

Principles of the hydrolysis assisted solidification (HAS) process for forming ceramic bodies from aqueous suspension

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Abstract

Hydrolysis-assisted solidification (HAS) is a new method for net-shaping ceramic green parts from aqueous suspensions in non-porous molds. The process exploits the thermally activated and/or accelerated hydrolysis of aluminium-nitride powder, which has been added to ceramic suspensions. Several simultaneously occurring effects accompany the hydrolysis of AlN: an increased solids content in the suspension due to internal water consumption, a decreased ζ -potential due to the pH change caused by ammonia formation, and the formation of Al-hydroxides. The overall result is a dramatic increase in the suspension's viscosity, which ultimately leads to the formation of a solid body. The contributions of individual mechanisms were studied and are discussed in this paper. At very high solids loading, each of these mechanisms can lead to a significant increase in the viscosity of the suspension. At lower solids loadings, the precipitation of aluminium hydroxide seems to play the major role in the suspension's solidification.

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1. Introduction

During the last few decades, systems containing agents which cause the setting of a water-based ceramic feedstock after a temperature change have been intensively studied and several new ceramic forming processes have emerged. Due to the ease of de-binding, the environmental benefits and the lack of fire and health hazards, the use of aqueous suspensions for forming ceramics is becoming increasingly popular. The earliest aqueous ceramic forming principles were those based on the gelling of methyl-cellulose during heating¹ or agar during cooling,² gel-casting³ used the polymerisation of an acryl amide monomer during heating, and direct coagulation casting (DCC)⁴ exploited an enzymatic decomposition of urea for setting the water-based feedstock. Most recently, temperature induced forming (TIF), a method based on bridging flocculation of poly-acrylic acid, has been reported.⁵ Kosmač and co-workers developed a method of ceramic forming based on setting due to the

hydrolysis of AlN powder, which is admixed in a small quantity into the aqueous ceramic suspension, i.e. the hydrolysis assisted solidification, or HAS process.⁶

Each of the mentioned setting principles can be used to form green parts in impermeable molds: they can be classified as “closed-mold” methods. The formation of the green body is not affected by externally applied pressure or water absorption by an absorptive mold, rather the processes exploit various thermally activated chemical processes in situ. After opening the mold, the solid green parts have only to be taken out and dried to remove the water. Industrial application of these processes, however, is still limited,⁷ because the reliability of the sintered ceramics is still in question. For this reason, further studies to better understand and improve the processes, are still needed.

This paper will focus on the mechanisms involved in hydrolysis-assisted solidification (HAS). The process exploits the hydrolysis of AlN powder to form aluminum hydroxides, which decompose to form aluminum oxide during sintering in the open air. The process is, therefore, suitable for those ceramic materials that contain alumina, at least as a minor phase, for example: all grades of alumina ceramics, alumina-toughened zirconia, sia-

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lones, etc.⁸ Fig. 1 shows a schematic of the HAS process.

In contrast to many other techniques, in HAS the setting agent does not increase the viscosity of the host suspension and no organic binders are needed. The hydrolysis reaction can be controlled by temperature and/or by modification of the AlN surface characteristics.⁹ The process is effective in both acidic and alkaline conditions,¹⁰ distinguishing it from the DCC process, and after de-molding, the liquid vehicle (water) is removed by simple drying. The HAS process can be used to produce large and complex-shaped parts with a green strength high enough to allow green machining.^{11,12}

The increase in viscosity during HAS and the final solidification of the ceramic suspension to form a solid green part was proposed to be mainly the result of (1) internal water consumption during the AlN hydrolysis reaction, (2) ammonia formation, and (3) particles dissolution and precipitation. These individual contributions have been analyzed and will be described and discussed below.

2. Experimental procedures

The powders used for the study were an AlN Grade B (H. Starck, Berlin) with a mean particle size of 1.2 μm and a surface area of 3.2 m^2/g , and Alcoa alumina A16 SG with a mean particle size of 0.7 μm .

The hydrolysis of the AlN powder was investigated by analysis before and after soaking in hot water (60°C) for different periods of time. SEM, TEM, XRD and BET were employed to observe the morphology and the composition of the formed phases.

Alumina was used as a model system and aqueous suspensions with different solids contents at its inherent pH, i.e. 9.5, were prepared by de-agglomeration and homogenisation in water containing a suitable amount of the commercial poly-electrolyte Dolapix CE64 (Zschimmer & Schwarz, FRG). In the last 10 min of the homogenisation, 1 wt.% of the AlN powder was added.

The viscosity of the suspensions was followed using a rotational viscometer (Haake, measuring system NV,

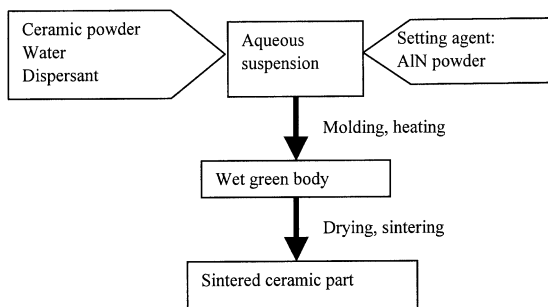


Fig. 1. Flow-chart of the HAS process.

shear rates up to 1000 s^{-1}) during heating from room temperature up to 80°C (heating rate $\approx 1^\circ\text{C}/\text{min}$). The time needed for the solidification of suspensions was estimated by measuring the viscosity within a limited range and by visual inspection of the green bodies formed.

3. Results and discussion

3.1. Viscosity increase in Al_2O_3 –AlN suspension

Fig. 2 shows the thermally activated viscosity increase for a suspension containing 58.7 vol.% alumina powder and 1 wt.% AlN (with respect to solids) in water. For comparison, the effect of temperature on the viscosity of a suspension without AlN is also shown. Both suspensions experience a slight decrease in viscosity at low temperatures, however, above 60°C the viscosity of the AlN-containing suspension starts to increase steeply and within a few minutes reaches values above the measuring range.

The AlN hydrolysis also proceeds at lower temperatures, even at room temperature, however, the viscosity increase occurs much more slowly: a suspension containing 58.7 vol.% alumina and 1 wt.% AlN needs more than one day to solidify at room temperature. Irrespective of the temperature, the final result is the complete transformation of a low viscous suspension into a wet solid green part.

3.2. Mechanisms involved in HAS

The hydrolysis of AlN powder has been studied by other authors^{13,14} and their studies have shown that the reaction at 20°C initially produces an amorphous AlOOH that transforms into crystalline bayerite $\text{Al}(\text{OH})_3$ by a dissolution-crystallization process.

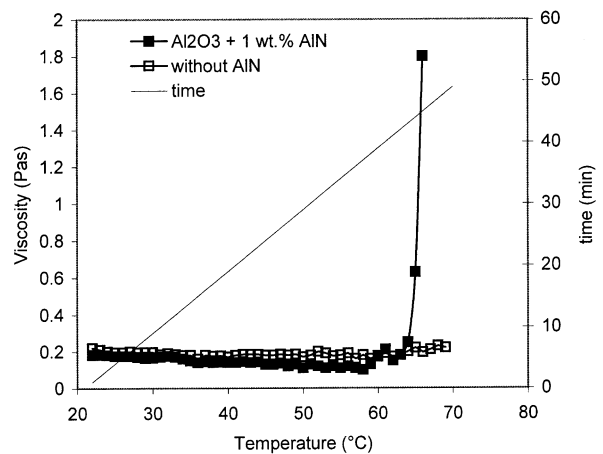
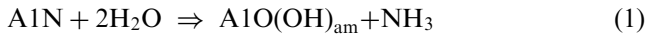


Fig. 2. Viscosity increase during heating for the suspension containing 58.7 vol.% alumina and 1 wt.% AlN in comparison with the suspension without AlN.



From the above reactions it is clear that (1) water is consumed during the hydrolysis of the AlN powder, (2) ammonia is formed and that (3) AlN particles dissolve and aluminum hydroxides are formed. The first phenomenon may contribute to an increase in the solids content and the second may have a significant influence on the pH of the suspension, that effects its electrokinetic and consequently its rheological properties. The dissolution of the AlN particles may affect the ionic strength in the suspension, and the precipitation of the phases formed by the reaction may result in an increase in the surface area of the solids or in a change in the rheological properties of the liquid media in the ceramic suspension. It is clear, that all these reactions may significantly change the rheological properties of the host aqueous ceramic suspension, and so the contribution of the individual effects was examined in this study.

3.3. Water consumption

The contribution to the increase in solids content due to water consumption during the AlN hydrolysis was analysed in alumina suspensions with different solids contents and the addition of 1 wt.% AlN powder. The suspensions were isothermally heated at 60°C in closed molds and the time needed for solidification was estimated by periodic visual inspection. The results given in Table 1 show that the time for solidification increases with decreasing solids content. The suspension with the highest initial solids content (58.7 vol.%) solidified within an hour, while the suspensions with less than 27.3 vol.% solids retained their viscous character even after one day.

Table 1
Solidification time for alumina suspensions with different initial solids contents and 1% AlN and the corresponding calculated final solids content^a

Initial solids loading, vol.% (wt.%)	Final solids content, vol.%	Time needed for solidification at 60°C, h
58.7 (85)	61.0	< 1
50.1 (80)	51.8	1
36.9 (70)	38.1	3
27.3 (60)	28.1	5
20.1 (50)	20.6	No solidification
14.3 (40)	14.7	No solidification

^a The solidification was observed in a closed plastic mold of dimensions $\phi = 35$ mm, $h = 15$ mm. The final solids content was calculated according to the reactions (1) and (3).

Table 1 also lists the final solids content, calculated according to reactions (1) and (3), assuming that all the added AlN powder had reacted. It is clear, that even in this utmost situation, the increase in solids content is rather small, for example just 1.3 vol.% for the suspension with the highest initial solids loading. In an attempt to quantify this effect, in terms of the relative viscosity (η_r) of the suspensions, the viscosity of several experimental alumina suspensions was plotted as a function of the relative solids loading, ϕ_r , (Fig. 3). The maximum solids loading, ϕ_m , was estimated by centrifugal sedimentation and was assumed to be 63 vol.% for the analysed suspension. As known also from the literature,¹⁵ the viscosity of ceramic suspensions increases exponentially with increasing solids content. At high relative solids loadings the particles are so close together that their mobility becomes limited, and with a further increase the suspensions tend to behave more like an elastic body. In the graph the initial solids contents for the HAS suspensions listed in Table 1 are represented as solid squares, while empty squares illustrate the calculated final solids contents and their corresponding viscosity. The exponential increase in viscosity with solids loading means that the viscosity of the suspension having an initial 58.7 vol.% solids, which corresponds to $\phi_r = 0.93$, could increase by a factor of 6 after AlN hydrolysis, whereas the suspensions with moderate initial solids contents (for example 50.1 vol.% solids, i.e. $\phi_r = 0.8$), show a negligible viscosity increase. This suggests that the contribution of the internal water consumption during AlN hydrolysis to the overall solidification is limited just to highly loading suspensions

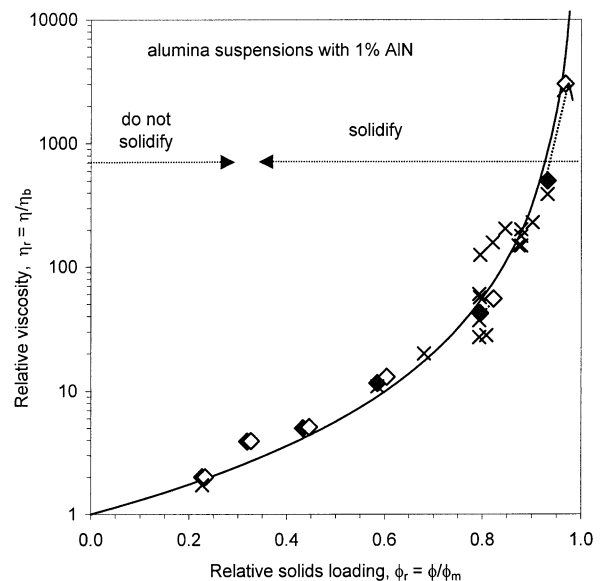


Fig. 3. Relative viscosity, η_r , for aqueous alumina suspensions as a function of relative solids loading, ϕ_r , at $D = 1000 \text{ s}^{-1}$ (η, η_1 = viscosity of suspension and of liquid, respectively; ϕ = solids loading, ϕ_m = maximum solids loading = 0.63).

and can not explain the solidification of suspensions with moderate solids loadings.

3.4. Ammonia formation

The hydrolysis of AlN is accompanied by the formation of ammonia. According to reaction (1), 1 mol NH₃ will be formed by the hydrolysis of 1 mol AlN. Assuming that the AlN particles in the alumina suspension react completely, 0.4 g of ammonia will be released per gram of AlN powder. Hence, in aqueous alumina suspension containing 58.7 vol.% solids and 1 wt.% AlN (with respect to solids), 2.6 g of NH₃ per litre of water will form, which is below the solubility of ammonia at temperatures less than 80°C. As a result, the pH of an alumina aqueous suspension with the addition of a small amount of AlN increases progressively from 9.5 to 11. In this pH range, the ζ -potential of alumina tends to decrease with increasing pH (Fig. 4a), which in turn causes an increase in the viscosity as shown in Fig. 4b. This increase is small for a suspension with a low solids content (dashed line), but much larger in a suspension with a higher solids loading (solid line). For the suspension containing 58.7 vol.% solids the viscosity increased by a factor of 4 after increasing the pH from 9.5 to 11. This result suggests that for alkaline suspensions the contribution of an ammonia-induced pH

change, and the resulting ZP decrease, to the solidification of the suspensions is rather small.

When starting from an acidic alumina suspension, the contribution of the pH change to solidification may be more significant, since an increasing pH will cross the iso-electric point (IEP) causing flocculation. This work, however, is only concerned with processes in the alkaline region, since most ceramic suspensions are alkaline by nature and the process is much more serviceable and economical in the alkaline region.

3.5. Dissolution and precipitation

Another proposed contribution to the hydrolysis-induced viscosity increase is the dissolution of solid AlN particles in the suspension and the precipitation of new phases.

Aluminum oxide, hydroxides and particularly nitride are moderately soluble in water; their solubility depends primarily on temperature and pH. Bell and co-authors⁵ suggest that a temperature increase and a simultaneous increase in pH result in a higher concentration of [Al(OH)_x]^{3-x} ions in the suspension. This may affect the ζ -potential because of an increase in ionic strength in the suspension⁵ and an increase in the viscosity. However, since this would result in the formation of solid aluminum hydroxides, dissolution is not thought to be significant for solidification and so has not been estimated quantitatively.

The precipitation of aluminum hydroxides, in contrast, has been examined [reactions (1) and (3)]. According to the literature data, amorphous mono-hydroxide Al(OH) is formed first, but after aging in the supernatant at room temperature, it crystallizes into bayerite Al(OH)₃ by a dissolution-precipitation process; aging at 80°C results in the crystallization of boehmite AlOOH.^{16,17} In order to examine the hydrolysis of AlN in the presence of a poly-electrolyte, we analysed the powder before and after soaking at 60°C for 1 or 22 h. The results are given in Table 2 and Figs. 5 and 6.

The morphology of the AlN powder changed drastically with the reaction and during aging, Fig. 5a–c. After soaking for 1 h, fine, clustered platelets (Fig. 5b), characteristic of boehmite were observed.¹⁸ After aging for 22 h in water, this fine structure was lost (Fig. 5c),

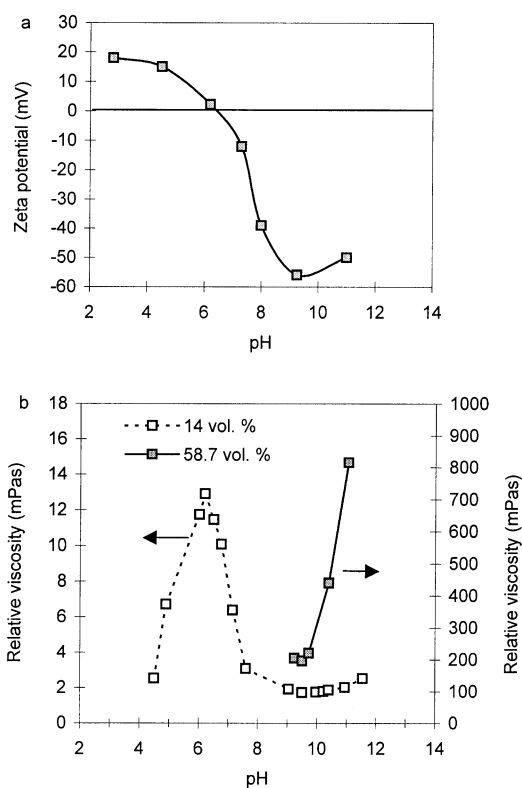


Fig. 4. (a) ζ -potential as a function of pH for an aqueous alumina suspension with a polyelectrolyte; (b) corresponding viscosity increase for suspensions containing 14 and 58.7 vol.% solids; $D = 1000 \text{ s}^{-1}$.

Table 2

The BET and XRD of the AlN powder before and after soaking in hot water

AlN powder	Specific surface area, m ² /g	Phases observed by XRD
As-received	3.2	AlN
Soaked at 60°C for 1 h	185.7	Boehmite, Nordstandite, AlN
Soaked at 60°C for 22 h	51.9	Boehmite

and necks were formed between the clusters by the dissolution and precipitation process.¹⁹

BET analysis of the as-received AlN powder and the powder after soaking for 1 h at 60°C confirmed an enormous increase in specific surface area from 3.2 to

185.7 m²/g. After 1 h of soaking, the phases determined by XRD were boehmite AlO(OH), nordstrandite Al(OH)₃ and the remaining un-reacted AlN, (Fig. 6a). After 22 h, the surface area decreased to 51.9 m²/g, and XRD shows only the presence of boehmite, (Fig. 6b).

The enormous increase in BET for the hydrolysed AlN powder, however, contributes only slightly to the average specific surface area of the dispersed powder in the suspension of alumina with 1 wt.% of the AlN, i.e. less than 1%, which implies a limited effect on the viscosity of the suspension. On the other hand, a much larger contribution to the solidification of the alumina suspension can be attributed to the boehmite, which was observed to form necks between the particles (Fig. 5c). It is reasonable to suppose that the boehmite formed in the fluid between the ceramic particles in the suspension connects them into a stiff body or at least drastically increases the viscosity of the aqueous ceramic suspension due to an increase in the viscosity of the fluid between the particles.

This assumption was strongly supported by TEM analysis of green alumina parts solidified at 60°C in a closed mold and dried in air at room temperature. The technique used to study the microstructure of the green parts and detailed results are described in Ref. 20. The

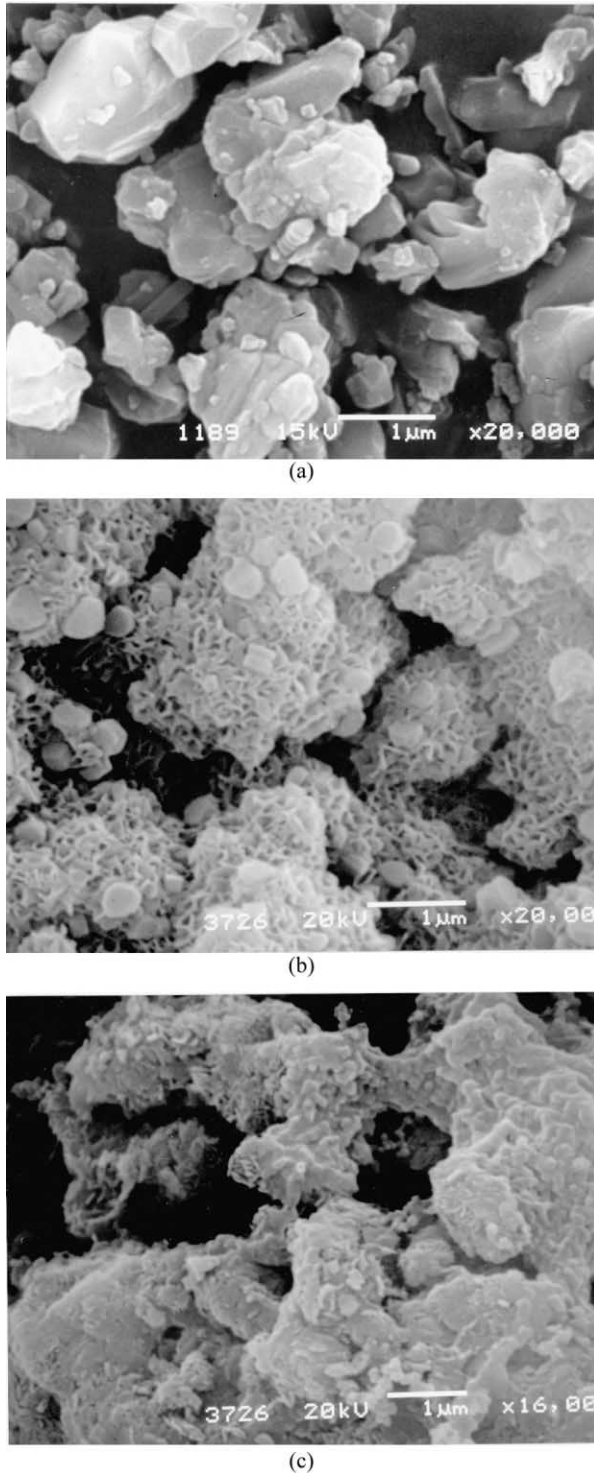


Fig. 5. SEM micrographs of (a) as received AlN powder and of the reaction products formed by the hydrolysis of AlN at 60°C (b) after 1 h and (c) after 22 h of soaking in hot (60°C) water.

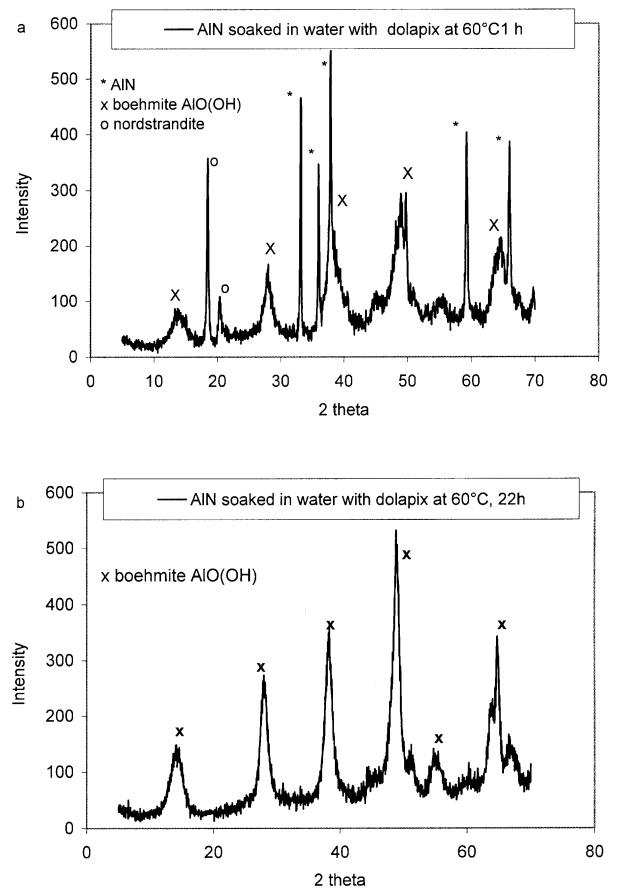


Fig. 6. XRD of the product formed by the hydrolysis of AlN soaked at 60°C for, (a) 1 h and (b) 22 h.

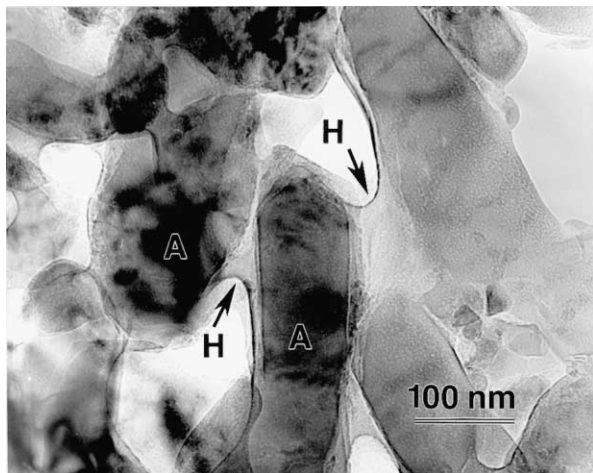


Fig. 7. TEM micrograph of the solid green alumina part (A-alumina particle, H-amorphous hydroxide layer).

micrograph in Fig. 7 shows that the alumina particles are covered by a continuous layer of mostly amorphous phase with some embedded nano-sized crystallites. We suppose that this phase plays an important role in the solidification of the ceramic suspension. When all the water is still present in the body (before opening the closed mold), the hydroxide uniformly precipitates in the liquid and hence causes the increase in its viscosity or the hydroxide precipitates preferentially on the surface of the ceramic particles forming necks between them. In both cases the mobility of the ceramic particles in the suspension becomes highly restricted. The presence of boehmite between the particles can also explain the high green strength of the solid bodies, which was also described in Ref. 4.

4. Conclusions

The hydrolysis assisted solidification (HAS) process was studied with the aim of explaining the mechanisms involved in the solidification of ceramic aqueous suspensions. The particular effects of the hydrolysis of the AlN powder, used as the setting agent, were analysed: water consumption, ammonia formation, dissolution of AlN particles and precipitation of new phases.

The results obtained in this study show that internal water consumption has a minor effect on the viscosity of the aqueous ceramic suspension. For suspensions containing high initial solids loadings, however, viscosity could increase due to this effect, but for the suspensions with a lower solids content the viscosity increase is negligible. Nevertheless, the suspensions with solids contents above approximately 27 vol.%, did eventually solidify.

The ζ -potential modification may be the result of two mechanisms: first, a pH change due to ammonia evolution and second, an increase in ionic strength due to the dissolution of particles. The contribution of the first

effect was estimated to be similar to that of the water consumption, while the increase in ionic strength was considered to be insignificant, since the concentration of ions in the solution decreased after the reaction product was formed. In general, the effect of the ζ -potential change seems to be moderate, but the resulting viscosity increase driven by this mechanism is not enough for solidification of the ceramic suspensions.

The enormous increase in surface area observed during the hydrolysis of AlN powder seems to be negligible in terms of the overall alumina suspension with its small AlN addition, since no isolated hydroxide particles were observed within the solid parts. Instead, the amorphous phase observed between the ceramic particles in the suspension using TEM seems to play an important role in the viscosity increase in ceramic suspensions.

Several different phenomena accompany the hydrolysis of the AlN powder added to an alumina aqueous suspension and finally result in the solidification of the suspension to form a solid green part. According to the results of this study, the solidification is a cumulative effect of internal water consumption, ζ -potential decrease and the formation of amorphous aluminum hydroxides within the liquid. The most significant role is believed to be played by the formation of amorphous aluminum hydroxides, either creating necks between the ceramic particles or increasing the viscosity of the liquid.

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References

1. Rivers, R. D. Method for injection molding powder metal parts. US Patent 4113480, 1978.
2. Fanelli, A. J., Silvers, R. D., Frei, W. S., Burlew, J. V. and Marsh, G. B., New aqueous injection molding process for ceramic powders. *J. Am. Ceram. Soc.*, 1989, **72**, 1833.
3. Janney, M. A., Omatete, O. O., Method for molding ceramic powders using a water-based gel casting. US Patent 5028362, 1001.
4. Gauckler, L. J., Graule, Th., Baader, F., Ceramic forming using enzyme catalysed reactions. *Mater. Chem. Phys.* 1999, **78–102**.
5. Bell, N. S., Wang, L., Sigmund, W. M. and Aldinger, F., Temperature induced forming: Application of bridging flocculation to near-net shape production of ceramic parts. *Z. Metallkd.*, 1999, **90**(6), 388–392.
6. Kosmač, T., Novak, S., Sajko, M. and Eterovič, D., A process for forming ceramic products from an aqueous suspension with a high solids content. Patent EP 0-813-508 BI, 1999.
7. Rak, Z. S., Advanced shaping techniques in advanced ceramics. *Ber. DKG.*, 2000, **77**(6), 6–16.

8. Kosmač, T. and Krnel, K., Microstructure and mechanical properties of HAS formed Al_2O_3 , Y-TZP and Si_3N_4 ceramics. In *Proc. 6th Int. Symp. on Ceramic Materials and Components for Engines*, ed. K. Niihara. Arita, Tokyo, 1998, pp. 663.
9. Krnel, K. and Kosmač, T., Reactivity of aluminum nitride powder in dilute inorganic acids. *J. Am. Ceram. Soc.*, 2000, **83**, 1375–1378.
10. Novak, S. and Kosmač, T., Interactions in aqueous Al_2O_3 -AlN suspensions during the HAS process. *Mater. Sci. Eng.*, 1998, **A256**, 237–242.
11. Novak, S. and Kosmač, T., Large alumina parts from aqueous suspensions, In: *Euromat '99 Proceeding: Vol. 8: Ceramics-Reliability, Tribology and Wear*. 2000, pp. 150–156.
12. Kosmač, T., Novak, S. and Sajko, M., Hydrolysis-assisted solidification (HAS): a new setting concept for ceramic net-shaping. *J. Eur. Ceram. Soc.*, 1997, **17**, 427–432.
13. Bowen, P., Highfield, J., Mocellin, A. and Ring, T. A., Degradation of aluminum nitride powder in an aqueous environment. *J. Am. Ceram. Soc.*, 1990, **73**(3), 724–728.
14. Mobley, W. M., Colloidal Properties, Processing and Characterization of Aluminum Nitride Suspensions, Thesis. Alfred University, New York, 1996.
15. German, R. M., *Powder Injection Molding*. Metal Powd. Ind. Fed., NJ, 1989, pp. 158.
16. Pierre, A. C. and Uhlmann, D. R., Gelation of aluminum hydroxide sols. *J. Am. Ceram. Soc.*, 1987, **70**(1), 28–32.
17. Yoldas, B. E., Hydrolysis of aluminum alkoxides and bayerite conversion. *J. Appl. Chem. Biotechnol.*, 1973, **23**, 803–809.
18. Yang, X., Pierre, D. R. and Uhlmann, A. C., TEM study of boehmite gels and their transformation to α -alumina. *J. Non-Crystalline Solids*, 1988, **100**, 371–377.
19. Brinker, C. J. and Scherrer, G. W., *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*. Academic, Boston, 1990.
20. Novak, S. and Dražič, G., Analytical electron microscopy of green ceramics formed from aqueous suspension. *J. Am. Ceram. Soc.*, 2001, in press.