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A study of ceramic-suspension solidification using complex-impedance spectroscopy

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Abstract

The degree of setting of an aqueous ceramic suspension was followed by complex impedance spectroscopy. Samples were measured in specially designed measuring cells at temperatures of 20 and 27°C. At each temperature the complex impedance of the suspensions in the frequency range between 0.1 Hz and 10 MHz was acquired at regular time intervals. During the solidification process the value of the impedance increased by more than an order of magnitude. The results have confirmed that the method is a useful tool for the study of the process of forming green ceramics bodies from aqueous suspensions.

Keywords: Al_2O_3; Impedance; Solidification; Suspensions

1. Introduction

The process of forming ceramic green bodies from an aqueous suspension by casting into a porous mould is an old technique with many disadvantages. For this reason, during the last decade, several new wet-forming methods have been developed that differ from conventional slip casting in the use of a closed non-porous mould. In these techniques a liquid vehicle remains in the sample during solidification which progresses with the aid of a setting agent, with the liquid being subsequently removed from the solid part by drying or evaporation. In the hydrolysis assisted solidification (HAS) method[1] the setting agent is fine aluminium-nitride (AlN) powder, which is added in small amounts to an aqueous suspension of the host ceramic powder. Due to hydrolysis of the AlN, ammonia is formed in the suspension and consequently the pH increases. Aluminium hydroxides are also formed.[2,4] A certain amount of water is consumed during the hydrolysis, but most of it remains in the solid body until it is exposed to atmosphere to dry. The overall result of the processes accompanying the hydrolysis is that a low viscosity AlN-containing ceramic suspension transforms into a stiff solid green part. The time needed for the solidification of the suspension depends on many process parameters, such as the amount of AlN, its particle size, solids content in the suspension, temperature, etc.[3–5] For the low-solid-loaded suspensions the progress of the process, i.e. the transformation of the viscous fluid to a solid body, can be in part followed by a viscosity measurement, though the process of solidification itself is disturbed during rotational or oscillatory measurements. For highly solid loaded suspensions (50–60 vol.%) this technique is even less suitable, so that only a periodic opening of the mould and visual inspection of the stiffness of the forming body seems to be appropriate for monitoring the process.

For this reason a need for another, non-destructive method, has appeared. Due to an extreme change in the consistency of the suspensions during the progress of the HAS process, a hypothesis that the solidification could be accompanied by a change in electrical properties was followed. Impedance spectroscopy, as a possible method for monitoring the processes taking place during the forming of a wet solid ceramic body from an aqueous suspension, was tested.

2. Experimental

An alumina suspension containing 50 vol.% of alumina powder (Alcoa A16SG) and 50 vol.% water with

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0.4 wt.% Dolapix CE64 (per solids) as a dispersing agent was prepared by homogenisation in a ball mill. In the last 10 min AlN powder was added in quantities of 0.5, 1 or 5 wt.% per solids. The suspensions were cast into specially designed measuring airtight cells.

The degree of setting of the aqueous alumina suspension was followed by impedance spectroscopy using a Solartron 1260 Impedance gain-phase analyzer. The measuring cells were comprised of four specially designed Pd-based electrodes prepared using thick-film technology. The electrodes were flat and rectangular with a surface area of 9×14 mm^2. Four-terminal electrical measurements were used. The samples were measured at temperatures of 20 and 27°C. At each temperature the impedance in the frequency range of 0.1 Hz to 1 MHz was acquired at regular time intervals.[6] The obtained Cole–Cole diagrams consisted of two arcs. While high-frequency arcs were normally complete, the low frequency arcs were truncated, but still in most cases well resolved. In this study the high-frequency resistance (R_h) was used, calculated from the high-frequency semi-circles using the equation $\omega_m RC = 1$ (where ω_m is the frequency at the maximum of the semicircle in Cole–Cole diagram, R and C are resistivity and capacitance) (Fig. 1). Besides the fact that low-frequency arcs were not complete the reason why high-frequency semicircles were used was the also much higher change of the resistivity, calculated from these circles during the solidification processes. In other measuring cells the pH was followed throughout the process and in another set of closed containers the solidification was inspected visually from time to time.

3. Results and discussion

The freshly prepared (10 min after homogenisation) aqueous suspensions containing 50 vol.% alumina powder and 0.5, 1 or 5 wt.% AlN were alkaline with pH values around 9. The variation of pH value with time was followed until the suspensions solidified. As shown in Fig. 2, the pH steadily increased with time. The rate of the pH change increased with the AlN content as well as with temperature. For the suspension containing 5 wt.% AlN, the pH reached a value of 10.4 within approximately 5 h at 27°C, while significantly longer times were needed for the suspensions containing 1 wt.% or 0.5 wt.% AlN.

In addition to the observed pH change, the electrical properties of the suspensions also varied with time. The diagram in Fig. 3 represents the high-frequency resistance (R_h) of the suspensions containing different additions of AlN as a function of time and temperature. At

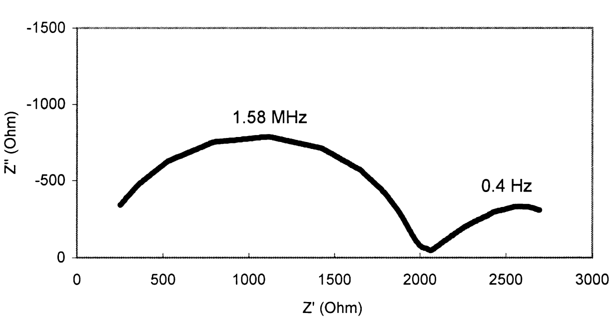

Fig. 1. Characteristic Cole–Cole diagram of the suspension containing 1 wt.% of AlN after 48 h at 27°C.

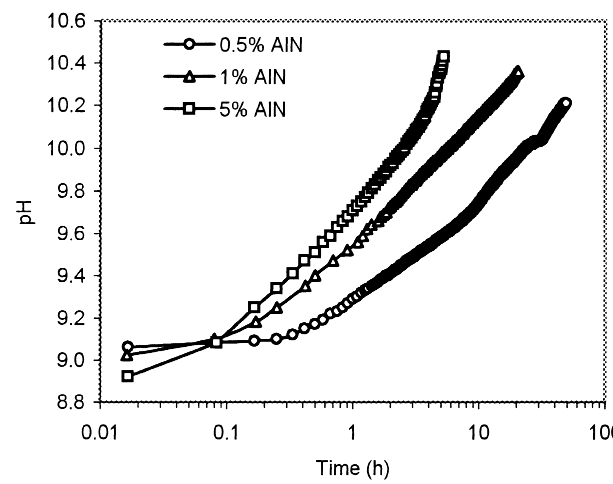

Fig. 2. The change in pH with time for an aqueous alumina suspension containing 0.5, 1 and 5 wt.% AlN at 27°C.

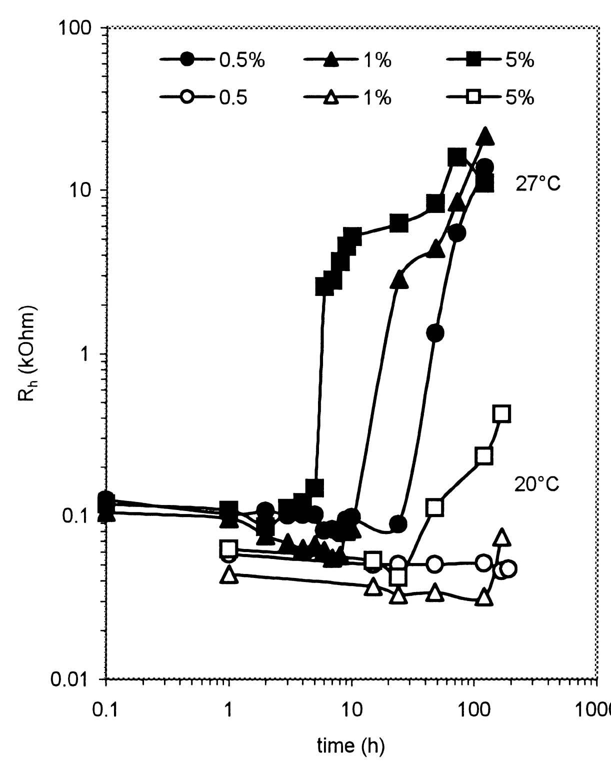

Fig. 3. High-frequency resistance (R_h) for aqueous alumina suspensions containing 0.5, 1 or 5 wt.% AlN as a function of time and temperature.

the beginning of the experiments at 27°C, the resistance reduced slightly, then, after a certain time, it increased sharply by more than an order of magnitude. The progressive increase in pH which, most likely is connected to an increase in the amount of NH_3 and consequently to an increase in concentration of $[NH_4]^+$ and $[OH]^-$ ions in the suspension, could explain the decrease in R_h within the initial phase. The time for the onset of the sharp increase in R_h decreases with the increased amount of the AlN, which is also illustrated in Fig. 4: 24 h for the suspension with 0.5 wt.% AlN, 10 h for 1 wt.% AlN and 5 h for 5 wt.% AlN. The sudden increase in R_h could not be explained by the change in pH value. At approximately the same time as the sharp increase in R_h occurred, the suspensions in the parallel moulds were determined to be solid by a simple impression test. The results strongly support the idea that the sudden increase in R_h corresponds to the point of solidification caused by the AlN hydrolysis.

At the lower temperature, i.e. 20°C, the hydrolysis reaction proceeds more slowly, which results in longer times being needed for the increase in R_h. The influence of the AlN content on the timing of the sharp increase in R_h appears, however, to be similar to that at higher temperatures.

It is interesting to note that the observed significant increase in R_h was obtained for samples in which almost all the water was present during the solidification process and the electrical measurements, since the measuring cell was tightly closed. If all the AlN in the suspension had reacted, only approximately 3 wt.% of the water would have been consumed by the reaction. So, the change in electric resistance cannot be ascribed to water (electrolyte) removal but only to a change in the electrical properties of the water-containing solid body in which the alumina particles are embedded.

In order to explain the observed variations of R_h during the suspension solidification we first verified, whether the high-frequency semicircles pertain to the bulk. In a set of experiments the distance between the measuring electrodes was varied. For all points measured before and after the sharp increase of impedance it was found that the R_h was proportional to the reciprocal of the distances between the electrodes.

Another mechanism that could presumably influence the electrical properties of the suspension during solidification is formation of aluminium hydroxides between alumina particles. In our current analytical-electron-microscopy study of the microstructure of green bodies prepared by the HAS method we have found that various types of aluminium hydroxides and hydroxy-oxides are present at the junctions of alumina particles. Secondary phase was found to be amorphous or in some cases, forming crystals of few tens of nanometers in size. In Fig. 5 a transmission electron micrograph (bright field) of a secondary phase between alumina particles in a dried green piece is shown.[7] This phase continuously distributed between the alumina particles in the suspension is presumably responsible also for the hindered mobility of the solid particles in suspensions reflecting in solidification.

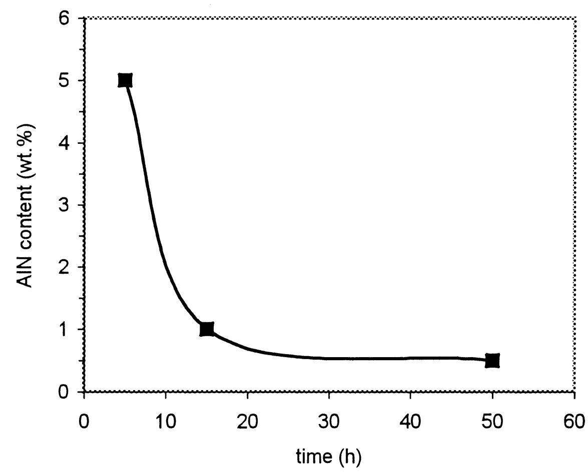

Fig. 4. Solidification time of aqueous alumina suspensions as a function of AlN addition.

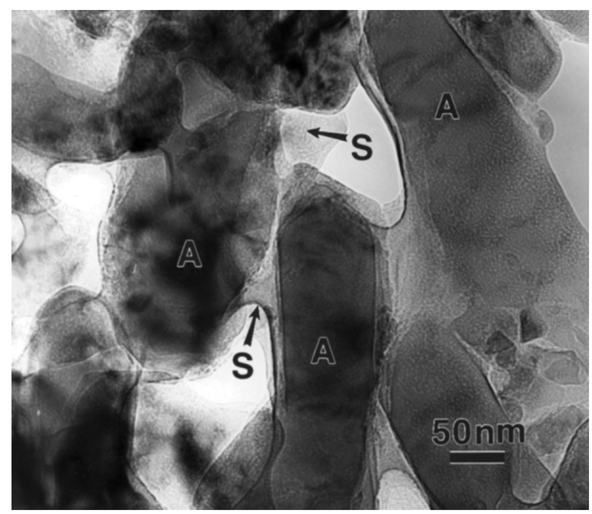

Fig. 5. TEM micrograph (bright-field imaging) of the secondary phase between alumina particles in a dry green body prepared using the HAS method; A — alumina particles, S — secondary phase.

A tentative explanation for the observed phenomenon is, therefore, that the water that contains charge-carrying ions is immobilised in some way in the newly formed skeleton of aluminium hydroxides and alumina particles. However, at the moment, explanations are more or less speculative and have to be studied further. Nevertheless, the results clearly show that the described method is useful for monitoring the solidification of aqueous ceramic suspensions prepared by the HAS process.

4. Conclusions

A sharp increase in the high-frequency resistance of the ceramic aqueous suspension, measured using impedance spectroscopy, was observed for the time interval where solidification of the suspension occurred. The timing of the increase in R_h was found to be a function of temperature and the amount of added AlN. Using four-terminal measuring cells and varying the distance between the electrodes it was concluded that the sudden change of impedance was not a consequence of some electrode processes but was rather a result of a change in the material's properties.

The results have confirmed that impedance spectroscopy is a useful tool for monitoring the process of forming ceramics from aqueous suspensions.

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References

1. Kosmač, T., Novak, S., Eterovič, D. and Sajko, M., A process for forming ceramic products from an aqueous suspension with a high solids content: European Patent No. EP 0-813-508 B1, 1999.
2. Bowen, P., Highfield, J. G., Mocellin, A. and Ring, T. A., Degradation of aluminium nitride powder in an aqueous environment. *J. Am. Ceram. Soc.*, 1990, **73**, 724–728.
3. 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.
4. Novak, S. and Kosmač, T., Interaction in aqueous Al_2O_3–AlN suspensions during the HAS process. *Mater. Sci. Eng.*, 1998, **A256**, 237–242.
5. Novak, S., Kosmač, T. and Krnel, K., Principles of the hydrolysis assisted solidification (HAS) process in slurry forming ceramic bodies. Submitted to *J. Eur. Ceram. Soc.*
6. Macdonald, J. R., *Impedance Spectroscopy*. John Wiley & Sons, NY, 1987.
7. Novak, S. and Dražič, G., Analytical electron microscopy of green ceramic parts formed from aqueous suspension (to be published).