

# Apparatus for Crystal Growth Studies in Glass

## A PLATINUM-WOUND DEVITRIFICATION FURNACE

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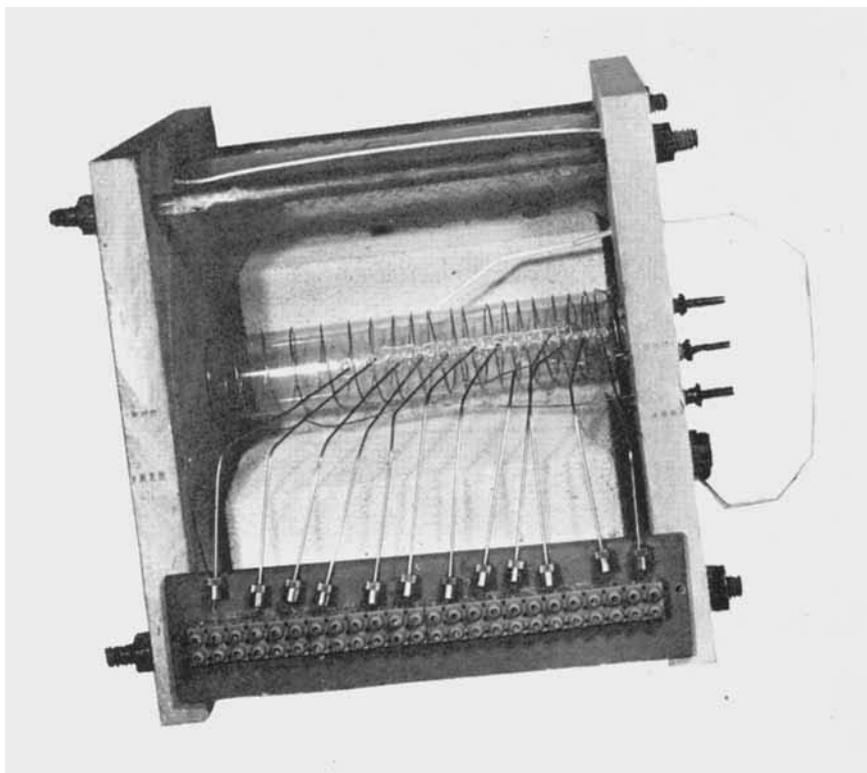
The absence of crystals is normally considered essential for a glass, but the crystalline state is a more stable one than the liquid one. The vitreous state is, therefore, to some extent an artificial condition since all glasses pass through an unstable condition with respect to one or more crystalline compounds on cooling from the melting temperature. It is because a glass has a relatively high viscosity in the crystallising region that complete crystallisation is inhibited and, by passing through this temperature zone as quickly as possible, a glass is produced in the form that is generally known. The temperature at which crystals first appear is designated the "liquidus temperature" and, on cooling the melt below this temperature, the rate of crystal growth rises to a maximum and then falls as the viscosity increases until it is completely inhibited at very high viscosities by the rigidity of the structure. Data on the liquidus temperature and the rate of crystal growth at various temperatures are obviously of great importance to the glassmaker because of the limitations they impose on the manufacturing processes involved in melting, forming and annealing.

Glass devitrification studies are often made by using the platinum boat method described by Silverman (1) and Preston (2). The glass being examined is placed in a platinum boat about 6 inches long and this is then put into a furnace which has a temperature gradient along its length. It is desirable that the boat should be so positioned in relation to this temperature gradient that the expected liquidus temperature comes at about the

centre of the boat. The sample is left under the action of the heat treatment for such a time as to make certain that crystals are formed; the soaking time may be minutes, hours or even weeks as it is dependent on the case with which devitrification occurs. After the heat treatment, the boat is removed and examined by means of a microscope to establish the highest temperature at which crystals have begun to grow. The temperature gradient of the furnace, as well as its level of temperature, must be accurately controlled for the whole of the heat treatment period and may be measured by either a sliding platinum:rhodium-platinum thermocouple or by a series of fixed thermocouples.

Because of the comparatively massive sample involved in this method, the heat treatment time is not precisely defined due to the necessary heating-up and cooling-down periods.

For studies of the rate of crystal growth, very small samples are used so that the glass is brought rapidly into equilibrium with the temperature of treatment and is as quickly quenched when it is removed from the furnace. The condition of the crystals grown is, therefore, frozen in to the sample and they are then examined under the microscope. The rate of growth of the largest crystal obtaining in the sample is calculated from the time of heat treatment assuming the nucleation time to be zero and the rate of growth to be linear. Swift (3) has shown that the latter assumption is correct provided that there is no interaction between crystalline zones.



*This demonstration model of the apparatus for investigating the rate of crystal growth in glass shows the rhodium-platinum furnace element with its centre tapping, the twelve platinum-clad thermocouples for determining the temperature gradient, and the control thermocouple*

The method used in this laboratory is shown in the photograph, which is of a demonstration model of the apparatus. A small horizontal electric furnace is wound with 10 per cent rhodium-platinum wire 1.2 mm in diameter, and the winding is provided with a centre tapping so that the power supplied to the two halves of the furnace can be changed. This enables a variable temperature gradient to be established along the centre section with the temperature level of the whole furnace adjusted to cover the devitrification zone of the glass sample. A sensitive and accurate temperature controller is used to maintain the desired condition over a long period of time. The temperature gradient along the furnace is obtained by means of twelve 1.6 mm diameter JMC platinum-clad platinum : rhodium-platinum thermocouples as shown

in the illustration although the arrangement in practice differs slightly in detail from this.

Each sheathed thermocouple is cemented through a separate hole in a refractory tile at 1 cm intervals so that the thermocouples occupy the centre section of the furnace and extend over the length of the sample holder, with their thermojunctions just above it. A continuous record of their output and hence of the temperature gradient is given by connecting them to a twelve-point electronic potentiometric recorder. A separate thermocouple, placed outside the furnace winding and adjacent to it, is used as the sensing element for the temperature controller. It has been found preferable to employ this separate element in close proximity to the winding to reduce hunting of the temperature about the desired level.

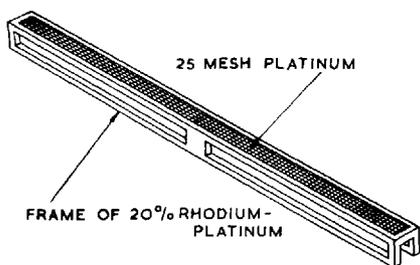
The sample holder consists of a strip of

25 mesh platinum gauze welded to a framework made of 20 per cent rhodium-platinum rectangular strip.

The glass to be examined is crushed, and pieces passing a 20 mesh sieve but retained by the 25 mesh gauze are placed along the top of strip to fill most of the cells formed by the mesh.

Thus we have in effect a large number of separate crucibles in which the glass is retained by surface tension when it is heated.

The sample holder is inserted into the furnace and pushed up against a stop cemented to the refractory tile so that it is in a known position in relation to the thermocouples. Because of the relatively low thermal capacity, the holder quickly attains



*The sample holder used in studying crystal growth phenomena consists of a strip of platinum gauze welded to a framework of rhodium-platinum. Measuring five inches in length, the holder provides a large number of "crucibles" in which the glass is retained by surface tension*

equilibrium with the temperature regime in the furnace. After it has been in the furnace long enough for crystals to have grown to a measurable size, the sample is removed and undergoes rapid cooling. It is then placed in a specially constructed cell attached to the stage of a travelling microscope which is equipped with scales for two directions of movement.

The cell is provided with pins which locate

in holes in the end members of the gauze supporting frame to locate the sample holder in a definite position relative to the microscope scales. The positions of individual crystals on the sample holder are obtained from the readings of these vernier scales and can be correlated with the known temperature gradient.

The sample can be returned to the furnace and the increase in size of particular crystals can be measured after given times of heat treatment to eliminate errors due to finite nucleation times. If the temperature level of the furnace is changed so that, on reinserting the holder, some of the crystals are above their liquidus temperature, they will begin to dissolve and the rate of solution can be measured.

The advantages of this method are as follows:

- (a) the relatively large amount of sample material of large surface area is useful in a glass which provides few nucleation centres;
- (b) fixed thermocouples enable a continuous record to be made and any faults in temperature reading immediately become obvious;
- (c) the glass is prevented from flowing laterally by surface tension; this is of value when studying glasses of low viscosity;
- (d) the sample is available for direct microscopic examination and can also be subjected to further heat treatment if required;
- (e) an adjustable temperature gradient makes possible exploratory measurements when the devitrification range is unknown since a steep gradient can be used; in normal operation a gradient of about  $10^{\circ}\text{C}/\text{cm}$  is used.

#### References

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|---|-----------------|----|----|----|--|
| 1 | W. B. Silverman | .. | .. | .. | <i>J. Amer. Cer. Soc.</i> , 1939, <b>22</b> , 378  |
| 2 | E. Preston      | .. | .. | .. | <i>J. Soc. Glass Tech.</i> , 1940, <b>24</b> , 101 |
| 3 | H. R. Swift     | .. | .. | .. | <i>J. Amer. Cer. Soc.</i> , 1947, <b>30</b> , 165  |