Monitoring the crystallization of glass

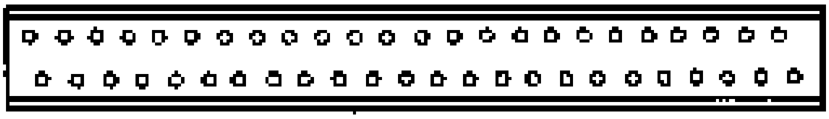
The liquidus temperature, the temperature of maximum crystallization rate, the maximum crystallization rate and the type of crystalline phase in the measured glass can be determined by the gradient method. The principle of the method is that the glass is exposed to a temperature gradient in the gradient furnace for a certain period of time.

Description of measuring equipment

The gradient furnace in which the measurement is made is a horizontal tubular electric furnace with platinum winding (Pt20% Rh wire of 0.5 mm diameter, 12 m length) with a maximum thread density at one end of the corundum tube. The winding density decreases towards the other end. Thus, the desired temperature gradient in the furnace (200 to 700°C) can be achieved. The required power, and hence temperature, is maintained by an automatic regulator. The furnace temperature is measured by a sliding thermocouple connected to a temperature indicator. The thermocouple in the furnace moves horizontally by 1 cm. After measuring the temperature gradient in the furnace, a ceramic stop is inserted into the detected maximum constant temperature zone to perform the measurement in the part of the furnace with decreasing temperature gradient.

Working procedure

The thermocouple is inserted into the furnace up to the stop; the furnace is closed with an asbestos plate to avoid temperature changes, and heated to a temperature above the expected liquidus temperature of the measured glass. A sample of glass is prepared during heating. Normal homogeneity of glass prepared in the laboratory is usually not enough. In this case, the glass sample should therefore be crushed in a mortar, sieved through a fine sieve and remelted. Optionally is possible to repeat this procedure two or three times. The homogeneity of industrially produced glass is usually sufficient. The homogeneous glass sample is roughly crushed and sieved with mesh sizes of 2.8 mm and 1 mm. In this way, about 5 to 10 grams of cullet are prepared, which remain on the finer mesh. It is then degreased in ethanol in a beaker and dried on filter paper. From such treated cullet, the appropriate ones (round or square massive pieces of glass, not scales) are picked with tweezers and inserted into the holes of the platinum bridge. The length of the bridge is 15 cm, the distance between the holes is 0.5 cm, while the bottom row of holes is offset by 0.25 cm from the top - see. picture.



Platinum bridge - top view

Care should be taken that the pieces of glass are not too small, since, after thermal exposure, these small pieces do not fill the whole hole of the bridge and observation under the microscope will not allow the correct reading of the largest crystal size in this hole.

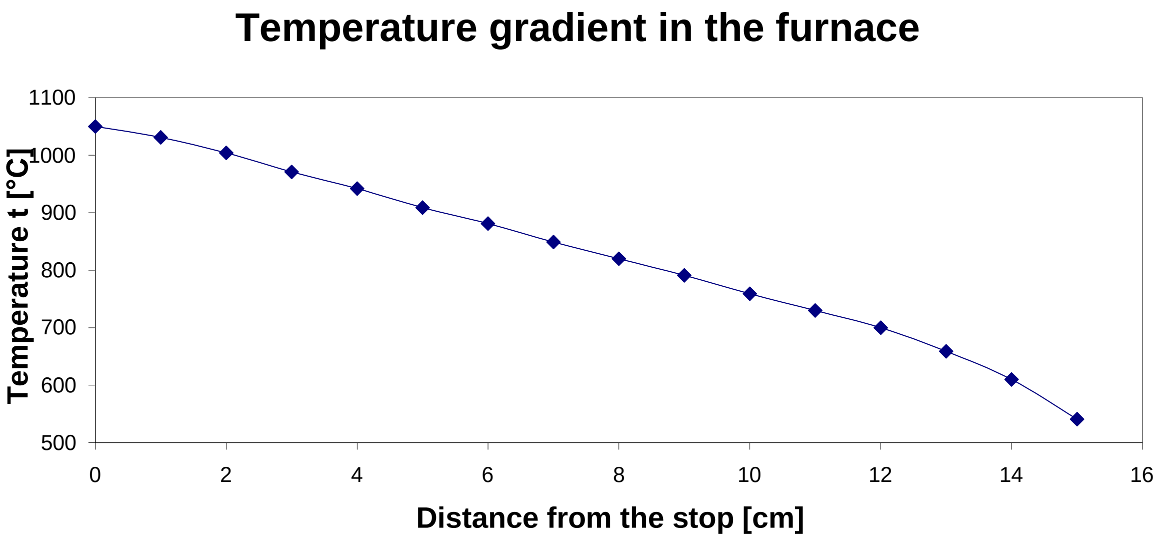
The full bridge with the pieces of glass is inserted up to the stop in the gradient furnace, the thermocouple is inserted under it (see picture) and the time is recorded.

Cross section of platinum bridge, furnace tube and corundum capillary for thermocouple

After about 20 to 30 minutes from the recorded time, the temperature gradient of the furnace is measured (after reading the temperature, the thermocouple shifts 1 cm out of the furnace and after 5 minutes, when the temperature is stable again, read the following temperature; up to 15 centimeters). Each time the thermocouple is moved, the asbestos plate must be pressed against the furnace. The temperature gradient is recorded in a table and graph. The temperature gradient graph is used to determine the temperature that corresponds to which hole in the bridge.

Temperature gradient of the furnace from the temperature maximum (furnace stop) towards the front opening of the furnace

distance [cm]	**t [°C]**	**Distance [cm]**	**t [°C]**
0		8	
1		9	
2		10	
3		11	
4		12	
5		13	
6		14	
7		15	



After some time exposure (1 hour to several hours or more - depending on the chemical composition of the glass), the bridge is removed from the furnace, the time of removal from the furnace is recorded and the bridge is allowed to cool in air.
The holes in the bridge are then examined by the microscope one by one away from the hot end, i.e. from the highest temperature. After several holes without crystals, the first small crystals in the shape of needles or spherolytes appear. The size of the largest crystal is determined in each hole using the rotary eyepiece scale
(1 unit of the eyepiece scale corresponds to 15.2 microns). The axis of the crystal must be parallel to the main axis of the eyepiece, i.e. the units on the main axis of the eyepiece must be perpendicular to the axis of the crystal.

<u>The liquidus temperature</u> (t_{liq}) is determined as the temperature of the bridge hole in which there are no crystals yet, but which is adjacent to the hole in which the first small crystals appeared.

<u>The crystallization rate</u> is calculated from the equation

$$KR = \frac{l}{2t} \quad ,$$

where l is the largest crystal size in μm,
t is the heating time of the bridge in the furnace in minutes.

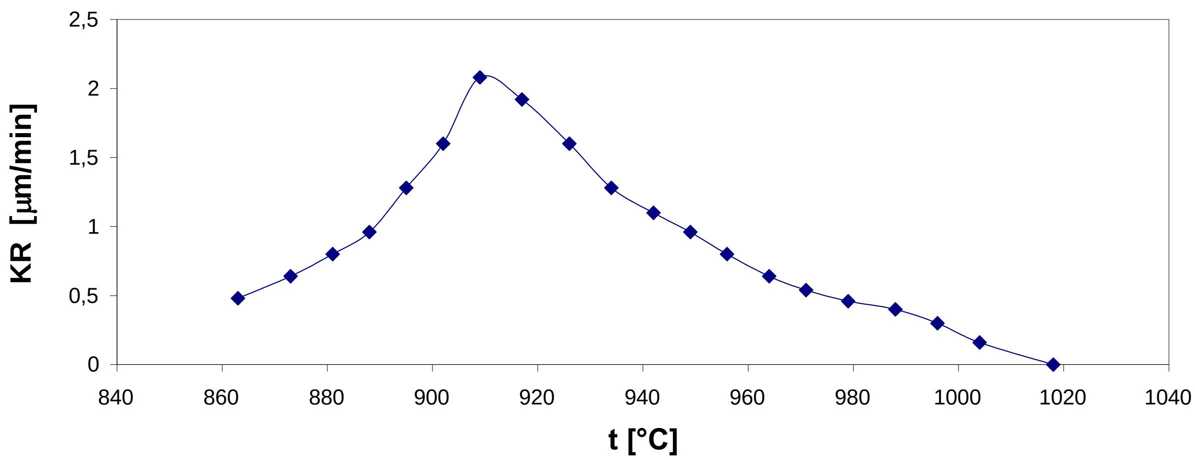
This relationship is used in the case of spherolytes or free-standing crystals that grow from a certain point in two or more directions. For crystals that grow out of the surface (for the platinum interface) and which have grown in one direction from the surface nucleus, it is used to calculate the crystallization rate an equation

$$KR = \frac{l}{t} \ .$$

The dependence of crystallization rate on temperature is shown in the table and graph - see. picture. The liquidus temperature corresponds to the intersection of the curve with the x-axis, i.e. the state where the crystallization rate is zero. The curve runs to maximum at the temperature of maximum crystallization rate t_{maxKR}, which corresponds to the maximum crystallization rate KR_{max} and approaches the temperature axis again at lower temperatures.

Distance [cm]	**Temperature [°C]**	**Number of units**	**Crystal size [μm]**	**KR [μm/min]**

Dependence of crystallization rate on temperature



Conclusion

In conclusion, give t_{liq}, t_{maxKR}, KR_{max} and the precipitated crystalline phase.

Instructions for drawing up the protocol

1. Describe the principle of the method.

2. Describe in details the measurement procedure.

3. Give the relations for calculating the crystallization rate.

4. Process the table and graph of the temperature gradient in the furnace.

5. Process the temperature dependence of the crystallization rate into the table and graph.

6. Determine and report the liquidus temperature, the temperature of maximum crystallization rate, the value of maximum crystallization rate and the precipitated crystalline phase.