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New method for the measurement of stress in thin drying gel layers, produced during the formation of ceramic membranes

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A new method has been developed for the measurement of stresses in thin gel layers during the drying process. The gel layers under investigation consist of boehmite, and are produced during the formation of γ-Al_2O_3 ceramic membranes. The method is based on the principle of the cantilever beam. Detection of beam deflections is carried out with a laser displacement meter, using a 760 nm infrared laser. Deflections of the beam can be measured continuously during the drying process, making it possible to monitor the stress in the layer also continuously. Examples illustrate that stresses may be as high as 180 MPa. Cracking of gel layers most likely manifests itself by a marked decrease in the stress. Uncracked gel layers may be stressed and subsequently unloaded by slowly lowering and increasing the relative humidity. An increase of temperature at constant air flow and relative humidity leads to an increase of the stress. Lowering the rate of air flow over the sample lowers the stress which is built up. The method which is described here can very probably also be applied to other coating materials, which are dried on rigid supports.

1. Introduction

In recent years, the interest in ceramic membranes, their formation mechanisms and applications (microfiltration, ultrafiltration, catalytic processes and gas separation) has steadily increased [1–8]. Ceramic membranes are of a composite type, with a macroporous rather thick support, and a thin top layer with a pore structure depending on the application. The formation of such a top layer is a three-step process involving preparation of a stable sol (e.g. γ-AlOOH or TiO_2), dip-coating with subsequent drying and calcination (e.g. [1]). Because the gel layers, being the precursors of the ceramic membranes, may not crack, it is of importance to study the buildup of the stress during drying in order to get insight into the parameters that govern the formation of cracks.

In the process of drying of porous gels, one can generally distinguish a constant drying rate period and a falling rate period [9]. During the constant rate period, drying of a free fluid layer takes place. At the end of the constant rate period, the fluid intrudes the pores of the gel. During drying the gel will shrink, and if it was formed as a layer on a porous support by colloidal filtration, extraction of liquid from the wet upper part of the support occurs to prevent the fluid meniscus entering the gel, in order to prevent an increase in the surface free energy. In the case of a supported gel, the layer is restrained from shrinking in a direction parallel to the support which will lead to a buildup of stress in the gel layer. During the second period of drying, capillary forces, due to the fluid menisci in the pores, present a source of stress in the gel layer. The moving drying front within the gel layer may also lead to cracking at pronounced surface irregularities. If the stress surpasses the elastic strength of the gel, or if relaxation (time) is insufficient, cracking will occur. A detailed physical model of the drying of gels which relates the drying behaviour to the buildup of stress, has appeared recently, e.g. [10–13]. This model includes the case of a thin gel layer constrained by a support, but the support is considered dense. To the best of our knowledge, there are no experimental data for the stress in gel layers during drying. The aim of this paper is to describe a method for the measurement of stresses in thin drying gel layers on porous (or non-porous) supports.

2. Concept of stress measurement

Concepts of the measurement of stress in thin layers are summarized by, for example, Hoffman [14] and Campbell [15]. Methods for measuring stresses in thin layers can be divided into several groups. Well-known methods are based on the "bending plate technique", in which the radius of curvature of a support in the form of a wafer is measured as a result of the buildup of stress in the thin top layer. A second technique, called the "bulge deflection method" is based on the

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difference in stress between support and top layer. When the support is etched away in a small circular region under the top layer, the top layer will, as a result of the stress, show a convex or concave shape over the hole, depending on the sign of the stress. The radius of the curvature is a measure for the magnitude of the stress. Other methods apply X-ray diffraction (XRD) techniques (e.g. [16]). Also well known is the cantilever beam technique. Because the supports of the ceramic membranes have diffuse reflecting surfaces, the "bending plate technique" which usually applies interferometric detection of the bending (for example in the case of coatings on silicon wafers), is not very suitable. As for ceramic membranes, both top layer and support consist of metal oxides (for example a γ-alumina top layer and an α-alumina support), the bulge deflection method, in which selective removal of the support is essential, is very difficult to realize. XRD techniques may only be used for the measurement of residual stresses. The cantilever beam method appeared to be the most suitable for the continuous measurement of stresses in thin gel layers [17]. A summary of the concept of this technique is given below.

3. Description of the method

A cantilever beam is a small strip of support material, clamped rigidly at one end. When a stress in the top layer occurs this will lead to bending of the support. The principle is demonstrated in Fig. 1. As a result of stress in the layer and the elastic counteraction of the support, the top layer is under tensile stress, if the support is forced to bend upwards, and under compressive stress if the support is forced to bend downwards (Fig. 1).

The end-deflection, δ, can be measured, and is related to the overall stress, σ, in the top layer by the relation [14, 15, 18, 19]:

$$\sigma = \frac{E_s d_s^2}{3L^2(1 - \nu_s) d_s} \delta \qquad (1)$$

where E is the Young's modulus of the substrate (support), d_s is the thickness of the support, L the free length of the support, ν_s Poisson's ratio of the support, and d_f the thickness of the top layer (film).

The equation is valid when $d_s \gg d_f$, when L is greater than twice the width of the support strip, and when $\delta < d_s$. A more detailed evaluation of Equation 1 can be found in Hoffmann [14] and Campbell [15]. Kinoshita [20] presents a solution for the case when δ is similar in magnitude to d_s. The elastic modulus of the film should then also be known. As in drying gel films, for this quantity, which is time dependent δ must not exceed $> d_s$. Also the layer thickness, d_f, changes during drying. Therefore, the layer thickness should, in fact, be measured as a function of time. However, we assume for simplicity that the layer thickness is constant. As will become clear from examples given at the end of the paper, this will lead to the situation that the initial stresses calculated are too high. But the final (residual) stress will be correct, because it is measured after the shrinkage period. An improvement of the method, in which the layer thickness variation is continuously measurable, simultaneously with δ and time, is at present under investigation.

The accurate and sensitive measurement of the deflection, δ (see Fig. 1) is very important. For the measurement of the deflection there are several possibilities, such as an optical method (with a microscope), magnetic and inductive methods [15], or capacitative methods for electrically conducting supports [21–25]. Also other constructions have been described, in which, for example, the end of the cantilever is attached to a microbalance, which measures the deflection by weight changes [26–29]. Also the electromagnetic sensorhead of a surface probe may be used to monitor the stress, because the needle can detect very small vertical movements [30]. It appeared, however, that most of these methods could not be applied, because either the support material was not suitable for it, or the method was not sensitive enough. Because it is necessary to dry the top layers under conditions of controlled humidity and temperature in a climate chamber, the apparatus must be able to withstand moderate air flows. The consequence is that methods which require that the end of the cantilever is attached to another device (for example, by a thin wire or similar) are also unsuitable. Unintentional movement of the wire may be caused by the air flow, leading to unacceptable noise in the data. We found that detection of the deflection with a laser displacement meter was appropriate [31]. Here, the displacement is measured by a triangular technique and with a detector which is sensitive for lateral displacements (Fig. 2). Such laser displacement meters are commercially available and we used the LC2010/2000 displacement meter/amplifier set from Keyence Corporation, Tokyo, Japan. Fig. 3 gives a schematic picture of the apparatus, including the sensors for measurement of humidity and air flow. Fig. 4

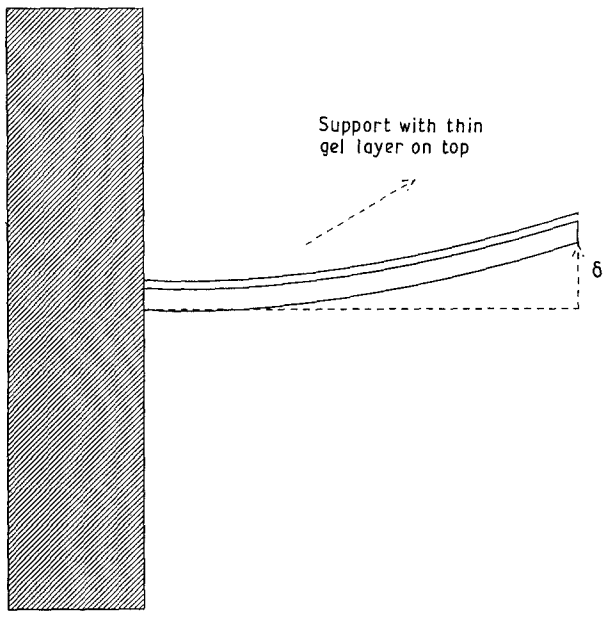

Figure 1 The cantilever beam principle. In the configuration shown here, the stress in the top layer would be tensile.

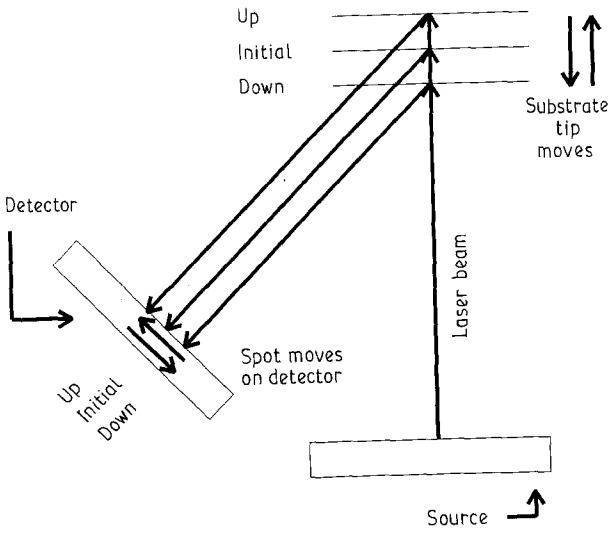

Figure 2 Triangular measurement of the deflection.

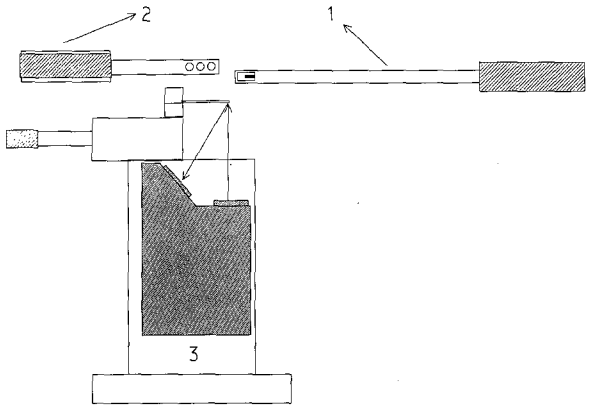

Figure 3 Schematic drawing of the apparatus based on the cantilever beam technique. 1, Anemometer; 2, humidity sensor; 3, cantilever beam apparatus.

shows a photograph of the apparatus in the climate chamber.

The laser displacement meter is calibrated using a reference sample which has steps at known heights. It appeared that the error in the measurement of the deflection is 0.8%. As can be seen from Equation 1, several other parameters appear which should be determined in order to calculate the stress. The Young's modulus of the support (porous alumina in our case) is determined using a four-point bending test. Poisson's ratio is taken to be equal to that of dense alumina [32]. From several determinations of the Young's moduli of the two different porous alumina support types, it appeared that the accuracy of the value of the Young's modulus was, respectively, 6% or 10%. For a series of experiments, the same support type is used, and the errors in these parameters are then of a systematic type. The values of d_s, d_f, and L should be determined for every experiment. The value of d_s is determined by the accuracy of the manufacturing of the support strips. The strips are sawed from larger blocks, and the variation in thickness is, at minimum, 0.02 mm. The relative error is 0.4%. This is acceptable for our purposes. Strips with larger variations are not used for experiments. However, the sawing induces stress, but this residual stress is removed by heating the supports over night at 500 °C. Measurements of residual stress in the supports with a standard XRD stress measurement technique indicated only rarely some almost negligible residual stresses after the heat treatment. The thickness of the support and also its free length are measured by an electronic marking gauge. The free length, L, is measured with an error of 0.5%. The largest relative error is involved in the measurement of the layer thickness. Layer thicknesses are measured by SEM after the experiment. Variations of thickness on one support appear to be caused by the roughness of the support (porous alumina) and variations in thickness between different supports by inaccuracy in time measurement in the dip-coating process. The reproducibility of the layer thickness of the different layers appears to be about 6%. However, this relatively large error may be very moderate on other smoother support materials, and with a better control of dipping time.

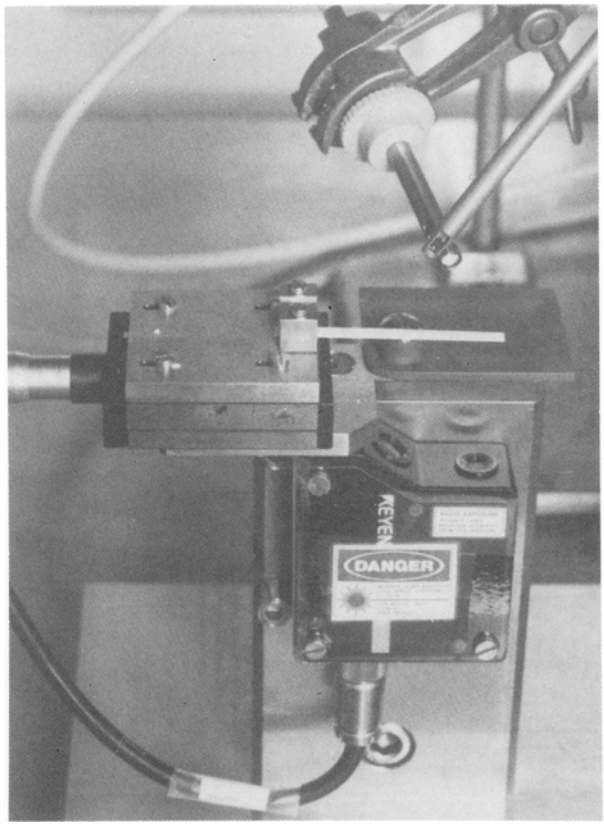

Figure 4 Photograph of the actual apparatus.

Data acquisition is effected by connecting the analogue output signal of the amplifier of the laser (V) to an A/D converter card placed in an XT personal computer. With the aid of appropriate software, the A/D converter card is scanned in very short time intervals. To reduce the noise level, the values of 50 scans (I/O points) are averaged, the average thus constituting one data point. Data points and (real) time are stored at least every 25 s. It appeared that under the conditions applied, the changes in stress (deflections) during drying with a probable physical meaning (i.e. other than obvious noise) took place in

the first 20 min. Experiments of several hours at constant drying conditions showed no more major changes after 20–30 min. The duration of measurements is therefore generally about 30 min.

4. Examples and discussion

Measurements were carried out for γ-AlOOH gel layers on porous α-alumina supports ($E = 65 \pm 4$ GPa). The porosity of the alumina supports is about 40%. Deflections during drying (Figs 5a, 6a, see below) are within the linear range of elastic deformation of the support.

Representative experiments are shown in Fig. 5a and b and in Fig. 6a and c. In Fig. 5a two experiments are shown for gel layers 2 μm thick (Curve 1) and 3 μm thick (Curve 2) on an α-alumina support. The drying conditions were 25 °C and 60% RH and 40 °C and 60% RH, respectively. The rate of air flow was 3.25 $\pm$ 0.2 m s^{-1}. The flow regime close over the surface of the drying gel layer was probably turbulent. Fig. 5a shows the deflection versus time for both curves, and displays additionally a blank experiment, i.e. a measurement of deflection of a porous support with time, without a top layer (Curve 3 in Fig. 5a). The deflections of the 25 and 40 °C experiments were converted

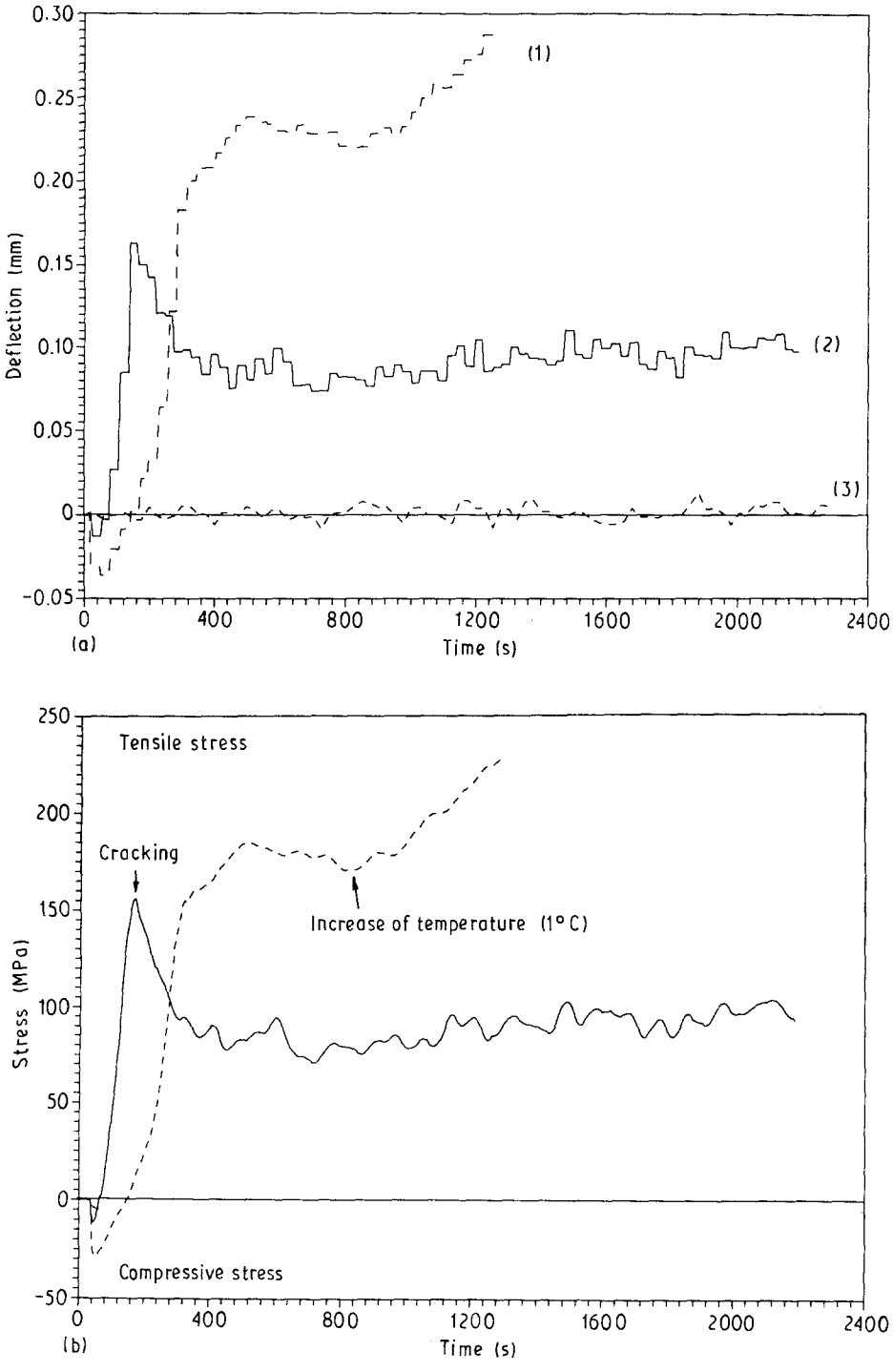

Figure 5 (a) Measured deflection data for two experiments, (1) at 25 °C and 60% RH (layer thickness 2 μm; run 0102902) and (2) at 40 °C and 60% RH (layer thickness 3 μm; run 3103902). The gel is boehmite, the substrate is porous alumina. Air flow over the sample during measurement 3.25 m s^{-1}. A blank experiment (no top layer) is also shown (3). (b) Stress values calculated from the data in (a) by applying Equation 1. Free length (– – –) 5.08 cm and (——) 3.71 cm. Support thickness 0.37 mm (both curves).

to stress with a computer program using Equation 1, with free lengths of, respectively, 5.08 cm (– – –) and 3.71 cm (——) and a support thickness of 0.37 mm (both curves). The data were smoothed with a method based on a combined least squares method and a convolution procedure [33]. In both experiments, the rise in tensile stress after a few minutes is clearly seen (Fig. 5b). The curve for 25 °C clearly shows a second rise in stress after about 900 s. This rise in stress was due to a deliberate increase in the temperature of the climate chamber of about 1 °C. After the experiment, no cracks were observed in the layer. Curve 2 in Fig. 5a and b shows a strong decrease after about 300 s. Afterwards, it was observed that this layer was cracked. The decrease is therefore interpreted as being stress relaxation after cracking. The irregular variations in the stress after the strong rise which were observed by both experiments, is likely to be noise, caused by the turbulence of the air flow in the climate chamber and irregular vibrations due to the cooling unit and pumps of the climate chamber (c.f. the blank experiment). It can be seen that the observed max-

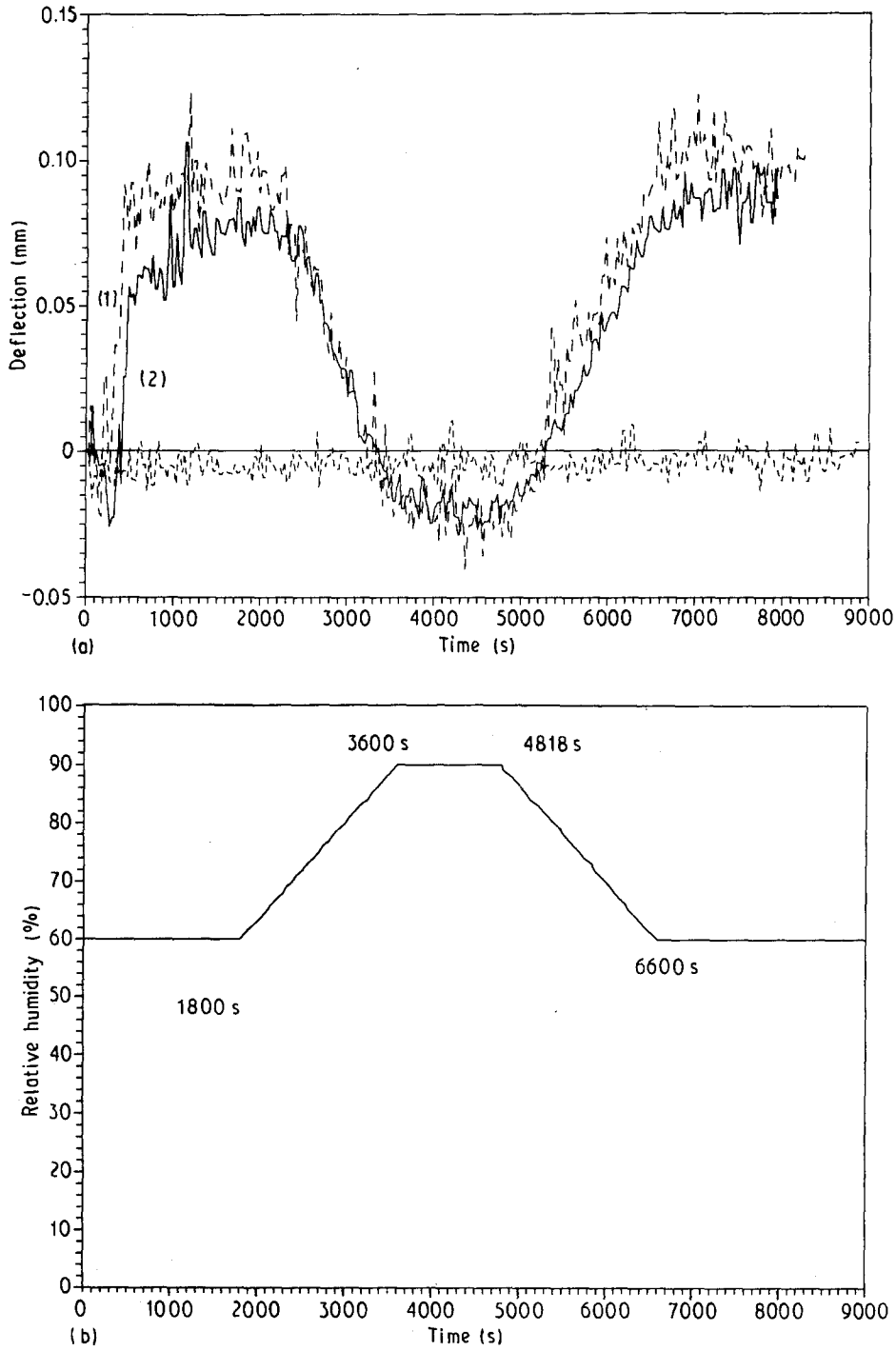

Figure 6 (a) Deflection values for two similar experiments (1, run 2707903; 2, run 3107902) carried out at 40 °C and a changing relative humidity. Layer thickness 5 μm for both runs. Support materials are as in the experiments of Fig. 5. Windscreens are now applied to shield the apparatus from strong air flow. Actual air flow ~ 0.5 m s^{-1}. A blank experiment (no top layer) is shown for comparison (3). (b) The variation in humidity set values plotted from a printout of the computer program which controlled the climate chamber. (c) Stress values calculated from the deflections of (a) by applying Equation 1. Free length 4.86 cm (both curves). Support thickness: (——) 0.51 mm and (– – –) 0.49 mm. Note that the stress returns to approximately its original value when the layer is dried again at 60% RH.

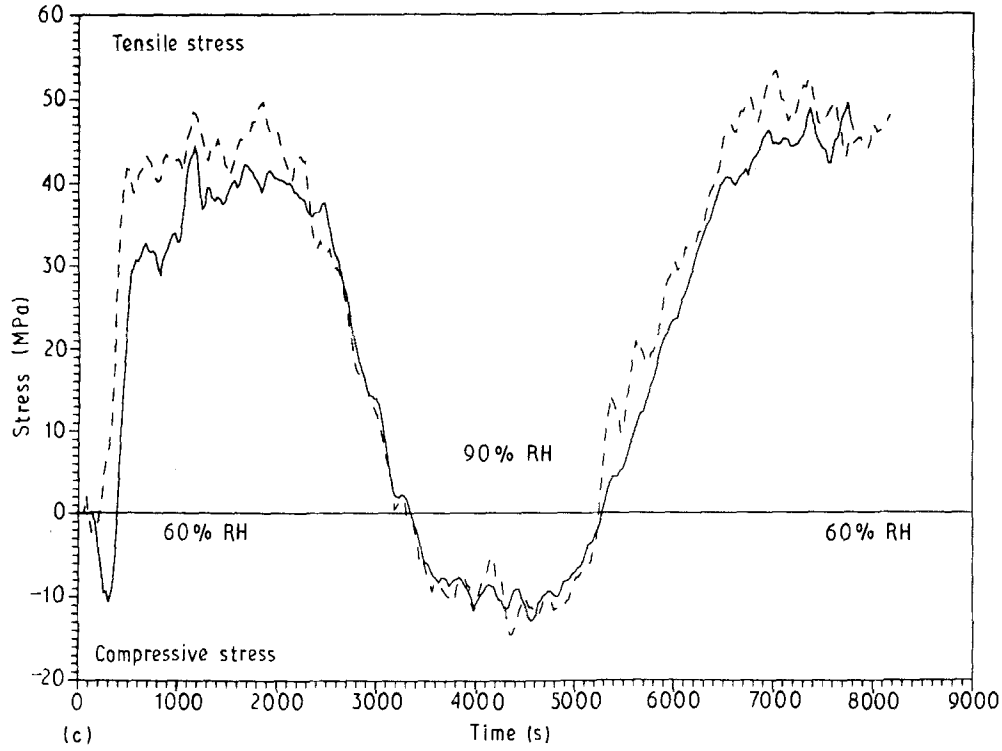

Figure 6 Continued

imum level of the stress for a layer with a thickness of 2 μm is about 180–200 MPa (Curve 1) or 150 MPa for a layer of a thickness of 3 μm (Curve 2). This means that stresses of this magnitude can be induced in these layers without immediate cracking. The initial variations in the stress, at short drying times, including the observed compressive stress may probably be physically meaningful, and related to support effects.

In Fig. 6a two similar experiments for a 5 μm thick boehmite gel layer on supports similar to those above, are shown. In these experiments, the temperature was kept constant, and the relative humidity was changed (Fig. 6b). Also, use was made of windscreens, shielding the apparatus from the strong air flow, a procedure which leads to lower maximum deflections (lower maximum stress) as drying is slower. The air flow was approximately 0.5 $m\,s^{-1}$. Fig. 6a shows the original raw data, and additionally again a blank experiment (no top layer; Curve 3). In Fig. 6b, the variation of the humidity set values is shown. Set values and actual values were generally the same, but when reaching 90% RH, an overshoot to 94% RH was noted which lasted a few minutes. The stress values from Fig. 6c were calculated from the deflections of Fig. 6a using Equation 1 and a free length of 4.86 cm (both curves) and support thicknesses of 0.51 mm (——) and 0.49 mm (– – –). The data were smoothed, similar to the data of Fig. 5a. It can be seen that the stress rises to a level of about 50 MPa when drying at 60% RH. This value is lower than for the previous experiments, because of the windscreens (lower air flow). With increasing humidity, the stress falls and becomes even compressive in nature. When the humidity is lowered again, the stress becomes again tensile and increases to the level previously attained. Uncracked gel layers of boehmite may thus be stressed and unloaded during drying by adjusting the relative humidity. More extensive discussions of the available data will be made in a separate paper which is in preparation.

Layer thickness varies during the process, due to shrinkage. The shrinkage of the constrained layer during drying is not known, but it is probable that this will be considerable. Free lateral shrinkage of the thick layer (1.5–2 mm before shrinkage) was measured by drying layers on mercury and monitoring the dimensions and thickness of the circular or oval patch of gel from the gelling point onwards until drying was complete. Free lateral shrinkage was found to be about 46%, whereas in the thickness direction the free shrinkage is about 75%. The rise in stress in the first few minutes, encountered in the experiments, is very likely due to the constrained shrinkage (c.f. [11]), so the peak value and stresses at greater time values will probably be correct. Only the initial values before the maximum stress (and thus shrinkage) is reached will actually be lower than shown in the curves. The actual stress buildup is therefore also even faster than shown. As the constrained shrinkage perpendicular to the support surface is not known, no value for the error can be given yet. If the free shrinkage in a rather thick layer, as mentioned above, can be extrapolated to a thin layer, a large shrinkage perpendicular to the support may be expected and thus large stresses seem not unrealistic. There is little literature on measured stresses in gels, but stresses above 100 MPa also evolve from measurements of the pressure exerted by a drying gel on a manganese wire ($\pm$ 1350 atm) [34]. Prediction of the stresses from physical models [10, 11] requires the knowledge of several parameters involved in the models which are not known or for which no reasonable assumptions can be made for the present situation. Also, as mentioned before, the

models are not derived for porous supports, but for dense ones. Even if the initial magnitudes of the stress may be somewhat uncertain, the results show that the measurement of stress/time curves will be of importance in research on ceramic membrane formation processes. It is important to know how stresses vary with time in the drying process and when or if cracking occurs. It can be seen that the first minutes of the drying process are crucial, as then large tensile stresses occur. The method can also be used to investigate for example the effect of the addition of polymer binders on the mechanical properties of the thin gel layers, or the influence of the water/alcohol ratio in the sol on the drying stress in the gel.

The method is likely to be potentially useful for other systems where a coating is drying on a rigid support. Some preliminary tests on other support material (glass) have been carried out.

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