

Methods of Measurement and Strategies for Binder Removal in Ceramics

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Abstract

Binder removal was investigated with various oxide and non-oxide ceramics and different binders. In situ measuring methods were used to obtain weight loss, dimensional changes, heat transfer and wetting properties and to identify evolved gas species during thermal debinding with conditions similar to production furnaces. In addition, gas permeation, strength and microstructure were investigated in partially debinded and quenched samples. A model free method was developed allowing prediction of debinding kinetics based on the experimental data. With small components weighing up to 100 g maximum safe rates were determined experimentally. Using the kinetic model considerable reductions in debinding times were obtained.

Introduction

During production of ceramics, organic additives such as binders, plasticizers and deflocculants have to be added to the inorganic raw materials, to achieve the required visco-elastic properties for forming and processing of the green parts. (In the following the organic additives are summarized as binder). After forming and before sintering, binder has to be completely removed, without affecting the microstructure of the inorganic components. During thermal debinding, binder usually is removed via the gas phase. The long chain binder molecules are thermally split or oxidized, producing CO_2 and H_2O if they degrade completely [1,2]. The gaseous reaction products have to reach the components surface via the pore channels. The flow resistance of the pore channels causes an overpressure inside the green bodies, when debinding is too fast, which can lead to cracks and fracture:

$$\frac{P_{\text{centre}}}{P_{\text{surface}}} = \left(1 + \frac{\mu \kappa R T}{M P_{\text{surface}}^2} L^2 r \right)^{1/2} \quad (1)$$

with P = gas pressure at centre respectively surface of the part, α = viscosity of gas, κ = permeability, R = gas constant, T = absolute temperature, L = characteristic

half-length of part (e.g. its smallest radius), r = reaction rate, M = molar mass of gas species [1].

If the binder fills the pores completely, the diffusion of volatile components within the binder controls the transfer to the surface of the components. When the vapor pressure of the volatile components exceeds the external pressure, blisters are formed within the binder which can deteriorate the green part [3]. Usually extremely small heating rates are required to allow for a release of volatile species through the binder. The diffusion within the binder can also control debinding in green components where the pore channels are partially filled with gas. In that case, the size of clusters formed by binder and inorganic particles is critical for the distance which has to be covered via the slow process by the volatile species [3].

On the other hand, a slow debinding process is expensive in industrial production. Therefore, the fastest debinding cycle has to be identified, which can be realized without risking any damage at the components. This task is made more difficult due to the fact that the reaction rates depend on the partial pressure of the reaction products. In addition permeation and diffusion of the gaseous molecules in the pore channels change with temperature as well as with debinding rate. An increasing degree of debinding, raises the binder free pore volume. Therefore, permeability and effective diffusion coefficient of gases in the pore channels increase as well. Further aspects for the optimization of debinding cycles come from the interac-

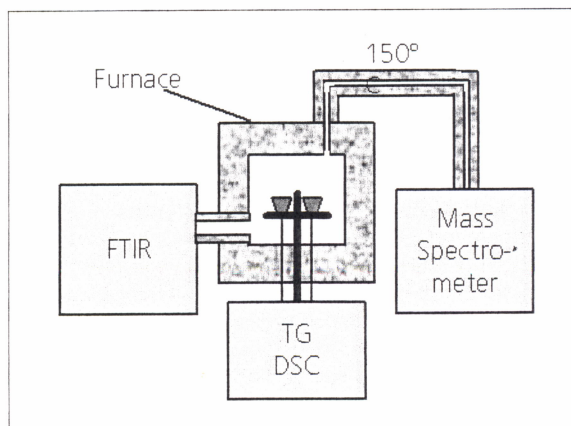


Fig. 1 Principle scheme of the TG-DSC-FTIR-MS device

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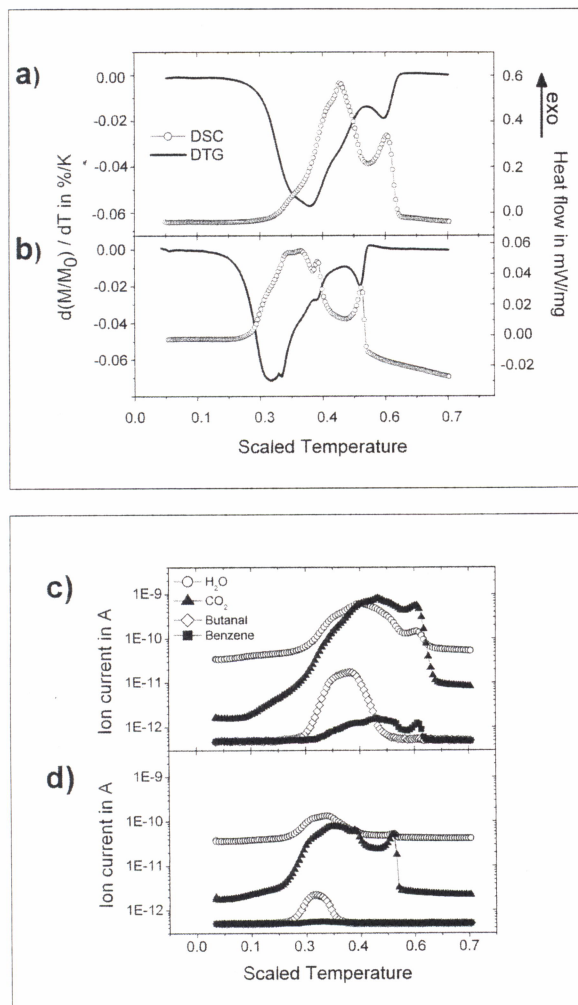


Fig. 2 Debinding of PZT green parts: Differential Thermogravimetry (DTG) and Differential Scanning Calorimetry (DSC) at a heating rate of 5 K/min [a] and 0,5 K/min [b] as well as intensity of the mass spectrometric signals of different gas species at a heating rate of 5 K/min [c] and 0,5 K/min [d]

tion of the residual binder with the inorganic particles. Thus, usually strength is decreasing during binder burnout, i.e. with proceeding degree of debinding, the acceptable overpressure is decreasing. Further interactions during debinding can appear with thermoplastic binders, because capillary forces can cause a redistribution of the ceramic particles and redistribution of the viscous binder in the pore network. Forming processes like cold isostatic or uniaxial pressing only demand a small binder fraction (< 2,5 %). Thus debinding is relatively unproblematic. To produce larger components and components of more complex shape, forming processes like tape casting and injection molding are increasingly applied. For that purpose, large fractions of binder in the green parts are requested. This causes massive problems during debinding, mainly in large components. Regarding non-oxide ceramics, such as AlN, SiC, BN, MoSi₂ or TiC, debinding creates additional problems, because it has to be performed without oxygen in an inert atmosphere. During pyrolysis in inert atmosphere non-volatile, elemental carbon occurs, which remains in the components. This residual carbon may affect sintering and the final quality of the components, e.g., it causes discoloration, density gradients and warpage. It is assumed that the intermediate for-

mation of aromatic hydrocarbons by the reaction of decomposition from the pyrolysis of the used aliphatic binders is responsible for the formation of elementary carbon [4].

Temperature gradients inside the green parts also play an important role for larger components respectively higher heating rates. A coupled simulation of temperature distribution, reaction rates and gas permeation was performed using Finite Element methods. Using this method, the dehydration reactions occurring during firing of high voltage insulators were considered in the optimization of the heating cycle [5]. In principle the binder removal can be optimized in a similar way. But considering the complexity of the related phenomena, many material data are required which are difficult to obtain. Therefore, simplified and more efficient models are to be preferred.

The present paper summarizes recent investigations [6], [7] on debinding of oxide and non-oxide ceramics, where various ceramic systems (PZT, AlN, SiC, MoSi₂ as well as a mixed oxide ceramics), and binders – based on polyvinyl butyral (PVB), polyvinyl alcohol (PVA) polyethylene glycol and wax emulsion – were included. At first, measuring methods are presented, which were essential for a description of debinding phenomena. Subsequently, strategies for the development of efficient debinding cycles are discussed.

Results and Discussion

The most important measuring method for investigation of binder burnout was Thermogravimetry (TG). By means of the weight loss, the degree of debinding was determined in situ very accurately after buoyancy effects have been corrected. Reproducibility was improved by conditioning of the green parts (previous storage at defined humidity and temperature) and maintaining constant sample dimensions. Small samples (approx. 100 mg) were analyzed with a customary Thermobalance (Netzsch STA 449c, Selb, Germany). Thereby, the heat of reaction was measured simultaneously. This was done qualitatively by differential thermal analysis (DTA) or quantitatively by Differential Scanning Calorimetry (DSC) in comparison to an inert reference sample. In addition, the evolved gas species during debinding were detected, using infrared spectroscopic methods FTIR (Bruker Tensor 27, Ettlingen, Germany) as well as mass spectroscopy (MS, Netzsch QMS 403 C, Selb, Germany) (Fig. 1). MS and FTIR methods provided additional information regarding the evolved gas species, for molecules without dipole moment were not IR active and molecules with equal ratio of ion charge to mass (e.g. CO₂ and N₂) could not be distinguished by MS. Exemplarily, measurements of PZT green parts produced by tape casting with a PVB based binder are shown in Fig. 2. Reaction rates changed considerably when the heating rates were varied, e.g., at the lower heating rate of 0,5 K/min, no aromatic hydrocarbons (benzene) were detected whereas a distinct benzene MS signal was obtained at 5 K/min. This was attributed to the lower partial pressure of hydrocarbons for the lower heating rate that decreases the reaction rate. Thus conclusions about reaction order could be obtained. More details on these measurements were given in [6].

Larger samples with approx. 100 g weight were measured with a special Thermo-Optical Measuring device