

The kinetics of crystal growth in an aluminosilicate glass containing small amounts of transition-metal ions

J. WILLIAMSON

Nuffield Research Group in Extraction Metallurgy, Imperial College, London, S.W.7

SUMMARY. Quantitative data are presented for the kinetics of crystal growth in an aluminosilicate glass to which a few wt % of a transition-metal oxide had been added. The composition of the base glass was CaO 30, MgO 2, Al₂O₃ 15, SiO₂ 53 wt %, to which the oxides of iron, vanadium, chromium, or zinc were added. Glasses were prepared with a range of high to low valency ratios in cases where the transition metal oxide could exist in two or more oxidation states.

Small quantities of Fe²⁺, Fe³⁺, Zn²⁺, V³⁺, V⁴⁺, and V⁵⁺ were all found to increase the kinetics of crystal growth from the glass phase. The magnitude of the effect is compared with additions of Mg²⁺ to the glass. Cr²⁺, Cr³⁺, and Cr⁶⁺ were found to decrease the rates of crystal growth. Values for the apparent activation energy for crystal growth ranged from ~50 kcal/mole to ~150 kcal/mole. The high values were found to be of the same order of magnitude as that for the activation energy for viscous flow in the glass at the crystallization temperature.

The results are interpreted in terms of the structure of the glasses and current theories on the rate of crystallization of glasses.

KINETIC studies on the crystallization of glasses provide information on both the structure and stability of the glass. The crystallization of glasses in the system CaO–MgO–Al₂O₃–SiO₂ is of interest for the production of glass-ceramic materials. In order to achieve a fine grained glass-ceramic, it is necessary to start with a homogeneous glass, to which a small quantity of a ‘nucleating agent’ is frequently added. The rates of nucleation and crystal growth can then be controlled during the heat-treatment process. Transition metal oxides have been found to be effective additives for controlling the rate of nucleation in many silicate glasses. Klemantaski and Kerrison (1966) have recently described the use of iron blast-furnace slags, which consist essentially of lime, magnesia, alumina, and silica, as a starting material for the production of a glass-ceramic material. The addition of a few wt % of iron oxide, chromium oxide, or zinc oxide to the slag glasses was found to assist in both the nucleation and crystallization of the glass.

In order to understand the complex processes occurring in the glasses during crystallization, a study has been made of the effect of additions of several transition-metal oxides to synthetic oxide glasses in the system CaO–MgO–Al₂O₃–SiO₂. The effect of the oxidation state of the transition-metal ion on both the nucleation and the crystallization process has been observed. This paper reviews the results obtained for glasses containing iron and vanadium oxides (Williamson *et al.*, 1968, 1969), and also the work of Keyworth (1969) on glasses containing chromium oxides.

New data are presented for the effect of zinc oxide on the kinetics of crystal growth from the glass. Some aspects of the nucleation processes involved are described by Rogers (1970) in a separate paper.

Results

The glass composition chosen for the study contained CaO 30, MgO 2, Al₂O₃ 15, and SiO₂ 53 wt %, to which a few wt % of the transition metal oxide was added. The base glass was prepared by fusing together AnalaR oxides and a pure form of silica at 1400 °C in platinum crucibles. Full preparative details have been given in an earlier paper (Williamson, Tipple, and Rogers, 1968), and this procedure was followed for the glasses containing iron, vanadium, and zinc oxides. Glasses containing chromium oxide were prepared at 1500 °C by Keyworth (1969) to increase the limited solubility of chromium oxides in the base glass.

Small pieces of glass approximately 10 mm square were crystallized in electric muffle furnaces. Chromel/alumel thermocouples were placed close to the specimens to measure the crystallization temperature. After heat treatment the specimens were sectioned and a thin section 20 to 30 μm thick made from one half of each specimen. The other half was retained for possible X-ray study or electron-probe investigation. All the glasses studied nucleated and grew crystals from the surface of the glass.



Fig. 1. Typical thin section of the crystalline surface layer of a heat-treated glass containing a small amount of chromium oxide. The crystals are an intimate mixture of wollastonite and anorthite. $\times 300$.

Fig. 1 shows a photomicrograph of a portion of such a thin section. The crystals can be seen to grow as thin needles from the surface of the glass

towards the centre of the specimen. The crystal-growth rates can therefore be derived from the depth of the surface crystallization. The layer of surface crystallization showed remarkable uniformity in thickness over all parts of the thin sections for most of the systems studied.

In all cases, X-ray powder diffraction of the crystalline surface showed that the phases were a mixture of anorthite and wollastonite. From the composition of the base glass, anorthite and wollastonite would be expected to crystallize in approximately equal proportions. It was not possible to distinguish between the crystalline phases in the thin section as individual needles were considerably $< 1 \mu\text{m}$ thick. In some thin sections, very small dendrites approximately $1 \mu\text{m}$ in size were visible at the surface of

the crystalline layer. Similar dendrites were frequently encountered in the bulk of the material and these were later shown by X-ray diffraction to be diopside.

Glasses containing iron oxides. The results for the glasses containing iron oxides have already been published (Williamson *et al.*, 1968) and can be summarized as follows: The rate of crystallization of the glass was found to be dependent on the amount of iron oxide added and also on the state of oxidation of the iron in the glass. Furthermore, it was shown that the rate of crystal growth was proportional to the square of the ferrous ion concentration, as shown in fig. 2. The crystal-growth rates were obtained from five glasses, all containing the equivalent of 5 wt % FeO, but with ferrous/total-iron ratios ranging from 26 to 70 %. The isotherms have been extrapolated in both directions to levels at which the iron would have been present either totally as Fe³⁺ (base line) or as 100 % Fe²⁺. Additions of Fe³⁺ to the glass are then seen to have only a marginal effect on the crystal growth rates compared to equivalent amounts of Fe²⁺.

Glasses containing iron oxides were found to have crystal-growth rates that remained linear with time only when crystallized at the lower temperatures. Fig. 3 shows the depth of surface crystallization versus time for a glass containing 5 wt % FeO in which 26 % of the iron is present as Fe²⁺. At the higher crystallization temperatures the rate of crystal growth increased considerably over a period of several hours. It has been found by using an electron-probe analyser that there is an increase in the concentration of the iron in the glass at the crystal/glass interface, and a corresponding decrease in the concentration of the iron in the crystalline layer compared with that in the bulk glass. It is now thought that the increase in the concentration of the iron at the crystal interface is sufficient to lower the viscosity of the glass in the region of the advancing crystal front and that this leads to the increase in the measured crystal-growth rates. This aspect of the work is to be dealt with in a paper by Scholes.

Glasses containing vanadium oxides. Vanadium can be present in silicate glasses as either V³⁺, V⁴⁺, or V⁵⁺ ions. Glasses were prepared in which the vanadium was present as mainly V³⁺ or V⁵⁺, with small amounts of V⁴⁺ in both cases. The effect on the crystal-growth rates of varying the total vanadium content and the ratio of oxidized to reduced vanadium has been observed (Williamson, Tipple, and Rogers, 1969). Glasses containing mainly V⁵⁺ ions were prepared by adding V₂O₅ to the glass before the final melting. The glasses were analysed for both total and reduced

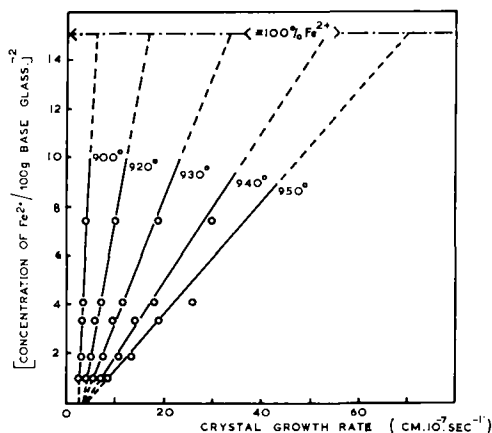


FIG. 2. Rate of crystal growth versus the square of the ferrous ion concentration for glasses containing the equivalent of 5 g FeO per 100 g base glass. The results for glasses with five different ferrous/ferric ratios are shown.

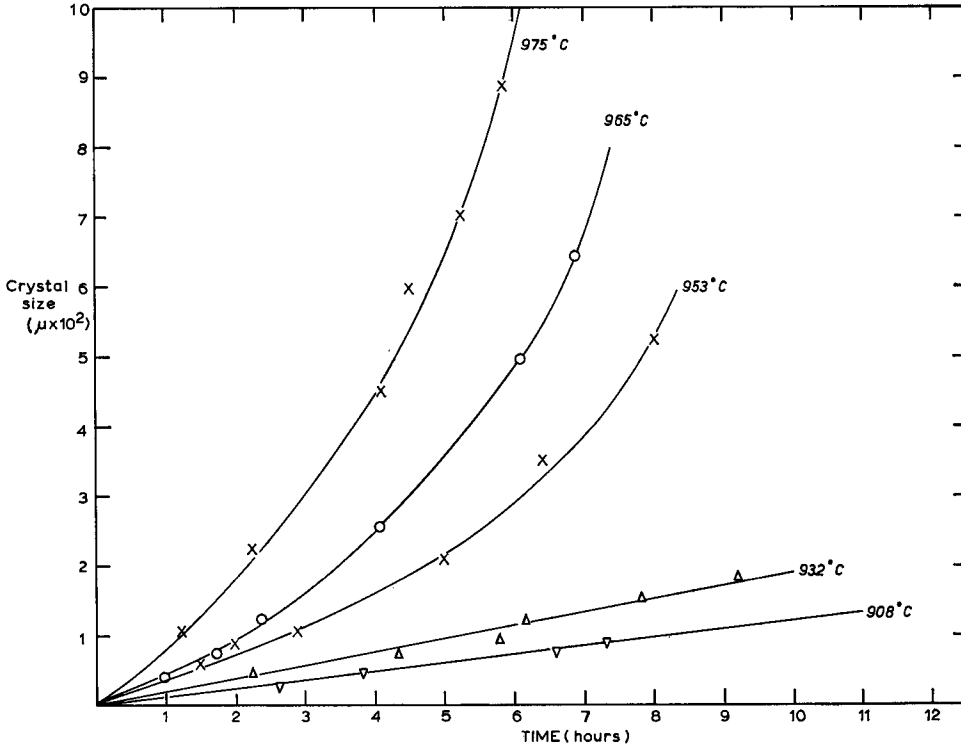


FIG. 3. Thickness of surface crystallization versus time for a glass containing 5 g FeO per 100 g base glass with 26% of the iron as Fe^{2+} .

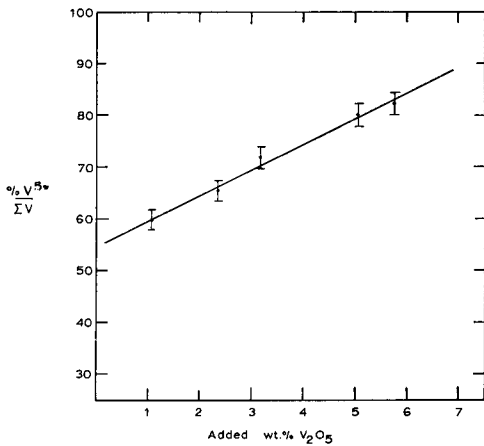


FIG. 4. Proportion of vanadium present as V^{5+} for glasses melted in air for one hour at 1400°C .

vanadium. The spectral evidence of Kakabadse and Vassiliou (1965) shows that the reduced vanadium would be essentially V^{4+} . Fig. 4 shows the results of the chemical analysis. The proportion of V^{5+} increased approximately linearly with increasing concentrations of V_2O_5 in the glass for glasses prepared under identical conditions. Fig. 5 shows the effect of additions of V_2O_5 to the glass on the rates of crystal growth. For crystallization temperatures between 900 and 980°C additions of V_2O_5 to the base glass initially increased the crystal-growth rates. The rates reached a maximum at between 2 and 4 wt% V_2O_5 depending on the temperature of crystal-

lization. Glasses containing mainly V^{3+} ions were prepared by the addition of V_2O_3 to the melt. The results for two glasses containing 2.3 and 4.1 wt % V_2O_3 , of which approximately 80 % of the vanadium was in a reduced form are shown in fig. 6. The solubility limit of V_2O_3 in the silicate melt at 1400 °C appeared to be close to 4.1 wt %,

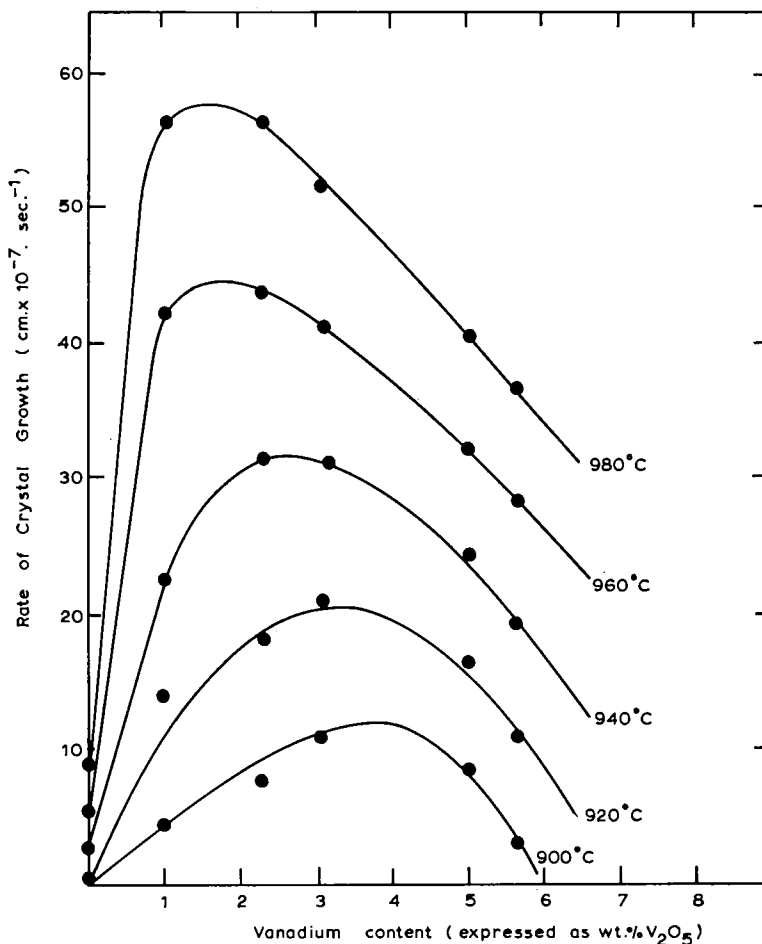


FIG. 5. Rate of crystal growth in glasses containing V_2O_5 .

as the last traces of the V_2O_3 were slow to dissolve. Comparison of figs. 5 and 6 shows that for small additions of vanadium oxide to the glass, V_2O_5 is more effective at increasing the growth rates than similar quantities of V_2O_3 . Little can be deduced about the effect of V^{4+} ions.

Glasses containing chromium oxides. A study of the effect of additions of chromium oxides to the same base glass on both the nucleation and crystal growth rates has been made by Keyworth (1969). Cr_2O_3 is only slightly soluble in these glasses. At 1500 °C

approximately 0.6 wt % Cr_2O_3 dissolved in the melt. The ratio $\text{Cr}^{6+}/\text{Cr}^{3+}$ for glasses melted under an air atmosphere was found to be 0.17. This ratio could be doubled by melting the glass under an atmosphere of pure oxygen. Glasses were also prepared by melting under an atmosphere of forming gas (10 % H_2 , 90 % N_2) and the ratio $\text{Cr}^{2+}/\Sigma\text{Cr}$ was found to be 0.85. Chromium oxides, unlike the other transition metal

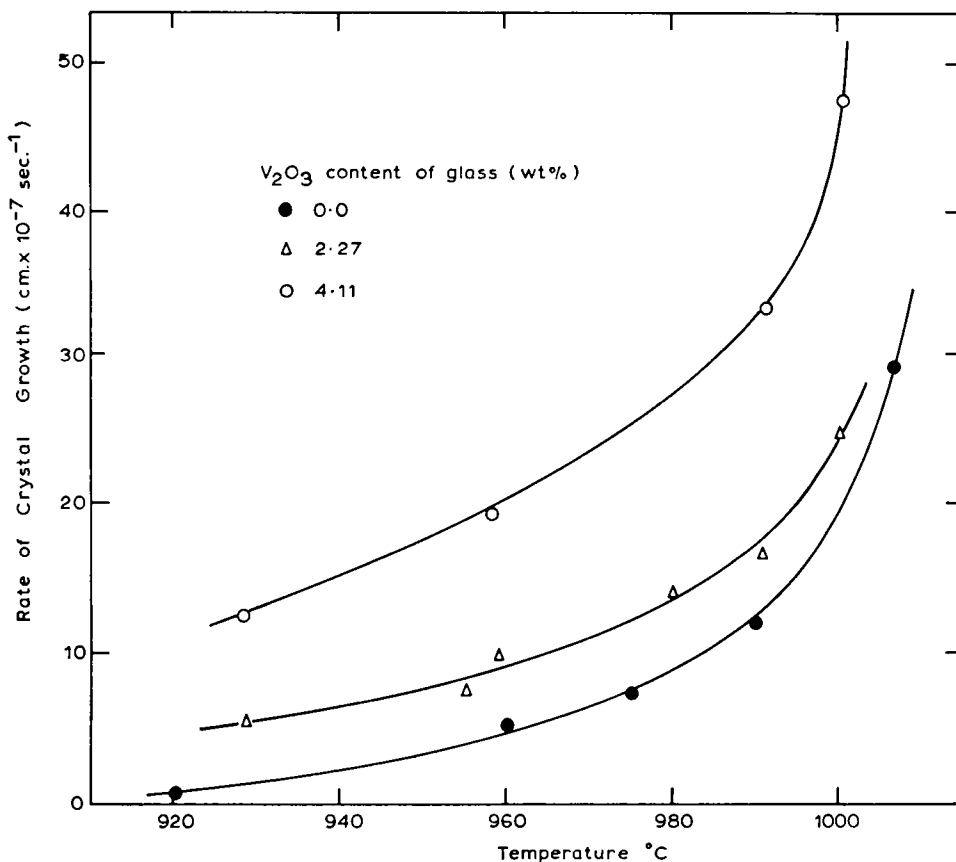


FIG. 6. Rate of crystal growth in glasses containing V_2O_5 .

ions studied, were found to decrease the crystal-growth rates. The results for the glasses melted in air and under reducing conditions are summarized in fig. 7. Glasses melted under oxidizing conditions were found to have almost identical crystal-growth rates to the air-melted glasses. An increase in the Cr^{6+} content of the glass has therefore negligible effect on the crystal-growth rates of the glass. The results obtained from the oxidized glasses have therefore been omitted from the figure for the sake of clarity. The magnitude of the reduction in the crystal-growth rates for the air-melted glasses increased almost linearly with increasing Cr^{3+} content for crystallization temperatures in the range 940–1000 °C. Fig. 8 shows the percentage reduction in the growth rate

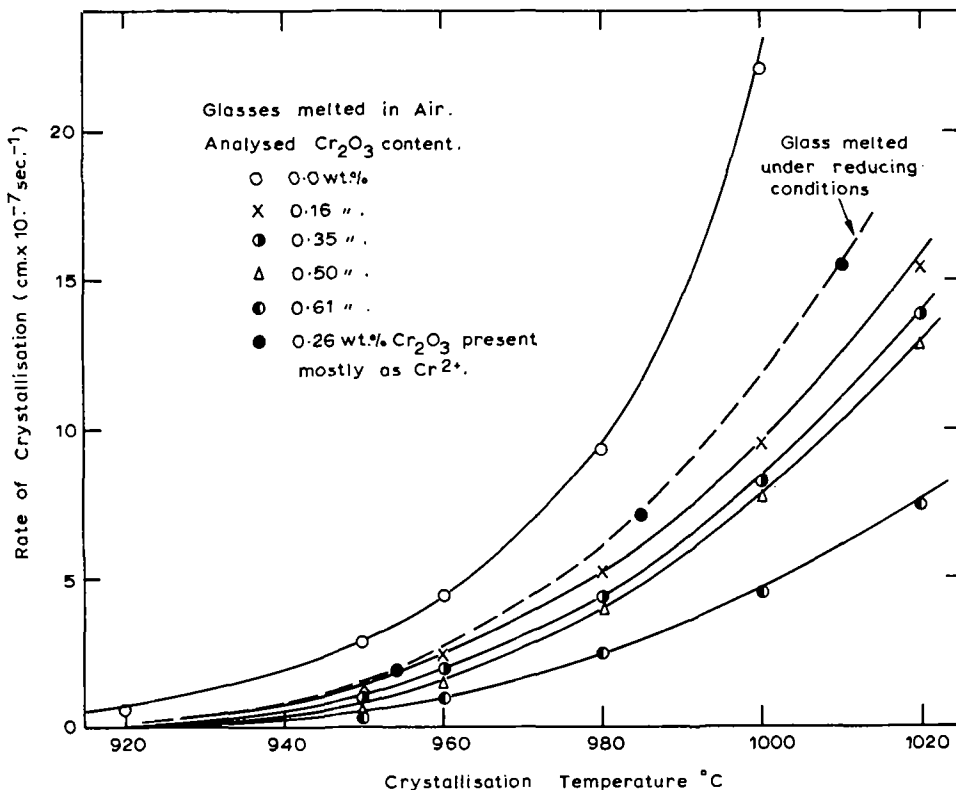


FIG. 7. Crystal-growth rates in glasses containing increasing amounts of chromium oxide, melted in air and melted under reducing conditions.

as a function of analysed Cr^{3+} content of the glass, expressed as wt % Cr_2O_3 . Reduction in growth rate = $(U_0 - U_1)/U_0$, where U_0 = growth rate of base glass at temperature T , and U_1 = growth rate at temperature T for given Cr^{3+} content. The results for the glasses prepared under reducing conditions and containing appreciable quantities of Cr^{2+} indicated that the reduction in the growth rate was not as marked as with the corresponding air-melted glasses. Evaluation of the results is difficult, due partially to the nature of the effect of the presence of small quantities of Cr^{6+} in the air-melted glasses. On a qualitative basis, Cr^{2+} does not appear to reduce the growth rates as much as Cr^{3+} and Cr^{6+} .

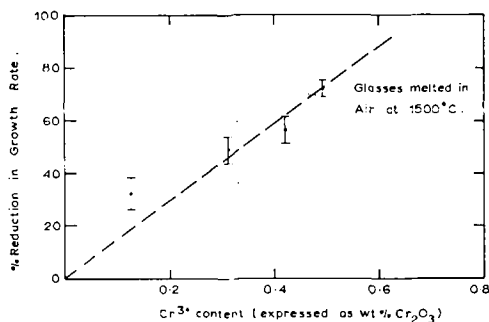


FIG. 8. Reduction in the rate of crystal growth as a function of Cr^{3+} content of the glass.

Glasses containing zinc oxide. Glasses were prepared containing up to 8 wt % ZnO and the crystal-growth rates determined between 900 and 1000 °C. The relationship between the crystal-growth rate and the temperature is shown for the base glass and four different concentrations of ZnO in fig. 9. The results obtained were similar to those obtained for the addition of iron oxide to the glass, although Fe^{2+} had a greater effect

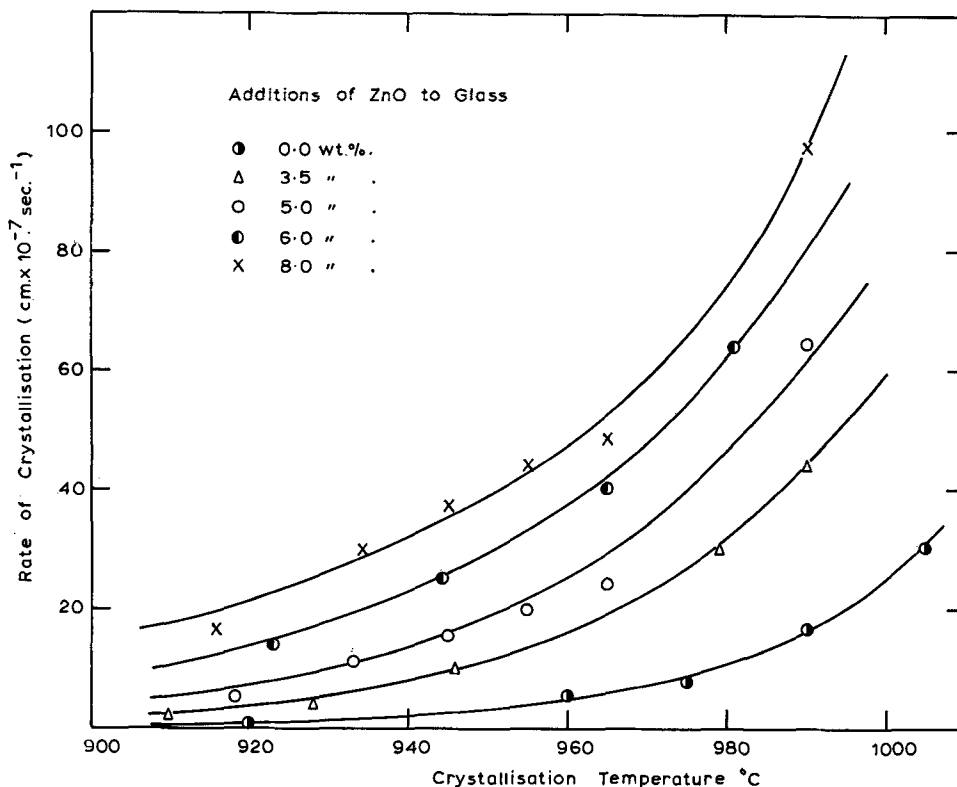


FIG. 9. Rate of crystal growth in glasses containing ZnO.

on the growth rates than Zn^{2+} . Fig. 10 shows that there was a linear relationship between the square of the zinc ion concentration and the crystal-growth rates over a greater temperature range than that observed for the iron-containing glasses.

The apparent activation energies for crystal growth varied from 110 kcal/mole for a glass containing 3.5 wt % ZnO to 65 kcal/mole for a glass with 8 wt % ZnO.

Discussion

Crystal-growth rates in both organic and inorganic glasses initially increase with the degree of supercooling. The growth rates pass through a maximum and eventually reach zero for extreme degrees of undercooling. The general equation for the rate of crystal growth, u , can be expressed as

$$u = a_0 v \exp[-\Delta G''/RT][1 - \exp \Delta G'/RT], \quad (1)$$

where a_0 represents the jump distance, ν is the vibrational frequency, $\Delta G''$ is the free energy of activation for an atom to move from the amorphous to the crystalline solid and $\Delta G'$ is the bulk free energy of crystallization. The first exponential term is known as the kinetic barrier to crystallization and the second exponential term the thermodynamic barrier. For small degrees of undercooling the second exponential term is

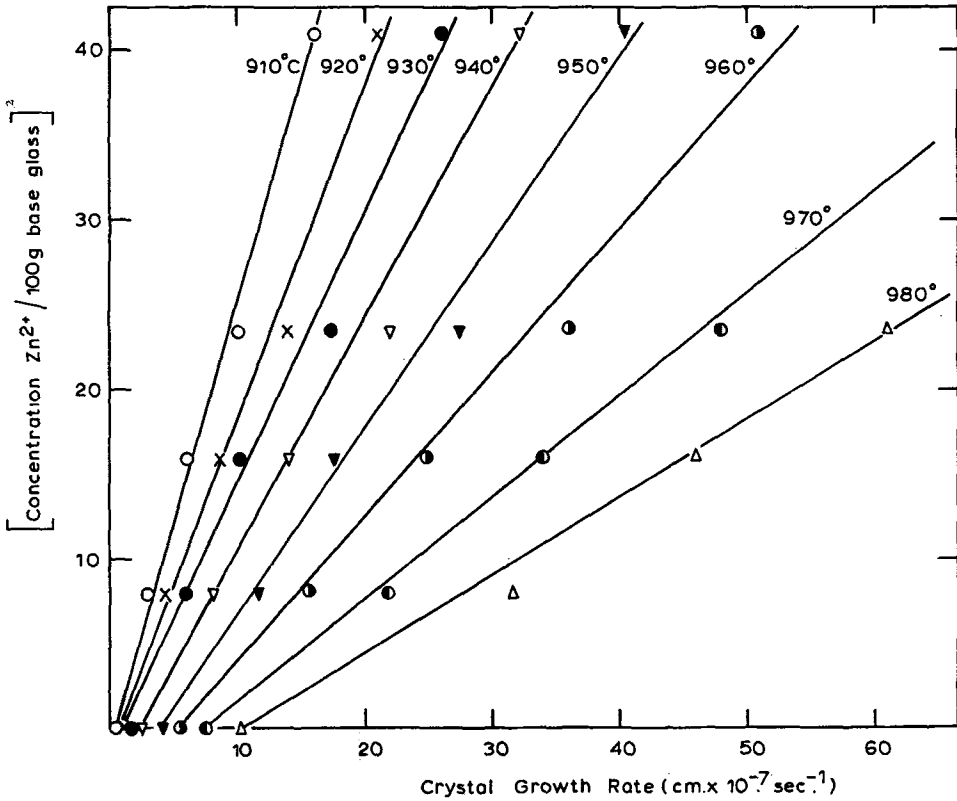


FIG. 10. Rate of crystal growth versus the square of the zinc ion concentration.

dominant and $\Delta G'$, and hence the growth rate, u , increases with increasing degrees of undercooling (ΔT). Eventually the kinetic term becomes the rate-controlling factor and the growth rates then decrease with increasing ΔT . Turnbull and Cohen (1960) suggested that for many substances the activation energy controlling the kinetics of crystal growth was equal to that for viscous flow in the same substance. The kinetic term in the above equation was therefore replaced by one to include the viscosity, η , so that $u = fRT[1 - \exp \Delta G/RT]/3Na_0^2\eta$, where f is the fraction of sites to which a molecule can be attached.

For small departures from the equilibrium temperature $\Delta G \approx L_v \Delta T/T_E$, where L_v is the latent heat of fusion per unit volume and T_E is the equilibrium temperature. Jackson (1958) has characterized materials with small entropies of fusion ($L/RT_E < 2$)

as having rough interfaces and has also shown that materials with large entropies of fusion ($L/RT_E > 4$) have smooth interfaces and anisotropic growth.

Hillig and Turnbull (1956) found that the use of equation (1) predicted values for the growth rates of cristobalite from pure fused silica that were in close agreement with the observed values. It would be unreasonable to expect the equation to satisfy more complex glasses. Multicomponent oxide glasses generally exhibit growth rates that vary less rapidly than equation (1) would predict. In the present case the bulk composition of the glass remains fairly constant, as do the phases crystallizing from the glass. However, a change in the viscosity of the glass with substitution of a different transition metal ion or with a change in the oxidation state of the ion, should have a marked effect on the crystal growth rates. The viscosity of some of the glasses has been measured in the temperature range 900–980 °C, the temperature at which the crystallization had been studied (Williamson *et al.*, 1968). It was found that the presence of a few wt % iron oxide mainly in the Fe³⁺ state slightly lowered the viscosity over the whole temperature range. The same amount of iron oxide present in the Fe²⁺ state lowered the viscosity even further, the effect being most noticeable at the higher temperatures. It was not surprising therefore that glasses containing Fe²⁺ ions had crystal-growth rates greater than glasses containing an equivalent amount of Fe³⁺.

The apparent activation energy for the crystallization of the glasses was calculated from the rates at zero time using the Arrhenius equation $k = A \exp(-E_a/RT)$. The activation energy for crystallization of the glasses containing iron oxides was found to vary from ~30 kcal/mole for a glass containing 5 wt % iron oxide in the Fe³⁺ state, to ~150 kcal/mole for a glass containing the same amount of iron oxide in the Fe²⁺ state. The activation energies increased linearly with increasing proportion of Fe²⁺ ion up to a ratio of Fe²⁺ : Fe³⁺ of 1 : 1, at which point there was a sharp increase in the slope; thereafter the activation energies rose steeply with increasing Fe²⁺ : Fe³⁺ ratio. It appeared that there were two mechanisms for crystal growth in the iron-containing glasses. The activation energy for viscous flow in the glasses containing ferrous ion was found to be ~150 kcal/mole. Glasses containing iron oxide with the iron present essentially as Fe²⁺ are therefore thought to crystallize by the movement of large anionic units to the advancing crystal interface, whereas glasses containing iron oxide with the iron as Fe³⁺ appear to crystallize by the diffusion of single cations to the crystal front.

Small additions of Mg²⁺ to glasses and melts in the system CaO–Al₂O₃–SiO₂ are known to reduce the viscosity (Machin, Yee, and Hanna, 1952) and Zn²⁺ is likely to have a similar effect. On the other hand Cr₂O₃ is known to increase the viscosity of a slag (Higgins and Jones, 1963), and this no doubt accounts for the reduction of the crystal-growth rates for additions of Cr₂O₃ to the glass. There appears to be no information available in the literature for the effect of additions of V₂O₅ on the viscosity of silicate melts or glasses. V₂O₅ itself forms a very fluid melt (Pantony and Vasu, 1968) and so it appears likely that small additions of V₂O₅ to the silicate glass will also reduce the viscosity.

A direct comparison of the effects of the different transition-metal oxides on the rates of crystal growth presents some difficulty. Cr²⁺, Cr³⁺, and Cr⁶⁺ all reduced the

crystal-growth rates, while the other transition ions increased the growth. Less than 1 wt % chromium oxide dissolved in the glass at 1500 °C whereas several wt % of the other oxides were soluble at 1400 °C. The effect of a few wt % MgO on the crystal growth rates has also been determined (Williamson *et al.*, 1968; Keyworth, 1969), and these results can be compared with those of the transition-metal ions. Table I lists the oxides studied and the crystal-growth rates at 950 °C. In order to make a direct comparison between the different transition-metal oxides, the growth rates corresponding to a cation fraction of 2 % have been determined. The oxides of chromium, all of

TABLE I. Rates of crystal growth at 950 °C for a cation fraction of 2 %

Oxide	g/100 g base glass to give cation fraction of 2 %	Rate of crystal growth $\times 10^{-7}$ cm sec ⁻¹	Cation radius	Oxygen-ion attraction <i>I</i>
VO _{2.5}	3.20	~ 35	0.59	2.5
FeO	2.54	32	0.76	0.86
ZnO	2.88	10	0.74	0.87
VO _{1.5}	2.66	8	0.74	1.31
MgO	1.43	4	0.65	0.95
FeO _{1.5}	2.83	~ 4	0.64	1.44
Base glass		3		
CrO	*	< 3	~ 0.84	0.80
CrO _{1.5}	*	≪ 3	0.69	1.31
CrO ₃	*	≪ 3	0.52	3.25

* Solubility limit of CrO_{1.5} ≈ 0.46 cation %.

which reduce the growth rates, are only slightly soluble in the glass, the solubility limit of Cr₂O₃ being approximately 0.46 cation % at 1500 °C.

The influence of the transition-metal ion on the silicate glass will depend largely on the charge and size of the ion. Excluding the chromium ions a rough correlation exists between the ionic potential (Z/r) and the effect on the growth rate. For the divalent ions, as the ionic potential increased the ion exerted less influence on the growth rate. A similar trend was found for the trivalent ions V³⁺ and Fe³⁺.

Dietzel (1942) used the attraction between a cation and the oxygen ion in contact with it as a means of classifying metal oxides in glass-forming systems. The oxygen-ion attraction, I , is defined as $2z/l^2$, where z is the charge on the cation and l is the sum of the radii of the cation and oxygen ion. Cations with $I > 1.6$ were classified as being strongly coordinated to oxygen atoms (i.e. network formers). Values for the oxygen-ion attraction, I , for the cations studied are included in table I. The treatment makes no allowance for the covalent character of the ions. Despite this, the trend is for the oxygen-ion attraction to increase as the rates of crystal growth decreased. Glasses containing V⁵⁺ ions show a marked deviation from this trend. A similar deviation is shown by glasses containing V³⁺ ions. The growth rates for glasses containing V₂O₅ exhibited a maximum in the curve of growth rate versus V₂O₅ content. At a cation fraction of 2 %, the crystal-growth rate was close to the observed maximum. A further increase in the V₂O₅ content

resulted in a lowering of the growth rate. Hence at a cation fraction greater than 2 %, V_2O_5 would appear much lower down in the table. No satisfactory explanation exists at present to explain the observed maxima in the growth-rate curve of the glasses containing V_2O_5 . The phenomena may well be related to the formation of vanadate complexes in the glass. The anomalous position of V_2O_3 in table I is also difficult to explain. This may be related to the V^{4+} also present in the glasses containing V_2O_3 . Little could be deduced of the effect of V^{4+} ions on the crystal-growth rates of the glass.

The evidence obtained from the presence of other transition-metal ions in the glass suggests that the stability of these glasses towards devitrification is conditioned largely by the size and charge on the transition metal ion added to the glass.

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