Formation of zirconia fibres on unidirectional freezing of a gel

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A zirconia hydrogel prepared by dialysing $ZrOCl_2$ aqueous solution against water buffer was unidirectionally frozen in a cylindrical polyethylene cell which was immersed in a $-78°C$ cold bath at various rates. Freezing rate, R, and temperature gradient, G, at the frozen gel front were continuously measured during freezing. It was found that zirconia fibres longer than 20 mm are formed when $G/R = 2$ to $8°C\,h\,cm^{-2}$. Either lower or higher G/R values gave only fragmental zirconia. The diameter, d, of the long zirconia fibres was changed from 25 to 55 μm with the temperature gradient and the freezing rate according to the equation $d = A/(GR) + B$, where A and B are constants. It was concluded that long fibres of the desired diameter are obtained by controlling both the freezing rate and the temperature gradient. These results were interpreted in terms of cellular growth of ice crystals.

1. Introduction

Unidirectional freezing of a gel was first applied to the preparation of amorphous silica fibres by Mahler and Bechtold [1] in 1980. Since then, amorphous or crystalline zirconia, titania, and alumina fibres have been successfully prepared by a similar method by Kokubo *et al.* [2] and Maki *et al.* [3, 4]. The mechanism of formation of the fibres during freezing is, however, not well understood.

In the present study, the process of formation of amorphous zirconia fibres on unidirectional freezing of a gel was investigated in detail, and the factors determining the length and diameter of the fibres are discussed.

2. Experimental procedure

2.1. Preparation of gel

Reagent grade $ZrOCl_2 \cdot 8H_2O$ was dissolved in distilled water to obtain a 1 M $ZrOCl_2$ solution. The solution was so acidic as to show a pH of 0.5. It was tried to neutralize the solution by adding 1 N KOH solution drop by drop to the solution which was cooled with ice-cold water under stirring with a magnetic stirrer. It was difficult to add more than 40 ml KOH solution to the 100 ml $ZrOCl_2$ solution, without conversion of the transparent solution to a milky solution. The pH of the solution was increased to 0.90 by the addition of KOH solution. About 2.5 ml of the partially neutralized solution was then put in a cellulose tube of 6 mm diameter, 120 mm length and 50 μm thickness, and dialysed against 2 litre distilled water buffer for 96 h. The cellulose tube had micropores of 2.4 nm diameter. The water was renewed every hour during the first 4 h, after the next 20 h and every 24 h during the following 72 h. The water was continuously stirred with a magnetic stirrer. As a result, the pH of the solution increased to the isoelectric point, i.e. about 7 [5]. The solution was transformed into a clear gel within 18 h.

2.2. Unidirectional freezing of the gel

The gel as-prepared in the cellulose tube was put into a polyethylene cylinder 10 mm inner diameter, 130 mm length and 0.5 mm thickness, the side wall of which was lined with a polyurethane foam, 1 mm thick, for thermal insulation. The cylinder was immersed in a $-78°C$ cold bath of a dry ice–ethanol mixture at various rates from 2 to 8 cm h^{-1} by moving the cold bath upward at a constant rate, as shown in Fig. 1. As a result, the gel was unidirectionally frozen upwards. After the whole mass of gel was frozen, it was allowed to thaw on a glass dish at room temperature for 24 h and water was decanted.

2.3. Measurement of length and diameter of fibre

Solid substances left on the glass dish after thawing were examined under metallurgical and scanning electron microscopes. The length and diameter of the fibres obtained were measured under the microscopes.

2.4. Determination of freezing point

The zirconia hydrogel prepared in the cellulose tube by the method described in Section 2.1 were cut into small pieces about 20 mm long. One of them was put into a polyethylene cylinder of the same size as that described in Section 2.2, but not lined with the polyurethane foam. A thin chromel–alumel thermocouple 0.1 mm thick was inserted into the centre of the gel. The whole mass of the gel was rapidly immersed into a $-10°C$ cold bath of ice–salt mixture. The temperature change of the gel with time was measured to determine the freezing point of the gel.

2.5. Measurement of temperature change during unidirectional freezing

Two or three chromel–alumel thermocouples 0.1 mm thick were inserted into the gel which was placed in the polyethylene cylinder described in Section 2.2, and
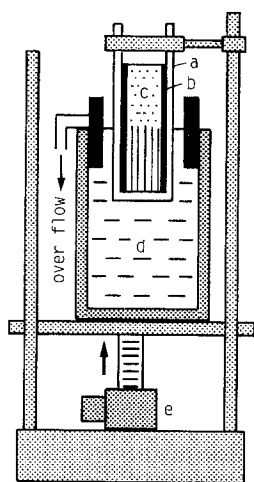
Figure 1 Apparatus for unidirectional freezing of the gel. (a) Polyethylene cylinder, (b) polyurethane foam, (c) gel, (d) dry ice–ethanol cold bath, (e) motor.

their junctions were located at various heights. The gel was unidirectionally frozen by the same method as that described in Section 2.2. During freezing, the temperature of the gel was continuously measured by the thermocouples located at the various heights. Two or three runs were conducted with different sets of thermocouples for one immersion rate. The freezing rate of the gel and the temperature gradient at the frozen gel front were calculated from the results of the measurements.

3. Experimental results

3.1. Length of fibre

The appearance of the solid substances left on the glass dish after thawing are schematically shown in Fig. 2 for the respective immersion rates of the cylinder. Detailed morphologies of the individual fibres have been reported elsewhere [2]. It can be seen from Fig. 2 that long fibres of about 100 mm in length, which are continuous from the bottom to the top of the cylinder, are obtained only for the immersion rates of 4 or 6 cm h^{-1}. At other immersion rates, lower or higher, the fibres are fragmental and shorter than 5 mm, except for portions near the bottom where relatively long fibres, 20 to 50 mm in length, are obtained.

3.2. Diameter of fibre

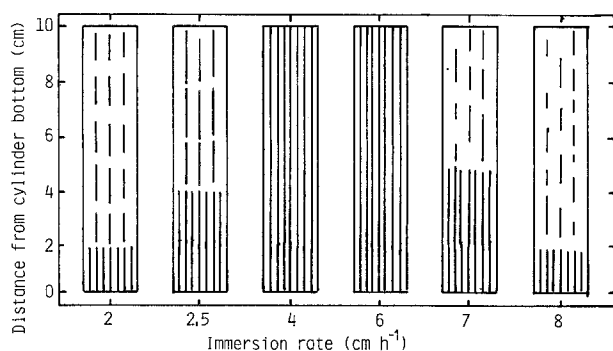Average diameters measured for the fibres longer than 40 mm are shown in Fig. 3 as a function of the distance
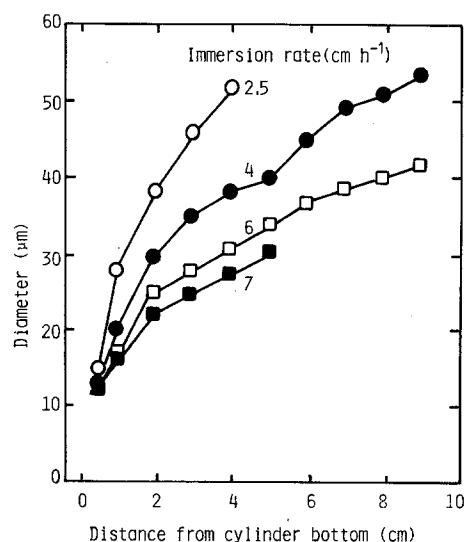

Figure 3 Diameter of fibres as a function of the distance from the bottom of the cylinder.

from the bottom of the cylinder for the respective immersion rates. It can be seen from Fig. 3 that the diameter of the fibres increases with increasing distance from the bottom of the cylinder and that the magnitude of the increase is larger for lower immersion rates.

3.3. Freezing point of the gel

When the whole mass of the small piece of the gel described in Section 2.4 was rapidly immersed into the -10°C cold bath, the temperature of the gel first gradually decreased with time and after a while showed a constant value. This constant value, -0.5°C, was taken as the freezing point of the gel.

3.4. Freezing rate of the gel

Fig. 4 shows the temperature change of the gel at various heights as the cylinder was immersed into the -78°C cold bath at a rate of 4 cm h^{-1}. It can be seen from Fig. 4 that the temperature of the gel at any height is gradually lowered from room temperature to below freezing point with progress of the immersion, although the lowering rate depends upon the height.
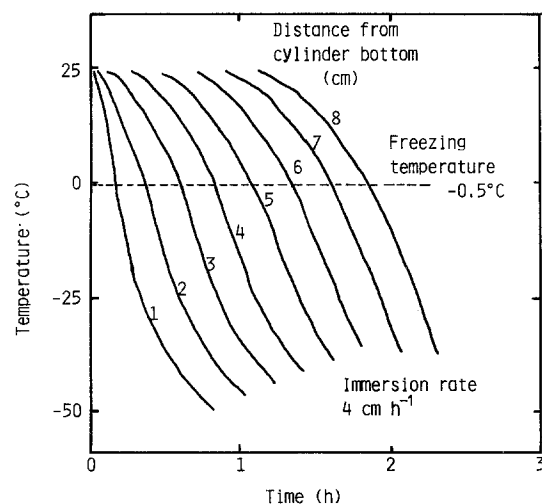

Figure 2 Appearance of solid substances left on the glass dish after thawing.

Figure 4 Temperature change of the gel at various heights of the cylinder with time on unidirectional freezing at an immersion rate of 4 cm h^{-1}.

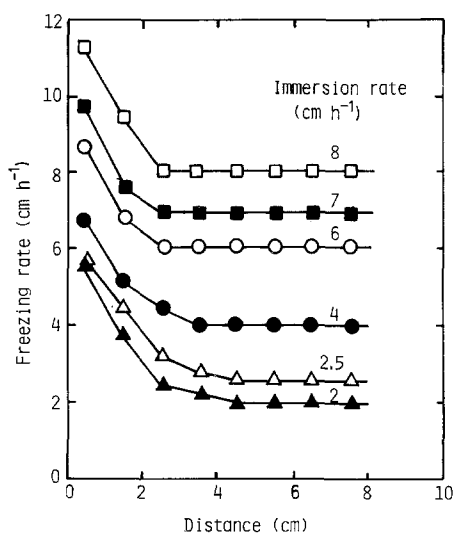Figure 5 Freezing rate as a function of the distance from the bottom of the cylinder.

Figure 7 The ratio of the temperature gradient to freezing rate G/R as a function of the distance from the bottom of the cylinder.

Similar results were obtained for other immersion rates.

From these results, the freezing rate of the gel can be calculated by the following method. For example, times t_1 and t_2 when the gel located at heights of 1 and 2 cm, respectively, reached the freezing point, can be read on Fig. 4. Dividing the distance between these locations, i.e. 1 cm by the period from t_1 to t_2, gives the average freezing rate around 1.5 cm in height. The freezing rates thus calculated at various heights are shown in Fig. 5 for the respective immersion rates. Fig. 5 shows that the freezing rate is generally higher than the immersion rate at the beginning of the immersion, but soon reaches almost the same rate as that of the immersion.

3.5. Temperature gradient at frozen gel front
The temperature gradient at the frozen gel front can also be calculated from the temperature change of the gel during unidirectional freezing by the following method. The rate of temperature change at the frozen
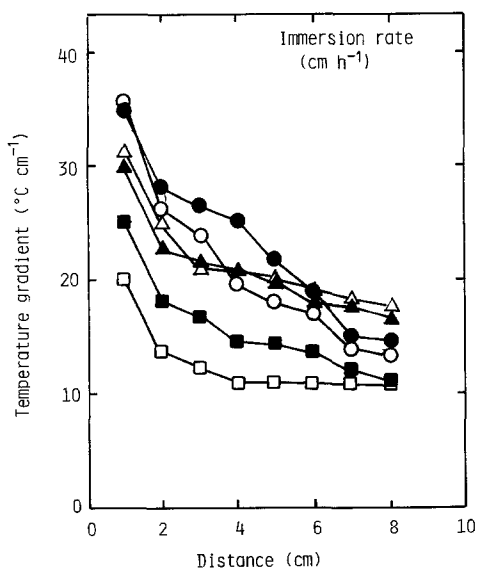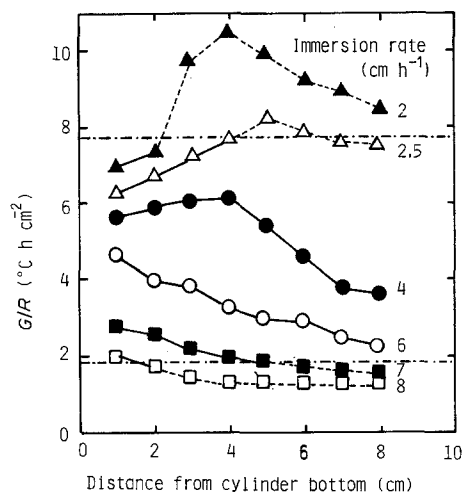
gel at various heights is obtained from the slope of the temperature–time curves as shown in Fig. 4 at the point where they cross the freezing point line. Dividing the rate of temperature change (dT/dt) by the freezing rate (dl/dt) at the corresponding height gives the temperature gradient (dT/dl) at the frozen gel front. The temperature gradients thus obtained at various heights are shown in Fig. 6 for the respective immersion rates. It can be seen from Fig. 6 that the temperature gradient decreases with increasing distance from the bottom of the cylinder for all the immersion rates, although the magnitude of the decrease depends upon the immersion rate.

4. Discussion
4.1. Length of fibre
The ratios of the temperature gradient, G, at the frozen gel front to the freezing rate, R, were calculated from Figs 5 and 6 at various heights for the respective immersion rates. The results are shown in Fig. 7 in which G/R values which gave fibres longer than 20 mm are connected by a solid line, and others are connected by a dotted line. It can be seen from Fig. 7 that the long fibres are obtained only when the G/R value is 2 to $8°C\,h\,cm^{-2}$, irrespective of the immersion

Figure 6 Temperature gradient at the frozen gel front as a function of the distance from the bottom of the cylinder. Immersion rate: (▲) $2\,cm\,h^{-1}$, (△) $2.5\,cm\,h^{-1}$, (●) $4\,cm\,h^{-1}$, (O) $6\,cm\,h^{-1}$, (■) $7\,cm\,h^{-1}$, (□) $8\,cm\,h^{-1}$.
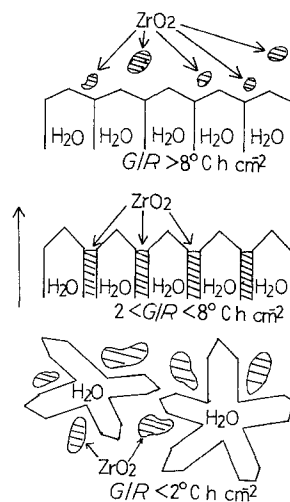

Figure 8 Schematic representation of unidirectional freezing of the gel.

rate. This indicates that an intermediate G/R value should be chosen to obtain long fibres.

When a melt is unidirectionally solidified fulfilling the following condition, columnar crystals of the solvent grow by taking a plane front structure, without forming grooves between them [6]:

$$\frac{G}{R} \geqslant - \frac{mC_0(1 - k)}{Dk} \qquad (1)$$

where m is the slope of the liquidus line, i.e. change of liquidus temperature per unit change of solute concentration, and C_0, k and D are initial concentration, partition ratio and diffusion coefficient in the liquid of the solute. In the present case, the solvent is water, and the solute is zirconia.

When the G/R value is large, the condition given by Equation 1 is fulfilled and columnar crystals of ice grow, taking the plane front structure without forming grooves between them, as shown at the top in Fig. 8. As a result, the solute of the zirconia is expelled only ahead of the ice crystal and fibrous zirconia cannot be formed.

When the G/R value is intermediate, Equation 1 is hardly fulfilled and the columnar crystals of ice grow forming a cellular structure with grooves between them, as shown in the middle of Fig. 8. As a result, zirconia is expelled into the grooves, and condensed and polymerized there into fibrous forms. Long fibres of zirconia are thus obtained in this case.

When the G/R value is too small, the ice crystals no longer grow in columnar form but in radial form, as shown at the bottom in Fig. 8, because largely super-cooled regions are formed ahead of the columnar crystals, and homogeneous nucleation of ice crystals occurs there. As a result, the zirconia is expelled randomly and long fibres cannot be formed.

Fig. 9 shows a longitudinal section of the gel which had been unidirectionally frozen up to half the height of the polyethylene cylinder with an immersion rate of $4\,cm\,h^{-1}$. It can be confirmed from Fig. 9 that the long zirconia fibres were actually formed as a result of the cellular growth of ice crystals when the G/R value was intermediate.

4.2. Diameter of fibre
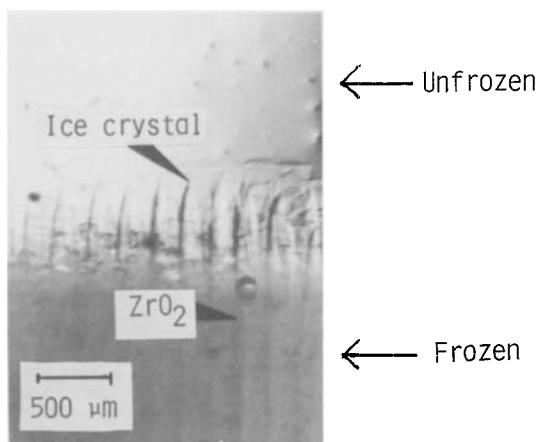Products of the freezing rate, R, and the temperature

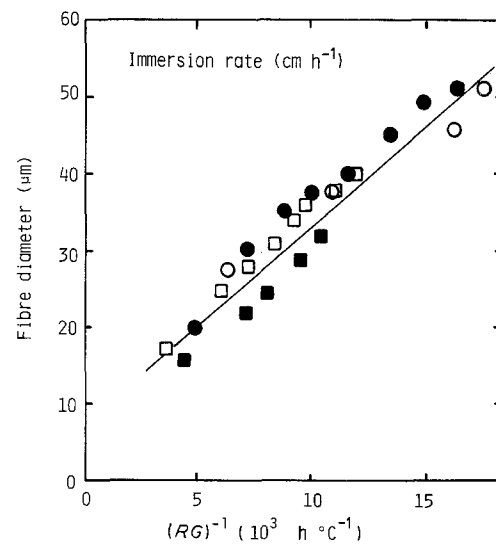*Figure 9* Longitudinal section of zirconia gel being unidirectionally frozen at an immersion rate of $4\,cm\,h^{-1}$.

Figure 10 Fibre diameter plotted against $1/(RG)$. Immersion rate: (O) $2.5\,cm\,h^{-1}$, (●) $4\,cm\,h^{-1}$, (□) $6\,cm\,h^{-1}$, (■) $7\,cm\,h^{-1}$.

gradient, G, at the frozen gel front were calculated from Figs 5 and 6 at various heights of the cylinder for the respective immersion rates. Fig. 10 shows a plot of fibre diameter against $1/(RG)$. It is seen from Fig. 10 that the fibre diameter, d, changes with $1/(RG)$ according to the following equation, irrespective of the immersion rate and the height

$$d = \frac{A}{RG} + B \qquad (2)$$

where A and B are constants. This indicates that it is necessary to maintain RG at a constant appropriate value in order to obtain fibres of a constant desired diameter.

When a melt is unidirectionally solidified with a cellular structure, the intercellular spacing, s, i.e. centre to centre distance of the cells, is given by the following equation [6]

$$s = \frac{A'}{RG} + B' \qquad (3)$$

where R and G are the solidification rate and the temperature gradient at the solidification front, respectively, and A' and B' are constants. The ice crystals in the present experiments might also grow with the cellular structure having the intercellular spacing given by Equation 3 under intermediate G/R conditions. In that case, the diameter of the interstices among the cells are also given by the same type of equation as Equation 3. Accordingly, the diameter of the zirconia fibres changed with $1/(RG)$.

Acknowledgement

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