Ultrasonic Monitoring of Slip Casting Kinetics of Silicon Nitride Ceramic

S. Appleton, D. A. Hutchins & M. H. Lewis

Departments of Engineering and Physics, University of Warwick, Coventry, CV4 7AL, UK

Abstract

An ultrasonic technique has been used to perform in-situ monitoring of ceramics formed by the slip casting of silicon nitride. The technique can monitor the cast thickness as a function of time. Experiments have been performed to study the casting kinetics as a function of slip pH and viscosity, and the results correlated with the resulting cast green density.

Es wurde ein Ultraschall-Verfahren angewandt, um die Formgebung von Silizium-Nitrid-Keramiken durch Schlickerguß in situ zu kontrollieren. Die angewandte Technik ermöglicht die Überwachung der Guß-Schichtdicke in Abhängigkeit der Zeit. Es wurden Experimente zur Untersuchung der Gieß-Kinetik als Funktion des pH-Wertes und der Viskosität des Schlickers durchgeführt. Die Ergebnisse wurden in Verbindung mit der resultierenden Gründichte des Gußkörpers gesetzt.

On a développé une technique ultrasonique pour réaliser un contrôle in situ de céramiques réalisées par coulage en barbotine de nitrure de silicium. Cette technique permet de contrôler l'épaisseur de la coulée en fonction du temps. Les expériences ont été réalisées afin d'étudier les cinétiques de coulage en fonction du pH de la barbotine et de sa viscosité, enfin les résultats ont été corrélés avec la densité 'en crue' des céramiques coulées.

1 Introduction

The production of ceramic components by methods which necessitate little or no post-firing treatment is of crucial economic importance to industry. Several techniques exist, including injection moulding, hot isostatic pressing (HIP) and slip casting. The latter technique is probably the simplest for both large-scale production and prototype development, because of the low cost of forming materials, and the versatility of the technique.

The processes involved in slip casting have been studied extensively.[1-4] The casting process involves the formation of a stable suspension of powder in a suitable liquid (the slip), which is then cast in an absorbent mould. Liquid is drawn from the slip by the suction pressure of the mould, leaving a cast layer which is removed once excess liquid has been poured off. The result is a ceramic in its green state, which requires drying and heat treatment to form the finished product.

It is now well-established that during slip casting, the thickness (x) of the cast ceramic layer increases with time (t) according to

$$x^2 = At \qquad (1)$$

provided that abnormal effects (such as saturation of the mould with liquid[5]) are not present. The rate of thickness increase is thus directly proportional to the constant, A, which will vary with the properties of both the mould and the slip.[3,6,7] Previous work has attempted to quantify the above relationship, using monitoring techniques during the cast. For example, γ-ray methods have been suggested as a means to estimate cast layer thickness,[8,9] and another study[10] has investigated the use of nuclear magnetic resonance (NMR) imaging for this purpose. However, a more simple, cheap and accurate approach is to use an ultrasonic technique.[11] This relies on an acoustic reflection of energy from the interface between the slip and the cast layer. Using a fixed transducer to both generate and detect ultrasonic pulses, at frequencies in the 1–10 MHz range, an echo can be detected which moves in time as the

layer grows in thickness. If the transducer is a known distance (d) from the mould wall, and the acoustic velocity in the slip is v_s, then the propagation time of an ultrasonic pulse to the layer/slip interface and back is

$$t_1 = 2(d - x)/v_s \qquad (2)$$

In addition an ultrasonic reflection from the mould wall can be detected. This has a transit time, t_2, where

$$t_2 - t_1 = 2x/v_c \qquad (3)$$

and v_c is the acoustic velocity averaged through the thickness of the cast. Thus, knowledge of v_s and d leads directly to the thickness (x) of the cast layer at any time. This in-situ monitoring has been shown to be useful in preliminary studies of slip-cast alumina ceramics.[11] In this paper, we will extend this work to another important engineering ceramic, silicon nitride (Si_3N_4), and show how the technique can be used to monitor casting kinetics as a function of the properties of the slip, such as pH and viscosity. In addition, it will be shown that the acoustic velocity within the cast layer (v_c) can be monitored with time, and correlated with both the casting kinetics and the resultant green density.

2 Apparatus and Experiment

The Si_3N_4 slips used in the present work were prepared from powders with a composition by weight of 95% Si_3N_4/5% Y_2O_3. The Si_3N_4 powder was manufactured by Ube Industries, Japan, and consisted of sub-micrometre particles. The Y_2O_3 powder was of 99·99% purity, and manufactured by Alfa Ventron. The powders were selected as being a frequently used source of Si_3N_4, with a reproducible

oxygen impurity content and containing a typical liquid-phase sintering additive (Y_2O_3). Both the surface oxygen impurity on Si_3N_4 and the sintering additive are known to influence the surface chemistry and charge of the major component particles, and hence the stability and viscosity of the slip for specific pH values. The powders were mixed to form a homogeneous dispersion by milling in a polyethylene container with alumina balls, and were then sieved to remove any coarser aggregates. An appropriate amount of deionised water was then added, to result in a 50% solid loading, and the result stirred to form a reasonable suspension. This was blended at high speed for 30 min, and subsequently degassed.

The variation of casting kinetics with pH was of interest in the present study. Hence, the pH of all slips was carefully controlled over the range 8·3–9·3 using ammonia solution, this range in pH causing a variation from high to low viscosity. The actual pH was measured using a Hanna HI1280 pH meter of the glass combination electrode type.

The viscosity of the slip at each pH was also measured, using a Brookfield LVDTV-I digital viscometer, fitted with a small sample adapter where appropriate. The viscosity was measured as a function of shear rate for each slip, using the spindle type appropriate to the viscosity being measured, and this data recorded for later comparison to the ultrasonic data. In addition, thixotropy was estimated for the slips by measuring the viscosity at a constant shear rate over a period of 30 min.

A schematic diagram of the apparatus used to study the casting kinetics of these slips using ultrasound is shown in Fig. 1. A Panametrics 5055PR pulser/receiver was used to both excite and receive ultrasonic signals from an immersion piezoelectric ultrasonic transducer. This was 12·5 mm in diameter, and operated at a centre
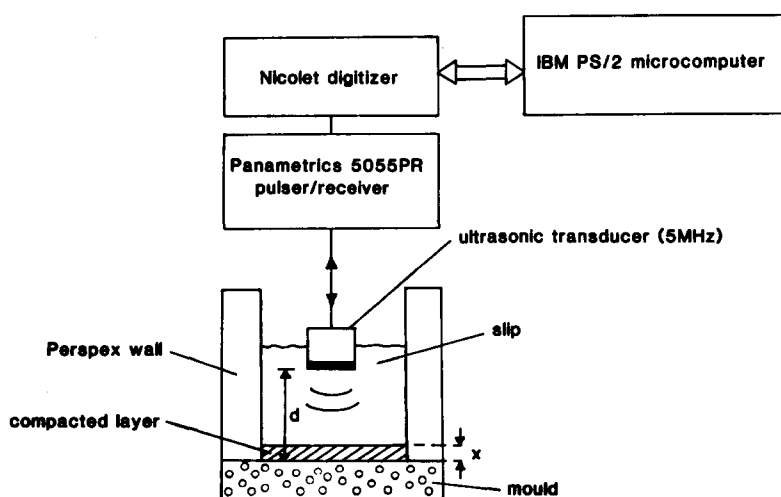

Fig. 1. Schematic diagram of the apparatus used for ultrasonic monitoring of slip casting.

frequency of 5 MHz. The transducer was held rigidly at a fixed distance, d, from the plaster of Paris mould wall, where d could be adjusted using a translation stage fitted with a micrometer. The surface of the mould and the transducer were aligned so as to be parallel, to maximise the ultrasonic signal reflected back to the transducer. The mould took the form of a single slab of plaster of Paris, with a perspex surround containing the slip. Suction was thus in one direction only.

When a cast was in progress, ultrasonic echoes were received from both the mould surface, and the interface between the liquid slip and the cast layer. The complete ultrasonic waveforms, including both reflections, were recorded at preset time intervals using a digital oscilloscope under computer control. Ultrasonic waveforms were transferred in real time to the IBM PS\2 microcomputer, for analysis after the cast was completed. Waveforms could be digitised at a minimum time separation of 10 s during each cast. If signal levels were low, fast signal averaging was available to reduce noise levels to an acceptable level.

In a typical test, a slip was poured into the mould, which contained the transducer mounted as in Fig. 1. The distance d was fixed at 5 mm at the start of the experiment, but this could be increased by known increments using the micrometer, if the slip/cast layer interface approached the transducer face.

A set of typical ultrasonic waveforms recorded during such an experiment is shown in Fig. 2. The times quoted are those after the initial filling of the mould with slip. There are several features of interest in these waveforms. The signal due to reflection from the boundary between the slip and the cast layer (labelled C in each waveform) can be seen to move to the left with increasing cast time. This is due to the interface moving towards the transducer, causing a decrease in the propagation time back to the transducer, as described by eqn (2). The other main features in the waveform are a noise signal from the excitation voltage on the transducer (V), and the reflection from the mould wall (W). Note that the latter signal also moves slightly with time, due to a different ultrasonic velocity in the cast layer (v_c) than in the slip (v_s). In fact, the propagation time (t_2) for this transient is given by

$$t_2 = 2[(d - x)/v_s + x/v_c] \qquad (4)$$

where v_c is the velocity in the cast layer.

In some cases, we wished to link the casting kinetics with the resulting green density of the cast layer. The green ceramic specimens formed by slip casting were approximately 8 mm thick, with an area
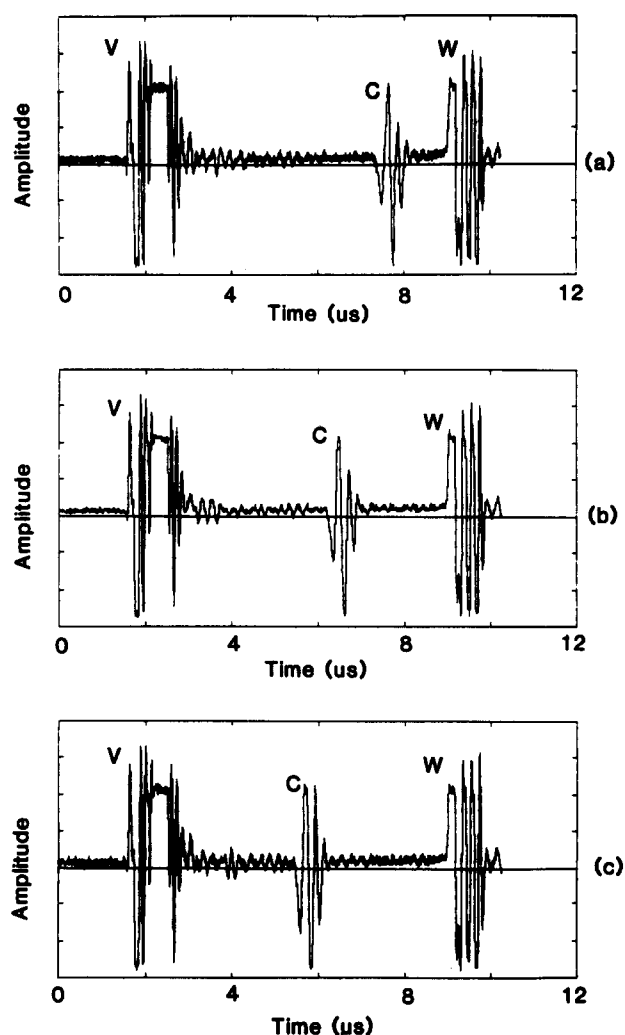

Fig. 2. Typical ultrasonic waveforms, obtained during slip casting of Si₃N₄ at a pH of 8·97, using the apparatus of Fig. 1. The waveform is shown after casting times of (a) 10 s, (b) 30 s and (c) 50 s.

of 50 × 50 mm. They were removed from the mould, and dried at room temperature for 24 h, followed by a further 24 h at 110°C. The green density was then estimated using Archimedes' principle. A small piece of each sample was placed in a constant volume capilliary-stoppered glass bottle after first closing the surface porosity by soaking in paraffin. Archimedes' principle of volume displacement was then used to estimate the density.

3 Results and Discussion

A series of experiments have been performed, to study the kinetics of casting for a range of Si₃N₄ slips with various pH and viscosity properties. Initial experiments were performed, to determine whether the parabolic law between layer thickness (x) and casting time (t) of eqn (1) held for these slips. The results of a typical cast, in this case for a slip pH of 8·49, is shown in Fig. 3. In Fig. 3(a), the cast layer
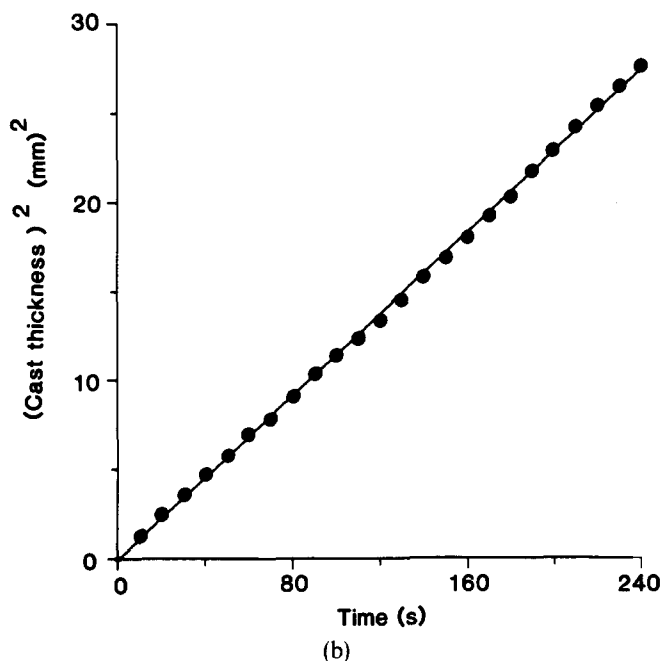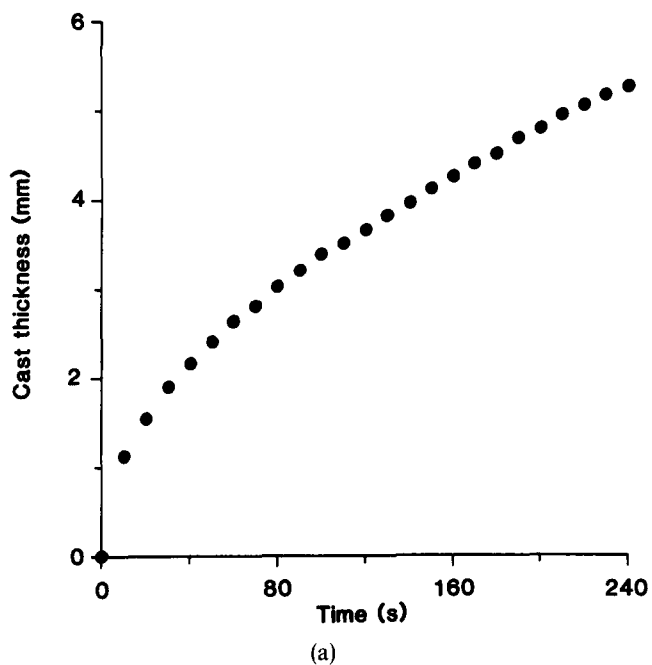
(a)

Fig. 4. Variation of constant A in eqn (1) with pH of Si_3N_4 slips.

(b)

Fig. 3. Cast kinetics for Si_3N_4 slip at pH = 8·49, showing (a) cast thickness and (b) the square of cast thickness as a function of time.

thickness is plotted directly as a function of casting time, and it is clear that the rate of layer build-up gradually levels off with time, as would be expected from a parabolic law. The adherence to eqn (1) can be tested more rigorously if x^2 is plotted as a function of t, as a straight line should then result. This is shown in Fig. 3(b), where indeed an excellent linear relationship exists. It was observed throughout the study that the Si_3N_4 slips followed such a behaviour closely. The slope of a graph such as that in Fig. 3(b) leads to a prediction of the constant A in eqn (1), which controls the casting rate.
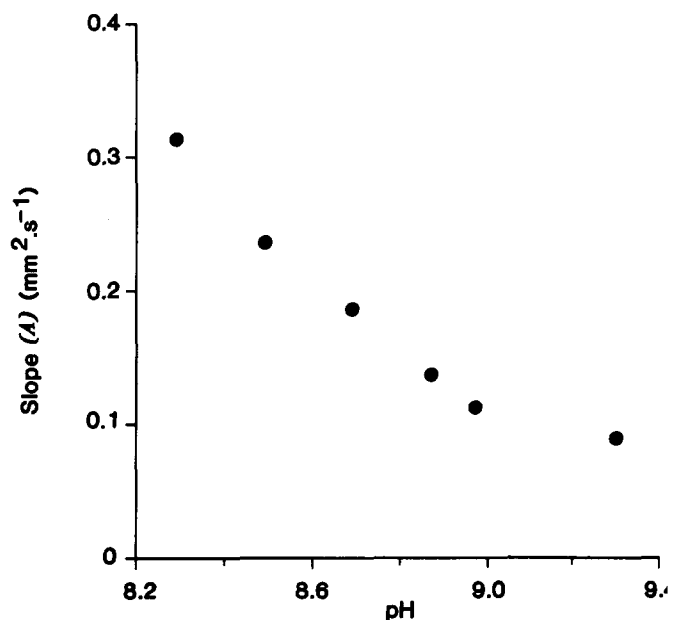
A series of such measurements have been made as a function of slip pH, and the results are presented in Fig. 4. They indicate a marked decrease in the casting rate (i.e. a decrease in the constant A) with an increase in pH, up to a value of pH = 9. Beyond this value, the casting rate tended to a constant value. The increase in casting rate at lower pH values is thought to be due to flocculation of the particles within the slip, due to attractive inter-particle forces. The development of attached particle networks would be expected to lead to poorer particle packing, and hence a lower green density. To test this hypothesis, the green density was measured as a function of pH, the results being shown in Fig. 5. At neutral pH values, the green density was found to be in the region of 53% of theoretical, whereas at higher pH values it was in excess of 70% of theoretical. Thus, the green density does increase with pH as expected, and this is accompanied by a decrease in the casting rate from Fig. 4. Note that a parabolic thickness–time relationship was maintained throughout the pH range studied, indicative of a rate control via pressure differential across the cast layers with different porosity. This is consistent with existing models for slip casting.

As was stated earlier in eqn (3), it is also possible to monitor the average acoustic velocity, v_c, in the deposited layer as a function of casting time. A typical result (for a particular pH of 8·87) is shown in Fig. 6(a). The velocity averaged through the thickness of the layer increases rapidly at first, and then at longer casting times tends to an asymptotic value, in this case of $1380\,\text{ms}^{-1}$. This is the same value as that recorded for the velocity of sound in the
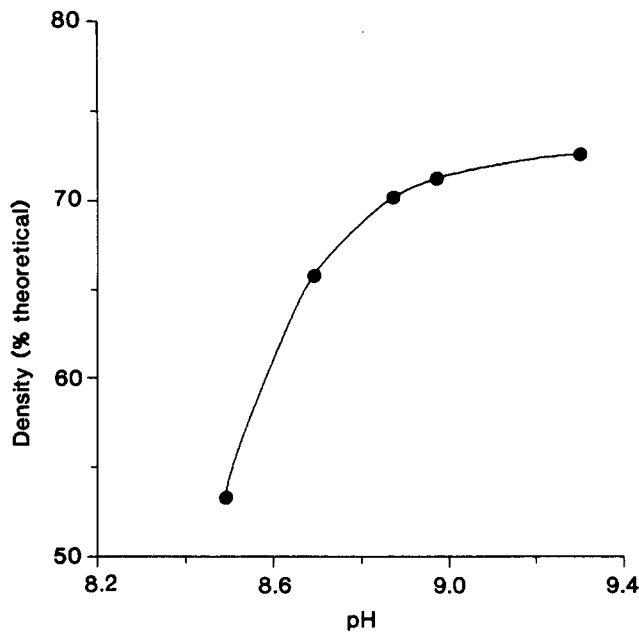
Fig. 5. Variation of green density of slip-cast Si_3N_4 with the pH of the slip.

Fig. 6. The acoustic velocity in the cast layer (v_c) as a function of time, estimated using eqn (3). (a) pH = 8·87, (b) pH = 8·3.

slip, in a measurement made prior to casting. For a lower pH of 8·3 (Fig. 6(b)), v_c also tended to the acoustic velocity in the slip, but reached it in a much shorter casting time. This agrees with the earlier observation that a lower pH leads to a faster cast, but also indicates that greater density variations are likely to be present in lower pH casts.

The evidence from the v_c measurements suggests that the density of the cast layer changes throughout its thickness, but that after a certain casting time (i.e. after a certain layer thickness has been cast) the deposited density will thereafter be close to a constant value. It is known from earlier studies of slip casting[1-3] that the ceramic density is expected to decrease with distance away from the mould wall, due to suction and to compaction effects in which some time-dependent rearrangement of particle networks is expected, especially in the lower pH casts. An additional influence on density gradient may be the transport of finer particles to pores within the larger particle network, which occurs preferentially in the initially cast region of the layer.[12] The acoustic data is consistent with such a density variation. The effective acoustic velocity also decreases with distance from the wall, and although the theory for acoustic velocity changes in fluid-saturated layers of particles is complicated, it would be expected that the acoustic velocity would decrease with a denser packing of ceramic particles (the wave exists primarily in the fluid, and not in the ceramic particles with very different acoustic properties). The ultrasonic experiment has thus demonstrated that it is possible to follow this change in
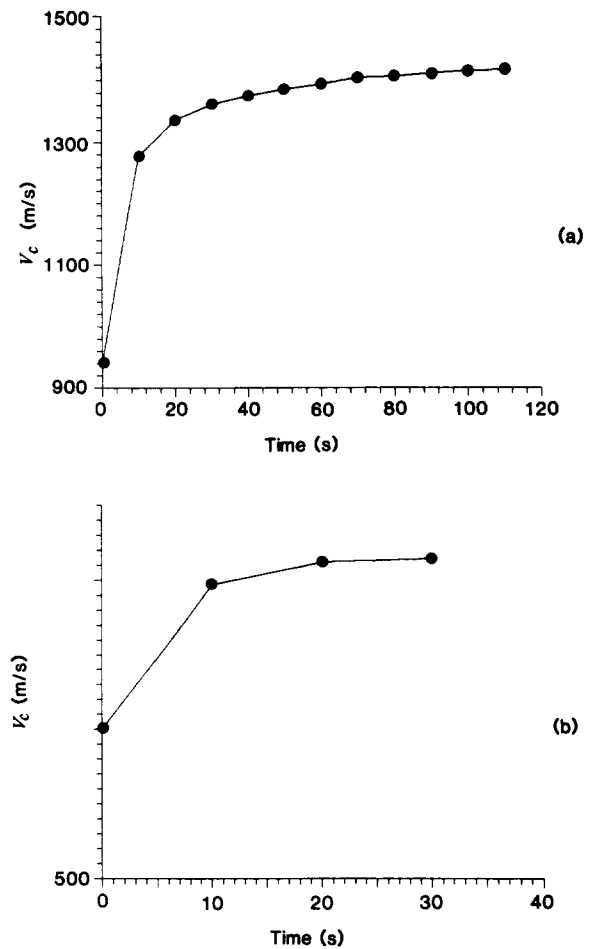
density, although it must be remembered that at a particular cast thickness, the velocity v_c is averaged throughout the total thickness.

Viscosity measurements were also undertaken on the slips, to determine the relationship between viscosity, casting rate and pH. The viscosity was, as expected, a strong function of pH, and as mentioned earlier, was also a function of the shear rate used in the measurement. This behaviour is shown in Fig. 7 for several pH values. At pH = 8·38, which resulted in a thick slip (and a high casting rate from Fig. 5), the viscosity was a maximum. This pH is close to the neutral pH of the Si_3N_4 slip. At this pH value, slightly thixotropic behaviour was observed, but this was reversible, i.e. identical viscosity/shear behaviour was seen after reblending and degassing. At higher pH values, no thixotropy was observed, but at pH values of 8·8 and 8·98, the viscosity was considerably lower than at 8·38. For all three viscosity values, the slips exhibited pseudoplastic behaviour, with the viscosity decreasing with increased shear rate. At pH 9·3, the viscosity was a low, near constant value, the slip being essentially Newtonian in behaviour.
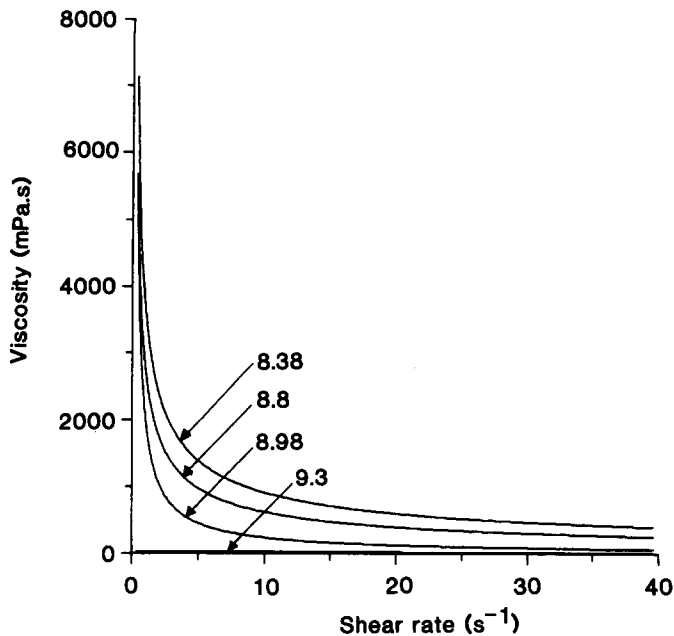
Fig. 7. Viscosity values at different shear rates, for four Si_3N_4 slips with selected pH values.

It is interesting to investigate the effect of viscosity on the casting kinetics. This was discussed briefly earlier, in that the slope of an x^2 versus casting time (t) graph was seen to decrease with an increase in pH in Fig. 4. In addition, Fig. 7 indicated that the viscosity of the slip decreased with an increased pH. To establish a quantitative relationship between slip viscosity and casting rate is complicated, in that the viscosity changes with shear rate in the viscosity measurement. To indicate the type of correlation that exists, a standard shear rate of $13.2\,s^{-1}$ was chosen, where the viscosity of the Si_3N_4 slips was not changing too rapidly with shear rate. At this shear

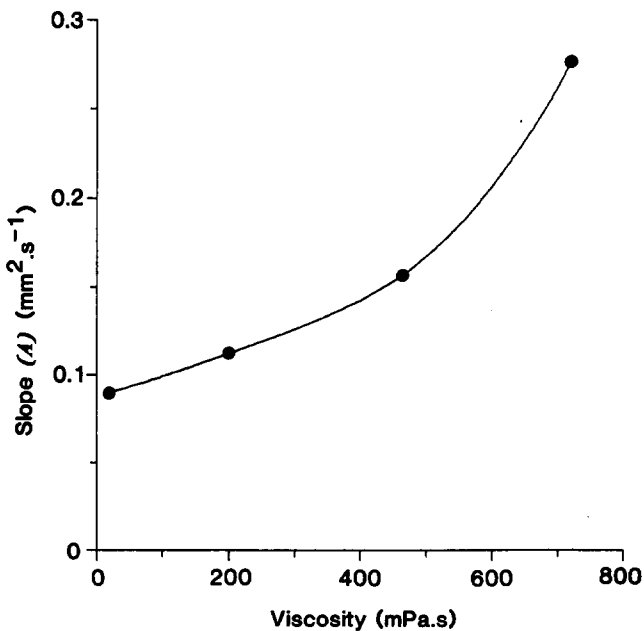rate value, the slope of the x^2 versus t graph was plotted against viscosity as in Fig. 8. This indicates that the casting rate, estimated from the ultrasonic data, does in fact increase with viscosity, in a continuous fashion.

4 Conclusions

The above has demonstrated that an ultrasonic method can be used with some success in slip casting to monitor the casting kinetics of Si_3N_4. It has been shown that the casting rate is a function of both slip pH, and the resultant viscosity. The casting rate has also been linked to the green density of the deposited layer, where it has been shown that a lower pH leads to a faster cast, but to a lower green density. It has also been shown from the ultrasonic data that the cast density varies throughout its thickness, as expected. It is thought that the method described can be applied to a wide range of ceramic materials, and to other processing methods such as pressure casting. This will be the subject of further work.

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Fig. 8. The value of the constant A in eqn (1), as a function of viscosity at a constant shear rate of $13.2\,s^{-1}$.