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Hydrolysis-Assisted Solidification (HAS): A New Setting Concept for Ceramic Net-Shaping

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Abstract

A new, hydrolysis-assisted solidification (HAS) concept for net-shaping of ceramic green parts from aqueous suspensions is presented. The process is based on thermally activated hydrolysis of aluminium nitride powder added to highly loaded ceramic suspensions. During hydrolysis of AlN, water is consumed and ammonia is formed, which in turn may increase the pH of the suspension. Both mechanisms can be used to increase the viscosity and ultimately to set a cast or injection-moulded ceramic green body. Different ceramic suspensions containing various amounts of AlN powder were prepared at ambient temperature without increasing their viscosity and subsequently set in heated impermeable moulds. The setting time ranged from a few seconds to a few minutes, depending on the solids loading, AlN addition and the thickness of the green body. © 1996 Elsevier Science Limited.

Introduction

The role of advanced ceramics in engineering structures largely depends on the possibility of reliable mass production of complex-shaped articles. Among wet-forming techniques enabling near-net-shaping, powder injection moulding (PIM) is most widely used for the production of a wide range of smaller ceramic components for high-performance application. The basic concept of the PIM forming technique, which has been known since the early 1930s[1] is based on mixing the ceramic or metallic powder with a liquid binder system (usually a blend of molten polymers or waxes) to create a viscous suspension, forming the part by injection moulding in a closed metallic die, removal of the binder usually through a moderate temperature heat treatment, and densification.[1,2]

During the last decade rapid technological and commercial progress in high pressure PIM has been made, so that PIM using polymer carriers and high injection pressures is now a well established process, in spite of some serious technological drawbacks and relatively high production costs. Therefore efforts have been made to find cost-effective alternatives to existing high-pressure systems, leading to reconsideration and modification of the low-pressure (LPIM) system using a hydrocarbon carrier.[3]

At the same time, LPIM systems containing gelling agents which cause setting of the feedstock on temperature change are being intensively developed. In Japan, for example, a nonaqueous nonpolar solvent, containing propylene + alkyl groups is used to dissolve hydroxystearic acid as a gelling agent,[4] whilst water-based systems are favoured in the USA. Due to the ease of debinding, the environmental benefits and the lack of fire and health hazards, these aqueous systems are certainly among the most promising ones.

Aqueous injection moulding is thus a relatively new ceramic forming process which has been first developed based on the thermogelling properties of methylcellulose polymers which are soluble in cold water and gel on heating.[5] Agar is a member of the same general chemical family but it is soluble in hot water and gels on cooling. The combination of two critical properties, namely, favourable rheology and high gel strength, makes agar systems more attractive for development of the injection moulding process for ceramic and metal powders. These materials form nonviscous solutions at a temperature near 100°C which solidify to rigid gels on cooling below the gel point temperature. Gels formed by these materials were reported to be strong for agar and even stronger for agarose. Moulded parts can be dried and fired without the use of adsorbent powders or special debinding operations.[6] A somewhat similar technique — gelcasting — favours acrylamide monomers for *in-situ* polymerisation on heating, through which a macromolecular network is created to hold the ceramic particles together.[7] The organic binder concentration in this system is significantly higher than in the case of agar and so is the viscosity of the suspension before gelling. This reduces the solids loading and hence the green density of the moulded part, which consequently leads to higher shrinkages of the ceramics. On the other hand, high green strengths have been reported for gelcast samples, which facilitates manipulation of the green parts and also enables green machining.

Besides gelling of water-soluble organic additives, other physical and/or chemical principles can be used in solidification of ceramic parts from aqueous suspensions. Thus for example, the 'quick-set' process is based on freezing of a suspension in a mould, kept below the freezing temperature of water,[8] whereas 'direct coagulation casting'[9] is based on the enzymatic decomposition of urea resulting in a shift of the pH value of the aqueous suspension toward the isoelectric point (IEP), which causes coagulation and setting of the highly loaded ceramic suspension.

It should be pointed out that each of the above mentioned setting principles can be applied either to casting in an impermeable mould or to injection moulding. Setting, i.e. solidification of the green body is not affected by the externally applied pressure, except in the case of 'adiabatic moulding' not mentioned above, which also requires pressure for the solidification of the slurry.[10]

In the present paper yet another concept suitable for casting or aqueous LPIM is presented, termed hydrolysis-assisted solidification (HAS), and its performance demonstrated. It is based on chemical bonding of water in a concentrated aqueous suspension by thermally activated and/or accelerated hydrolysis of added aluminium nitride powder.

Theoretical Considerations

The HAS concept of using thermally activated and/or accelerated hydrolysis of added aluminium nitride powder is based on the following considerations:

(i) The relative viscosity of a concentrated suspension exponentially increases with the solids loading, which can be described by an empirical equation in the form:[2]

$$\eta_r = A\left(1 - \frac{\phi}{\phi_c}\right)^n \qquad (1)$$

where η_r is the relative viscosity, ($\eta_{\text{suspension}}/\eta_{\text{dispersant}}$), ϕ the volume fraction of the solid in the suspension and ϕ_c the critical solids loading. The critical value corresponds to the composition where all particles are in close contact and all void space between the particles is filled with dispersant.[11] The coefficient A (typically near unity) and the exponent n (typically near 2·0) contain factors such as the shear rate sensitivity of the suspension, the packing density of the powder and its interaction with the liquid vehicle,[2,12] which, however, are not a main concern for the theoretical considerations relevant to HAS.

According to eqn (1), the relative viscosity of a suspension approaches infinity as the solids loading approaches the critical value. At $\phi \geq \phi_c$ the fluid character of the suspension is lost, i.e. the mixture becomes too stiff to be considered viscous. Depending on the capillary and/or interparticle forces holding the particles in place such a 'saturated solid' or cake may behave plastically or elastically.[13] Equation (1) generally holds for any concentrated suspension, regardless of the powder(s) and dispersant(s) used and regardless of how the solids loading is increased.[14] Thus, solidification of an aqueous suspension can be achieved not only by incremental addition of powder to the suspension but also by physical separation of water by centrifugation or by external removal of water in a porous mould, as in the case of slip casting. Solidification will also occur if a sufficient amount of water is internally consumed by a chemical reaction with one of the solid constituents in the aqueous suspension, as for example by hydration or hydrolysis. Of course, in wet ceramic forming by internal chemical bonding of water, such additives should be chosen as will react with water under technologically acceptable conditions, but which will not hinder the subsequent densification nor reduce the functional properties of the sintered ceramics.

(ii) If a polar liquid is used as a vehicle, the viscosity of the ceramic suspension at a given solids loading depends on the particle surface charge, usually described by the zeta potential on the shear plane of the electrical double layer; this can be greatly influenced by changing the pH of the suspension. In general the viscosity is a maximum in the pH range close to the isoelectric point (IEP) of a given system and decreases with increasing zeta potential, regardless of the sign of the surface charge. Hence, if a chemical reaction between solid particles and water results in a change in the pH of the suspension, the surface charge and consequently the viscosity can be changed as well, which can be exploited for setting a cast or moulded ceramic green body in a similar way to that in the DCC process.[9]

(iii) Besides ordinary hydraulic binders, several metal nitrides are known to react with water, forming metal oxides or hydroxides and ammonia. Thus, one of the problems in the production of AlN ceramics is the reactivity of the AlN powder with water or humidity. The hydrolysis of AlN follows the reaction scheme:[15]

$$AlN+2H_2O \rightarrow AlOOH_{amorph.} + NH_3 \quad (2)$$

The reaction rate is temperature-dependent, being rather low at room temperature or below and greatly accelerated at higher temperatures.[16] According to eqn (2), during hydrolysis of AlN, water is consumed and ammonia is formed, which in turn may increase the pH of the suspension. As described previously, both can be used to increase the viscosity and ultimately to set a cast or moulded ceramic green body. In addition, gelling of Al(OOH) can further assist solidification of the slurry and/or contribute to the green strength of the solid body thus formed.

Experimental Procedure

Concentrated aqueous suspensions were prepared by wet ball milling of selected commercial ceramic powders: alumina (Alcoa A-16 SG); yttria stabilised tetragonal zirconia (YTZP; Hüls Troisdorf Dynazircon F5Y); silicon nitride (H. C. Starck, LC 12) in distilled water. Appropriate electrolytes and deflocculants were used to assist deagglomeration and formation of a stable dispersion of the powder, in order to maximise the solids content at a viscosity enabling mould cavity filling by casting, or low-pressure injection moulding. Technical grade AlN (H. C. Starck, Grade B) powder was mixed with the fully deflocculated aqueous suspensions, which were cast or injected in a heated non-porous mould. After demoulding, the green parts were dried in air and sintered under conditions appropriate to the materials selected. The characterisation methods encompassed viscosity measurements, green and sintered density measurements and microstructural examination of the sintered ceramic parts.

Results and Discussion

The variation in pH of an aqueous suspension containing 1·5 wt% of AlN powder on continuous heating (1°C/min) is represented in Fig. 1 for two starting pH values: firstly the inherent pH value, after dispersing AlN powder in deionised water and secondly pH 4·8 developed in 15 min after dispersing AlN powder in deionised water, at pH 3·3, adjusted by the addition of a diluted (0·1 N) HCl. To avoid continuous dissolution of CO_2 from the ambient atmosphere in the suspension during stirring, the pH measurements were performed under a protective (N_2) atmosphere. In the case of the inherent pH of the suspension, the initial pH value starts to increase steadily with temperature, the hydrolysis being greatly accelerated at temperatures above 45°C and at 60°C the maximum pH is reached. In the latter case the starting pH of 4·8 decreases slightly up to *c*.45°C where it starts to increase rapidly and reaches the equilibrium pH value at *c*.70°C. In both cases the variation in pH on heating is very similar to that reported by Barba *et al.*[17] and Egashira *et al.*[18] for the time-dependent pH variation of suspensions containing 10 wt% AlN and 0·05 wt% AlN at room temperature, respectively. It is worth mentioning that above *c*.45°C the addition of HCl to adjust the starting pH of the suspension to the value of 4·8 does not show any significant influence on the hydrolysis of dispersed AlN powder on further heating. It can thus be expected that several technically important ceramic suspensions can be prepared in the acidic region enabling attainment of a positive zeta potential on the particles' surface (e.g. on the left-hand side of the IEP) which can be subsequently set by using both mechanisms of HAS, i.e. water consumption and pH shift toward the IEP due to ammonia formation.

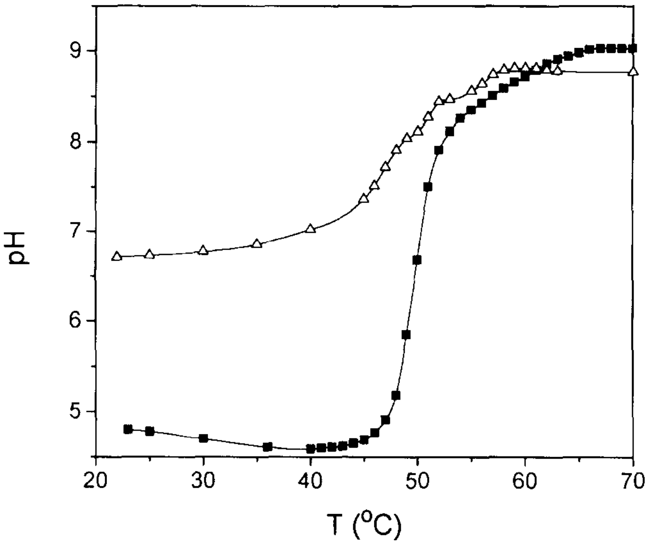

Fig. 1. Variation in pH of an aqueous suspension containing 1·5 wt% AlN powder, starting from two different pH values: Δ, the inherent pH; and ■, pH 4·8 adjusted by the addition of dilute HCl.

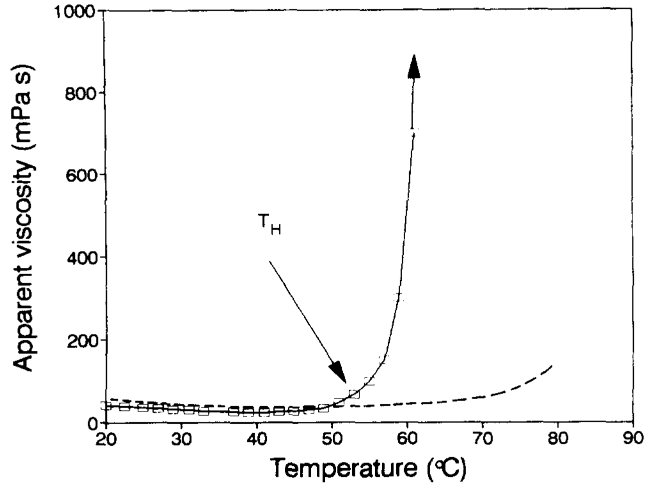

Fig. 2. Temperature dependence of the apparent viscosity of an aqueous suspension of alumina (80 wt% solids loading at pH 9·8), containing 1 wt% AlN powder. The viscosity–temperature profile of the same alumina suspension without AlN addition is represented by the dashed line.

The temperature dependence of the apparent viscosity of an alkaline (pH 9·8) aqueous suspension containing 80 wt% alumina powder and 1 wt% of AlN addition is represented in Fig. 2. At a certain temperature T_H (indicated by the arrow), which corresponds well to the onset of a sharp rise in the pH of a diluted aqueous AlN suspension on heating (with reference to Fig. 1), the viscosity starts to increase rapidly until at *c*.70°C the liquid character of the suspension is lost. Since the apparent viscosity of the same alumina suspension without AlN addition (represented by the dashed line in Fig. 2) starts increasing at temperatures above 80°C along with water evaporation, the abrupt rise in viscosity at T_H can be mainly ascribed to the decreased water content in the suspension due to thermally activated hydrolysis of AlN. Namely, at pH 9·8 the surface charge of dispersed alumina particles is negative (the IEP of this particular alumina powder is at pH 8·2) and sufficiently high to enable almost complete deflocculation. Since even at higher concentrations NH^+_4 is not a powerful enough counterion to reduce the thickness of the electrical double layer, any further increase in pH due to ammonia formation by AlN hydrolysis can only increase the repulsive forces between dispersed alumina particles but cannot lead to electrolytic coagulation.[19] The contribution of coagulation to the solidification of an alkaline alumina suspension is thus negligible, revealing that chemical bonding of water due to thermally activated hydrolysis of the 1 wt% AlN powder added to the suspension alone has the potential to set it in an impermeable mould.

Suspensions containing various amounts of AlN can thus be prepared at temperatures below T_H without increasing their viscosity, and subsequently set in a nonporous mould, kept at/or above T_H. As discussed previously, the assistance of pressure during mould cavity filling has no influence on the setting kinetics, so that either casting or injection moulding can be used for forming ceramic parts using the HAS concept. Most of our forming experiments were performed using a low-pressure injection moulding machine of our own construction. Moulded parts were rectangular 5 × 5 × 50 mm bars, various water seals and laser reflectors, the latter two geometries being commercially produced by LPIM using a paraffin-wax carrier. The setting time ranged from a few seconds to a few minutes, depending on the solids loading in the suspension, AlN addition and the thickness of the green body formed. For rectangular bars, setting times are listed in Table 1 for three different ceramic suspensions, together with the corresponding green and sintered densities. Due to the high solids loading in alumina and zirconia (YZTP) suspensions, the setting times are short and high green densities (60% of theoretical) can be obtained. In contrast, Si_3N_4 powder cannot be dispersed in water at such a high solid loading. Consequently, higher amounts of AlN and longer times are needed for setting and the green density is correspondingly low. An addition of 4 wt% Y_2O_3 was deliberately chosen to assist pressureless sintering of these SiAlON specimens, which will certainly need major corrections to optimise the microstructure and to design the required phase composition.

Table 1. Setting times and corresponding green and fired densities of rectangular 5 × 5 × 50 mm bars injection moulded from various aqueous ceramic suspensions

Starting materials	*AlN addition*[a] *(wt%)*	*Setting time*	*Green density*[b] *(% T.D.)*	*Sintered density (% T.D.)*
Al_2O_3	1	15 s	60	98[c]
YZTP	3	30 s	58	99[c]
$Si_3N_4(Y_2O_3)$	17	10 min	40	~94[d]

[a] Referred to the solid content in the suspension.

[b] Roughly corresponds to the entire solids loading in the suspension.

[c] After sintering in air for 4 h at 1580°C.

[d] After sintering for 2 h at 1800°C in flowing N_2.

The corresponding microstructures of sintered parts formed by low-pressure injection moulding of alumina, YTZP and $Si_3N_4(Y_2O_3)$ suspensions, containing 1, 3 and 17 wt% of AlN, respectively, are represented in Fig. 3, which also illustrates the potential of the HAS process for shaping high-performance ceramic parts. During sintering in air, the hydrolysed AlN particles are ultimately

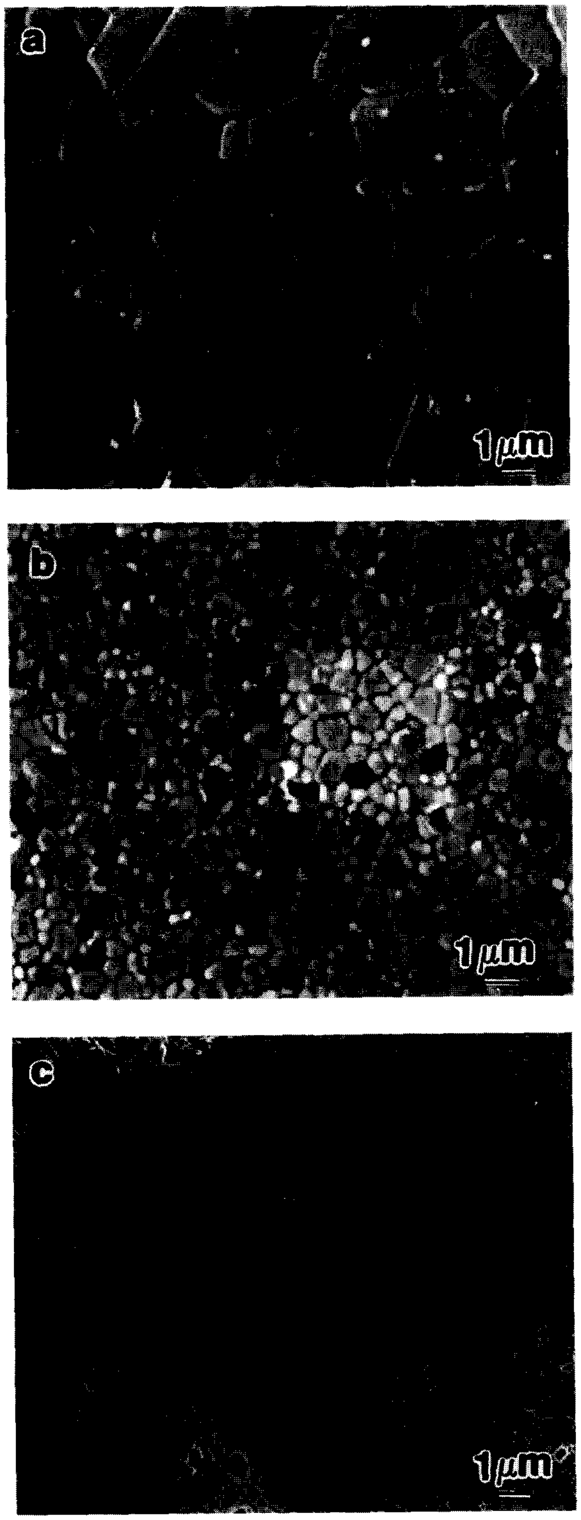

Fig. 3. Microstructures of sintered ceramic parts formed by LPIM of aqueous suspensions using thermally activated hydrolysis of added AlN powder: (a) Al_2O_3 + 1 wt% AlN, 1580°C, 4 h in air, (b) YTZP + 3 wt% AlN, 1580°C, 4 h in air and (c) Si_3N_4 (4 wt% Y_2O_3) + 17 wt% AlN, 1800°C, 2 h in flowing N_2.

transformed into α-Al_2O_3 so that they cannot be distinguished in the microstructure of sintered alumina. They are, however, visible in the SEM micrograph of sintered YZTP as dark grains, also indicating the distribution of former AlN particles in the suspension. From the micrograph of sintered SiAlON it is also evident that the very low fractional density of green parts does not allow a high sintered density to be reached, although the major contribution to the rather low sintered density (94% T.D.) arises from the trapped air bubbles in the suspension (not shown in Fig. 3c), emphasising the importance of de-airing before mould cavity filling.

Summary and Conclusions

- Thermally activated hydrolysis of aluminium nitride powder, added to highly concentrated and fully deflocculated aqueous suspensions, was used for fast setting of wet-formed ceramic parts.
- During hydrolysis, water is consumed, thereby increasing the solids content in the suspension while ammonia formation can be used to shift the pH of the suspensions toward the isoelectric point, resulting in coagulation of solid particles; both effects result in rather fast solidification of the slurry within the mould.
- By using the HAS (hydrolysis assisted solidification) process, high green and sintered densities were obtained indicating the potential of this forming concept for the near-net-shaping of various high-performance ceramics.

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