calculated binder loss distribution in the sample does not fit anymore the experimental one. Binder loss throughout the sample is more uniform than predicted by the diffusion model which may be due to a liquid phase redistribution. As the temperature is now higher than the melting point of the paraffin mix (measured equal to 56 °C on a torque rheometer), liquid wax is able to move from the heart to the surface of the sample where it is removed by the supercritical fluid flow. As shown by Cima *et al.* [14], the driving force responsible for such a flow is given by the difference in capillary pressure ΔP resulting from the different pore radii present in the sample:

$$\Delta P = 2\gamma \cos \theta \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \quad (6)$$

where γ is the surface tension of the liquid, θ is the contact angle between the liquid and

Fig. 10 — Evolution of the porosity with debinding time at 52 °C and 62 °C

the pore wall, R_1 is the radius of a small pore and R_2 the radius of a larger pore.

Melted wax may thus be drained from large pores within the samples to small pores near the surface during binder extraction.

4.4. POROSITY DEVELOPMENT. — The evolution of the porosity during debinding will depend on the mechanisms of organic removal and should thus be different between the solid state at 52 °C and the liquid state at 62 °C or 72 °C.

In order to determine how the porosity develops during wax extraction, samples are debinded under 28 MPa, at 52 and 62 °C, for one, two and three hours. In parallel with these experiments, another sample is completely thermally debinded (with an heating rate of 1 °C min⁻¹ up to 200 °C, an hold up time of 4 hours and a final heating rate of 1 °C min⁻¹ up to 500 °C before cooling) to evaluate the final pore size distribution of the ceramic injected bulk.

Pore size distributions of debinded samples are measured by mercury porosimetry and given in Figures 6, 7 and 8. Depending on the temperature, the evolution of the opening of the porosity is different. At 52 °C, small pores are first opened whereas large pores appear first at 62 °C. Two classes of pores can be distinguished at both temperatures, one ranging from about 0.1 to 0.7 μm, the other one ranging from about 0.7 to 5 μm. If the following ratio, volume of pores between 0.7 and 5 μm over volume of pores between 0.1 and 0.7 μm, is plotted as a function of the debinding time (Fig. 9), it becomes evident that the opening of porosity differs completely between the two temperatures tested.

At 52 °C, evacuation of solubilised wax molecules by diffusion only opens small channels (the median "channel" diameter is equal to 0.39 μm) in the binder phase located in the largest pores between the ceramic particles. As wax molecules are further removed during the treatment, these largest pores (with a median diameter of 1.5 μm) become entirely open. Then, during the third hour of treatment, new small pores appear which can correspond to the smallest pores of the green body (Fig. 6).

At 62 °C however, it becomes obvious that capillary flow occurs and combines with diffusion. The smallest pores remain filled up with binder whereas bigger ones open. After one hour of extraction, the 0.7–5 μm pore class is far more developed than the smaller one: the median pore diameter is equal to 2.8 μm (to compare with the 0.39 μm value obtained at 52 °C after 1 hour). Pore size distribution corresponding to two hours of extraction is difficult to explain as pores develop due to both capillary flow and diffusion. This distribution suggests that capillary migration open large pores and diffusion of solubilised polymer by supercritical CO₂

open small ones. During the third hour of extraction, capillary migration may become less important than diffusion as more than 70 wt.% of the organic phase mainly located in large pores is removed and small open pores become larger due to the diffusion process of solubilised species.

In our case, the porosity has nearly completely opened at 62 °C whereas roughly 70% of the porosity is opened at 52 °C (Fig. 10).

5. Conclusion

In a previous study [1] on supercritical debinding of ceramics, two mechanisms of extraction of organic additives in a solid state, namely solubilisation of binder molecules and diffusion of solvato-complexes, were found to involve in the extraction process and a model based on diffusion equations was developed.

In the presence of a low melting point binder system however, a third mechanism of removal based on capillary flow is activated when the temperature of extraction is higher than the melting point of the organic phase. Porosity development in the sample during debinding confirms that, in this case, a liquid phase redistribution, governed by the differences in capillary pressure between pores of different sizes, occurs in the green body.

The diffusion model developed remains in good agreement with experimental results for a temperature treatment below the melting point of the binder. But this model will have to be completed with a capillary migration term to fit the results obtained at a temperature above the melting temperature.

Finally, the contribution of capillary flow allows faster extraction rates. A too important liquid phase however induces sample deformation. Optimisation of supercritical fluid extraction cycles will thus need to facilitate but to control the evolution of such a liquid phase to avoid deformation of the green part.

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