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The Effect of Vanadium Oxides on the Crystallisation of Silicate Glasses

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The influence of vanadium oxides as catalysts for nucleation and crystal growth in $CaO–MgO–Al_2O_3–SiO_2$ glasses has been investigated. The effect of varying the total vanadium content and the ratio of oxidised to reduced vanadium ions has been observed. No internal nucleation was observed, but the rate of growth of crystals of anorthite and wollastonite from the surface was increased by additions of V_2O_5 and V_2O_3. The values of the growth rates and the analysed V^{5+} content in both oxidised and reduced glasses suggest that V^{5+} ions are the most active species. Increasing concentrations of V_2O_5 in the glass gave maxima in the growth rates between 2 and 4 wt % for crystallisation temperatures between 900 and 980° C.

1. Introduction

Glasses in the system $CaO–MgO–Al_2O_3–SiO_2$ are of interest as potential starting materials for the formation of glass-ceramics. Compositions within this system can be made using metallurgical slags and other waste materials. The achievement of a fine-grained glass-ceramic depends on starting with a homogeneous glass which includes a small quantity of added nucleating agent. This addition is necessary in order to control the rate of nucleation of the crystalline phases from the glass during the subsolidus heat-treatments. Of the large number of nucleating agents for silicate glasses that have been studied, Sawai [1] describes the use of transition metal oxides, including V_2O_5. He suggested that the presence of transition metal ions, capable of valency changes during heat-treatment, may lead to points of local energy difference which result in an increased rate of formation of nuclei. In particular, glasses containing vanadium oxides are of interest since their resistivity/temperature characteristics enable them to be classified as semiconductors. Williamson, Tipple and Rogers [2, 3] have shown that additions of iron oxides to silicate glasses have profound effects on both the nucleation and crystallisation rates within the glass. They found that the nucleation rate was affected by the ferric ions in the glass while the ferrous ions controlled the rates of subsequent crystal growth.

Because of the potential use of vanadium oxides as nucleating agents, it was decided to investigate the effect of vanadium ions in various oxidation states on both the nucleation and crystallisation processes. Such an investigation, taken in conjunction with information already available for other variable valency ions in glass, should help in understanding the role of transition metal oxides as catalysts for nucleation and growth.

2. Experimental

The starting materials for all the glasses were a pure fused quartz powder and "Analar" grade $CaCO_3$, MgO and Al_2O_3. The quartz was crushed to less than 200 mesh and dried at 1000° C. The calcium carbonate was dried at 135° C and the magnesia and alumina at 1350° C. Vanadium oxide was added to the glass as either V_2O_5 (GPR grade) or V_2O_3.

The V_2O_3 was prepared by the reduction of V_2O_5 powder in a stream of forming gas (10% H_2, 90% N_2). The temperature was held at 600° C for approximately 17 h and then raised to 1000° C for a further 6 h to complete the reduction. The lowest liquidus temperature in the system $V_2O_5–V_2O_3$ occurs at 680° C and hence the initial low temperature reduction avoided the formation of a liquid phase. X-ray powder diffraction patterns of the reduced material showed no trace of V_2O_5.

The composition of the base glass was the same as that used for the previous study [2] and contained CaO 30, MgO 2, Al_2O_3 15 and SiO_2 53 wt %. The base glass was prepared in 100 g batches by fusing the dried starting materials in a 70 ml platinum crucible using an electric muffle furnace. The glass was fused, quenched and ground to a fine powder and then remelted. This process was repeated three times to ensure homogeneity of the base glass. The vanadium oxide was added to the powdered glass before the final melting and the time for the final melt was kept to less than 1 h. The object of the short final melting time was to ensure that as much as possible of the vanadium oxide was retained in the original oxidation state.

The glass was finally quenched by pouring the melt in the form of a long thin strip on to a brass plate. The quenched glass was then cut into pieces approximately 1 cm square suitable for heat-treatments and analysis.

2.1. Chemical Analysis

Glasses to which V_2O_5 had been added were analysed for total vanadium content, expressed as V_2O_5 and for the proportion of the vanadium present in a lower oxidation state. Approximately 0.3 g of finely powdered glass was dissolved in concentrated sulphuric acid solution to which a few drops of hydrofluoric acid had been added. The solution was diluted and titrated with 0.01 N $KMnO_4$ to give the reduced vanadium. The resulting solution was then titrated with standard ferrous ammonium sulphate solution to give the total vanadium present. The results are expressed in table I showing the total vanadium present in the glass, expressed as V_2O_5, and the proportion of the vanadium present in the glass as V^{5+}.

Glasses to which V_2O_3 had been added were dissolved in the acid mixture in the presence of a known excess of ammonium metavanadate solution. Ammonium metavanadate oxidises V^{3+} to V^{4+}, and is itself reduced to V^{4+}:

$$V^{3+} + V^{5+} \rightarrow 2V^{4+} .$$

The solution was then titrated with 0.01 N $KMnO_4$ solution to give the V^{3+} present in the glass. Titration with standard ferrous ammonium sulphate solution gave the total vanadium after due allowance had been made for the added ammonium metavanadate solution. Barium diphenylamine sulphonate was used as the indicator for titrations with ferrous ammonium sulphate.

2.2. Heat-Treatments

Small pieces of glass were heat-treated in electric muffle furnaces. The temperatures were measured with chromel/alumel thermocouples placed alongside the samples. All the glasses studied crystallised from the surface. After heat-treatment each of the specimens was sectioned and a thin section 20 to 30 μm thick was made from one half of the specimen. The other half was retained for possible X-ray powder diffraction. Examination of the thin section under the optical microscope showed that all the glasses had nucleated at the surface of the glass, and the crystalline phases then grew as thin needles towards the centre of the sample. In view of this mode of crystallisation, the depth of surface crystallisation or the advance of the crystal front gave the rate of crystal growth. Glasses containing mainly V^{5+} ions showed remarkable uniformity in the thickness of the crystalline layer over all parts of the thin section (see fig. 1). Fig. 2 shows a thin section of a glass containing V^{3+} ions. The crystalline layer was less regular than for those glasses containing V^{5+} ions, showing occasional crystals growing ahead of the general crystal to glass interface.

3. Results

3.1. Crystallisation of Glasses Containing Mainly V^{5+} Ions

Fig. 3 shows the depth of surface crystallisation versus time for a series of crystallisation temperatures for a glass containing 5.7 wt % V_2O_5. The curves remain linear with time indicating a constant growth rate. A similar series of curves was obtained for all the other glasses studied. The results of the crystal growth rates for all the glasses to which V_2O_5 had been added have been summarised in fig. 4. This shows the rate of crystal growth versus V_2O_5 content for a series of isothermal temperatures between 900 and 980° C. The growth rates for the base glass [2] without added vanadium oxide have also been included. The curves show that the addition of V_2O_5 to the base glass initially increased the rate at which the crystals grew. This rate reached a maximum at between 2 and 4 wt % V_2O_5 depending on the temperature of crystallisation. Thereafter, further additions of V_2O_5 decreased the crystal growth rates.

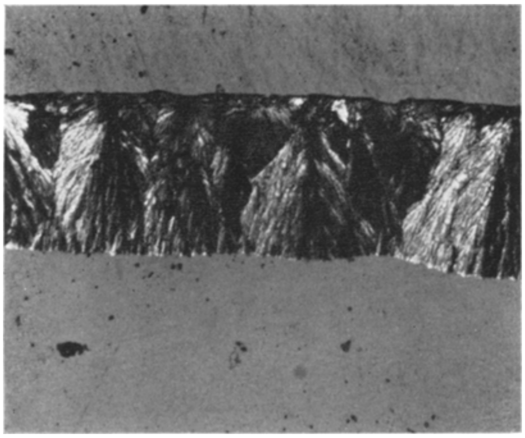

Figure 1 Thin section of a glass containing 3.14 wt% V_2O_5 crystallised at 938° C for 3 h. Crystals are a mixture of anorthite and wollastonite (× 150).

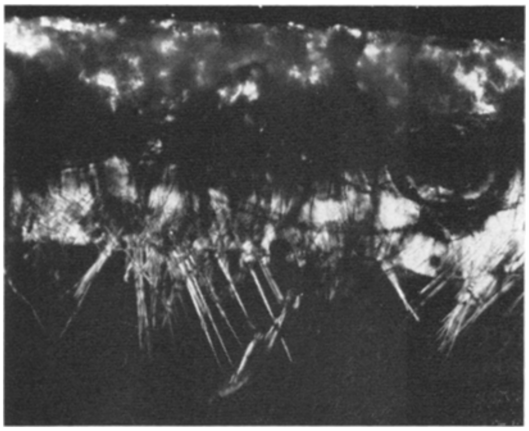

Figure 2 Thin section of a glass containing 2.27 wt% V_2O_3 crystallised at 990° C for 4 h (× 150).

3.2. Crystallisation of Glasses Containing Mainly V^{3+} Ions

The results for glasses containing added V_2O_3 are more limited as only two compositions were studied. These contained 2.27 and 4.11 wt % V_2O_3 respectively; the latter appeared to be close to the solubility limit of V_2O_3 in the silicate melt at 1400° C. The results for the rate of crystal growth in these glasses at temperatures between 920 and 1000° C are shown in fig. 5. Additions of V_2O_3 to the base glass composition increased the rate of crystal growth at all temperatures, the curves showing a similar rate of growth versus temperature distribution as the base glass.

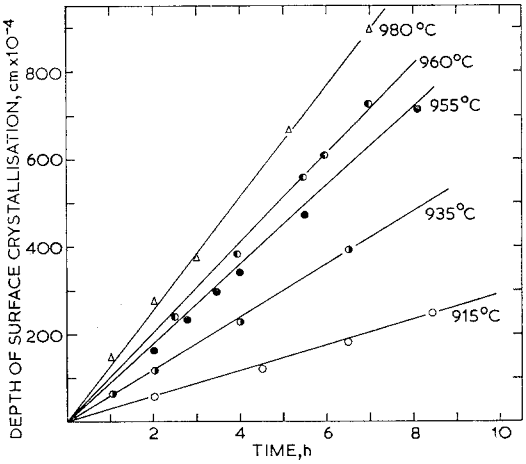

Figure 3 Depth of surface crystallisation versus time for crystallisation of glass containing 5.70 wt % V_2O_5 at temperatures between 915 and 980° C.

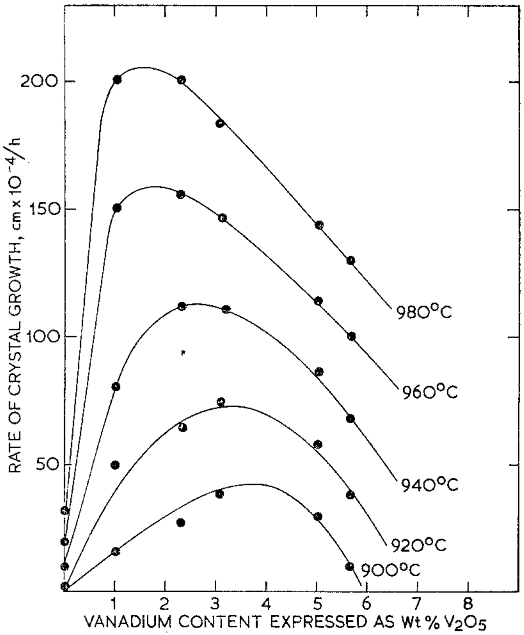

Figure 4 Rates of growth of crystalline surface layers for temperatures from 900 to 980° C for the glasses containing V_2O_5.

3.3 Crystalline Phases

X-ray powder diffraction patterns of the crystalline surface layer were obtained on both a conventional 11.54 cm Debije Scherrer camera and a Guinier focusing camera. The X-ray powder diffraction patterns indicated a mixture

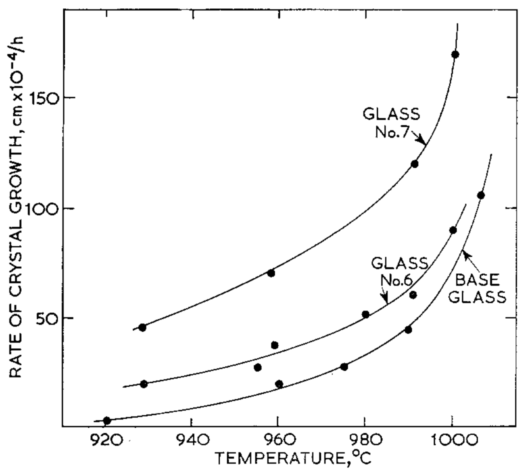

Figure 5 Rate of growth of crystalline surface layers as a function of temperature in glasses containing 2.27 wt % V_2O_3 (No. 6) and 4.11 wt % V_2O_3 (No. 7).

TABLE I Analysis of vanadium glasses.
Glasses with added V_2O_5

Glass no.	Total vanadium expressed as wt% V_2O_5	% vanadium present as V^{5+}
1	1.05	59.0
2	2.34	66.3
3	3.14	74.0
4	5.09	79.0
5	5.70	81.8

Glasses with added V_2O_3

Glass no.	Total vanadium expressed as wt% V_2O_3	% vanadium present as V^{5+}
6	2.27	23.0
7	4.11	20.0

of wollastonite ($CaO.SiO_2$) and anorthite ($CaO.Al_2O_3.2SiO_2$). In the specimens containing V_2O_5, the needles were extremely thin, generally less than 1 μm, and hence it was not possible to distinguish optically between the phases. Glasses containing V_2O_3 showed slight irregularity in the surface crystallisation with a few needles protruding beyond the general layer of surface crystallisation into the residual glass, fig. 2. Comparison with previously published micrographs suggests that the needles are wollastonite [4].

3.4 Internal Nucleation of Crystalline Phases

Glasses containing either V_2O_3 or V_2O_5 were subjected to a variety of both single and double stage heat-treatments. Apart from the occasional internal dendritic or spherulitic crystal no crystallisation of the bulk glass was observed.

4. Discussion

Little is known about the effect of additions of vanadium oxides on the properties of silicate glasses. The optical spectra of V^{5+}, V^{4+} and V^{3+} in sodium disilicate glasses have been investigated by Johnston [5], who showed that it was possible to have all three oxidation states of vanadium present in the glass at the same time. These findings were also supported by Kakabadse and Vassiliou [6]. For this reason, the chemical analysis of the vanadium glasses in table I shows only the total vanadium and the proportion present as V^{5+}. The remainder is present as reduced vanadium which may be either V^{3+} or V^{4+}. Once V_2O_5 had been added to the glass, the melting time was kept to under 1 h. The quenched melt would therefore be far from equilibrium between the various oxidation states. The previous investigation with additions of iron oxide to melts of the same composition showed that, under similar experimental conditions, the equilibrium between Fe^{2+} and Fe^{3+} and the air atmosphere was established only after at least 50 h melting at 1400° C [2]. A study of additions of Cr_2O_3 to similar melts at 1500° C required 25 h for equilibrium to be obtained between Cr^{3+} and Cr^{6+} [7]. Hence by keeping the melting time of the vanadium glasses to the minimum necessary for the formation of a homogeneous bubble free glass, an attempt was made to keep the maximum proportion of the vanadium present in its original oxidation state. Despite this, glasses low in V_2O_5 contained an appreciable amount of vanadium present in a reduced form. Table I shows that the proportion of reduced vanadium present after 1 h of melting, decreased with increasing V_2O_5 content. This would be consistent with the equilibrium reactions proposed by Johnston [8] for the loss of oxygen from the melt.

Data for glasses containing V_2O_3 were more limited, since only two glasses were prepared containing 2.27 and 4.11 wt % V_2O_3 respectively. In the case of the latter glass, the V_2O_3 was slow to dissolve and this could be due to proximity of the solubility limit of V_2O_3 in the silicate melt at 1400° C.

The rates of crystal growth in the glasses containing both V_2O_5 and V_2O_3 showed complete linearity with respect to time for the advance of the crystal front. This was in contrast to the glasses containing small additions of either iron oxides [2] or chromium oxides, both of which exhibited increasing growth rates with time. Electron probe microanalysis of the crystal/glass interface [9] has shown an increase in concentration of either iron oxide or chromium oxide in the glass as the crystals advance into the residual glass. It would therefore appear that these ions are not readily included in the crystalline structures. Both ferrous and ferric ions have been shown to reduce the viscosity of the glass and it is thought that this leads to an increase in the crystal growth rates. Although the viscosity of the chromium containing glasses was not measured, it is thought that a similar effect takes place. The linearity of the crystal growth rates of the glasses containing both V^{3+} and V^{5+} ions suggests that both these ions can be accommodated in the crystal lattices.

Fig. 4 shows that increasing the V_2O_5 content of the glasses initially increases the rate of crystal growth. The crystal growth rates reach maxima at between approximately 2 and 4 wt % V_2O_5, with the position of the maximum depending on the temperature of crystallisation. V_2O_5 itself, unlike P_2O_5, forms a very fluid melt [10] and small additions of V_2O_5 to a silicate glass might reasonably be expected to lower the viscosity of the glass. This explains why the rates of crystal growth initially increase with increasing V_2O_5 content. It does not, however, explain the maximum in the crystal growth rates, nor why the rates decrease so rapidly after the maximum.

The apparent activation energy for crystallisation of the V_2O_5 glasses was calculated using the Arrhenius equation $K = A \exp - E_a/RT$, where E_a is the activation energy. A plot of log K versus $1/T$ gave slopes with apparent activation energies ranging from 62 to 73 $\pm$ 5 kcal/mole.

The effect of V_2O_3 on the crystal growth rates of anorthite and wollastonite in the silicate glasses was more predictable. Fig. 5 shows the growth rates of the two V_2O_3-containing glasses with that of the base glass included for comparison. The limited solubility of V_2O_3 in the melt precluded the preparation of glasses containing more V_2O_3. The general trend is for the growth rates to increase with increasing V_2O_3 content with no sign of a maximum in the growth rates as found with the V_2C_5. The apparent activation energies for crystallisation were 58 and 63 $\pm$ 5 kcal/mole for the glasses Nos. 6 and 7 respectively. The activation energies are of the same order of magnitude as those obtained for the crystallisation of the glasses containing ferric ions [3], but considerably lower than those obtained for glasses with ferrous ions in the glass. In the latter case activation energies of the order of 140 kcal/mole were obtained and found to be of the same order as the activation energy for viscous flow in the glass.

Comparison of figs. 4 and 5 shows that at all temperatures additions of V_2O_5 to the glass were more effective than V_2O_3 at enhancing the rates of crystal growth. The glasses containing additions of V_2O_3 were shown by analysis to contain approximately 20% of the vanadium present as V^{5+}. Hence glasses Nos. 6 and 7 (fig. 5) contain sufficient V^{5+} alone to account for the enhanced rates of crystal growth as compared with those of the base glass. This leads to the assumption that both V^{3+} and V^{4+} have little effect in increasing the growth rates and may in fact tend to decrease them. These assumptions then indicate that the results shown in fig. 4 are attributable solely to the presence of V^{5+} ions in the glass.

All the glasses studied were subjected to a variety of single and double stage heat-treatments in an attempt to induce internal crystallisation of the glasses. Apart from the occasional internal dendritic crystal no nucleating effect due to either V_2O_3 or V_2O_5 was detected. Additions of approximately 5 wt % V_2O_5 were made to a glass of composition CaO 28, MgO 10, Al_2O_3 20, SiO_2 42. This composition lies just within the field of primary crystallisation of spinel; it had previously been found that the addition of a few wt % Fe_2O_3 to this glass was effective in producing a fine-grained crystalline material by a two-stage heat-treatment. V_2O_5 added to the same glass and given similar heat-treatment gave no internal crystallisation. It must therefore be concluded that V_2O_5 and V_2O_3 by themselves do not act as nucleating agents for the alumino-silicate glasses studied. However, taken in conjunction with concurrent work on glasses containing other transition metal oxides, this work should help towards a structural interpretation of nucleation and crystal growth phenomena.

Acknowledgement

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