

Behaviour of silicate and borosilicate glasses in contact with metallic sodium. Part 2. Borosilicate glasses*

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When sodium borosilicate and sodium aluminoborosilicate glasses were heat treated in contact with metallic sodium at temperatures between 300 and 400°C, glasses with lower Si/B ratios exhibited coloration while those with higher Si/B ratios developed a crystalline sodium metasilicate product layer. Both processes were shown to be diffusion controlled. In the coloration process, low (less than 1.1 wt%) levels of atomic sodium were absorbed reversibly by the glass. In the crystallisation process, high levels of sodium were incorporated into the product layer which caused severe deterioration of the glass surface. Glasses which colour rather than crystallise are recommended as sealing glasses in sodium environments.

The development of Na-S battery systems has created a need for glasses capable of sealing α to β Al_2O_3 which are resistant to the metallic sodium environments encountered within the battery at its operating temperature (typically 300–350°C).

Since few basic investigations of the effect of metallic sodium on glass have been reported in the literature, possible reaction mechanisms of metallic sodium with two and three component alkali silicate glasses were initially determined.⁽¹⁾ Two distinct diffusion controlled processes were observed as a result of heat treatments with metallic sodium: reddish-orange coloration and crystallisation.

In glasses with higher sodium contents, a uniform layer of colour with a sharp front advanced into the bulk until the glasses were uniformly coloured. Values of the apparent activation energy associated with the colour boundary movement were similar to those predicted from a model of atomic sodium diffusion in

which the square root of the activation energy is proportional to the molecular diameter of the diffusing specie.⁽²⁾ Each glass composition which became coloured exhibited a characteristic intensity of colour which was relatively independent of the temperature and duration of the heat treatments over the experimental ranges investigated. The coloration process was found to be at least partially reversible, which suggested that the absorbed atomic sodium did not react chemically with the glass.

In glasses with higher silica contents, crystallisation of sodium metasilicate, rather than coloration, occurred at the sodium/glass interface. This process requires some reduction of the glass constituents. Since the thermodynamics of the reduction of silica by metallic sodium become favoured in sodium silicate glasses as the silica content of the glasses is increased,⁽³⁾ it was concluded that a critical silica content was necessary for crystallisation to occur. The sodium metasilicate crystalline phase was separated from the bulk glass by a planar boundary and advanced into the glass as a function of the square root of time as described by a parabolic rate law. The crystallisation process was considered detrimental to glass durability in metallic sodium environments.

This study has been performed on sodium borosilicate and sodium aluminoborosilicate glasses which, due to thermal expansion matching, are capable of sealing α to β alumina. Two series of glasses containing approximately 60 and 70 mol% silica were investigated. Within each series, Al_2O_3 was substituted for B_2O_3 at a constant Na_2O and SiO_2 content so that the Al/Na ratio varied from 0 to approximately 2. Borosilicate glasses were chosen for this study because rather low melting glasses of the correct thermal expansion could be formed which contained silica contents low enough so that coloration, rather than crystallisation, might be favoured.

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Experimental procedure

Thoroughly mixed reagent grade SiO_2 , B_2O_3 , Al_2O_3 , and Na_2CO_3 powders were melted in platinum crucibles in an induction furnace until an optically homogeneous glass was obtained. Cylindrical rods averaging 5–8 mm in diameter were drawn from the melt and annealed. The resulting glasses were analysed for Na, Al, and Si by atomic absorption spectrometry, and B was determined by subtraction. The analysed compositions are shown in Table 1, along with corresponding coefficients of linear thermal expansion.

Sections of the glass rods, 3 cm in length, were encapsulated with metallic sodium as described elsewhere.⁽⁴⁾ The glass samples were heat treated isothermally at temperatures ranging from 300 to 450°C for from 1 day to several months and then quenched to room temperature.

After the heat treatment, the recovered glasses were sectioned perpendicularly to the long axis, polished with oil based diamond abrasives, and stored in a desiccator.

Using a scanning electron microscope equipped with an energy dispersive spectrometer, sodium concentration profiles were determined and crystallised regions were photographed. In samples which became coloured, corresponding optical density profiles were measured with a microphotometer to determine the depth of colour penetration. Optical transmittance measurements were also used to estimate levels of absorbed sodium too low to be easily measured by energy dispersive spectrometry. In this technique, equal thicknesses of coloured glasses of known metallic sodium content were used in a plot of logarithm of relative transmittance as a function of atomic sodium content. By assuming that the logarithm of the optical transmittance was a linear function of the concentration of the colouring specie (Beer's Law), extrapolation of this plot was used to estimate levels of absorbed sodium which were less than 1 wt%.

Ion thinned sections of the coloured glasses were observed in bright and dark field by transmission electron microscopy at 200 kV. For samples which developed a crystal layer, crystal growth measurements were made from scanning electron photomicrographs and crystalline phases were identified by x-ray diffraction analysis. Thermal gravimetric analysis was performed on certain samples in vacuum or in oxidising atmospheres using a thermal analytical balance.

Table 1. Analysed glass compositions (mol %)

Series	Glass number	SiO_2	B_2O_3	Al_2O_3	Na_2O	Coefficient of linear thermal expansion 25–300°C
S 60	1	58.0	32.3	—	9.7	60.7
	2	57.3	27.6	5.9	9.2	60.4
	3	57.8	19.7	12.9	9.5	55.3
	4	57.9	13.8	18.6	9.7	66.2
S 70	1	70.6	19.9	—	9.5	60.5
	2	71.4	13.5	6.7	9.6	72.7
	3	70.1	6.6	12.5	9.7	58.9

Experimental Results

Series 60

As a result of the heat treatments with metallic sodium, reddish-orange coloration or crystallisation was observed. These effects were similar to those previously observed in sodium silicate glasses.⁽¹⁾ In glass 1, a uniformly coloured region with a sharp boundary advanced from the reaction surface toward the interior of the glass sample until, at a sufficient reaction time, the glass became uniformly coloured. The sodium concentration and corresponding optical density measured radially across the Na/glass interface are shown in Figure 1 for glass 1 heated for 24 h at 382°C. The coloured region of glass 1 corresponds to a uniform addition of approximately 1.1 wt% sodium to the bulk glass composition. The position of the colour front, approximately 1.1 mm from the reaction surface, is characterised by a sharp increase in optical transmission along with a sharp decrease in sodium concentration.

At a constant SiO_2 and Na_2O content, substitution of Al_2O_3 for B_2O_3 reduced levels of sodium absorption for glasses 2 and 3. From optical transmittance measurements, the absorbed sodium level resulting in coloration was estimated to be 0.2 wt% for glass 2 and 0.4 wt% for glass 3. These values were relatively independent of reaction time and temperature.

For all glasses that showed the colour effect, the position of the colour front was measured as a function of time at each reaction temperature. The results of these measurements are shown in Figure 2 for glass 2. At all temperatures, the data obey a parabolic rate law in which the square of the boundary position is linear with reaction time, indicating a diffusion controlled process. Figure 3 shows a similar plot comparing colour boundary movement for glasses 1, 2, and 3 at 400°C. Since the slopes of these lines are proportional to a diffusion coefficient, it appears that Al_2O_3 substitutions for B_2O_3 at first lower the sodium diffusivity and then increases it.

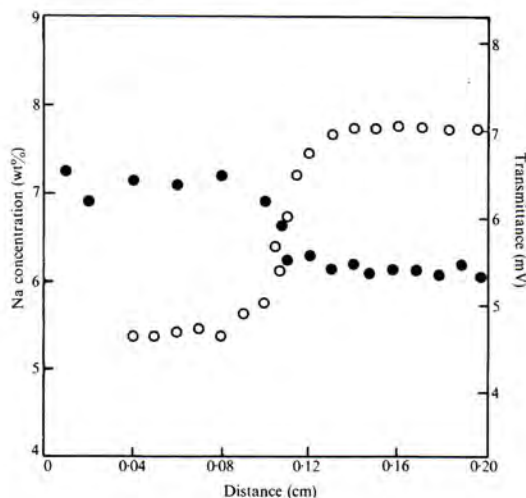


Figure 1. Variation of sodium content (●) and transmittance (○) with depth in glass 60-1 after heat treatment for 24 h at 382°C

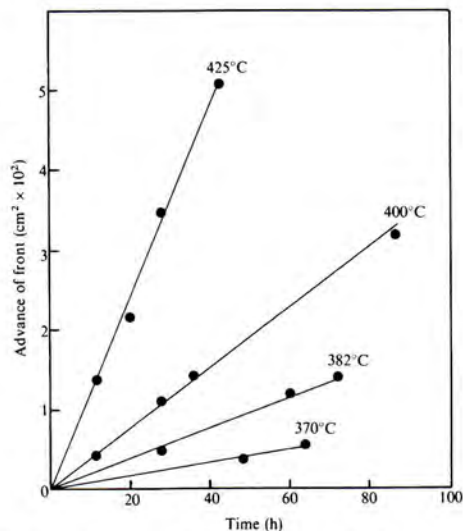


Figure 2. Time dependence for advancement of colour front in glass 60-2 at 370, 382, 400, and 425°C

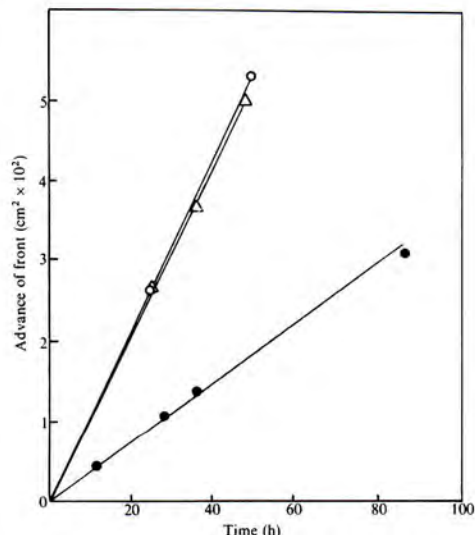


Figure 3. Time dependence for advancement of colour front in Series 60 glasses at 400°C

- glass 1
- glass 2
- △ glass 3

Further substitutions of Al for B resulted in the development of a black crystalline product layer as shown in Figure 4 for glass 4. At temperatures of 400°C and above, crystallisation also occurred in glass 3. The sodium concentration measured radially across the product layer toward the interior of the glass is shown in Figure 5 for glasses 3 and 4, reacted for 14 days at 450°C. These measurements show a linear gradient of sodium through the product layer and a discontinuity in sodium concentration at the product layer/glass interface. The sodium content measured at this interface is approximately that of sodium metasilicate, the major crystalline phase identified by x-ray diffraction analysis.

The discontinuity observed in the sodium concentration indicates that the formation of sodium



Figure 4. Section of glass 60-4 after heat treatment for 48 days at 375°C (bar = 0.01 mm)

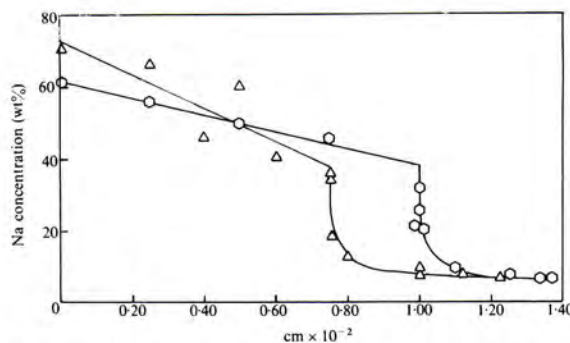


Figure 5. Variation of sodium content with depth for Series 60 glasses after heat treatment for 14 days at 450°C

- △ glass 3
- glass 4

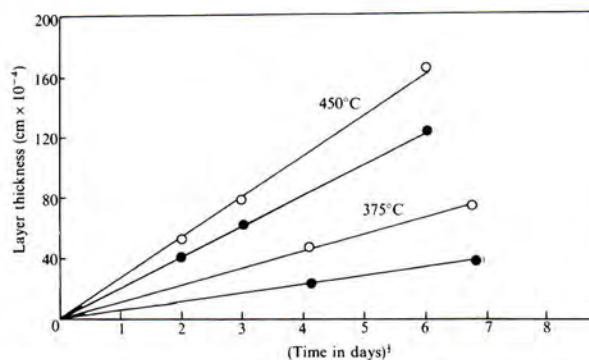


Figure 6. Product layer thickness as a function of time for Series 60 glasses

- glass 3
- glass 4

metasilicate at the crystal/glass interface is more rapid than the transport of sodium through the product layer. When this is the case, the product layer is expected to grow at a rate proportional to the square root of time. This is shown in Figure 6 for glasses 3 and 4.

Higher $\text{SiO}_2/\text{B}_2\text{O}_3$ ratios apparently favour the crystallisation process, as all three glasses in this series crystallised when heated with metallic sodium. Glass 2 exhibited both coloration and crystallisation in the temperature range 375–425°C; however, coloration only occurred where there were breaks in the crystalline product layer. The crystalline layer apparently acts as a barrier to the coloration process.

The concentration of sodium measured radially through the product layer, as shown in Figure 7, is similar to that of the Series 60 glasses (Figure 5). Product layer growth was proportional to the square root of time as shown in Figure 8.

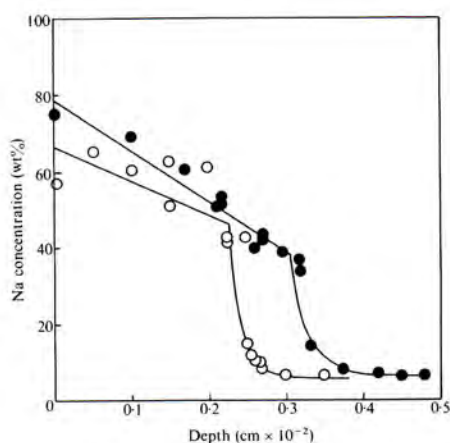


Figure 7. Variation of sodium content with depth for Series 70 glasses after heat treatment for 46 days at 375°C

○ glass 1
● glass 2

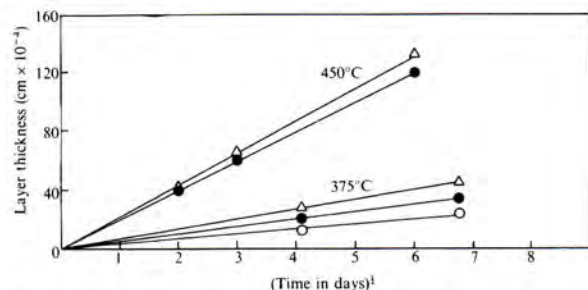


Figure 8. Product layer thickness as a function of time for Series 70 glasses at 375 and 450°C

○ glass 1
● glass 2
△ glass 3

Discussion of results

Coloration

From plots of the square of the colour boundary position against time, e.g. Figure 2, slopes determined as $\text{cm}^2 \text{s}^{-1}$ were used in an Arrhenius plot to determine the apparent activation energy of diffusion for the coloration process. Figure 9 shows Arrhenius plots for Glasses 60-1 and 60-2. Comparative data⁽¹⁾ are

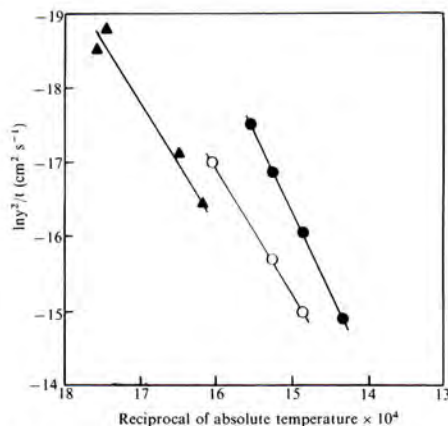


Figure 9. Relationship between rate of advancement of colour front and temperature for Series 60 glasses

○ glass 1
● glass 2
▲ glass 60, Reference 1

shown for a binary $\text{Na}_2\text{O} \cdot \text{SiO}_2$ glass (58.2 SiO_2 , 41.8 Na_2O mol%). The calculated values of apparent activation energies over the temperature range 300–425°C are 33.6 kcal/mole (140 kJ/mole), 42.7 kcal/mole (179 kJ/mole), and 34.0 kcal/mole (142 kJ/mole) for glasses 1 and 2 and the sodium silicate comparison glass, respectively.

It is hypothesised that, in atomic diffusion, the square root of the apparent activation energy is proportional to the molecular diameter of the diffusing specie.⁽²⁾ In fused silica, an activation energy of 29 kcal/mole (121 kJ/mole) represents a diffusing specie with a molecular diameter of 3.4 Å, the molecular diameter of gaseous sodium metal.

For an atomic diffusion process, modifier additions to fused silica are expected to increase the activation energy for diffusion because more energy is required to move the diffusing atom from one interstitial site to another.⁽⁵⁾ Therefore, it is expected that sodium diffusion in glass 1, which contains only 9.7 mol% modifier, would not have as high an activation energy as in the sodium silicate glass, which has 41.8 mol% modifier. This apparent contradiction is explained by assuming phase separation into a sodium borate rich matrix phase and a silica rich droplet phase. In such a glass, silica rich phase with its high sodium diffusivity would be isolated, so that the apparent activation energy for diffusion would be much higher than expected from consideration of the modifier content alone. As shown in Figure 10, direct transmission electron microscopy of a chemically thinned and ion milled sample of glass 1 reveals silica rich droplets isolated in a $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ rich matrix.

Substitution of Al_2O_3 for B_2O_3 reduced the sodium absorption and increased the apparent activation energy for diffusion for glass 2; however, further substitutions had the reverse effect. This is similar to atomic diffusion phenomenon in sodium aluminosilicates in which substitutions of Al_2O_3 for SiO_2 reduce helium diffusivity and solubility when $\text{Al}/\text{Na} < 0.5$ and increase the values of these parameters when

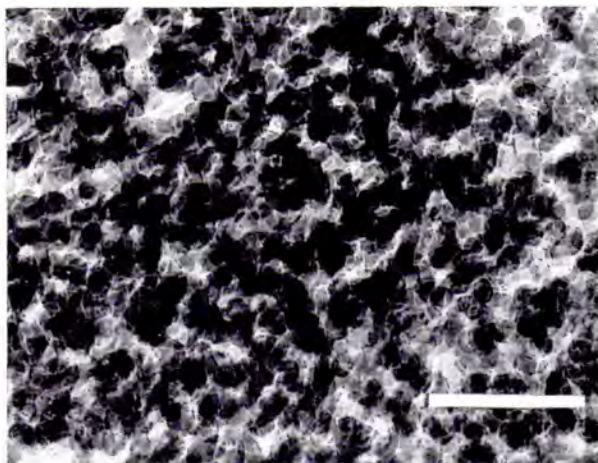


Figure 10. Electron micrograph of glass 60-1 showing phase separated microstructure (bar = 10^{-3} mm)

Al/Na > 0.5.⁽⁶⁾ Currently, there is no model to explain this behaviour.

Certain coloured glass samples, when heated in flowing dry air to 400°C, became colourless without any weight change. The colourless samples, however, were photoluminescent. This same phenomenon is observed in glasses containing atomic silver.⁽⁷⁾ Atomic silver can exist in glass as single atoms, in which case the glass is colourless but photoluminescent, or as very small silver crystals, in which case the glass is coloured but not photoluminescent. Since the coloured glasses containing sodium behave in a similar manner, it is expected that the colour centres are small crystals of atomic sodium. Figure 11 shows the electron diffraction pattern and dark field image (corresponding to $d = 1.52 \text{ \AA}$) for a coloured sample of glass 70-2. The diffraction rings result from fine ($< 100 \text{ \AA}$) randomly oriented crystals which can be seen as small bright spots in the dark field image. The D spacings calculated from the diffraction pattern closely matched those of atomic sodium.

Coloured glass samples, when heated in vacuum, became appreciably colourless with a corresponding

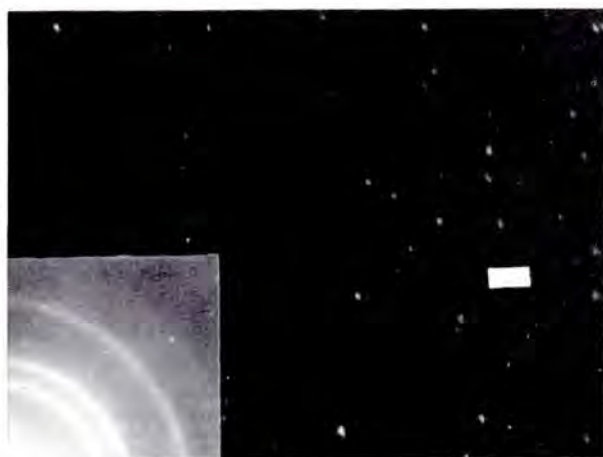


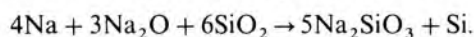
Figure 11. Electron diffraction (inset) and dark field electron micrograph of glass 70-3. Bright areas correspond to $d = 1.52 \text{ \AA}$ (bar = 10^{-4} mm)

weight loss. This is likely due to sodium volatilisation, which implies that the absorbed sodium does not react chemically with the glass network as in a reduction reaction and that the sodium absorption process is at least partially reversible.

Crystallisation

It appears from the present investigation of borosilicate and aluminoborosilicate glasses that increased Si/B ratios favour the crystallisation of sodium metasilicate. Small substitutions of Al_2O_3 for B_2O_3 at a particular SiO_2 level resulted in coloration, but larger substitutions resulted in increased crystal growth rates (Figures 6 and 8) as did substitutions of SiO_2 for B_2O_3 at a particular Al/Na ratio.

The formation of sodium metasilicate by the reduction of metallic sodium with glass requires some reduction of the glass constituents. In the sodium silicate glass system, it was observed that a critical silica level was necessary to favour the reaction⁽¹⁾



The crystallisation effects observed in the present investigation suggest that a critical silica content may be necessary for the crystallisation of sodium metasilicate in borosilicate glasses as well.

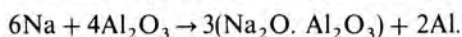
To test this hypothesis, glass 60-3 was heat treated slightly above its transformation temperature prior to immersion in metallic sodium. The heat treatment caused extensive phase separation which isolated some of the silica from metallic sodium at the sodium/glass reaction interface. This phase separated glass coloured rather than crystallised during the metallic sodium heat treatment, demonstrating the importance of silica content to the crystallisation process.

In all observed cases, the rate at which crystals grew into the bulk glass was proportional to the square root of time, indicating diffusion controlled growth. Sodium concentration profiles measured across the crystal/glass interface (Figures 5 and 7) suggest a diffusion controlled mechanism which involves transport of sodium through the crystal layer to the crystal/glass interface where sodium metasilicate is rapidly formed with a corresponding reduction of silica to metallic silicon. The very high levels of sodium measured in the crystal layer were probably a result of excess sodium metal penetrating into fine channels and cracks which formed in the product layer on cooling due to the large thermal expansion mismatch between the sodium metasilicate crystals and the glass.

The formation of a crystal layer apparently precludes the coloration process; this suggests that coloration might occur whenever the thermodynamics are unfavourable for the reduction of silica. The corollary of this statement is also implied. Namely, crystallisation will occur only when the thermodynamics allow the reduction of silica.

The role of Al_2O_3 is less apparent. Burggraaf, *et al.*⁽⁸⁾ have shown that the reduction of alumina by

sodium is also possible according to the reaction⁽⁸⁾



However, sodium aluminate and Al were never detected by x-ray diffraction analysis in the final product layer. Since increased crystal growth rates occurred when Al_2O_3 was substituted for B_2O_3 , it is difficult to determine whether crystal growth was stimulated by alumina additions or by the higher Si/B ratios which resulted.

The crystallisation process results in extremely high levels of sodium being incorporated into the glass surface both as crystals of sodium metasilicate, which adhere poorly to the bulk glass, and as excess free sodium. As such, the crystallisation process severely deteriorates the glass surface and is considered detrimental to the fabrication of a corrosion resistant sealing glass.

Conclusion

When borosilicate and aluminoborosilicate glasses are heat treated with metallic sodium at temperatures between 300 and 450°C, two different diffusion controlled phenomena are observed. The first, which occurs primarily in glasses with low Si/B ratios, is characterised by low (<1.1 wt%) levels of sodium absorption resulting in coloration of the glass. The second, which occurs in glasses with high Si/B ratios, is characterised by a high level of absorbed sodium which is incorporated into a crystalline product layer.

The coloration effect was observed at all temperatures investigated for glasses 60-1 and 60-2, which contained the lowest Si/B ratios. Each glass exhibited a characteristic absorption level which was independent of reaction time and temperature. The apparent activation energy for diffusion associated with the coloration process for glass 1, which contained 9.7 mol% modifier, was approximately that of a sodium silicate glass, which contained 42.6% modifier. This was explained by the phase separated microstructure of glass 1 in which the silica rich phase with a high sodium diffusivity existed as isolated droplets in the sodium borate rich matrix. Small substitutions of Al_2O_3 for B_2O_3 in glass 1 greatly reduced the amount

of absorbed sodium and increased the apparent activation energy for diffusion (glass 2). Calculated values of the apparent activation energy are consistent with a model of atomic sodium diffusion. Small (<100 Å) crystals of metallic sodium were identified in the coloured glasses and are believed to be colour centres. The absorption of sodium resulting in coloration was shown to be at least partially reversible, which suggests that the absorbed sodium does not react with the glass network.

Higher Si/B ratios resulted in crystallisation of sodium metasilicate at the glass/metallic sodium contact surface. At a particular silica level, substitution of Al_2O_3 for B_2O_3 resulted in increased crystal growth rates as did substitution of SiO_2 for B_2O_3 at a particular Al/Na ratio. The thickness of the crystal layer increased proportionally to the square root of time, which implies diffusion controlled crystal growth. The sharp decrease in sodium concentration, which was observed at the crystal/glass interface, implies that the reaction between metallic sodium and glass, which results in sodium metasilicate and reduced silicon, is very rapid. However, it appears that a critical silica content is necessary to favour this reaction.

The sodium metasilicate product layer is easily corroded and, due to its mismatch in thermal expansion, is not very adherent to the bulk glass. Therefore, glasses which crystallise in contact with metallic sodium are not recommended for use as sealing glasses in sodium-sulphur batteries. Glasses which become coloured when in contact with metallic sodium are recommended as possible sealing glasses because coloration involves low levels of absorbed sodium, which does not appear to react chemically with the glass.

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