

# Protein forming — a novel shaping technique for ceramics

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## Abstract

A new consolidation method for the forming of ceramics using globular proteins as consolidators/binders was developed. Various protein products: bovine serum albumin (BSA), albumen (egg white powder) and whey protein concentrate (WPC), were shown to work as gelling agents, which was confirmed by rheological measurements and forming experiments. Suspensions of Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> powders with various solids loadings (44–55 vol.%) were prepared, proteins were added and the resulting slips were poured into simply shaped moulds and consolidation (gelling) took place through heating at 80°C. Through an optimisation of the process, it was possible to sinter to high density values (> 99% of theoretical) using gas pressure sintering (GPS) of Si<sub>3</sub>N<sub>4</sub> materials, and using pressureless sintering in air of the oxides. Among the globular proteins studied, WPC showed the most favourable properties with less serious slip thickening, limited foam formation, faster gelling, sufficiently high green body strength to make demoulding in wet state possible and less cracking during drying. However, a larger amount of WPC was needed to achieve a proper gelling compared with the other proteins. This negatively influenced the sintering conditions by lower density of shaped bodies, which required ceramic powders that sinter more easily to full density. The most critical steps in the processing were to efficiently remove air, to break foam formations, and to avoid cracking during the demoulding and drying of the cast bodies. None of the proteins gave rise to critical stresses during the burnout operation and sintering was carried out without deformation or cracking. © 2000 Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** Al<sub>2</sub>O<sub>3</sub>; Globular protein; Protein forming; Shaping; Si<sub>3</sub>N<sub>4</sub>; ZrO<sub>2</sub>

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## 1. Introduction

The shaping of powders into rigid bodies is a critical step in the manufacture of ceramic components. To achieve optimal sintering, adequate material properties and dimensional tolerances, dense and homogeneous particle packing as well as evenly distributed additives are required. New forming techniques are continuously being developed to meet these requirements and to obtain a cheaper, more environmentally friendly and reliable processing of ceramics.

One group of recently developed powder-forming methods can be referred to as “*Direct consolidation techniques*”. Consolidation is, for example, achieved through polymerisation reactions (*gel casting*),<sup>1</sup> polycondensation reactions (*hydrolysis assisted solidification, HAS*),<sup>2</sup> destabilisation (*direct coagulation consolidation,*

*DCC*),<sup>3</sup> freezing (*quick set*)<sup>4,5</sup> or by using starch as consolidators/binders.<sup>6</sup> In these methods, the particle structure of the ceramic slips is consolidated without powder compaction or removal of liquid. This means a transformation from an optimal state in suspension to rigidity, potentially without affecting the homogeneity. An inhibited migration of additives and the control of the final dimensions of shaped components will consequently enhance the material properties.

A new direct-consolidation technique, *protein forming*,<sup>7</sup> has recently been developed, in which globular proteins, such as albumin, form gels in water when heated to 70–80°C. This process can be used to solidify water-based ceramic suspensions (slurries) into rigid bodies.

In this work, various ceramic powders (Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and yttria-stabilised ZrO<sub>2</sub>) were shaped into rigid bodies using globular proteins in aqueous media. The processing was more thoroughly evaluated with Si<sub>3</sub>N<sub>4</sub> powders. Various globular proteins were studied with regard to their rheological and gelling properties in water

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solutions and in powder suspensions. Shaped ceramic bodies were fired in air to burn out the organics, and gas pressure sintered in nitrogen ( $\text{Si}_3\text{N}_4$ ) or pressureless sintered in air ( $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ). The sintered density was measured and the microstructure of the various materials characterised by SEM. The entire processing was evaluated and optimised to achieve highly dense materials.

## 2. Protein chemistry — protein forming

The new forming method for manufacture of dense ceramics evaluated in this work is based on the fundamental property of some types of globular proteins: their gelling (coagulation) ability in water when heated to a certain temperature.<sup>8,9</sup>

*Globular proteins* such as albumin (which exists in blood plasma and egg white) are characterised by regular structural elements of amino-acid sequences mixed with randomly extended chain segments. In the initial state the protein molecules are folded into spherical configurations with the size of some nanometres. In this state they appear as small particles with specific surface chemistry and charging in water depending on the pH. Under certain conditions (thermal, chemical, etc.), globular protein molecules can gel in water. Prior to the gel formation a denaturation process occurs.

*Denaturation* of globular proteins can be accomplished by irradiating with UV or X-rays, heating, adjusting the pH, increasing the interfacial area, or adding organic solvents, salts, urea, detergents, etc. Denaturation means loss of native structure and biological activity of a protein through a breakdown of the structure (Fig. 1). Non-covalent bonds, such as

hydrogen bonds, are broken and random coil or metastable forms are formed. Denaturation is generally reversible if the peptide chain is stabilised in its unfolded state, which inhibits any intermolecular reactions. The native conformation can then be re-established after removal of the agent. Irreversible denaturation occurs when the unfolded peptide chain is stabilised by interactions with other chains. This is the case of albumin, in which the thermal unfolding (denaturation) exposes amino acid side-chains, which, in turn, may take part in intermolecular interactions. The polypeptide chains become tangled to form a three-dimensional and thermo-irreversible gel network (*coagulation*) through the formation of new hydrogen bonds between the chains. In a ceramic suspension a sufficient amount of globular protein will gel in the aqueous phase when heated up, which transforms the suspension into a rigid body (Fig. 2).

Globular proteins also show surface-active properties, for example by attraction to air/water interfaces, which gives a tendency to foam formation in water; a disadvantage if the purpose is to produce fully densified ceramic materials using this method. When adding a globular protein to a ceramic slip through a mixing operation, air bubbles are introduced, and the protein molecules are adsorbed at the interface between air and water via hydrophobic areas, and a partial unfolding (surface denaturation) occurs. The decrease in the surface tension caused by protein adsorption facilitates the formation of new interfaces and more bubbles are created. The ability of protein molecules to form and stabilise foam depends on the diffusion rate and denaturation ability. An anti-foaming agent must be added to avoid critical bubble formation and foam stabilisation. Foams are destroyed by lipids and organic solvents, e.g. higher

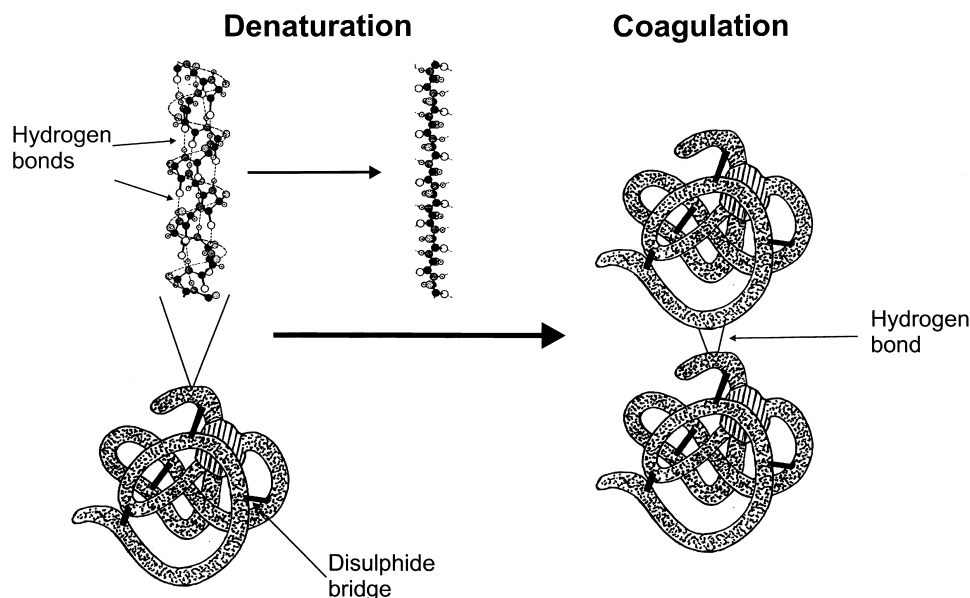


Fig. 1. Schematic illustration of the denaturation of globular proteins.

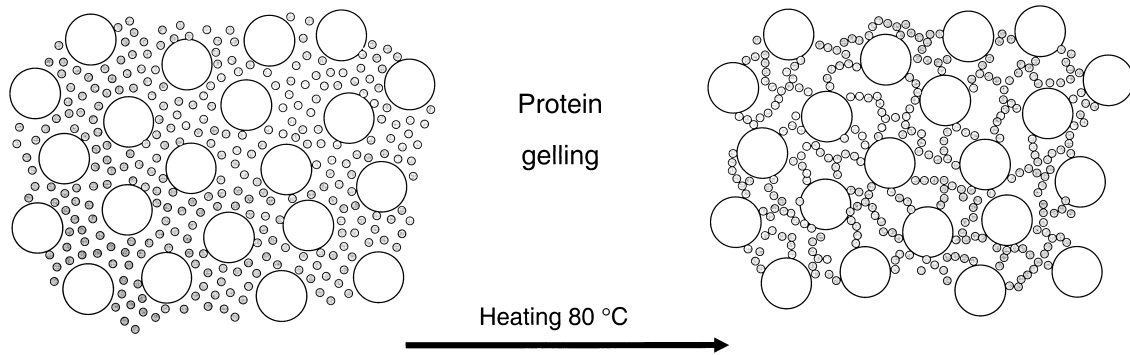


Fig. 2. Schematic illustration of the gel formation with a globular protein in a ceramic powder suspension.

alcohols, which, by their hydrophobicity, displace the protein molecules from the surface of the gas bubbles preventing further formation of stable films.

### 3. Materials

The ceramic powders used in this study are listed in Table 1. Among the  $\text{Si}_3\text{N}_4$  powders, the SN-E10 powder is more expensive and purer with a higher degree of  $\alpha$ -phase than the P95H powder. Furthermore, the P95H powder has a much broader particle size distribution than the SN-E10 (see Fig. 3), which is an advantage when high solids loaded suspensions are to be prepared but, usually, a drawback when it comes to sintering and the ultimate material properties.

As sintering aids,  $\text{Y}_2\text{O}_3$  was used for silicon nitride and  $\text{MgO}$  for alumina. As dispersant, a polyacrylic acid (Duramax D-3021, Rohm & Haas, USA) was used and as anti-foaming agent, a commercial product (Contranspum Conc., Zschimmer & Schwarz, Germany).

Three different types of globular protein products were studied: *bovine serum albumin* (A4503, Sigma-Aldrich Chemie, US), *albumen* (Källbergs Industries AB, Sweden) and a *whey protein concentrate* (AMP-800, AMPC Inc., US). Bovine Serum Albumin (BSA) is extracted from bovine blood plasma and consists mainly of albumin (96%), the principal protein also in egg white. Albumen is produced by spray drying liquid

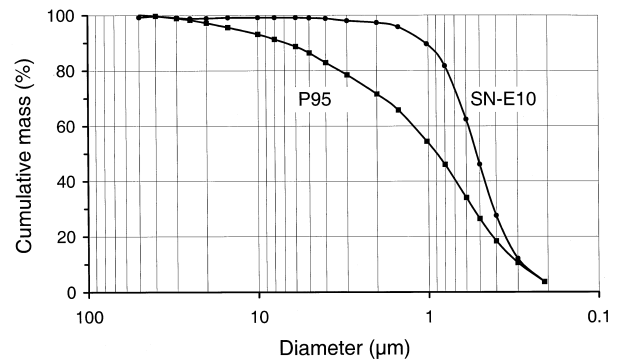


Fig. 3. Particle size distributions of the two  $\text{Si}_3\text{N}_4$  powders used in this study, as measured by the X-ray sedimentation technique (SediGraph 5100, Micromeritics).

egg white from hen's eggs. In this product the degree of purity, according to the albumin content, is much lower (< 82%). The WPC was a spray-dried powder derived by ultra-filtration of whey. This WPC consisted of about 80% milk proteins (except casein), mainly  $\alpha$ -lactalbumin and  $\beta$ -lacto globulin. The density of the protein products as measured with a helium pycnometer (Accupyc 1330, Micromeritics, US), was 1.32, 1.32 and 1.18  $\text{g}/\text{cm}^3$  for BSA, Albumen and WPC, respectively. Analysis of the proteins was also made to check their content of sulphur, phosphor and metals (see Table 2) using a plasma-emission spectrometer (ICP-AES, Svensk Grundämnesanalys AB, Sweden). Albumen and WPC are cheap bulk products for the food industry,

Table 1  
Ceramic powders used in this study

Material	Trade name	Specific surface area ( $\text{m}^2/\text{g}$ )	Manufacturer
$\text{Si}_3\text{N}_4$	P95H	9.9 <sup>a</sup>	Permascand AB, Sweden
$\text{Si}_3\text{N}_4$	SN-E10	9.4 <sup>a</sup>	UBE Industries Ltd., Japan
$\text{Al}_2\text{O}_3$	AKP 30	7.5 <sup>a</sup>	Sumitomo Chemical Co., Ltd., Japan
$\text{ZrO}_2$	HSY-3	7 <sup>b</sup>	Zirconia Sales Ltd., UK
$\text{Y}_2\text{O}_3$	Grade C	10–16 <sup>b</sup>	HC Starck GmbH & Co., Germany
$\text{MgO}$	Analytic	–	Merck KGaA, Germany

<sup>a</sup> BET (Flowsorb II 2300, Micromeritics, US).

<sup>b</sup> Data from producer.

Table 2

Measured ICP-AES (plasma-emission spectrometry) data for the used protein products and possible addition of corresponding metal oxides in  $\text{Si}_3\text{N}_4$  materials based on the preparation of slips with 52 vol.% solids and an addition of 10% BSA and albumen or 16% WPC

Element	Measured element amount (ppm)			Calculated amount in $\text{Si}_3\text{N}_4$ material (wt.%)		
	BSA	Albumen	WPC	BSA	Albumen	WPC
Ca	141±1	505±1	3220±8	0.0006	0.0023	0.0243
K	< 100	11 800±26	5450±19	< 0.0004	0.0455	0.0355
Mg	344±3	992±4	391±4	0.0018	0.0053	0.0035
Na	4430±10	16 300±41	12 100±21	0.0191	0.0703	0.0786
P	52.1±5.8	1050±7	5600±191	(0.0002)	(0.0034)	(0.0302)
S	19400±234	15 900±35	10 800±144	(0.0621)	(0.0509)	(0.0346)

whereas BSA is an expensive purified chemical for medical uses.

#### 4. Experimental procedures

##### 4.1. Protein solutions

Water solutions of various concentrations, 10–16 wt.%, of the proteins were prepared by stirring for 1 h to properly solve the protein before the pH and rheological measurements (described in Section 4.3) took place. A whipping experiment to illustrate the foaming ability was carried out with 100 ml of 10 wt.% protein solutions and powerful stirring during 5 min.

##### 4.2. Slip preparations

Water-based slips (180 ml) with various powder compositions according to Table 3 were prepared using a planetary mill (Retsch PM400, Germany) with  $\text{Si}_3\text{N}_4$  containers (500 ml) and spherical ( $\varnothing = 10$  mm)  $\text{Si}_3\text{N}_4$  balls. Milling was carried out at 200 rpm for 60 min with the exception of the slips containing SN-E10 powder (sample E) and the zirconia powder, in which it was necessary to add the powder in portions and a total milling time of 120 min was required. Different dispersing concepts were used to obtain well-stabilised slips with high solid loading (> 40 vol.%).

The  $\text{Si}_3\text{N}_4$  powder with the wider particle size distribution, P95H, is produced by a direct-nitridation process and a certain amount of  $\text{NH}_3$  (g) slowly evaporates from this powder. This gives an adjustment of pH

to about 10 when mixed with water. Since the isoelectric point ( $\text{pH}_{\text{iep}}$ ) of P95H is roughly 5, the  $\text{Si}_3\text{N}_4$  particles will be highly negatively charged and an electrostatic stabilisation occurs in a natural way without additions of surfactant or a pH modifier. The other powders were dispersed with the addition of various amounts of polyacrylic acid, small quantities for the SN-E10 powder and larger ones for the oxides. The solids content of the slips vary depending on the specific powder (see Table 3).

After milling, the slips were aged (slowly stirred) for at least 12 h before the various proteins were added in varying amounts (10–16 wt.%) based on the water phase. Subsequently, 10 drops/150 ml slip of anti-foaming agent were added. After one hour of propeller stirring, the slips were treated in vacuum (for about 10 min), to get rid of air, before the rheological measurements and forming experiments took place. An exception from this procedure was made for the slips based on P95H, as these required longer ageing time (3–4 days) to allow the evaporation of  $\text{NH}_3$  (g) to cease.

##### 4.3. Rheology

The rheological studies (viscosity, viscoelasticity) were conducted with a rotational controlled-stress rheometer (StressTech, ReoLogical Instruments AB, Sweden) and a concentric cylinder measurement device ( $\varnothing = 25$  mm) with a 1 mm gap. The pH of the protein solutions, of the powder and of powder/protein suspensions was also measured.

Steady-shear measurements of the equilibrium viscosity (apparent) at various shear rates were performed in the shear rate range of 1 to 700  $\text{s}^{-1}$  (seven steps). To achieve equal rheological history of each slip sample, all suspensions were exposed to a pre-shearing at 400  $\text{s}^{-1}$  for 2 min followed by a rest of 2 min before the measurements took place.

To characterise the gelling behaviour, protein solutions and  $\text{Si}_3\text{N}_4$  slips with protein added were subjected to oscillation at a constant frequency (1 Hz) and strain ( $10^{-3}$ ) during increasing temperature ( $5^\circ\text{C}/\text{min}$ ) from

Table 3

Ceramic slip compositions prior to protein addition

Material	Powder	Sintering aids (wt.%)	Dispersant (wt.%)	Solids loading (vol.%)
$\text{Si}_3\text{N}_4$	P95H	3	–	52
$\text{Si}_3\text{N}_4$	SN-E10	3	0.02	44
$\text{Al}_2\text{O}_3$	AKP 30	0.02	0.4	55
$\text{ZrO}_2$	HSY-3	–	0.3	45

25 to 85°C. The measurements were performed at intervals of 20 s. During this operation, the temperature in the suspension was measured using an external thermocouple placed in the upper part of the slip sample. The gelling was defined by an increase in the storage modulus ( $G'$ ), also called dynamic rigidity.  $G'$  represents the elastic component of the complex shear modulus  $G^* = G' + iG''$ , where  $G''$  is the loss modulus representing the viscous component of the viscoelastic properties.<sup>10</sup>

#### 4.4. Forming

Spherical discs ( $\varnothing = 50$  mm,  $h \approx 10$  mm;  $\varnothing = 25$  mm,  $h \approx 15$  mm) were formed by pouring the slip into cylindrical moulds, which were placed in a warming cupboard for consolidation (gelling) at 80°C for 45–60 min. The cylinders were covered to avoid evaporation of water before and during consolidation. After consolidation, the cast specimens were cooled to room temperature before demoulding took place. Complete drying was then conducted at room temperature for 24 h and subsequently at 120°C for 12 h.

#### 4.5. Burnout and sintering

To remove the proteins, the shaped  $\text{Si}_3\text{N}_4$  samples were fired to burn out the organics in air with a heating rate of 1°C/min up to 500°C and 60 min dwell time. After this operation the  $\text{Si}_3\text{N}_4$  samples were sintered in nitrogen using a gas pressure sintering (GPS) furnace (FPW-250/300, FCT, Germany) following different schedules regarding temperature (1900–2000°C) and pressure (2–10 MPa).

The burnout and sintering of the shaped alumina and zirconia samples were carried out by an integrated operation in air atmosphere. Initially, a slow temperature increase of 1°C/min up to 500°C was used for the burnout sequence, followed by a ramp (5°C/min) up to the sintering temperature, 1500°C for  $\text{ZrO}_2$  and 1650°C for  $\text{Al}_2\text{O}_3$  (60 min dwell time).

#### 4.6. Investigations of sintered materials

The densities of the sintered bodies were determined using the water immersion method according to Archimedes' principle. Before the measurement, the bodies were dried at 120°C for 3 h and kept in a desiccator during cooling to avoid moisture take-up.

The microstructure of the sintered material, mainly the overall homogeneity and grain structure, was studied using a SEM (JXA-8600, Jeol, Japan). The  $\text{Si}_3\text{N}_4$  samples were first polished and then subjected to  $\text{CF}_4$  plasma etching, whereas the oxide samples were thermally etched at a temperature that was 50°C below the sintering temperature.

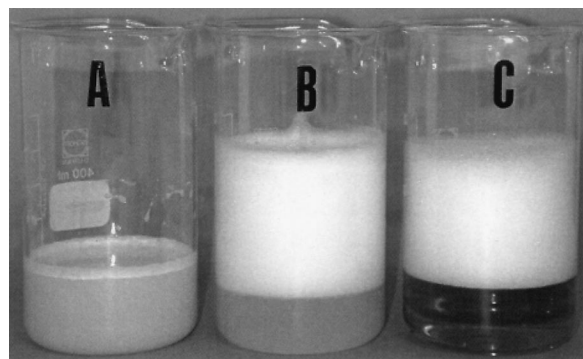


Fig. 4. Photo of whipped 10 wt.% protein solutions: (A) WPC, (B) albumen and (C) BSA.

## 5. Results and discussion

### 5.1. Protein solutions

Fig. 4 illustrates the foaming ability, by the height of foam formed during whipping (fast stirring), of various protein solutions. The lowest level of foaming was clearly achieved with the WPC, whereas Albumen and BSA showed a similar strong ability to form and stabilise foam.

The gelling behaviour of the three proteins in water solutions was characterised by oscillatory measurements at increasing temperature. It was found that each protein needed to be used at a certain minimum concentration to achieve a significant gelling behaviour. Fig. 5 shows that, in the case of WPC, at least 12% was required. However, 14–16% appeared to be more favourable as the gelling became stronger and occurred at a lower temperature. The corresponding amounts required for gelling were approximately 8% with BSA and 5% with albumen. A lower concentration of albumen was consequently needed to achieve gelling despite albumen's basic consistency of albumin (as BSA). This indicated that other compounds present in this product might support the gelling. Initially, 16 wt.% of WPC and 10% of BSA and albumen were chosen as additions to the ceramic slips, as this gave approximately the same gel strength in terms of storage modulus (see Fig. 6). However, differences can be observed. Albumen and WPC gave a more rapid and distinct gelling than BSA, which gave a prolonged gelling process. Fig. 7 shows viscosity curves for solutions with the same protein concentrations. Albumen gave the highest viscosity at lower shear rates indicating a more pronounced structure because of stronger interactions between the protein molecules and other constituents present. It can be noted that albumen gave clearly higher pH than BSA, which might be unfavourable for the charging, and, hence, the separation of the albumin molecules in albumen. WPC gave a Newtonian behaviour (the viscosity was independent of shear rate), whereas BSA gave the lowest overall viscosity level.

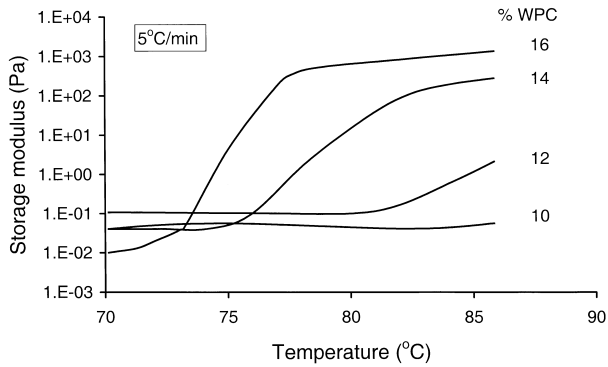


Fig. 5. Storage modulus at constant strain ( $10^{-3}$ ) versus temperature ( $5^{\circ}\text{C}/\text{min}$ ) for WPC solutions with various concentrations.

### 5.2. Powder suspensions with and without protein additions

After the ceramic slips were prepared by milling and conditioning (ageing), the addition of protein always resulted in a certain foaming, which was less pronounced with WPC than with BSA and albumen, despite the fact that slow stirring was used. By adding an anti-foaming agent, the foaming was considerably reduced. However, during vacuum treatment a large amount of still entrapped air was removed. The need of a vacuum treatment can be explained by the tendency of the anti-foaming agent to segregate to the surface of the suspension, which might reduce its efficiency to remove air from the bulk.

The addition of protein to a powder suspension dilutes the system in terms of ceramic powder concentration, but the total solids loading increases. In the case of P95H, the  $\text{Si}_3\text{N}_4$  powder concentration decreased from 52 vol.% to about 50 or 48.8 vol.%, whereas the total solids loading (including protein) increased to 53.8 or 55 vol.% when adding 10 wt.% (BSA and albumen) or 16 wt.% (WPC) protein (based on water). Because of the increase in solids loading caused by the protein additions, a general and expected thickening of the powder suspensions occurred as is

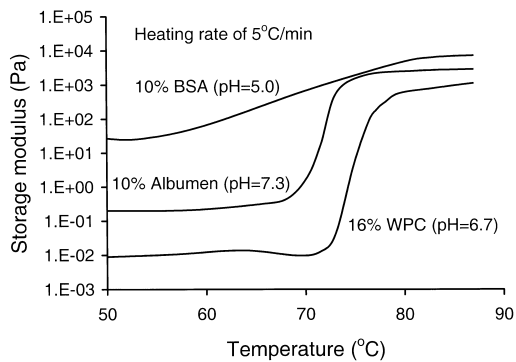


Fig. 6. Storage modulus at constant strain ( $10^{-3}$ ) versus temperature ( $5^{\circ}\text{C}/\text{min}$ ) for various protein solutions.

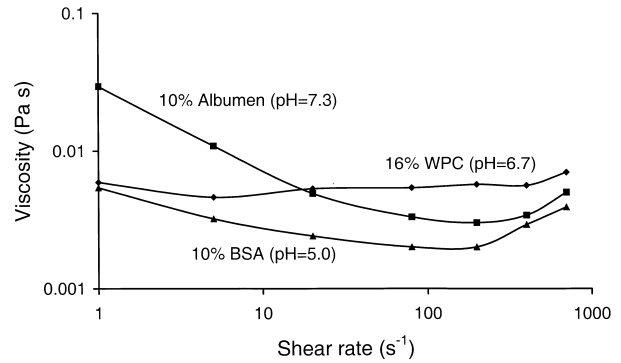


Fig. 7. Equilibrium apparent viscosity versus shear rate for various protein solutions.

exemplified in Fig. 8. The degree of viscosity increase of the  $\text{Si}_3\text{N}_4$  slips varies depending on the specific protein added, but is less pronounced with WPC in spite of the fact that a larger amount of this protein was added. Albumen gave the largest viscosity increase, along with a severe shear thickening (dilatancy). This is not favourable, either in the mixing step, in which the protein is added to the powder suspension, or in a subsequent mould filling operation. For this reason, smaller amounts (5–8 wt.%) of albumen were used in the later forming experiments, despite the lower gel strength obtained.

Fig. 9 shows the results of oscillatory shear at increased temperatures and illustrates the gelling process of slips with P95H with the addition of 16% WPC or 10% BSA. As in the case of pure protein solutions, the difference in gelling behaviour when these two proteins are used is clearly shown. In the same way, WPC gave a more distinct and rapid increase of the storage modulus than BSA, which showed a high storage modulus already from start. Fig. 9 also shows the results when the other  $\text{Si}_3\text{N}_4$  powder (SN-E10) was used in combination with WPC. The gelling behaviour appeared to be essentially the same as with P95H, but arrived at a slightly lower  $G'$  in the end. A reasonable explanation to this is the lower solids loading used with this  $\text{Si}_3\text{N}_4$  powder giving an overall lower rigidity.

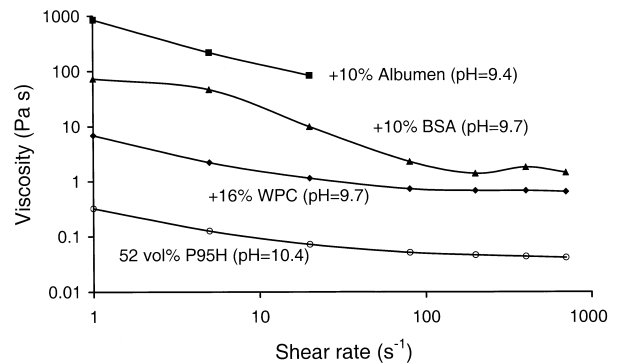


Fig. 8. Equilibrium apparent viscosity versus shear rate for P95H suspensions with and without protein additions.

### 5.3. Forming–binder removal

The forming process was evaluated mainly by visual observations during the gelling, cooling and drying stages and by the handling properties during demoulding. The heating time to obtain gelling was estimated from the rheological measurements. However, by touching the specimens during the heat treatment the time needed for gelling was also roughly determined in practice. In general, a complete gelling was obtained after 30–45 min when  $\text{Si}_3\text{N}_4$  bodies were formed, slightly faster for samples containing WPC and albumen than for those containing BSA. After cooling to room temperature and demoulding, all bodies showed a more or less elastic consistency. Certain care was necessary in demoulding and handling of shaped bodies to avoid damage (not always visible) of the gel structure. This damage resulted in crack formation and propagation during the subsequent drying. In this sense, the bodies formed with WPC were more robust and had less cracking tendency. During drying, the elastic appearance changed into a rigid and very hard consistency.

It was also observed that the presence of gas within the slip, for example remaining air, gave serious problems during gelling. Any gas present will create expanding cavities during the thermal treatment, which expose the gel network to stresses with cracking as a consequence. However, by a sufficient ageing (especially with P95H), the addition of an anti-foaming agent and a proper vacuum treatment, there were fewer problems with gas bubbles and cracking.

Utilising the described experiences, crack-free specimens of  $\text{Si}_3\text{N}_4$  using the two powders (P95H and SN-E10) and the different proteins were obtained. Samples of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  were obtained in a similar way.

After drying, all shaped and crack-free bodies were heated to burn out the organics ( $1^\circ\text{C}/\text{min} \rightarrow 500^\circ\text{C}$ ) without any cracking, regardless of the ceramic material or protein used. The organic material (< 15 vol.% based on solids), which was essentially decomposed from a solid to a gas, could easily be removed without critical stresses.

### 5.4. Investigation of sintered materials

#### 5.4.1. Composition–densification

The compositions, the type and amounts of the proteins used and the densities of the sintered samples are listed in Table 4. Regarding the results for the  $\text{Si}_3\text{N}_4$  materials, high density was achieved with the P95H powder only if BSA was used as a gelling agent. On the other hand, it was possible to reach nearly complete densification with samples of SN-E10, irrespective of the protein used as gelling agent in the forming step. Despite the fact that much lower solids loading was used with SN-E10, e.g. much lower green densities were obtained, this powder gave much better densification

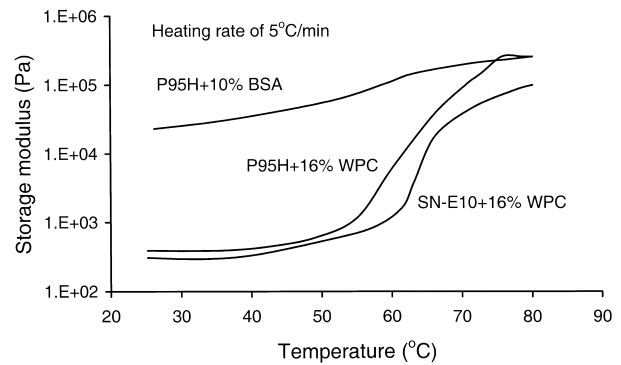


Fig. 9. Storage modulus, at constant strain ( $10^{-3}$ ), versus temperature ( $5^\circ\text{C}/\text{min}$ ) of  $\text{Si}_3\text{N}_4$  suspensions with additions of WPC and BSA.

and showed less sensitivity to the quality of the protein used.

The analysed data (Table 2) of the protein showed that BSA had much lower content of metals than albumen and WPC, which might explain the better sintering performance when using this protein in the forming step. Despite the fact that the metal content appears to be quite low based on ceramic powder, its influences on the material properties after sintering cannot be neglected. In the case of the  $\text{Si}_3\text{N}_4$  materials the major concern is the possible influence on the high-temperature properties through the effect on the inter-granular phase composition.

Regarding the alumina samples, the best result was achieved when using BSA as a gelling agent. It was not possible to reach full densification when using WPC and Albumen, even if the amount of protein was kept at the lowest possible level to obtain gelling. On the other hand,  $\text{ZrO}_2$  sintered to nearly full density irrespective of the protein used in the forming step. As in the case of high-quality  $\text{Si}_3\text{N}_4$  (SN-E10), the zirconia appeared to be insensitive to any negative effects that large amounts of a lower quality protein-product might cause.

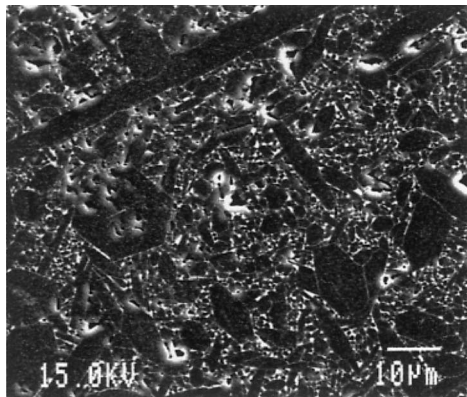
Fig. 10 shows the microstructure of the most dense samples obtained with the  $\text{Si}_3\text{N}_4$  powders (P95H and

Table 4  
Protein-formed and sintered ceramic materials

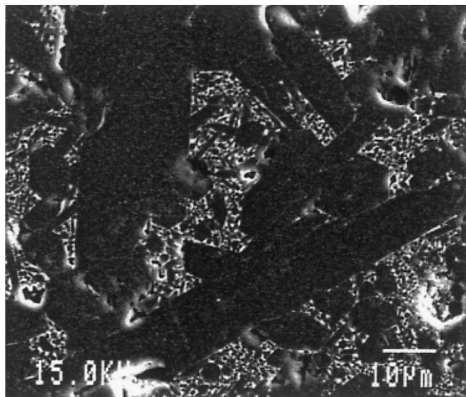
Material	Powder	Protein (wt.% in water)	Sintered density (% of theoretical <sup>a</sup> )
$\text{Si}_3\text{N}_4$	P95H	BSA-10	99.1
$\text{Si}_3\text{N}_4$	P95H	WPC-16	88.9
$\text{Si}_3\text{N}_4$	SN-E10	WPC-16	99.8
$\text{Si}_3\text{N}_4$	SN-E10	Albumen-8	99.7
$\text{Si}_3\text{N}_4$	SN-E10	Albumen-5	99.8
$\text{Al}_2\text{O}_3$	AKP 30	BSA-10	99.2
$\text{Al}_2\text{O}_3$	AKP 30	Albumen-5	97.9
$\text{Al}_2\text{O}_3$	AKP 30	WPC-12	96.4
$\text{ZrO}_2$	HSY3	WPC-16	99.4

<sup>a</sup> Theoretical densities ( $\text{g}/\text{cm}^3$ ):  $\text{Si}_3\text{N}_4$ : 3.215,  $\text{Al}_2\text{O}_3$ : 3.98,  $\text{ZrO}_2$ : 6.05.

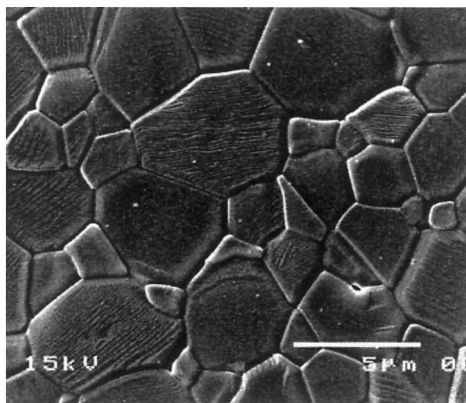
SN-E10) and alumina, respectively. The difference in the grain size distribution of the two  $\text{Si}_3\text{N}_4$  materials is mainly a consequence of differences in properties between the two  $\text{Si}_3\text{N}_4$  powders used. The SEM image of alumina shows a well-densified material with very limited porosity.



$\text{Si}_3\text{N}_4$  (P95H)



$\text{Si}_3\text{N}_4$  (SN-E10)



$\text{Al}_2\text{O}_3$

Fig. 10. SEM images of protein formed and GPS sintered  $\text{Si}_3\text{N}_4$ , obtained with P95H (P1) and SN-E10 (E1), and pressureless sintered alumina (A1).

## 6. Summary and conclusions

The globular proteins used in this study have all been shown to gel in water suspensions during heating and act as consolidators in the shaping of  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  bodies. Among the protein products investigated, whey protein concentrate showed the most promising properties: (1) less serious viscosity increase, (2) less foam stabilising ability, (3) faster gelling process and (4) less crack tendency during drying of shaped bodies. One disadvantage of using WPC was the requirement for larger amounts to achieve proper gelling. This diluted the system more regarding the ceramic powder and, hence, gave rise to lower shaped (green) density. When it comes to sintering performance, bovine serum albumin as gelling agent in the forming step gave the best result. All shaped materials were fully densified using this protein. When using WPC, full density was only reached if forming was carried out with the high quality  $\text{Si}_3\text{N}_4$  powder (SN-E10) or the zirconia powder.

When using protein forming of ceramics, great attention must be paid to the slip preparation to avoid critical foam formation. Addition of an anti-foaming agent and a proper vacuum treatment are therefore necessary. Furthermore, care has to be taken in the drying of the shaped ceramic bodies as the formed gel network has limited strength and cracking occurs more easily if the drying is too fast. All the tested protein products contained some amount of alkali metals (especially WPC and albumen) that might affect the sintering and the ultimate material properties. Further evaluations such as chemical analysis and mechanical testing of sintered materials are needed to verify this.

By a proper process control, the protein forming offers a promising and environmentally friendly shaping technique, which has great potential for the manufacture of various ceramic components.

## 7. Future developments and possibilities

This study was basically aimed at an initial testing and illustration of the protein-forming technique, in which only a few globular protein products were tested. Protein chemistry is a large field of research, which can appear complex but which also opens up a lot of possibilities. There are a large number of globular protein products in terms of type, concentration and pre-treatment which are interesting to use as gelling agents. Gelling cannot only be induced by heat but also by (or in combination with heat) salt addition or enzymatic treatment. Other processing aids such as dispersants and anti-foaming agents can also play essential roles in the gelling performance and must be considered. More results regarding protein forming using whey protein will shortly be presented.



The foam stabilising ability of globular proteins is a problem when dense ceramics are to be manufactured but can be utilised when the purpose is to produce porous ceramics. Strong whipping of a water suspension containing ceramic powders and globular protein results in a highly foamed structure. The cellular structure obtained will be preserved by the gel formation during the thermal treatment and will be permanent after the sintering of the ceramic. The final ceramic material will have a sponge-like structure with pore sizes and an amount of porosity, which depends on the overall solids loading of the original slip, the type and amount of protein, and the degree of slip agitation before gelling.<sup>11</sup>

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