REMOVAL OF THERMOPLASTIC BINDERS FROM CERAMIC GREEN BODIES

MARTIN TRUNEC, JAROSLAV CIHLÁŘ

Department of Ceramics, Institute of Material Engineering Technical University Brno, Technická 2, 616 69 Brno

Received November 15, 1996.

INTRODUCTION

Plastic forming methods of ceramic bodies have an important position among advanced ceramic forming methods, as they allow the manufacturing process to be automated and precise products of complex shapes to be formed. Injection moulding, extrusion and tape casting are the most familiar representatives of the plastic forming methods. Recently, experiments have been made with introduction of other methods taken over from the plastics industry, such as vacuum forming and blow moulding. To achieve a suitably plastic state, the ceramic powder has to be mixed with a one- or multi-component binder, mostly of thermoplastic type. Following the forming of the thermoplastic ceramic suspension, all organic components have to be eliminated from the green body. The binder removal is regarded as the most critical step in particular in the case of injection moulding where the amount of binder may reach as much as 50 vol.%. Removal of the binder from thick-walled parts is a demanding operation which can take as long as several weeks [1]. This is also due to the fact that debinding was in the past paid inadequate attention in comparison with the other steps of the injection moulding technology, and systematic research was only started some years ago. German [2] divides the debinding methods into the following categories:

- 1. Thermal debinding:
 - debinding with permeation
 - debinding with diffusion
 - wicking
- 2. Solvent debinding:
 - solvent debinding by immersion
 - supercritical debinding
 - solvent vapour debinding.

Thermal debinding is based on binder removal at elevated temperatures. One of its variants, wicking takes place at a temperature where the binder is liquid and has an adequately low viscosity allowing the binder to be sucked by capillary forces into an ambient porous medium. The other thermal debinding methods are based on evaporation of components with low molecular weights, or that of products of thermal decomposition and their removal through the porous medium of the already partially debinded body by diffusion or permeation.

Solvent debinding is based on extraction by immersion during which one component of the binder is dissolved, thus creating a porous structure suitable for subsequent thermal extraction. In the case of supercritical debinding, the green body is subject to extraction in a solvent under conditions above the critical point of the solvent. The last of the solvent debinding methods, solvent vapour debinding, uses solvent vapours at elevated temperature to create a porous structure in the green body. The techniques mentioned above are frequently combined in order to speed up the debinding process.

MECHANISMS AND PROCESSES OF THERMAL DEBINDING

Thermal debinding represents the most widely employed way of removing binders from ceramic green bodies, mainly thanks to the relative simplicity of the method and of the necessary plant. Although already employed for a number of years, its mechanism has not so far been satisfactorily explained. It also has its disadvantages such as the long time required for defect-free debinding of thick-walled and fine-grained ceramic parts and the risk of blistering, cracking and warpage involved [3].

Thermal extraction of a polymeric binder from ceramic green body is effected by three mechanisms [3, 4, 5], namely evaporation, thermal degradation and oxidative degradation. Binders with a low molecular weight are not subject to scission of the polymeric chain and the loss in weight is mainly effected by diffusion of the components towards the body surface or to the liquid-gas interface, and by subsequent evaporation which is mostly independent of the character of the ambient atmosphere [6]. Inert atmosphere is usually employed to achieve degradation of higher molecular weight binder components. The thermal degradation proceeds uniformly throughout the volume of the polymer phase. The degradation products diffuse towards the surface of the body or to the liquid-gas interface where they evaporate. Presence of oxygen in the ambient atmosphere during thermal debinding brings about oxidative degradation of the polymeric binder at the body surface and its propagation into the interior is restricted by diffusion of oxygen onto the binder, as well as by diffusion of the degradation products towards the surface and by their evaporation. Still another debinding mechanism can take part in the process when the body is surrounded by a porous medium (powder bed, porous pad) which creates capillary flow helping to remove the binder by absorbing it.

Evaporation

Binder evaporation from a ceramic green body proceeds similarly to drying of a porous body [7]. On the onset of extraction, all the pores between the ceramic particles are filled with the liquid binder. The tendency preventing formation of a energetically disadvantageous solid-gas interface during decrease in the volume of the liquid phase due to evaporation leads to curvature of binder menisci in the pores. Capillary tension P in the liquid depends on meniscus radius r and is given by the Young-Laplace equation:

$$P = -\frac{2\gamma_{\rm LV}}{r} \tag{1}$$

where γ_{Lv} is the interfacial energy at the liquid-gas interface. When the curvature centre of the liquid surface is in the gaseous phase, it is negative and the liquid is in tension. The maximum capillary tension is achieved when the meniscus radius is small enough to penetrate into the pore interior. The minimum meniscus curvature radius for a liquid in a cylindrical pore r_p in radius is

$$r = -\frac{r_{\rm p}}{\cos\Theta} \quad , \tag{2}$$

where Θ is the contact angle. The pores in actual bodies are not cylindrical in shape, but the maximum tension P_r can be expressed by the ratio of surface area S_p to pore volume V_p using the equation [7]:

$$P_{\rm r} = \frac{(\gamma_{\rm SV} - \gamma_{\rm SL})S_{\rm P}}{V_{\rm P}} = \frac{\gamma_{\rm LV}\cos\Theta S_{\rm P}}{V_{\rm P}} \quad , \tag{3}$$

where γ_{SV} and γ_{SL} are interfacial energies at the solid-gas or solid-liquid interface. The S_P/V_P ratio can be expressed by means of specific surface area S of the porous body using the equation [7]:

$$\frac{S_{\rm P}}{V_{\rm P}} = \frac{S\rho_{\rm S}\rho}{1-\rho} \quad , \tag{4}$$

where ρ is the relative density of the porous (binder-free) body, and ρ_s is the density of the solid phase.

Apart from capillary pressure, additional forces such as osmotic pressure may arise during evaporation [7]. . Preferential evaporation of one component may occur in the case of a multicomponent binder. The binder at the surface then can have a composition different from that at the centre. The corresponding concentration gradient may produce osmotic pressure, and this can only be relieved by diffusion in the pores.



Figure 1. Schematic representation of the movement of liquid binder from large pores (B) into the smaller ones (A) by the effect of capillary forces during binder evaporation [8].

Capillary tension is responsible for shrinkage of the body due to decreasing distances between the individual particles. At the point when the particle motion is blocked, the stress attains a maximum and the gas-liquid interface penetrates into the pore interiors. The interface does not advance uniformly throughout the specimen as the largest pores are the first to be emptied, passing the liquid into the smaller pores (cf. figure 1). Liquid flow from the larger pores to the smaller ones is controlled by Darcy's law which provides the following equation for liquid flow J_p (in volume units per surface area of the porous body per unit time) [7]:

$$J_{\rm P} = \frac{K}{\eta_{\rm L}} \, \nabla P_{\rm L} \quad , \tag{5}$$

where ∇P_L is the pressure gradient in the liquid, η_L is the viscosity of the liquid, and *K* is the permeability. A number of equations were derived for calculation of permeability of a porous medium. A simple one is represented by the Carman-Kozeny equation:

$$K = \frac{(1-\rho)^3}{5(\rho S \rho_S)^2} \ . \tag{6}$$

The distance from which the liquid can be conveyed by viscous flow to the phase boundary at which it can

evaporate, is given by the pressure loss during steady state flow through the porous medium. The pressure loss ΔP in a fully saturated porous medium is given by Kozeny's equation [8]:

$$\Delta P = \frac{36k_{\rm p}\,\eta_{\rm L}}{d^2} - \frac{(1-\varepsilon)^2}{\varepsilon^3} hv \quad , \tag{7}$$

where ε is the proportion of pores in the porous body, d is the size of particles composing the porous body, k_p is a constant given by the pore geometry, v is the liquid flow velocity and h the distance over which the flow takes place. If the porous body is not fully saturated, equation (7) has to be modified so as to take into account a decrease in liquid conductivity. The pressure difference ΔP responsible for liquid flow from the larger pores to the smaller ones can be estimated on the basis of interfacial energy of the liquid γ_{Lv} and on that of particle size d of the porous body [8]:

$$\Delta P = \frac{2\Delta\phi\gamma_{\rm LV}}{d}\cos\Theta \quad , \tag{8}$$

where $\Delta \phi$ is a factor depending on arrangement of the particles. For $\Delta \phi = 8$, one obtains the limit bottom estimate of capillary forces [8]. Comparison of equations [7] and [8] yields the equation:

$$\frac{h}{d} = \frac{\Delta \phi \varepsilon^3}{18k_{\rm p}(1-\varepsilon)^2} \frac{\gamma_{\rm LV}}{\nu G} \quad , \tag{9}$$

where $v (= \eta_L \rho^{-1})$ is the kinematic viscosity and $G (= \rho v)$ is the mass flow.

The right-hand side of equation (9) specifies the characteristic distance over which the capillary forces are significant. Equation (9) shows that the distance will increase with increasing surface tension and decrease with increasing viscosity and increasing amount of the liquid being transferred. Distance h gives the depth of the region partially saturated with the liquid (funicular region) separating at the interphase boundary in the porous body the fully liquid-saturated region from that having a porosity no longer allowing transport of the liquid by capillary forces (pendular region). Binder transport in the porous region can only be effected by vapour diffusion.

The rate of evaporation $V_{\rm E}$ is proportional to vapour pressure of the liquid $p_{\rm v}$ and to the ambient vapour pressure $p_{\rm a}$ [9]:

$$\dot{V}_{\rm E} = k_{\rm e} \left(p_{\rm v} - p_{\rm a} \right) \quad , \tag{10}$$

where k_c is a constant depending on temperature, flow of gases and geometry of the system. Vapour pressure of the liquid depends on tension P in the liquid

$$p_{\rm v} = p_{\rm v}^{\rm o} \exp\left(-\frac{-PV_{\rm L}}{RT}\right), \qquad (11)$$

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where p_v^{o} is the liquid vapour pressure above a planar interface, V_L is the molar volume of the liquid, *R* is the gas constant and *T* is temperature.

From equations (1), (10) and (11) is follows that evaporation will proceed until

$$p_{a} < p_{v}^{0} \exp \left(\frac{2V_{L}\tau_{Lv}}{RTr} \right).$$
(12)

Vapour pressure does not depend on the presence of an inert gas above the liquid. However, this applies only to small partial pressures of the inert gas. If these pressures are high, the inert gas also affects the steady-state vapour pressure above the liquid [10]. Evaporation from polymeric solutions is controlled by partial vapour pressures which can be determined from the activities of the individual binder components. The polymer-solvent systems generally do not conform to Raoult's law so that the activities of components have to be determined by means of the Flory-Huggins equation [11]:

$$a_1 = V_1 \exp(V_2 + \chi V_2^2) \quad , \tag{13}$$

where a_1 is the activity of the binder component, V_1 , V_2 are the volume proportions of binder components, and χ is the interaction parameter. Vapour pressure p_1 of the component above the solution is thus given by the equation:

$$p_1 = p_1^{\circ} V_1 \exp(V_2 + \chi V_2^2) \quad , \tag{14}$$

where p_1^0 is the vapour pressure of the pure component. If the binder system contains components with various vapour pressures, the binder composition will mostly change during evaporation from the porous body. The surface layer will be enriched with the non-volatile component. If the diffusion of this component against the liquid flow is not adequately fast, concentration of the non-volatile component will increase and the rate of evaporation decrease. It can be shown that the liquid flow is faster than the diffusion when the pore size is larger by several factors than the liquid molecule diameter [7]. Even in the case of adequately fast diffusion the rate of evaporation should gradually decrease as a result of decreasing concentration of the volatile component in the binder. However, no such effect was observed. The phenomenon was explained and its mechanism experimentally verified by Cima et al. [8, 12]. Figure 2 shows an idealized arrangement of ceramic particles with a broad pore size distribution. At first, the liquid is sucked by capillary forces into the smallest pores which are gradually filled with the non-volatile component. The small pores go on sucking liquid from the larger pores until also becoming filled with the non-volatile binder component. The process is repeated and advances into the ceramic body interior (cf. figure 3). The volatile material can diffuse through the polymeric binder in the direction perpendicular to the arising pores and the diffusion path

thus remains unchanged. The evaporation rate is therefore the same because the conditions of diffusion, which is the

Figure 2. The effect of capillary forces on binder redistribution. The non-volatile component settles in the smallest pores (diagonal hatching) [8].



Figure 3. Schematic model of two-component binder redistribution and removal during thermal debinding [13].

limiting process of evaporation, have not been affected. The diffusion rate of the volatile component in the binder can be estimated by means of the following equation [13]:

$$J_{\rm D} = -D_{\rm eff} \frac{\Delta c}{l} \quad , \tag{15}$$

where J_D (kg m⁻² s⁻¹) is the diffusion flow, D_{eff} is the effective diffusion coefficient, Δc is the concentration

difference and l is the diffusion distance. The effective diffusion coefficient takes into account the presence of ceramic particles and can be estimated by means of diffusion coefficient D of the volatile component in the pure binder [13]:

$$D_{\rm eff} = \frac{D\varepsilon}{\tau} \quad , \tag{16}$$

where ε is the proportion of pores in the porous body and τ is the tortuosity factor. The latter expresses the difference in the diffusion path due to the presence of ceramic particles and that in their absence, and ranges from 3 to 7. Evans [14] presents a survey of relationships for determining the effective diffusion coefficients in the form of:

$$D_{\rm eff} = f(D, V) \quad , \tag{17}$$

where V is the volume proportion of the dispersed ceramic phase. However, these relations do not take into consideration the particle shape and size distribution. Shrinkage in the course of evaporation will certainly affect diffusion as a result of increasing proportion of the solid phase and decreasing proportion of pores ε . In the case of fine particles (< 1 µm), a significant part will also be played by the layer adsorbed on the particle surface. This layer increases the effective volume proportion of the solid phase V_{eff} [4]:

$$V_{\rm eff} = V(I + k_{\rm a} \rho_{\rm c} S l_{\rm m}) \quad , \tag{18}$$

where ρ_c is the density of the ceramic material, S is the specific surface area of the ceramic particles and l_m is the size of the chain of the absorbed organic molecule. The constant k_a ($0 \le k_a \le 1$) defines the thickness of the adsorbed layer in which diffusion of the volatile component is zero. On considering the limit case of a minimum size pore in a system of spherical particles, this size would be 0.078 d (for closely packed spherical particles). For a powdered material of 0.4 µm mean particle size, the smallest pore would be roughly 30 nm in size. A comparison with the size of molecules, e.g. that of microcrystalline wax ($M_n = 300$) and polyethylene $(M_n = 2900)$ corresponding to about 3 nm and 14 nm respectively [14] shows that with submicrometric particles both binder flow and diffusion can be significantly restricted by the organic layer adsorbed on the surface of ceramic particles [4].

Shaw et al. [15, 16] showed that in the early stages of thermal debinding, surface and interconnected porosity is substantially less extensive that would be expected from the loss in weight. At a binder loss of 30 wt.% the porosity amounted to as little as 5 vol.% (in a system with initial ceramic phase content of 50 vol.%). This is due to shrinkage of the body caused by the particles moving closer together during binder departure [17] and to binder redistribution in the body [18]. However, the maximum shrinkage at the point of binder removal does not correspond to the optimum possible arrangement of particles for the given type of powder [19, 20]. Although the movement of particles during the shrinking is small (5 - 15nm) [21], the resultant non-uniformity of mutual contacts between the particles may be considerable. Song at al. [22] showed that the transfer of particles is due not only to capillary forces during binder removal, but also to London's attractive forces. Flocculation, which causes eracking, occurs in particular in systems with low-viscosity binders and non-stabilized ceramic particles.

Thermal and oxidative degradation

Thermal debinding involves degradation of binders. The polymers polymeric thermoplastic decompose thermally at temperatures depending on the polymer type as well as on the character of the ceramic powder. A typical range of thermal degradation is degradation proceeds 200 - 600 °C, and the simultaneously throughout the body volume. A diagram of the most probable thermal degradation reactions is shown in figure 4. Heat may affect the main chain bonds (A) or the substituents and the side chains (B). The main polymer chain may be subject to random scission or to scission of weak bonds, depending on the actual polymer structure. The macroradicals formed by main chain scissioning may undergo depolymeration reactions, where the chain length of the products depends on the polymer structure and on the exposure temperature. The chain ends have often labile structures promoting initiation of thermal degradation. This effect was observed on polymethyl methacrylate terminated by a double bond, or on polyoxymethylene with a terminal -OH group. Macroradicals formed by primary scission of these polymers tend to stabilize by releasing their monomers. Crosslinked decomposition products can be formed when the main chain contains double bonds.

The side bonds are weaker than those of the main chain and are thus more likely to be eliminated. Elimination of substituents by reactions of the type

was found with polyvinyl chloride. In the case of polyvinyl butyrate and polyvinyl alcohol, scission of side chains was found to produce butyraldehyde and water respectively [23]. Free radicals need not be necessarily produced by the reactions. If these are formed by scission of side chains, they may affect scission of the main chain as follows:



Cyclization is another frequent reaction of the side chains. The respective mechanisms may proceed simultaneously, with one of them being always predominant.



Figure 4. Diagram of the most probable reactions taking place during thermal degradation of polymers.

Degradation of alkanes and polyolefins, which are the most frequent binder components, was studied extensively and explained by means of the free radical mechanism [24, 25]. The following degradation mechanism was proposed for linear high-density polyethylene [25], where R represents the macromolecule and R^{\prime} is a small alkane group:

1. Initiation:

$$R - R \longrightarrow 2R^{-} . \tag{21}$$

2. Propagation:

$$R^{-} \longrightarrow R^{-} + CH_2 = CH_2$$
 (22)

3. Intramolecular transfer followed by decomposition reaction:

$$\begin{array}{ccc} \mathbf{R}^{\cdot} & \longrightarrow & \mathbf{R} - \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H}_2 - \mathbf{R}' & \longrightarrow \\ & \longrightarrow & \mathbf{R}^{\cdot} + \mathbf{C}\mathbf{H}_2 = \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H}_2 - \mathbf{R}' \end{array}$$
(23)

$$\begin{array}{ccc} R^{\cdot} & & & \\ & & \\ \hline \end{array} & & R - \dot{C}H - CH_2 - R' & \\ \hline \end{array} \\ & & & \\ R - CH = CH_2 + R'^{\cdot} & . \end{array}$$
(24)

4. Intermolecular transfer followed by decomposition reaction:

 $R-CH_2-R+R' \longrightarrow R-\dot{C}H-R+RH$ (25)

 $R-\dot{C}H-R \longrightarrow R-CH=CH_2 + R^{-1}$ (26)

5. Termination:

 $\mathbf{R'} + \mathbf{R'} \longrightarrow \mathbf{R'} - \mathbf{CH} = \mathbf{CH}_2 + \mathbf{R'H}$ (27)

$$\mathbf{R}^{\prime \cdot} + \mathbf{R}^{\prime \cdot} \longrightarrow \mathbf{R}^{\prime} - \mathbf{R}^{\prime} \quad . \tag{28}$$

The thermal degradation is initiated by scission of the weak bonds in the main chain, or possibly by random scission of C-C bonds of the main chain yielding free radicals. Depolymeration of radicals to ethylene competes with intramolecular and intermolecular transfer of radicals. The ratio of ethylene to other degradation products depends on degradation temperature. The secondary radicals formed by intramolecular transfer disintegrate to alkene and alkane radicals. These may further decompose or become stabilized while forming gaseous products (alkenes and alkanes). Degradation of n-alkanes, polypropylene and the other vinyl-type polymers proceeds by a similar mechanism [24]. However, in the case of paraffins, it is evaporation of the non-degraded components which is in particular involved in the debinding of ceramic green bodies.

The degradation products have to diffuse through the polymeric binder towards the body surface or to the gas-liquid interface where they can evaporate. The concentration profile and the activity of the degradation products in the body are therefore determined by the cumulative effect of formation of the products, their diffusion and evaporation [4].

Oxidative degradation of polymeric binders takes place side by side with thermal degradation in the presence of oxygen. The mechanism of polymer oxidation [26] includes oxidation of the primary radical producing a peroxy radical which in turn removes hydrogen from another polymeric macromolecule. The process yields a hydroperoxide molecule and a secondary radical, and can be described by the following reactions:

$$R' + O_2 \longrightarrow ROO'$$
 (29)

 $ROO' + RH \longrightarrow ROOH + R'$. (30)

Hydroperoxide ROOH is not stable and decomposes forming radicals:

$$ROOH \longrightarrow RO + HO$$
(31)

The radicals react with other macromolecules, causing branching of the macromolecule chains, formation of water and radicals suitable for further oxidation. The process can be described by the reactions

$$RO' + RH \longrightarrow ROH + R'$$
 (32)

$$HO + RH \longrightarrow HOH + R \tag{33}$$

The process is terminated by formation of inert products yielded by reaction of two oxidized radicals. The oxidative degradation is restricted to the surface layer of the body, being controlled by diffusion of oxygen into the polymeric binder, and by retrodiffusion of the oxidation products to the surface where they evaporate [27]. A suitable model for oxidative degradation advancing from the body surface towards its centre is represented by Szekel's shrinking unreacted core model [27]. When the gradual debinding from the body surface towards its centre forms a solid outer debinded layer while the core is still plastic, the resulting non-uniform shrinkage may lead to defects [28].

Thermal degradation is a process with a high activation energy (150 - 200 kJ mol⁻¹). In contrast to this, oxidative degradation including autocatalytic oxidation initiated by free radicals requires a lower energy (30 - 40 kJ mol⁻¹) and will therefore dominate at lower temperatures [6, 29]. Products of oxidative degradation may react mutually, producing compounds of higher molecular weight and possibly with a cross-linked structure. Their elimination would require an oxidative medium and higher temperatures [30]. In spite of this, extraction in pure oxygen was successfully utilized for debinding injection-moulded bodies at temperatures of max. 400 °C [31].

Degradation of polymeric binders may also be influenced by the ceramic material proper. It was shown that in the presence of oxidic materials, the degradation reactions are catalyzed and shifted towards lower temperatures [32]. The effect is much more pronounced in air atmosphere than in an inert gas [33]. The degree of the catalytic effect was proved to be affected by the character of the polymer and that of the solid particles, their amount and their specific surface area [34]. However, the effect of specific surface area on catalysis of thermal degradation was not positively established in the case of alumina [14]. Following the end of thermal debinding, a certain amount of polymer remains in the body in the form of carbon residues. These substances may negatively influence the final properties of the sintered material [35]. The amount of the carbon residues depends in particular on the type of the powder material and on the atmosphere of debinding. Masia et al. [33] showed that alumina with 2 wt.% polyvinyl butyral heated at 1000 °C in air atmosphere and in argon

atmosphere contained 80 ppm and 565 ppm of carbon respectively. Thermal degradation of polyvinyl butyral alone leaves behind no solid residues. Higgins et al. [36] demonstrated that the amount of carbon residues after debinding in an inert atmosphere was independent of the original amount of the organic phase (polymethyl methacrylate), but was directly proportional to the specific surface area of the powdered alumina employed. They also showed that very strong bonds between the degradation products and active OH groups on the surface of the oxidic material are formed.

Wicking (capillary extraction)

Evaporation or boiling of the binder and its degradation products bring about a multiple increase in volume during transition from the liquid to the gaseous phase, and this may result in defects in the bodies being debinded. In contrast to this, wicking is capable of removing the binder in its liquid phase from a porous body. When the body is surrounded with a porous medium (powder bed or a porous pad), the difference in the capillary forces in the body and porous medium is responsible for a capillary flow of the binder from the body into the porous medium. The difference in capillary pressures ΔP depends on the difference in pore size between the body and the powder bed according to the equation:

$$\Delta P = 2\gamma_{\rm LV} \quad \left(\frac{\cos\Theta_1}{r_{\rm p1}} - \frac{\cos\Theta_2}{r_{\rm p2}} \right), \tag{34}$$

where Θ_1 , Θ_2 are contact angles of the binder in the powder bed and in the body respectively, r_{p1} , r_{p2} are the respective powder bed and body pore radii, and γ_{LV} is the interfacial energy at the gas-liquid interface. The capillary flow in an isotropic medium is described by equation (5) which can be written in the form:

$$\frac{Q}{A} = -\frac{K\Delta P}{\eta_{\rm L}h} \quad , \tag{35}$$

where Q/A is the volume flow per unit area, η_L is the binder viscosity, *h* is the distance over which pressure difference ΔP is effective, and *K* is the permeability of the porous medium.

The above relationships show that wicking will be the more effective the greater the difference in the pore sizes of the powder bed and of the body, and the lower the binder viscosity. Permeability of the porous medium is another parameter affecting the capillary flow. German [37] suggests that the wicking should be arranged so that:

$$d_1 < d_2$$
 and $K_1 > K_2$, (36)

where d is the particle size, K is the permeability and subscripts 1 or 2 designate the powder bed and the body

$$P = \frac{10\gamma_{\rm LV}\cos\Theta}{d} \quad , \tag{37}$$

and

$$K = \frac{\varepsilon^4 d^2}{90(1 - \varepsilon)^2} \quad , \tag{38}$$

where ε is the porosity of the medium.

However, Bao and Evans [38, 39] showed that none of the relationships for permeability of the powdered medium correlated with experimental values. Mass transport in such a medium is affected by agglomeration and arrangement of the particles. Wright and Evans [40] found that wicking was capable of removing a part of the binder even when the body and the powder bed comprised the same powdered material. Maximum debinding can be achieved in the case of a very fine-grained powder bed (relatively with respect to the body particle size), but its rate will be controlled by powder bed permeability. It was found that the residual binder was distributed uniformly throughout the body and that the binder loss was accompanied by reduced filling of pores in the body [40]. In contrast to this, the powder bed had a constant partial filling of the pores and the boundary of extracted binder advanced towards the powder interior. Only a part of the powder bed pores was filled with the extracted binder, this being due to a broad pore size distribution in the loosely arranged or clustered powdered material [39]. Only the smaller pores are capable of producing a capillary pressure difference for wicking the binder from the body.

The partial filling of the powder bed pores with the liquid, the pore size distribution, their inhomogeneous distribution and the variable filling of pores in the body with binder in the course of the wicking process make the estimation of the mean capillary pressure difference and that of the permeability very difficult, and this also leads to considerable differences between the calculated and the experimental values of the wicking process.

OPTIMIZING THE THERMAL DEBINDING PROCESS

The types of defects arising in the course of thermal debinding can be divided into two groups [41]. One includes defects which actually arise during debinding, but have their origin or cause in the forming stage, for example relieving of residual stresses after forming, inhomogeneity of the ceramic green body, flow lines, cracks, air bubbles, and the like. Most of such defects are imperceptible after forming and appear only after debinding. Some of them can be eliminated by suitably adjusting the conditions (residual stresses), but the majority cannot be eliminated in the thermal debinding stage. The other group of defects is represented by those caused by unsuitable debinding conditions. These include e.g. warpage and cracking due to the gravity effect, bubbles, blisters and cracks caused by liberation of the gaseous phase, cracks produced by non-uniform binder removal, surface layers or structural defects resulting from the effects of thermal debinding residues. Many defects are caused by gases developed inside the body. Boiling of binder degradation products and low-molecular binder components generates multiple volumes of gases generating overpressure and damaging the body [42]. The boiling takes place approximately at the time when their vapour pressure p_x exceeds ambient pressure p_o , i.e. when

$$p_{v} > p_{0} \tag{39}$$

A large number of experimental studies were carried out with the aim to eliminate these defects while ensuring acceptable times of thermal debinding. However, the factors influencing the debinding process are so numerous that the transfer of results and experience from certain systems to others is very difficult and any generalization must be formulated with extreme caution.

Although the character and scope of defects in bodies cannot be correlated with the results of thermal analyses of mixes or small specimens [43], the results may provide suitable guidelines for selection of binder components, for designing the heat treatment schedule and the conditions of debinding [44, 45]. A suitable binder composition and a non-linear heating rate allow the loss in weight to be spread over a wider period of time and thus to prevent rapid generation of large amounts of gaseous products [46, 47]. Pinwill et al. [48] proposed an experimental method for determining the optimum debinding heating schedule. The method yields a diagram of temperature vs. heating rate, specifying the limits of maximum allowable debinding heating rates. However, the method is very time consuming and experimentally demanding and its results apply solely to the particular product. The critical temperature region was that closely above the softening point of the suspension, where the rate of heating must be significantly reduced. A comparison of results for various products showed that doubling the body thickness requires the total debinding time to be increased by a factor of roughly four.

Application of overpressure (0.1 to 1 MPa) permits the maximum admissible debinding heating rate to be increased [49]. The main advantage of such conditions is based on raising the boiling point of the degradation products and of the low-molecular weight binder components. The viscous flow rate as well as the diffusion rate are likewise increased with increasing temperature, so that the higher rate of debinding does not involve the risk of the gaseous phase forming in the sample.

Johnson et al. [50, 51] have devised equipment allowing the time of thermal debinding to be cut in half. The weight of the ceramic parts is monitored during the process and the temperature is controlled according to the weight loss so as to achieve a constant weight loss rate. At first, the temperature follows a pre-programmed curve until the weight loss rate exceeds a preset critical value; then the temperature is immediately decreased. As soon as the weight loss rate is stabilized, the temperature will further rise in line with the program. In this way the system controls the conditions throughout the entire debinding process. The system was further perfected by Carlström et al. [52] who replaced the on-off control by proportional heating rate control regulated to achieve a constant weight loss rate. It was proved that in this way the fluctuation of weight loss rate can be significantly suppressed and the time of debinding a ceramic turbocharger rotor was shortened by a factor of ten. A similar plant was developed for debinding multilayer ceramic capacitors [53]. As the critical weight loss rate value, use was made of the maximum value established at a conventional linear temperature rise rate. The kiln temperature control ensuring a constant weight loss rate was based on a cascade system of three PID controllers. In this way it was possible to achieve a very close agreement between the required and the actual weight of the charge.

Some of the defects arising during the debinding of massive parts cannot be eliminated without modifying the basic materials and the debinding conditions. Bandyopadhyay and French [54] showed that use of powder with a broad particle size distribution may lead to transfer of the fine particles to the body surface by binder migration in the course of wicking. This effect may result in compaction of the surface layer which prevents shrinkage and contributes to formation of internal cracking [55]. Defects of other types were found in bodies where the binders are not liquid during debinding, such as with the use of thermosetting resins, namely cracks in pores between the particles instead of the typical bubbles and blisters arising with thermoplasts [56]. With thermosets, evaporation of volatile components does not involve binder redistribution by capillary forces and microcracks are formed.

MODELS OF THERMAL DEBINDING

Several attempts have recently been made at developing a model which would simulate removal of thermoplastic binders from ceramic green bodies. The first model of extraction of a single-component binder was proposed by German [37] on the assumption that transport of gaseous components through free pores of a porous body is the controlling factor of thermal debinding. For isothermal conditions he derived the total time required for binder elimination. In the case of gaseous component transport by diffusion through the pores, the time t required was given by the equation:

$$t = \frac{\omega^2 \left(MkT\right)^{1/2}}{2d\Delta p \varepsilon^2 V_{\rm S}} , \qquad (40)$$

where w is the specimen thickness, M is the molecular weight of vapours, k is the Boltzmann constant, T is absolute temperature and d is the diameter of ceramic particles. Δp expresses the pressure difference between the pressure of the gaseous phase p at the interphase boundary and ambient pressure p_{a} , where the pressures include the vapour pressures and those of the ambient gases, ε is the porosity and V_s represents the molar volume of the solid binder. In the case of vapour transport through the pores by permeation, the derived equation acquires the form:

$$t = \frac{22,5\omega^2 (1-\epsilon)^2 p \eta_G}{\epsilon^3 d^2 F(p^2 - p_0^2)} , \qquad (41)$$

where η_G is the viscosity of vapours and *F* is the volume ratio of the solid binder to that of gaseous components at pressure *p*. From the relations it follows that the total time of debinding is proportional to the specimen thickness squared. The models were derived on the basis of simplifying assumptions and estimates of some parameters, so that the time estimate may involve an error of approximately 50%. However, the assumption that vapour transport through porous medium is the controlling factor of the debinding can only hold after a certain time of debinding, when the interphase boundary has already shifted into the specimen interior. The models in question do not take into consideration any criteria associated with the formation of defects.

Baron and Ulicny [57] devised a model which calculates the hydraulic pressures caused by thermal expansion of the organic binder in the initial stages of thermal debinding. The authors consider evaporation and thermal degradation as the mechanisms involved in binder elimination at elevated temperatures. The thermal degradation products in the body are transported in liquid phase by capillary forces. The model assumes that the ceramic particles constitute a rigid lattice in which the organic binder expands. This assumption does not correspond to the idea of dispersed ceramic particles separated by layers of organic binder, allowing the suspension to flow as a fluid. Experimental measurements have proved the existence of thermal expansion of ceramic suspensions in both solid and liquid states, and thus also the ability of particles to move freely [58].

On the basis of experimental measurements Angermann and Van Der Biest [59. 60] proposed a

partially dissolved in the other polymeric component (polyethylene or polypropylene) [61]. They focused their attention on the initial stages of debinding when there are none or only few free pores and a high risk of defect initiation exists. Over this temperature range the polymer degradation is negligible and the entire weight loss can be attributed to evaporation of low molecular weight components. They describe the removal of low molecular weight components in the subsequent steps. In the first step, open pores arise in the body, as shown in figure 5. The pores propagate from the surface into the interior and may be formed early, as soon as the binder is capable of viscous flow. Elimination of the components with a low molecular weight proceeds in step two by diffusion through the thermoplastic binder to the pore-binder boundary. Then follows evaporation (step 3), transport of gaseous components through the body porous structure to the surface (step 4) and their removal from the surface by inert gas flow (step 5). Steps 2 through 5 are represented in figure 5 by arrows. The slowest step was found to be the diffusion of low molecular weight components through the thermoplastic binder. The debinding is therefore controlled by diffusion and the weight loss values should be described by the equation:

model of removing a two-component binder comprising

a low-molecular weight component (stearic acid, paraffin)

$$\frac{m_{\rm SA}(t)}{m_{\rm SA}(0)} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(n+1)^2} \exp\left(-(2n+1)^2 \frac{\pi^2}{4} \frac{D_{\rm eff}}{l^2}t\right),$$
(42)

where $m_{SA}(0)$ is the total weight of the removable component with low molecular weight at temperature Tfrom specimen w in thickness, $m_{SA}(t)$ is the weight of this component remaining in the specimen at time t. Equation (42) is a solution of one-dimensional diffusion through a plate l in thickness with the initial condition that at time t = 0 the low-molecular component is distributed uniformly throughout the plate l in thickness. For further evaluation, use was made only of the first term of equation (42) for n = 0, as the other terms have values lower by several orders of magnitude and their neglecting would not affect the result. Equation (42) thus acquires the form:

$$\frac{m_{\rm SA}(t)}{m_{\rm SA}(0)} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2}{4} \frac{D_{\rm eff}}{l^2} t\right) , \qquad (43)$$

where D_{eff} is the effective diffusion coefficient of the low molecular weight component in the ceramic specimen which can be determined from equation (16).

The plot of log $(m_{\rm SA} (t)/m_{\rm SA} (0))$ vs. time of debinding t was linear for the individual temperatures, and the slopes of the straight lines allowed the factor $\pi^2 D_{\rm eff}/4l^2$ to be determined. From the logarithmic plot of $\pi^2 D_{\rm eff}/4l^2$ vs. reciprocal specimen thickness 1/w,

Angermann and Van Der Biest established the relationship:

$$l \sim \omega^{0.45} \approx \sqrt{\omega}$$
 (44)

This relationship indicates that the diffusion did not proceed throughout the specimen thickness, but only down to the boundary of the inner pore. The reason why the diffusion lenght increases with specimen thickness was not fully elucidated. Similarly to German's model, this model also does not include conditions for the formation of defects.



Figure 5. Idealized porous structure of a ceramic body, and representation of the individual thermal debinding steps [59].

Calvert and Cima were the first to introduce a model based on diffusion of degradation products in the binder and taking into account formation of bubbles when the critical concentration has been exceeded. Their model was concerned with the decomposition of methyl methacrylate yielding the monomer. If the monomer is produced at rate \dot{Q} (kg m⁻³ s⁻¹) and diffuses at a rate given by coefficient D_{eff} towards the surface, then the steady-state concentration C at distance x from the centre (x = 0) of plate 2l in thickness, is given by the equation:

$$C = \frac{\dot{Q}}{2D_{\text{eff}}} \left(l^2 - x^2 \right) + C_i \quad , \tag{45}$$

where C_i is the monomer concentration at the specimen surface. This concentration can be considered as being zero when the ambient gas is replaced at a high rate. The depolymeration rate at constant temperature was determined from the depolymeration activation energy. Cracks were considered to form at the moment when the monomer vapour pressure in the solution exceeds the atmospheric pressure. The model demonstrated that within an acceptable period of time (less than 7 days) it is impossible to remove the binder from specimens thicker than 3 mm. The debinding kinetics is significantly accelerated when uniform porosity is produced in the body following the initial stage of decomposition.

Evans et al. [11] have prepared an experimentally verified numerical model considering diffusion of degradation products in the thermoplastic binder under inequilibrial temperature conditions and allowing formation of defects in the debinded products to be predicted. The kinetics of thermal degradation of the polymeric binder (poly- α -methylstyrene) to its monomer is combined with non-linear numerical calculation of the diffusion of degradation products in the polymer solution. The monomer concentration at the centre of an infinite cylinder is used to calculate the monomer vapour pressure in the binder and to determine the time of defect initiation. The defects arise when the vapour pressure exceeds the ambient pressure (≈ 105 kPa). Analysis of the kinetics of thermal degradation permitted the weight fraction x of the residual non-degraded polymer at a given absolute temperature T to be calculated:

$$x = \exp\left\{-\frac{K_0 RT^2 \exp(-E/RT)}{ZE} \left[1 - \frac{2RT}{E} + \frac{6(RT)^2}{E^2}\right]\right\},$$
(46)

where K_0 is a specific rate constant and E is the activation energy of thermal degradation, R is the gas constant and Z is the rate of heating the ceramic body. On the assumption that degradation of polyalpha methylstyrene is a first-order reaction, the rate of monomer formation \hat{Q} (kg m⁻³ s⁻¹) in a ceramic suspension is given by the equation:

$$\dot{Q} = \rho_{\rm p} V_{\rm p} K_{\rm 1} x = \rho_{\rm p} V_{\rm p} K_{\rm 0} \exp[-E/(RT)] \exp\left\{-\frac{K_{\rm 0} RT^2 \exp(-E/RT)}{ZE} \left[1 - \frac{2RT}{E} + \frac{6(RT)^2}{E^2}\right]\right\},\tag{47}$$

where K_1 is the rate constant of thermal degradation, ρ_p is the density of the polymeric binder and V_p is the volume proportion of the binder. At time *t* the concentration profile of the monomer C = C(r,t)in an infinite cylinder r_0 in radius is given by the equation:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D_{\rm CT} \frac{\partial C}{\partial r} \right) + \dot{Q} \quad , \tag{48}$$

where D_{CT} is the effective, concentration and temperature dependent diffusion coefficient of the monomer in the ceramic suspension, and t is the time.

Calculation of the monomer vapour pressure from its concentration in the body, which is highest at its centre, was effected by means of Flory-Huggins' equation (13) and equation (14). Vapour pressure p_0 of the pure monomer at various temperatures can be established from the Clausius-Clapeyron equation when evaporation enthalpy ΔH_{vap} is known:

$$\ln p^0 = -\frac{\Delta H_{\rm vap}}{RT} + i \quad , \tag{49}$$

where i is a constant. In this way one can determine the condition for the maximum admissible monomer concentration and calculate the permissible heating rates for various body thicknesses. The model was further extended to include two types of porosity arising in the course of debinding [63]. In the first case, the interphase boundary atmosphere-binder is assumed to move uniformly into the body interior while a porous surface layer is produced [64]. In the other case the porosity is formed uniformly throughout the body volume. Figure 6 shows the dependence of critical heating rate on the cylinder radius for the basic model and for the two extended ones including porosity. The assumption of homogeneous porosity permits the rate of heating to be increased by a factor of up to 2.7. The diagram in figure 6 illustrates the distinctly very sharp decrease of the critical heating rate for larger body dimensions. Matar et al. [65] used the model to evaluate those properties of the organic component which are important with respect to defect formation. The evaporation enthalpy and the constant in the Clausius-Clapeyron equation for vapour pressure are the most significant properties of the monomer, as they influence its boiling point. The properties of the polymer should allow it to be degraded at high temperatures where the diffusion coefficient increases. The diffusion rate is affected by the same parameters as is the binder viscosity, and it is therefore desirable that the polymer viscosity should have a low temperature dependence, thus avoiding the risk of defects arising at the lower temperatures.



Figure 6. Critical heating rate vs. the radius of infinite cylinder for models including various types of porosity [63]. \Box - no porosity, \Diamond - porous shell, \Box - distributed porosity.

ALTERNATIVE DEBINDING METHODS

Supercritical debinding

A supercritical fluid is defined as a substance existing at temperatures and pressures above its critical point [66]. In this state a liquid is indistinguishable from a gas. Although the densities of a liquid and of a supercritical fluid are similar, the diffusion coefficient in a supercritical fluid is significantly higher whereas its viscosity considerably lower [67]. Carbon dioxide is frequently used as solvent in supercritical debinding. It has the advantage of a low price, non-toxicity and an adequate critical point pressure and temperature (cf. figure 7). The main factors causing occurrence of defects due to thermal debinding, such as binder redistribution in liquid phase and diffusion of degradation products, do not come into play in supercritical debinding. Debinding in a supercritical fluid proceeds in two steps, namely by dissolution and diffusion of the dissolved organic binder through the porous structure [67]. The highest solubility in a supercritical fluid is ensured when

$$\delta_{\rm S} = \delta_{\rm SCF} \quad , \tag{50}$$

where δ_s and δ_{scF} are Hildebrand's solubility parameters of the binder and of the supercritical fluid respectively [69]. The solubility parameter of a supercritical fluid can be calculated from the equation

$$\delta_{\text{SCF}} = 1.25 \sqrt{p_c} \frac{\rho_{\text{SCF}}(p, T)}{\rho_1} , \qquad (51)$$



Figure 7. Phase diagram of carbon dioxide [68].

where ρ_{SCF} is the density of the supercritical fluid at temperature *T*, pressure *p*, ρ_1 is the density of the fluid and p_c is the critical pressure. Equations (50) and (51) show that the highest solubility of the polymer will be achieved with the use of a supercritical fluid meeting the condition

$$\rho_{\rm SCF}(p, t) = \frac{\delta_{\rm S} \rho_1}{1.25 \sqrt{p_{\rm c}}} \quad , \tag{52}$$

Knowledge of changes in the density of the supercritical fluid in terms of temperature and pressure allows the optimum debinding conditions to be determined. The results showed that CO_2 is a satisfactory solvent for non-polar compounds and for components with a low molecular weight. It is less effective for polar components and those with a high molecular weight. In determining the debinding conditions one has also to take into account diffusion of the dissolved products through the porous medium out of the body. Experimentally verified was a model of diffusion of the dissolved polymer, based on the classical diffusion equation for an infinite cylinder:

$$\frac{\partial C(r, t)}{\partial t} = D_{\text{eff}} \left[\frac{\partial^2 C(r, t)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r, t)}{\partial r} \right] , \qquad (53)$$

where C(r,t) is the local polymer concentration and D_{eff} is the diffusion coefficient. The solubility and diffusion of the dissolved components are inversely dependent on temperature and pressure. This means that the conditions for the highest solubility are not necessarily identical with those providing the highest debinding rate. Chartier et al. [70] demonstrated that use of the supercritical method allows the removal of binder from ceramic green bodies

to be shortened from the 18 hours required for thermal debinding down to mere 3 hours. The mechanical properties of the supercritically debinded products after firing were comparable to those subjected to thermal debinding.

Catalytic debinding

The BASF company has developed a polyacetalbased binder which can be removed catalytically in an atmosphere containing vapours of nitric acid [7]. The catalytical reaction proceeds at a temperature below the softening point of the binder. Thanks to the low decomposition temperature no liquid phase is formed in the body so that viscous flow and capillary forces cannot bring about any deformations. The gaseous catalyst does not penetrate into the polymer and the decomposing reaction is restricted to the gas-solid binder interface. This rules out formation of internal stresses. The binder is removed by decomposition of the polyacetal to gaseous formaldehyde according to the equation

$$(CH_2O)_n \xrightarrow{HNO_3} nCH_2O$$
(54)

The commercially available polyacetals do not meet the requirements laid down for binders for injection moulding of ceramics. The high crystallinity and viscosity of polyacetal cause defects in the course of injection moulding. The binder for catalytic debinding therefore contains certain additional admixtures. The copolymers and amorphous polymers reduce the crystallinity and organic buffers neutralize the acidic or basic nature of the surface of ceramic particles which could attack the polyacetal. The sensitivity of polyacetal to high torsional stresses resulted in the design of special mixing equipment which rules out degradation of the polymer during the mixing process.

Solvent debinding

The binders used for solvent debinding consist of a small proportion of an insoluble polymer in a soluble solid component. The individual binder components are mutually soluble but differ in their solubility in the selected solvent [72]. At room or elevated temperature, the soluble component can be leached out of the ceramic body by some conventional solvent (e.g. water). The insoluble polymeric component remains solid and holds the body together. Following removal of the soluble component the body becomes porous and this facilitates rapid and safe removal of the residual binder by thermal debinding. The water-soluble substances include for example polyethylene glycol (PEG). Chung and Cao [72] specify the following binder composition for injection moulding of silica-based ceramic cores: 65 wt.% PEG,

25 wt.% polymethyl methacrylate (PMMA), 10 wt.% oxidized polyethylene wax (OPEW). OPEW is added to suppress the solubility of polyethylene glycol and thus to rule out binder swelling during the debinding. Anvar et al. [75] solved the problem of poor solubility of PMMA in PEG by dissolving the latter in an aqueous suspension of a ceramic powder and fine particles of PMMA (0.2 μ m). The suspension can be dried and granulated, and used as a ceramic mix for injection moulding. The Höchst company supplies commercially a binder for injection moulding, specially designed for solvent debinding. According to the manufacturer, 45 to 50 wt.% of the binder can be removed from the ceramic green body by dissolving in water at 60 °C.

CONCLUSION

The defects stemming from the debinding of plastic-formed ceramic greenware force the manufacturers to prolong the process and impose limits on the maximum viable dimensions of the ceramic products. The present review is concerned with describing the processes taking place in the course of debinding and with analyzing the causes of the associated defects. The proposed models of thermal debinding strive to describe the behaviour of ceramic green bodies during binder removal, and to establish conditions for the preparation of defect-free ceramic products. However, none of the models is capable of describing generally the behaviour of all thermoplastic ceramic mixes. Owing to the simplifying assumptions used in the derivation of the models the existing models are so far unsatisfactory for the design of defect-free removal of most of the currently employed binders. Further research in the field of debinding has the aim to work out a model which would make possible to design binders including the process of their safe elimination. This would provide conditions for further development of injection moulding as well as of the other plastic forming methods.

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Translated by K. Němeček.