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DEVITRIFICATION OF ALUMINOSILICATE GLASSES UNDER APPLIED ELECTRIC FIELDS

II. $Al_2O_3 \cdot 2SiO_2$ GLASSES CONTAINING TRANSITION METAL IONS

K. J. D. MacKenzie and I. W. M. Brown

Chemistry Division, D. S. I. R., Gracefield, Wellington, New Zealand;
Chemistry Department, Victoria University of Wellington, Wellington, New Zealand

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The effect of electrolysis on the devitrification of aluminosilicate glasses containing 2–10 wt.% Ti, V, Fe, Co and Ni was studied by DTA. In all cases the devitrification temperature is lowered under electrolysis by an amount greater than that which would be achieved by independently electrolysing or doping with the transition metal ion. The relative effect of the different transition metal ions on devitrification is explained in terms of the strengths of the respective metal-oxygen bonds and the octahedral/tetrahedral site preferences of the ions. The electrolysis mechanism is similar to that of the undoped base glass, but also includes migration of the transition metal ions to the cathode and the possibility of interaction between these species and the residual protons of the base glass.

In a previous paper [1] it was shown that when electric fields are applied to aluminosilicate glasses derived from kaolinite, their devitrification temperature are lowered by as much as 35°. The devitrification temperature can also be lowered by the addition of small amounts of certain transition metal oxides to the glass during fusion [2]; in this case the amount by which the devitrification temperature is lowered depends on the nature and concentration of the transition metal ion present. The present paper describes an investigation of the combined effect of electric fields and transition metal ion doping on the devitrification reaction.

Experimental

The glasses were prepared from the kaolinite described previously. Before fusion, transition metal oxides were added in amounts calculated to give a range of compositions from approximately 2–10 wt.% of the metal ion. The transition metals investigated in the present study were Fe, Ni, V, Ti and Co. In some cases, particularly with V and Ti dopants, it was impossible to prepare samples of the necessary dimensions containing more than about 2% transition metal as these glasses tend spontaneously to devitrify unless quenched extremely quickly. Small globules of the glasses were prepared for electrolysis as in the previous study [1]. The DTA electrolysis cell and operating conditions have been described in the previous paper [1]. The electrolysed product was examined by X-ray diffractometry, i.r. spectroscopy, electron microprobe analysis, optical and scanning electron microscopy as previously described [1].

Results

(1) *Effect of voltage on devitrification*

This was studied using samples containing 2% Fe; since this cation is known to have the greatest effect on the devitrification reaction in the absence of a field [2] its electrolysis behaviour was considered to provide an indication of the maximum effect which might be encountered. The effect of the applied voltage on glass of this composition is shown in Fig. 1, which indicates similar behaviour to the undoped glasses [1]. In contrast to the undoped glasses, however, no relationship appears to exist between the heat-of-reaction ΔH and the applied voltage although the heat evolved from the iron-containing samples is in all cases greater than from the undoped, the average ΔH values being -17.9 and -9.4 kcal/mol respectively. This difference is similar to that observed in the heat-of-reaction values of unelectrolysed iron-containing and undoped aluminosilicate glasses [2]. X-ray examination of the iron-containing glass after prolonged electrolysis at ~50° above the devitrification temperature revealed at the cathode face an extremely crystalline phase with an X-ray pattern (ASTM 11–579) similar to that observed in undoped electrolysed samples and attributed to an alkali aluminium silicate [1], together with crystalline iron oxide. Optical examination of the cathode face (Fig. 2) revealed a pitted surface covered with oxide flakes which on X-ray examination proved to be Fe_2O_3. By contrast, the anode material contained small amounts of poorly crystalline mullite and cristobalite in approximately equal amounts; moreover, the surface was smooth and retained a glassy appearance.

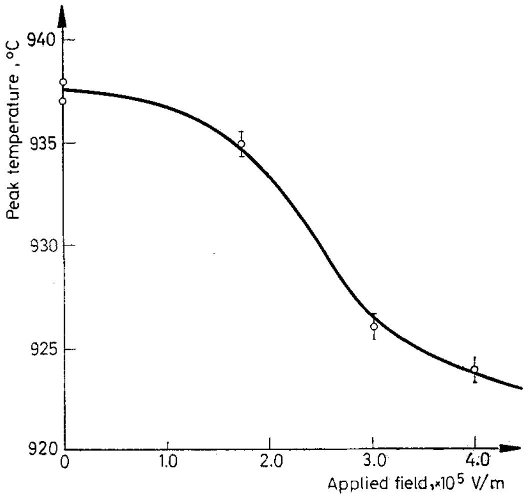

Fig. 1. Variation of DTA devitrification peak temperature with applied electric field. Dopant: 2% Fe, heating rate: 10°/min, ambient atmosphere

Electron microprobe examination of an electrolysed iron-containing pellet sectioned across its diameter showed an increased concentration of iron at the cathode face (Fig. 3). Also clearly evident in the region of the cathode were narrow striations running parallel to the electrode faces and containing extremely high iron concentrations. These striations were found only in a region about 30 μm thick behind the cathode face, and did not occur in unelectrolysed samples, in which the iron was homogeneously distributed both before and after devitrifica-

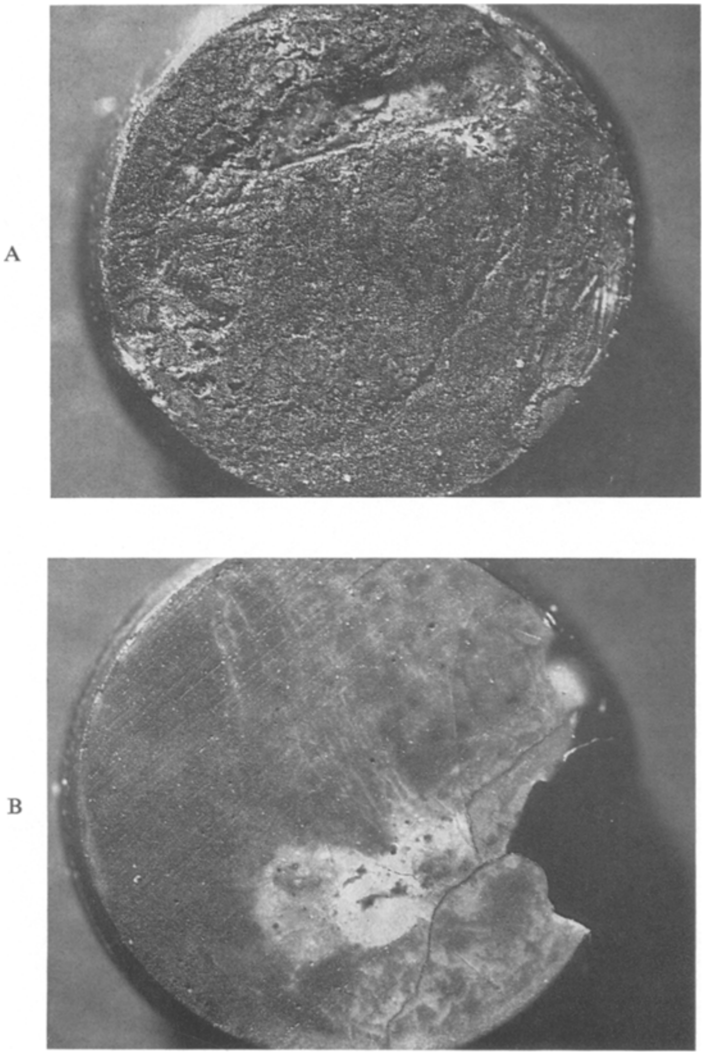

Fig. 2. Micrograph of 2% Fe doped glass after electrolysis for 6 h at 1000°. Magnification: 20×. A: Cathode face. B: Anode face

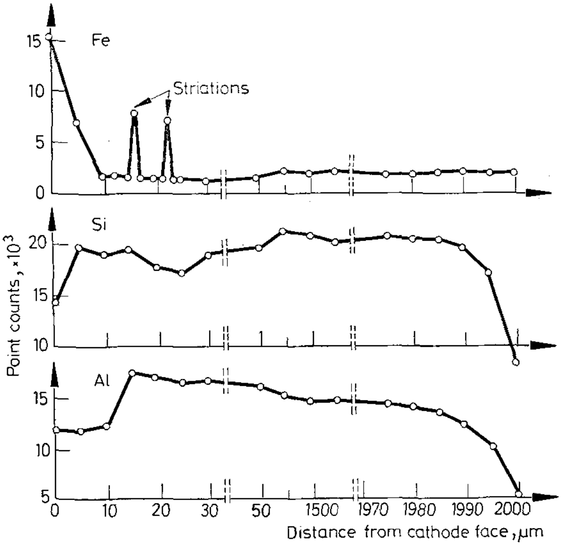

Fig. 3. Electron microprobe point counts along cross section of 2% Fe doped glass electrolysed for 6 h at 1000°

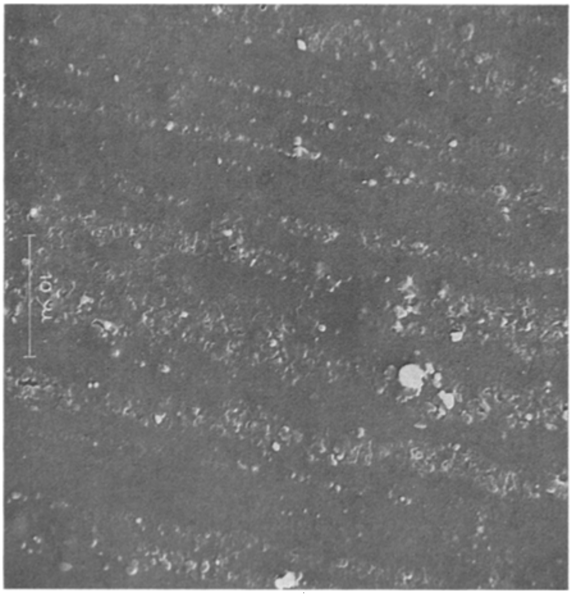

Fig. 4. Scanning electron micrograph of the cathode region of 2% Fe doped glass electrolysed for 6 h at 1000°, showing bubbles associated with the iron-rich striations

tion. The cause of these iron-rich striations is not known at present. Scanning electron microscopy showed them to occur in conjunction with lines of high bubble concentrations (Fig. 4); similar bubbles were found to occur in high concentration at the cathode region of undoped electrolysed samples [1] and are considered to indicate the loss of water or its constituents from regions of high proton concentration [1].

Electron microprobe analysis showed a depletion of both aluminium and silicon at the pellet faces, the depletion being slightly greater at the anode face (Fig. 3). This result may however be an artifact resulting from a slight bevelling of the edges during polishing as appeared to occur with the undoped glass [1]. The microprobe result for iron shows a significant increase in concentration at the cathode, which is considered to result from electrolysis.

(2) *Effect of the transition metal ion on devitrification*

The devitrification temperatures of glasses containing 2% by weight of Ti, V, Fe, Co and Ni are shown in Fig. 5, on which is plotted the values obtained under a field strength of $4.0 \cdot 10^5$ V/m and, for comparison, the peak temperatures of unelectrolysed samples. The mole fractions of transition metal ions in all these samples are comparable, ranging between 0.0717 for Co to 0.0895 for Ti. Also plotted on Fig. 5 is Δt, the reduction in peak temperature due to electrolysis. In all cases the devitrification temperature is lowered by electrolysis, the greatest effect being obtained for the iron-containing glass as is shown by the plot of Δt.

The change in heat-of-reaction ΔH with the transition metal ion is shown in Fig. 6, from which it is seen that in progressing along the periodic table from Ti to Ni the evolved heat increases in a similar manner to the increase in peak temperature. The increase in evolved heat corresponds to an increased resistance

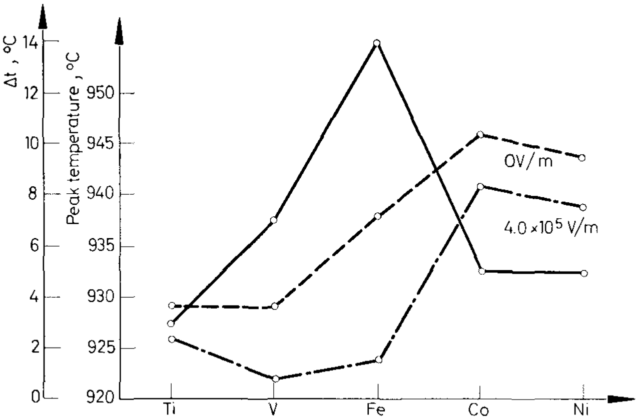

Fig. 5. Variation of DTA devitrification peak temperature and Δt with transition metal ion (2% concentration). Broken lines: peak temperature, solid line: Δt

to devitrification; the Ti and V-containing glasses are extremely difficult to prepare and tend spontaneously to devitrify whereas Co and Ni glasses containing higher metal concentrations (5 – 10% by weight) can be readily prepared. With the exception of the ion-containing glasses the ΔH values recorded under electrolysis are all slightly more exothermic than for unelectrolysed samples. These differences are probably significant, being just outside the reproducibility of the heat-of-reaction measurements (3%). The parameter χ (ΔH unelectrolysed $-$ ΔH electrolysed), representing the field-induced change in ΔH is also plotted in Fig. 6, from which it is seen that the trend in χ across the periodic table is similar to that for Δt.

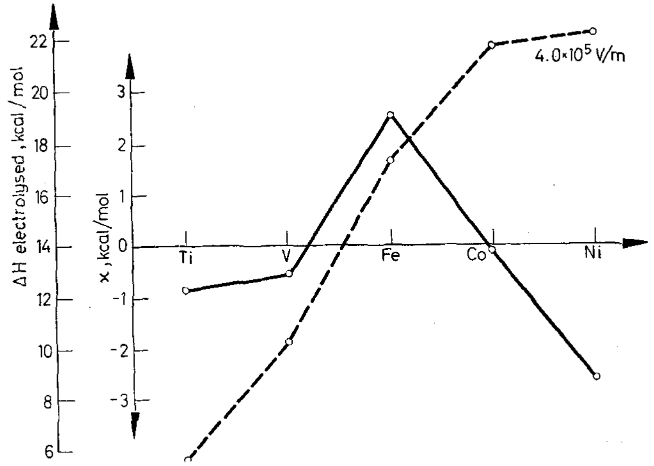

Fig. 6. Variation of heat of reaction ΔH and κ with transition metal ion (2% concentration). Broken line: ΔH electrolysed, solid line: χ

(3) *Effect of transition metal ion concentration on devitrification*

The effect of metal ion concentration was investigated in two of the glasses on which electrolysis had the greatest influence, namely the Fe and Ni glasses. The results of these experiments are summarised in Table 1. In each case, increasing the concentration of transition metal ion decreases the devitrification temperature, but also leads to a decrease in the effect of the electric field, as reflected by Δt (in the case of Ni the effect of the field at the higher concentration is to *increase* the devitrification temperature above the unelectrolysed value). Thus, at higher concentrations, the effect of the transition metal ion increasingly predominates over the effect of the field. The behaviour of the parameter χ suggests that the effect of the field on ΔH is independent of metal ion concentration in the Fe- glass but in the Ni-glass is decreased with increasing concentration. Thus, the heats of

Table 1

Effect of transition metal ion concentration on the electrolysis of aluminosilicate glasses

Ion	Concentration		Field strength, $\times 10^5$, V/m	Peak temp. °C	Δt, °C	$\Delta H_{\text{electrolysed}}$, kcal/mol	χ, kcal/mol
	Wt.%	Mole fraction x					
Fe	2.0	0.0755	3.01	926	12	−20.52	+2.64
Fe	9.76	0.307	3.01	870	5	−23.46	+2.58
Ni	2.0	0.0724	4.00	939	5	−22.33	−2.60
Ni	5.0	0.1681	4.00	920	−6	−23.94	−0.53

reaction of these two glasses under electrolysis exhibit different behaviour when the transition metal ion concentration is changed.

(4) *The product phases formed on electrolysis*

In all glasses electrolysed for several hours, the X-ray diffraction pattern of the anode region revealed reflections corresponding to poorly crystalline mullite and cristobalite in approximately equal intensity, while the cathode region, as in the electrolysed undoped glasses [1] exhibited a strong X-ray pattern of well crystallised alkali aluminium silicate similar to kalsilite (ASTM 11−579). Also occurring at the cathode after extensive electrolysis at the devitrification temperature were small amounts of other crystalline substances, the nature of which depended on the transition metal ion present. Thus, at the cathode the Fe-glass formed Fe_2O_3, the Co-glass formed $CoAl_2O_4$. The appearance of the transition

Table 2

Comparison of observed values of Δt with values calculated by additive combination of Δt_1 due to doping and Δt_2 due to electrolysis

Ion	%	Δt_1* ($t_{\text{base}} - t_{\text{doped}}$) ±4°C	Δt_2** ($t_{\text{unelec.}} - t_{\text{elec.}}$) ±4°C	$\Delta t_{\text{calc.}}$ ($\Delta t_1 + \Delta t_2$) ±8°C	$\Delta t_{\text{obs.}}$ ±4°C	($\Delta t_{\text{calc.}} - \Delta t_{\text{obs}}$)
Fe	2.0	18	21	39	35	4
	9.76	88	14^+	102	89	13
Ni	2.0	7	21	28	20	8
	5.0	29	21	50	39	11
V	2.0	19	21	40	37	3
Ti	2.0	20	21	41	33	8
Co	2.0	10	21	30	19	11

* Taken from Ref. 2.
** Taken from Ref. 1.
$^+$ This measurement was made at a lower field strength.

metal-containing phase at the cathode suggests that all the ternary glasses behave similarly under electrolysis to the iron-containing glass which was investigated fully by the electron microprobe analyser. The crystalline transition metal oxides and alkali aluminium silicate occur as a thin surface layer; when this is ground off, reasonably well crystallised mullite is found to have formed in the cathode region immediately behind the surface layer. On devitrification, the i.r. spectrum in the hydroxyl stretching region behaved similarly to the undoped glass [1], sharpening markedly and shifting to the characteristic wavelength for Si – OH groups (2.7 μm).

Discussion

The effect observed when electric fields are applied to aluminosilicate glasses containing transition metal ions results from a combination of two separate influences which are superimposed on the system, namely, the influence of the field and the influence of the dopant. Previous studies have shown that when applied independently, both the field [1] and the dopant [2] in most cases act to reduce the temperature of devitrification of the base glass. Thus it might be expected that the combination of electric fields and transition metal dopants will act together to reduce the reaction temperature below that observed in systems in which the two effects act independently. That this is the case is illustrated by Table 2, in which the Δt values recorded in the present experiments for doped electrolysed glasses are compared with Δt values calculated by additive combination of Δt_1 (the temperature change in the base glass caused by doping alone) and Δt_2 (the temperature change in the base glass caused by electrolysis alone). In all cases the calculated values are slightly higher than the observed values, but are still within the estimated experimental error. Thus, in all cases the decrease in devitrification temperature brought about by a combination of doping and electrolysis can be accounted for in terms of the contributions of the two separate influences.

Similar considerations for χ show that electrolysis alone reduces the heat evolved by the base glass (i.e. χ_2 is positive) [1] whereas doping alone increases the heat evolved by the base glass (i.e. χ_1 is negative) [2], with the exception of Ti and V-containing glasses. The experimental values of χ recorded in the present study show that the combination of doping and electrolysis usually *increases* the heat evolved by the base glass (with the exception of Ti and V glasses); the similarity between this result and those of the unelectrolysed doping experiments suggests that doping exerts the dominant effect on χ, the effect of the field on this parameter being much less significant. Certainly the observed values of χ cannot be explained in terms of an additive combination of the heats of the two contributing phenomena, even when the large errors in the heat measurements are allowed for.

Transition metal nucleating agents such as TiO_2 could act on the $Al_2O_3-SiO_2$ system in two possible ways [3], (i) by occupying tetrahedral sites, thus displacing tetrahedral Al into octahedral sites, or (ii) by entering the octahedral network directly. In both cases the instability of the system is increased by an increase in the number of cations in the immiscible octahedral aluminous network. Previous work [2] has shown that the effect of transition metal ions on the recrystallisation reaction probably depends on factors such as the octahedral site preference of the ion and its effect on the viscosity of the ternary glass, which in turn influences the degree of phase separation taking place during the initial quenching process. The effect of electric fields on the reaction in the base glass has been ascribed to the migration of positively charged species such as alkali ions and protons to the negative electrode [1]. That such a mechanism also operates in the case of transition metal ion-containing glasses is demonstrated by the appearance at the cathode surface of alkali aluminium silicates similar to those observed in the electrolysed base glass. In addition, migration of the transition metal to the cathode is also evident from the appearance of the respective oxides at that electrode face. Thus, since the alkali ion and hydroxyl content of the doped glasses is likely to be very similar to the undoped (these having been prepared under identical conditions from the same kaolinite), any differences in the electrolytic behaviour of the doped glasses should depend on the electrolytic behaviour of the transition metal ion.

According to Uhlmann [4], the most important factor in recrystallisation is the atomic mobility, which may be locally increased in phase separated systems where interfacial regions between phases can be enriched in some component, thus providing a chemical driving force for crystallisation. The polarising effect of electric fields should act similarly, setting up regions of high alkali or transition metal ion concentration and increasing the atomic mobility of all species.

In a previous study of the effect of transition metal ion dopants on the present aluminosilicate system [2], the most important factor in determining the effect of the transition metal ion on the devitrification reaction was found to be its site preference characteristics, i.e. those ions with similar site preference energies to the glassforming aluminium component exerted the greatest effect on Δt. The results of the present experiments, similarly plotted against octahedral site preference energies taken from McClure [5] and Dunitz and Orgel [6] are shown in Fig. 7.

Fig. 7 shows similarities with the corresponding diagram for the unelectrolysed glasses [2]. For the electrolysed glasses, the maximum value of Δt and χ occurs at an octahedral site preference energy of about 4 kcal/mol, corresponding to the Fe glass. However, the Ti and V glasses do not conform to the previously observed trend [2]; both the Δt and χ values for these glasses are smaller than those of the Fe glass although the unelectrolysed values [2] lead to the expectation that the Ti and V glasses should exhibit Δt values greater than or at least equal to that of the Fe glass. It thus appears that electric fields depress Δt for the Ti and V-containing glasses.

In the previous study of the unelectrolysed aluminosilicate glass [2], a simple relationship could not be demonstrated between Δt or χ and either the metal-oxygen bond strength, the transition metal cation radius or the cation field strength. Analogous plots of the present electrolysis results again show little evidence of a simple dependence on any of these parameters. In addition to their independent nucleating action, the transition metal ions are also acted upon by the electric field, and take part in the normal electrolysis mechanisms of the undoped base glass. This is indicated by the appearance of transition metal compounds at the cathode, and in the case of the iron-containing sample, by the coexistence of iron-rich striations and bubbles. If, as seems reasonable, the latter occur by a proton-hydroxyl (or proton-proton) reaction such as was postulated for the electrolysis of the base glass [1], the high concentration of bubbles in the regions of high Fe(II) concentration could be explained in terms of redox reactions such as

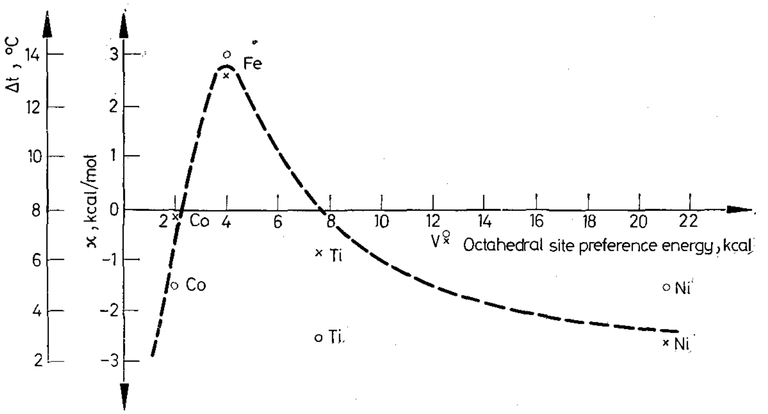

Fig. 7. Variation of Δt and κ with octahedral site preference energy of transition metal ions, taken from McClure [5] and Dunitz and Orgel [6]. Metal ion concentration 2%, field strength 4.0×10^5 V/m. $\odot = \Delta t$, $\times = \chi$

$$2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2\uparrow$$

Reactions of this type are known to occur in aluminosilicate systems containing low hydroxyl concentrations and variable valency impurities such as Fe, Cr and Mn [7]. Thus the presence of variable valency ions may modify the electrolysis process by assisting the removal of protonic species as well as by self migration under the electric field.

The relationship between Δt, χ and kinetic parameters

Although in the present study no attempt has been made to extract kinetic data from the DTA results, a qualitative explanation can be given for the behaviour of the peak temperature and peak area in terms of the kinetic parameters of the reaction. Reed et al. [8] have shown by computer simulations of DTA curves that an increase in the pre-exponential factor A or a decrease in the activation energy E leads to a lower peak temperature and higher peak area. Doping alone would be expected to increase the pre-exponential factor, whereas electrolysis should increase the activation energy by distortion of the energy barriers. Thus the combined effect of these factors on the DTA peak is consistent with that predicted from the work of Reed et al. [8]. Since electrolysis of the undoped glass [1] causes a decrease in *both* peak temperature and area, the effect of electrolysis on E is apparently a second order effect compared with the effect of doping on A. Thus if the treatment of Reed et al. [8] is appropriate to solid systems, the behaviour of the doped, electrolysed system compared to the undoped can be explained in terms of the reaction kinetics.

Conclusions

Changes in the devitrification behaviour of transition metal-containing aluminosilicate glasses under applied electric fields are greater than the changes brought about in the base glass by doping or electrolysis independently. The effectiveness of the transition metal ion in assisting devitrification is related to its octahedral site preference energy; the greatest effect is observed in iron-containing glasses in which the transition metal ion can participate in tetrahedral or octahedral co-ordination with approximately equal facility.

The electrolysis mechanism is similar to that of the undoped glass, in which alkali metal ions and protons proceed to the cathode, forming a layer of alkali aluminium silicate. In the electrolysed glasses containing transition metal ions, the latter species also migrate to the cathode, forming the metal oxide or aluminate in that region. The presence of variable valency transition metal ions may also modify the electrolysis mechanism by providing a means of proton elimination by a redox reaction. At higher transition metal ion concentrations the effect of the dopant on Δt increasingly predominates over the effect of electrolysis.

If the computer simulations of Reed et al. [8] are applicable to solids, the behaviour of these glasses under electrolysis can be explained in terms of an increase in the pre-exponential factor (caused by doping) and to a lesser extent a decrease in activation energy (caused by the electric field).

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ZUSAMMENFASSUNG — Der Einfluß der Elektrolyse auf die Entglasung von Alumosilikatglas-Arten mit 2 bis 10 Gew.% Ti-, V-, Fe-, Co- und Ni-Gehalten wurde mittels DTA untersucht. In allen Fällen wird die Entglasungstemperatur stärker herabgesetzt als bei unabhängig durchgeführter Elektrolyse oder Zusatz des Übergangs-Metall-Ions. Die relative Wirkung der verschiedenen Übergangs-Metall-Ionen wird aufgrund der Stärke der betreffenden Metall-Sauerstoff-Bindungen und des Vorrangs der tetraedrischen bzw. oktaedrischen Stellen der Ionen erklärt. Der Mechanismus der Elektrolyse ist ähnlich wie bei Gläsern ohne Zusatz, umfaßt aber auch die Wanderung des Übergangs-Metall-Ions zur Kathode und die Möglichkeit der Aufeinanderwirkung dieser Arten und der Restprotone des Grundglases.

RÉSUMÉ — On a étudié par ATD l'effet de l'électrolyse sur la dévitrification de verres types aluminosilicates contenant 2 à 10% en poids de Ti, V, Fe, Co et Ni. Dans tous les cas la température de la dévitrification est abaissée d'une manière plus importante sous électrolyse que si celle-ci est effectuée indépendamment ou que par dopage par des ions des métaux de transition. L'effet relatif des divers ions des métaux de transition s'explique en termes de forces des liaisons respectives du métal et de l'oxygène ainsi que par la préférence des ions pour les sites octaédriques ou tétraédriques. Le mécanisme de l'électrolyse est similaire pour les verres sans additifs. Il comprend cependant aussi la migration de l'ion du métal de transition vers la cathode et la possibilité de l'interaction de ces espèces avec les protons résiduels du verre de base.

Резюме — Влияние электролиза на расстекловывание алюмосиликатных стекол, содерщащих 2—10 весовых процента Ti, V, Fe, Co и Ni, было изучено с помощью ДТА. Во всех случаях температура расстекловывания понижалась при электролиза на величину, большую, чем была получена только при электролиза или только при добавлении в качестве присадок ионов переходных металлов. Относительное влияние различных ионов переходных металлов на расстекловывание обьяснено на основе прочности соответствующих связей металл-кислород и октаэдрической/тетраэдрической конфигурации ионов. Механизм электролиза подобный тому, как и в случае исходного стекла без присадок, но также включает миграцию ионов переходных металлов к катоду и возможность взаимодействия между этими частицами и оставшимися протонами основного стекла.