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Clot-forming: the use of proteins as binders for producing ceramic foams

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Abstract

This project uses the change of functional properties of proteins for ceramic and powder metallurgical shaping. Albumin (Bovine Serum Albumin, BSA) as a major constituent of blood was added as a model binder to an aqueous powder suspension, which then showed a sufficiently low viscosity for mould filling. The flow behaviour showed a structural viscosity being best described by a Herschel–Bulkley model. Temperatures higher than 66 °C lead to a significant increase of viscosity caused by irreversible changes in the spatial-structure of the protein molecule. Albumin, however, had a second effect in this process. Since albumin has amphiphilic properties its solutions are prone to foaming. A fine cellular foam structure of approximately 50–300 μm cell diameter was formed, probably due to a stable arrangement at the liquid gas interface. The combination of foaming and increase of stiffness lead to a stable protein-ceramic foam structure. After burn out and sintering final densities in the range from 8 to 20% t.d. were achieved. Fine cellular structures have more isolated pores while larger cells are typically interconnected. Typical applications would be high temperature insulation, catalyst carriers or scaffolds for cell technology.

Keywords: Al_2O_3; Biomaterials; Casting; Coagulation; Foams; Proteins

1. Introduction

This work was started to use the change of physical and chemical properties on heating of proteins for purposes of ceramic shaping. Almost all ceramic shaping technologies in technical ceramics are done in the presence of organic additives. To provide the required deformability of masses or suspensions. Binders however, are also added for machineability in the green state and to create the handleability of components.

All shaping techniques start from a liquid or plastic state in which the shaping takes place. As a very important step the system undergoes then the *transition from liquid to solid*. This might be triggered by the increase of solid content due to drying (spray drying, slip casting, colloidal filtration, extrusion drying) or melting/cooling (injection moulding, freeze dying).

The liquid-to-solid transition can also be established by gelation or flocculating.[1–4] In gel-casting the powder is dispersed with in an acrylate precursor which hardens in a mould. The comparably high viscosity of the gel hinders a degassing leaving a porosity behind. A very successful system is based on the enzyme reaction which changes the pH-value of the aqueous slip causing a flocculation of the system (DCC, direct coagulation casting).[5]

The structure and chemistry of proteins, which are basically condensation products of amino acids, is entirely different from conventional binders. The main chain of protein molecule is characterized by covalent peptide bonds, while their (conformation) is stabilized by weak, mostly non-covalent bonds. A change in the situation of these bonds leads to a change in physical and chemical properties of the molecule. The thermal activated loss of this structure is called denaturation. In this work the denaturation of a protein is used for ceramic processing. Proteins are prone to foaming because of their amphiphilic character like tensides. The foaming process of this work contains a protein assisted foaming followed by consolidation due to protein denaturation.

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2. Literature

2.1. Deflocculants and binders

In most of the aqueous systems the suspensions are stabilized by a deflocculant and additionally also by a binder. Typically binders are long chain molecules with functional groups (polyvinyl alcohol, polyvinyl butyral, cellulose ester, polycarbonic acids, polysaccharides). The functional groups enable both the solubility within the solvent and the coupling to the powder surface. The physical properties are primarily a function of the structure of the molecule, the type and amount of the functional groups as well as the residual solvent content. In typical consolidation processes, the properties of the binder molecules are prone to permanent changes, which, however, occur in a steady curve.

2.2. Proteins

Proteins are high molecular compounds, which are formally understood as condensation products of amino acids. Their amino acid R groups are responsible for the great variety of proteins in their physical and chemical properties. These groups are the key to understanding the chemical interactions with the ceramic material, on which the good binder properties of proteins are based, such as adhesion on the surface of the used alumina oxid particles or to dispersant molecules. The amino acid sequence, also called primary structure, stipulates the room-structure of the molecule, the secondary and tertiary structure. These room structures are based on intramolecular hydrogen bridge bonds as well as on ionic and hydrophobic interaction. The two dominating elements of secondary structure are the α-helix on the one hand and the β-sheet and β-turn on the other hand. Furthermore, there are random coil sections. The tertiary structure is defined by the spatial association of these structural elements to each other and is partially stabilized by disulphide bridges. The quarternary structure is founded on the spatial association of some similar or different peptide chains that form a protein complex.[6,7]

The more or less polar character of the amino acid R groups is resposible for the formation of differently charged sections in a protein molecule in solution and its individual adsorption properties. The process of adsorption is a two-step process. The fast punctual adsorption is followed by a slow realignment of the amino acid R groups to match oppositely charged surface groups. This change of conformation explains the increase of the adsorption layer thickness after the first process of adsorption.[8]

Caused by the alignment of the amino acid R groups between aqueous dispersing agent and particle surface, proteins show micellar effects. The amphiphilic character of these molecules, mainly based on the polar and apolar amino acid R groups, causes a decrease of surface tension, therefore the good foaming properties (“Maragoni” effect).[9,10]

These foaming properties are influenced by the amino acid sequence or rather the number of polar and apolar side chains as well as molecule flexibility. Another interesting property of proteins is their denaturability. In the process of denaturation secondary valency bonds, such as hydrogen bridge bonds, ionic bonds, hydrophobic bonds and disulphide bridges, which stabilize the native conformation of the protein, are partially modified. In consequence of the partially or totally unfolding of the protein, larger random coil structures are formed. Between these unfolded protein chains new bonds are statistically formed. This leads to consolidation and a decrease of solubility.[11] The structural change or denaturation occurs at rather low temperatures,[12,13] or by slight variations of solvent characteristics,[14] of charge distribution in the molecular surrounding,[16] comparable with the process of adsorption, or under the influence of shear force.[17]

2.3. Foam producing processes

Three main routes are in use for producing ceramic foams. The oldest method is the replica method, first patented or Schwarzwalder and Somers in 1963.[18] A reticulated polymer foam is infiltrated with a ceramic slurry and dried. After polymer decomposition, the green body is sintered. This route results in open pored, spongeous foams with low densities and low strengths, because of defects resulting from polymer removal.

The placeholder technique[19] consists of co-dispersing a ceramic powder with an easily burnable second phase, forming a green body, burning out the second phase and sintering the body. The resulting foams can be closed or open pored, depending on the volume fraction of placeholder. Cell size of the foam is easily controlled by placeholder particle size distribrution. As burning out of the placeholder leads to great amounts of gas, this process has to be controlled carefully.

Bubble-forming techniques are based on producing and stabilizing bubbles within the mass. These bubbles can be produced by physical or chemical processes resulting in gaseous components, including steam,[20,21] by bubbling gas into the mass[22] or by foaming surface active dispersions by turbulent mixing.[23–25] Technically this process is highly developed in polymer industry, for example, the extrusion of polystyrol foams. In this case an overpressure of gas is applied within the extruder which cause an volume expansion unloading. The foams are mostly closed or semi-open porous, process parameters determining the structure.

Egg foams have been investigated by Tuck and Evans.[26] One constituent of egg white is the protein lysozym which may be characterized as relatively stiff,

ellipsoidal and small molecule. The charges are not uniformly distributed which enables a tenside character and foaming. The materials had a closed cellular porosity which is less than the open cellular morphology of the replica method. Lindsten et al.[27] used albumin containing suspensions for foaming. The albumin was used in a double function as a deflockulant as well as a binder.

Foam generation by turbulent mixing is determined by three phases: gas inclusion and distribution by turbulences from the air–mass surface into the interior, bubble modification by mechanical agitation and foam drainage.[28] Hanselmann and Windhab[29] give a model of turbulent mixing in a rotor–stator system based on the systems Reynolds and Weber number. Under constant mixing parameters and constant time, high viscosity masses will result in less and finer bubbles than low viscosity masses, as higher viscosity will result in a less turbulent flow, mixing less air into the mass and the critical shear stress needed to disrupt a bubble is reached easier. During mixing, there will be an equilibrium between bubble build-up and drainage. After mixing foam drainage will lead to larger bubbles with high viscosity masses being more drainage resistant.

Bubble growth during thermal consolidation is a biaxial extensional process,[30] comparable with baking of bread,[31–33] where a correlation of the extensional characteristics of a dough and its viscosity parameters was not yet established.[31,32]

2.4. Fundamentals of the chosen process

In the process described hereafter the properties of proteins are used to produce foamy masses by turbulent mixing, which consolidate rapidly by low heat exposure. The thermal induced heat denaturation of proteins limits the increase of the pore size of the ceramic foam, driven by rising water vapour pressure.

There is no final judgement on the ideal structure of a protein foaming agent until now. Only a small selection of the natural polymers is stable enough for these technical processes and available at a low price level. Thus, for first trials on ceramic clot-foaming, bovine serum albumin (BSA) has been chosen as a protein. Being a major constituent of blood plasma, it is readily available and relatively cheap.

Because of its good capability to bind water, its main function is osmoregulation. Furthermore it serves as a protein reserve and, due to its property to develop reversible bonding to lipophilic molecules,[6] as a carrier molecule.

BSA has a molecular weight of 67 000 Da and consists of 565 amino acids,[34] which show approximately 100 carboxylic groups and 100 basic R groups.[35] The secondary structure is subdivided into 53% helical areas, 17% β-sheet structure areas and the aperiodic contents, in which this conformation is stabilized by 17 disulphide bridges.[36]

The heart-shaped tertiary structure of BSA could be approximated to a roughly equilateral triangle with sides of 8 nm and a depth of 3 nm.[37] The size varies with the influence of temperature, especially if the coagulation temperature of 65 °C at pH 6.4[38] is exceeded during the consolidation, or with the change of pH. Values for the isoelectric point (IEP) vary between of pH 5.5[37,39] and 4.9.[40]

The charge and the flexibility of the BSA molecule allows adsorption on positively as well as on negatively charged surfaces, with higher amounts of adsorpted protein found on positive surfaces.[41–43] The described flexibility facilitates the arrangement of the different charged amino acid R groups on the surface and the partial unfolding of the molecule during the process of adsorption.[16] Permanent alternation of hydrophobic and hydrophilic areas (visual analysis of 3D-structure of crystalline structure of human serum albumin from[15] enables adsorption on any kind of surface without far-reaching changes in secondary or tertiary structure).

3. Experimental

Ceramic masses have been produced from alumina (AKP50, Sumitomo Chemicals, BET-Surface 6.9 m^2/g), bovine serum albumin (Fraction V, ICN 160069, 98–99% pure) and distilled water. As it showed, that mass dispersion was not stable, Darvan C (Vanderbilt Co.) or Sokalan CP10S (BASF) were added as dispersants. Homogenization and prefoaming was done in a RETSCH PM4 planetary mill using PE-milling pots for 15 min at a standardized speed, volume of mass and milling ball content. The solid content in the masses was varied between 31 and 44 vol.%, the binder content between 1.3 and 6.25 M% (3.7–17.7 vol.%) based on the alumina content. The dispersant content was 0.5 M%, again based on alumina content, except for the masses prepared with 1.3% albumin, where 0.7% dispersant were needed for stable dispersion. Rheological data were measured using a rotational viscosimeter (HAAKE RV20/SV2 measuring device). The clotting behaviour was measured at a ramp of 1 °C/min.

The resulting masses were filled into PTFE-moulds of different dimensions ranging from 1.8 to 70 cm^3. Covering the moulds with a silicon oil made demoulding easier and led to better surface qualities.

Thermal consolidation was done in a conventional household microwave oven (BOSCH HMT876G) with a maximum microwave power of 900 W. Lower output (600, 360, 180, 90 W) was realized by interval control. For comparison, some specimens were consolidated by conventional heating in a drying oven (Heraeus VT5042EK) at various temperatures with the moulds preheated for at least 15 min before filling. The drying

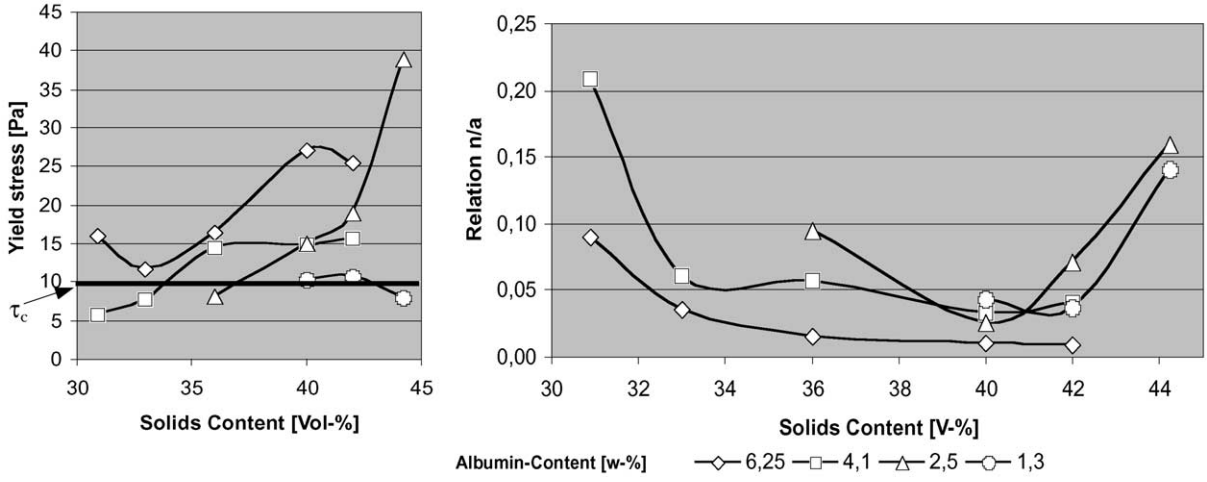

Fig. 1. Viscosity parameters according to Herschel–Bulkley model. (a) Yield stress, (b) n/a ratio.

of the specimens was done in the same drying oven at 80 °C.

The debindering characteristic of albumin has been evaluated in a thermobalance (NETZSCH STA429) under air with a heating rate of 5 °C/min.

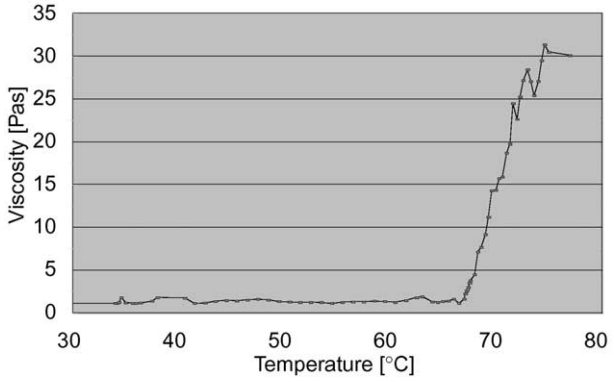

Fig. 2. Temperature induced consolidation behaviour of an albumin containing alumina mass.

For debindering, the specimens were heated in a chamber furnace (NABER N11) at 3.7 °C/min to 700 °C and held there for 30 min. Sintering took place in a chamber furnace (NABER HT 17/4). The temperature program consisted of a heat-up of 10 °C/min up to 1500 °C, a dwell time of 30 min and cooling at 10 °C/min.

The measurement of density of the sintered specimens followed a procedure, suggested by Engin and Tas[24] using the Archimedes principle. The specimen was weighed dry (m_t), infiltrated with water (m_n) and immersed in water (m_w). Infiltration with water was done in hot water (70 °C) under vacuum (<1 mbar) for 1 h.

After that, the specimens were cut perpendicular to the horizontal during consolidation as to show density gradients evolved during processing. The cut specimens were monitored with a SEM (PHILIPPS XL20). Pictures taken for monitoring the cellular structure were evaluated with a semiautomatic image analyses program IMAGE C (IMTRONIC) giving a cell size distribution and a size distribution of inter-cell connections.

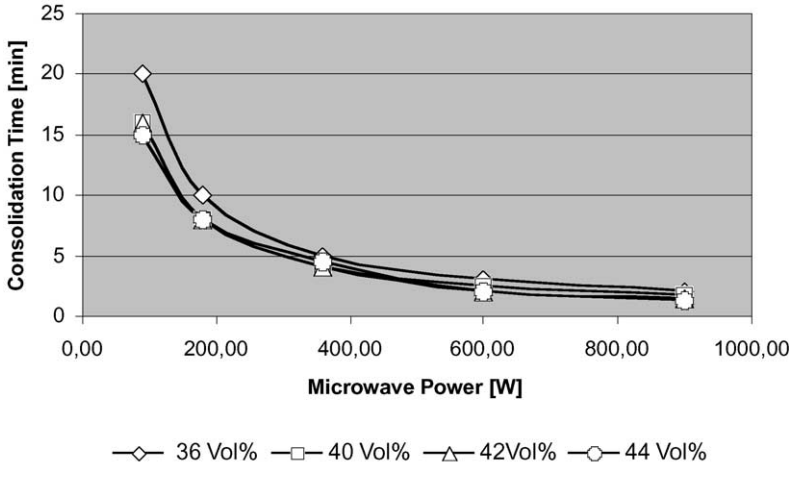

Fig. 3. Consolidation times for microwave heating.

4. Results and discussion

4.1. Mass dispersion

While dispersions of alumina in albumin–water solutions were not stable, those with a dispersant added were stable. Using Darvan C (ammonium polymethacrylate) led to dispersions with a pH of 9.5, while Sokalan CP10S [non-neutralized modified poly(acrylic acid)], led to dispersion with a pH of 6.5. At pH 9.5 both alumina and albumin bear a positive net charge.

The Darvan C stabilized masses showed shear-thinning behavior, best described by the Herschel–Bulkley model

$$\tau = \tau_0 + a\mathrm{D}^n \quad (1)$$

with a yield stress τ_0. Foaming requires both a critical yield stress τ_C (Fig. 1a) and an extensibility which may be described by the ratio n/a (Fig. 1b). Some irregularities in these data, as decreasing yield stress with increasing volume content may be due to different bubble content and size distribution.[44]

Masses prepared with Sokalan CP10S, were slightly less stiff. and dispersion was more stable. This was due to alumina now bearing a negative net charge, while albumin still bears a positive net charge.

4.2. Consolidation behaviour

Fig. 2 shows the viscosity increase during consolidation with an onset temperature of 66.6 °C. The plateau value reached at temperatures >75 °C is due to slip in the measuring device. While no significant drop in viscosity can be seen during heating before the coagulation temperature is reached, the coagulation is combined with a viscosity increase factor of 12 within the first 5 °C of temperature increase. The water loss during this time was insignificant, so that clotting seems to be the only responsible mechanism for this increase.

Fig. 3 shows the development of consolidation times needed at different microwave power settings. A proportionality between both parameters can be seen. These times were determined as the times needed for extracting the specimen from the form without damage.

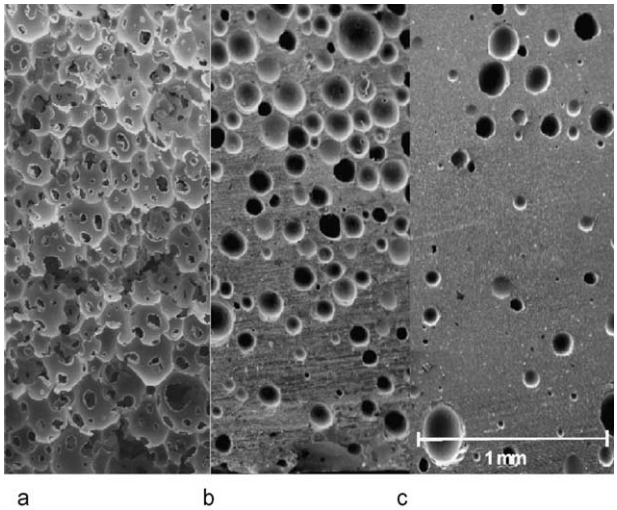

Fig. 4. Structures of foams, dependent on rheological characteristics of ceramic mass. (a) Good foamability, (b) too small yield stress, (c) too stiff.

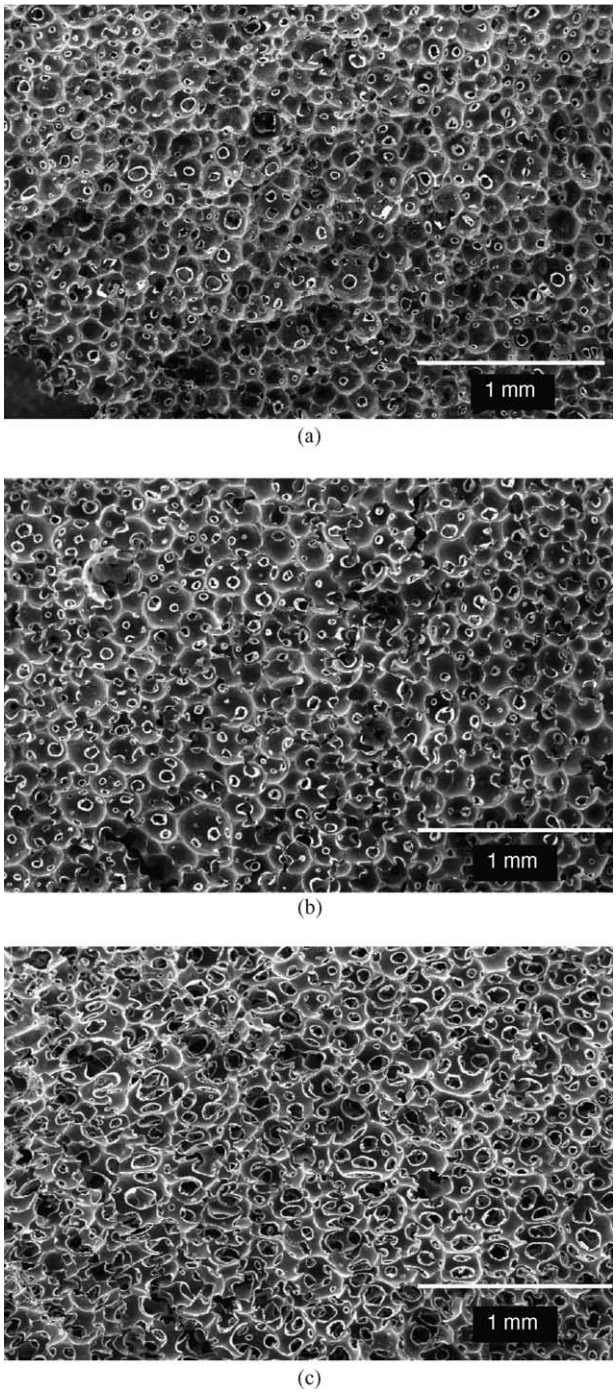

Fig. 5. Influence of consolidation heat on cellular structure after microwave foaming and subsequent sintering at 1500 °C. Power input of (a) 90 W, (b) 360 W, (c) 600 W. High power input leads to more interconnections.

At times too short for handleability, the specimens still had liquid phase or broke at about 1/3 of their height from the tip.

While no significant influence of the binder content on the consolidation times can be seen, there is an influence of solids loading, higher loading leading to shorter processing times. This is explained by the observation, that about 10% of the original water content of the specimens were lost during consolidation, before they were demouldable without damage.

4.3. Structure development during consolidation

Fig. 4 shows three basic foam structures. Fig. 4a is characterized by a good cell distribution without extended dense areas and with inter-cell connections, the size of the latter being consolidation dependent, as shown in Fig. 5. Fig. 4b shows a foam, with a stable foam structure at the free surface (top side) of the specimen, while cell size and cell density are decreasing further downward. The slurries producing these structures have a low viscosity and the structure shown results from bubble ascent and drainage. These structures are characteristic for a yield stress (Herschel–Bulkley model) lower than 10 Pa.

Fig. 4c shows a structure with few and far apart bubbles dispersed homogeneously in the specimen. These structures result from foams with too high a viscosity to allow a mixing turbulent enough to form sufficient bubbles under given mixing parameters.

Fig. 5 shows the development of the cellular structure as a function of microwave power used for consolidation. A higher power input leads to an interconnected pore network. Extending the time of heating over the limit needed for handleability led to formation of cracks parallel to the surface of the specimen, starting at about 1/3 of the specimen height, measured from the free surface. Generally the process of foaming has to be carried out prior to the stiffening of the protein. At low temperatures the material has still a remaining extensibility which allows the deformation of the bodies. However if the pressure is applied at a too high stiffness cracks are unavoidable. This is comparable with the moment of dough rupture in the process of baking bread, which is caused by similar mechanisms, as shown by Bloksma[31,32] or Fan et al.[33] Thus, control of processing time is crucial for producing foams of high structural integrity and good mechanical properties.

4.4. Debindering

Fig. 6 shows the debindering characteristics of BSA. The onset of weight loss is at ~250 °C with a maximum decomposition rate at 320 °C, followed by a slower rate process up to 540 °C. This broad debindering interval allows a well controlled debindering process.

4.5. Final density

Fig. 7 shows the dependence of relative density reached at 90 W microwave power on the alumina and protein content of the masses used followed by a 1500 °C sintering in air. In spite of the high sintering temperature no pore collapse did occur and the shape change of the body was very small. For each binder content, the results show a minimum density. Lower binder content shifts this minimum to higher solids loading. Furthermore, the

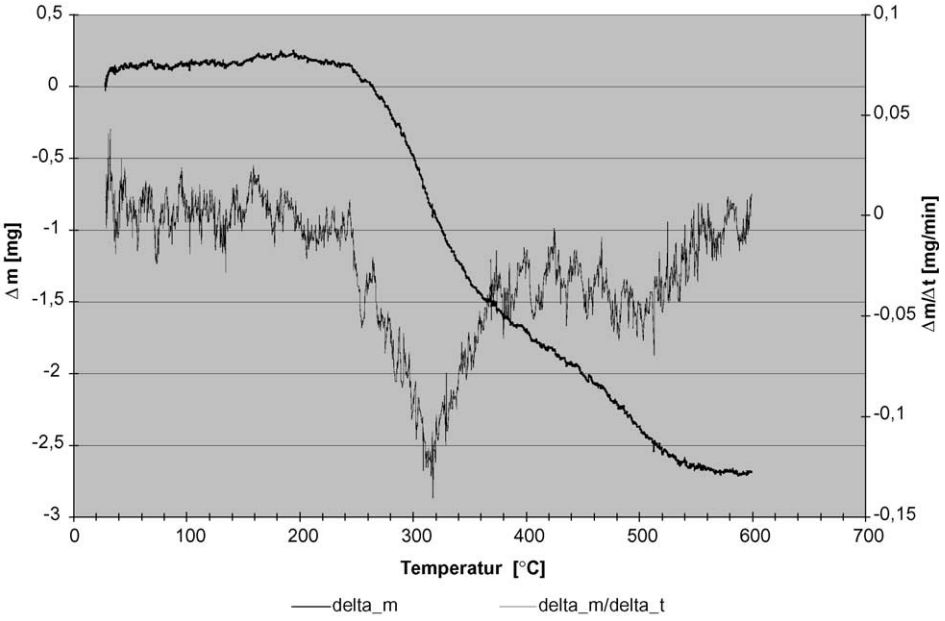

Fig. 6. Decomposition behaviour of albumin containing alumina foam, TGA and DTG versus temperature. Debindering requires a final temperature of 600 °C.

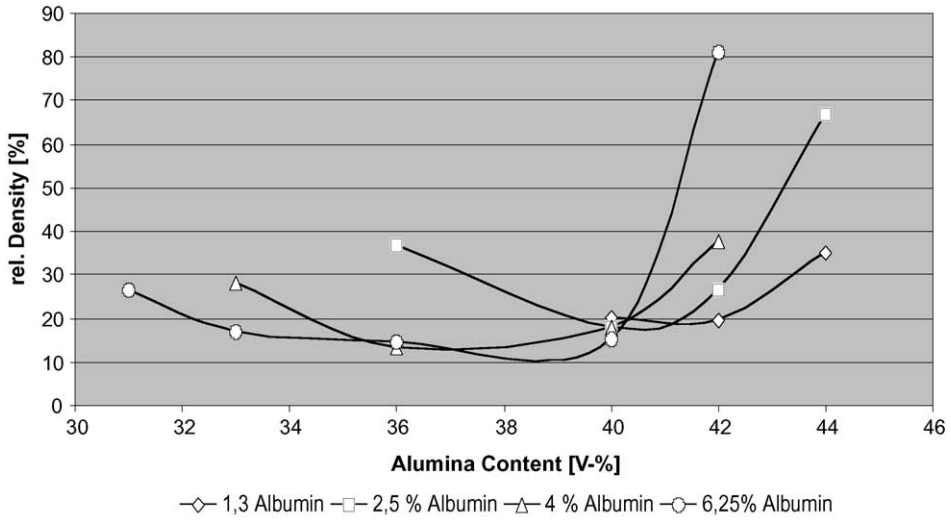

Fig. 7. Correlation of sintered density with both solid content and protein content (90 W input) .

interval, in which low densities are obtainable, becomes narrower with increasing binder content. Higher microwave power shifts these curves towards lower densities, with 7.7% of theoretical density being the lowest density obtained.

The relative density these foams is a result of a turbulent mixing process followed by a biaxial extension[33] flanked by draining processes.[28] All of these processes are viscosity dependent, so it was tried, to relate viscosity describing parameters to foam characteristics. Comparing Fig. 7 with Fig. 1b shows some similarities. This led to Fig. 8, showing the sintered density versus the n/a ratio. There seems to be a linear connection between both parameters for masses with high cell densities. The deviating point at 6.25% albumin and low n/a ratio belongs to a mass with a very low cell density and therefore extensional processes had no significant influence on the foam structure during consolidation.

4.6. Formation of dense structures

To check, whether the use of albumin for ceramic production is limited to the production of foams, it was tried to produce dense structures by filter pressing a foamy mass (30 vol.% alumina, 6 M% albumin) and sintering the filter cake. This produced a body of >98% of theoretical density.

5. Outlook

The solidification techniques which are used in food production show some striking similarities to the shaping processes in ceramics. The rapid change of viscosity of protein solutions due to the structural changes on denaturation can be used for shaping. The bodies undergo a fast stiffening in the mould without a high change in the content of solid. Thus, fast solidification

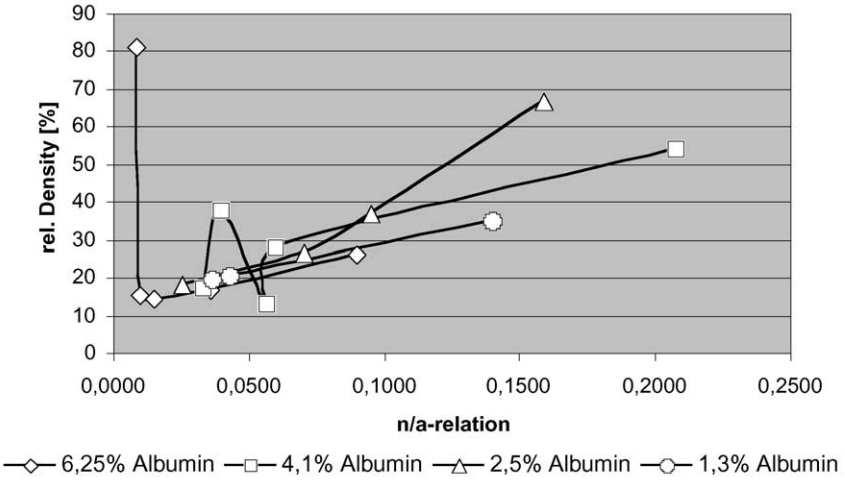

Fig. 8. Correlation of sintered density with relation of flow parameters n/a (90 W input).

times can be achieved. A total stiffening could be reached after a further dewatering of about 10%.

Since proteins are coupling with most surfaces the technology can be applied to wide spectrum of powders and there are no constraints with respect to the materials composition. Beside the reported alumina foams, Ti- and Al-metal foams as well as WC–Co and zirconia foams have be prepared sucessfully.

6. Uncited reference

Ref. 39

Acknowledgements

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