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Alkali Volatilization in TV Screen Glass Melts

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The alkali volatilization of TV screen glass melts with various K_2O/R_2O mole fraction was investigated by dependence of weight loss on time. The melt conductivity was also determined to evaluate relative alkali diffusion in melts. Based on the results of time dependence and compositional dependence of volatilization combining the results of conductivity, the rate determining process of the volatilization was suggested. From the viewpoint of the production and the application of TV glass it was also discussed a correlation between the dependence of properties on K_2O/R_2O and the present commercial composition.

Key words: Volatilization, Weight loss, Alkali diffusion, Conductivity

I. Introduction

Vaporization of volatile components during glass melting is undesirable, since it results in uncontrolled changes in composition, particularly in the surface layers that are consequently a potential source of inhomogeneities.[1] The escaping vapors react with refractories of furnace superstructure and corrode them. Condensates and reaction products tend to clog regenerators and thus reduce their life and efficiency. The major volatile components in commercial glass melts are alkali oxides, boric oxide and lead oxide etc.

Theoretically, the vaporization from the glass melt consists of three processes,[2-4] 1) diffusion transport of volatile species in the melt 2) their reaction with gases of the atmosphere at melt surface, namely conversion of the component from melt to gaseous state 3) diffusion transport of vapors through the atmosphere. According to some theoretical approaches, mass loss measurements as a function of time provide information concerning the rate controlling steps in the vaporization process. Therefore, most vaporization studies of glass melts have involved only measurement of weight loss for some commercial[4-11] and noncommercial[12-14] glass compositions containing alkalis without relative evaluation of diffusion transport of volatile species in the melt. There have been no studies in which the compositional dependence of weight loss and mobility of alkali ions in melt is treated.

Commercial TV screen glass is a typical mixed alkali glass containing Na_2O and K_2O. In the present work the compositional dependence of volatilization and electrical conductivity as function of K_2O/R_2O ($R_2O=Na_2O+K_2O$) was investigated in TV screen glass melts. The main objective of this work is to examine the influence of alkali ion mobility on the volatilization of mixed alkali glass melts and to discuss the present K_2O/R_2O of commercial TV glasses from the viewpoint of refractory corrosion.

II. Theory of Volatilization

In Figure 1 volatilization process of Na_2O from glass melts into the atmosphere containing H_2O is described schematically with effective parameters on volatilization. From the analogy with evaporation of liquids, it can be expected that the rate of vaporization from a melt surface into atmosphere is proportional to partial pressure of the volatile component. Here, it must be assumed that the surface reaction is rapid enough to keep the equilibrium vapor pressure at the surface, and that the vaporized component is supplied at a suitable rate from the deeper melt layers to the surface. This concept is in agreement with the fact that the

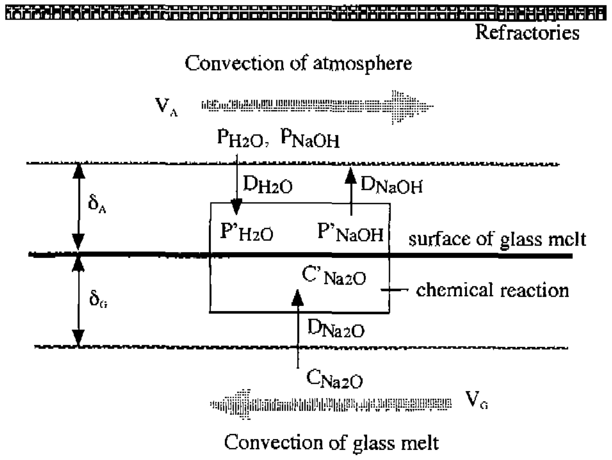

Fig. 1. Description of volatilization process of Na_2O from glass melt. V_A: flow rate of gas in atmosphere, δ_A: thickness of boundary layer in atmosphere. V_G and δ_G are corresponding values for glass melt. D: diffusion coefficient, P: parttial pressure, C: concentration.

temperature dependence of the vaporization rate for glasses is similar to that of the vapor pressure, in particular at the beginning of the process when the vaporization occurs at a constant rate.12) In this case, the vaporization kinetics is given by the transport rate of volatile component vapors through adjacent layer of the atmosphere gases. If the melt volume is large in comparison with the surface area exposed and the amount volatilized is small, the total change in concentration of the volatile component in melt can be neglected and the rate of volatilization is approximately constant (independent of time) within a considerable time interval. This behavior occurs whenever the volatile component is transferred to the surface by intensive convection in the melt.

However, the majority of experimental studies have shown that the rate of volatilization from molten glasses decreases after a long period of time according to parabolic time dependence. There is evidence that this is due to reduced concentration of the volatile component on the melt surface.9,14) This reduction brings about a decrease in vapor pressure at the interface and diffusion of the volatile component in melt becomes the controlling process. This effect does not arise when the melt has the same compositions as the escaping vapors (congruent vaporization) or when the melt is agitated, the surface being thus continuously renewed.

As indicated in the introduction, the vaporization of a volatile substance from a multicomponent melt can be finally divided into three processes; diffusion transport of volatile species in the melt, chemical reaction around melt surface and diffusion transport of reaction products in the atmosphere. Practical results show that only two of these processes must be considered, namely diffusion in the melt and the surface process.7,14)

Assuming that the rate of volatilization can be described by the diffusion in the melt involving surface reaction, following equations have been derived.15)

If the melt were static and diffusivity independent of concentration, transport within the melt would be governed by Fick's second law, $\partial c/\partial t=D(\partial^2 c/\partial x^2)$ where c is the concentration of volatile species, D is the diffusion coefficient which is assumed to be independent of concentration, t is time, and x is the distance from the surface. If the glass melt is regarded as an infinite body having initial concentration of volatile component $c=c_i$ for $x=0$, $t=0$ and $c=c_i$ for $t>0$, $x>>0$, the surface process rate will be directly proportional to the difference between actual concentration of the volatile species at melt surface c_s and concentration c_0 which would be in equilibrium with vapor pressure of those species in atmosphere (usually $c_0=0$), namely $dm/dt=\alpha(c_0-c_s)$. The solution for the total volatilized quantity m_t per unit area has the following form16):

$$m_t= (c_i-c_0)/h[\exp(h^2Dt)\cdot \mathrm{erfc}\{h\sqrt{(Dt)}\}-1+(2/\sqrt{\pi})h\sqrt{(Dt)}] \qquad (1)$$

where $h=\alpha/D$, α is the proportionality constant of the surface process, and D is the diffusion coefficient of the volatile component in melt. For very long periods of time, the erfc term is close to zero. By neglecting it one obtains7)

$$m_t=-(c_i-c_0)/h+2(c_i-c_0)\sqrt{((Dt)/\pi)} \qquad (2)$$

This relationship allows simple evaluation of h and D from the diagram $m_t-\sqrt{t}$. The slope of the straight line portion is $2(c_i-c_0)\sqrt{(D/\pi)}$ and the intersect on ordinate m_t ($t=0$) defines the value $-(c_i-c_0)/h$. If the surface process is very fast ($a>>D$ and $h\rightarrow\infty$), the volatilization is controlled by diffusion in melt,

$$m_t=2(c_i-c_0)\sqrt{(D/\pi)} \qquad (3)$$

Acording to equation (3), the rectilinear plot of m_t-$\sqrt{t}$ should pass through the origin. However, this is usually not the case in practice, since the initial stage is controlled by the surface process.

III. Experimental

The base glass composition in mol% was $72SiO_2$, $(14-x)Na_2O$, xK_2O, $10(SrO+BaO)$ and other inevitable minor components for TV screen glass as ZrO_2, TiO_2, Al_2O_3, CeO_2 with x=0, 3.5, 5.5, 7, 10.5 and 14 in which the K_2O/R_2O ($R_2O=Na_2O+K_2O$) mole fraction takes the value of 0, 0.25, 0.39, 0.5, 0.75 and 1. Among these compositions, the commercial TV glass composition has the value of $K_2O/R_2O=0.39$. The raw materials used were sand and reagent grade carbonate chemicals etc. As a fining agent sodium antimonate ($Na_2OSb_2O_5$) was used. The batches were mixed thoroughly and melted in a Pt/20Rh crucible at temperatures between 1500-1550°C in an electric furnace, depending on the composition. Sufficient time (4-6 hours) was allowed for the melts to become visibly homogeneous. The glasses were remelted at 1550°C after casting on a graphite plate and homogenized by using Pt/Rh-stirrer, and bubble free homogeneous glass melts were prepared.

Volatilization experiments of glass melt were carried out by a simple thermal gravimetric method in air atmosphere. A Pt/20Rh bucket with about 6 cm^3 volume which can contain maximum 5 g of glass was hang on the digital recording micro-balance (D-101, Cahn, USA). A mullite tube was used as a closed reaction tube. The vaporization products were carried with He gas to the outlet of the tube. A small piece of glass (about 4 g) was placed in a bucket and then inserted into a furnace. The weight loss at 1400°C versus time was continuously detected by the microbalance. The measurements ran for 12 hours. The experiment was reproducible within the range of ±10%. The vaporization products of some melts were collected by filter placed at outlet of the closed reaction tube and analyzed qualitatively by EDX (Link Oxford 6232, England). The EDX analysis indicated that the major volatile constituents are Na_2O and K_2O. In order to evaluate the ion mobility indirectly, the electrical conductivity of each melt was determined. For the electrical measurement of glass melts, a dipping electrode arrangement was applied. The conductivity cell consists of an alumina crucible filled with glass melt and two Pt/30Rh electrodes immersed at 10 mm depth from melt level. Electrical conductivity was measured between two electrodes separated by 15 mm. As measuring bridge, a precision LCR meter (Hewlett Packard 4284A, USA) was used. The conductivity measurements were performed at 1 MHz. The details of the cell and the calibration are described elsewhere[17].

IV. Results and Discussion

1. Compositional dependence

Fig. 2 shows weight loss per unit area (m_t) for six glasses as a function of square root of time ($\sqrt{t}$). The plotting of m_t–$\sqrt{t}$ does not follow the equation (2) or (3), namely it produces no straight lines like the studies in another melt systems.[7,14] The deviation from linearity in the initial stage means that both diffusion of volatile species in the melt and the surface reaction take part in the rate determining step of the volatilization. The weight loss increases with increasing time but the order at constant time does not follow the K_2O/R_2O mole fraction. The glass melt with $K_2O/R_2O=0.75$ shows the largest weight loss. From this it is expected a nonlinear dependence of the volatilization on K_2O/R_2O. Fig. 3 shows compositional dependence of the weight loss at two different heat treatment times of 300 and 600 min. The weight loss increases slightly with increase of K_2O/R_2O, and after passing through $K_2O/R_2O=0.5$ mole fraction a dramatic increase occurs to $K_2O/R_2O=0.75$ and it decreases steeply. Hence, the both curves exhibit extreme values at $K_2O/R_2O=0.75$. In order to evaluate which of the two processes (diffusion in the melt and the surface process) contributes dominantly to compositional dependence of melt volatilization, the results of melt electrical conductivity are introduced in the next.

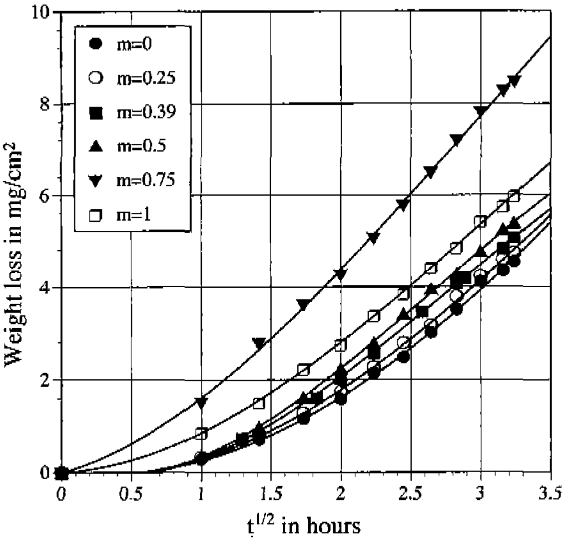

Fig. 2. Weight loss as a function of time at 1400°C for six glasses, $m=K_2O/R_2O$.

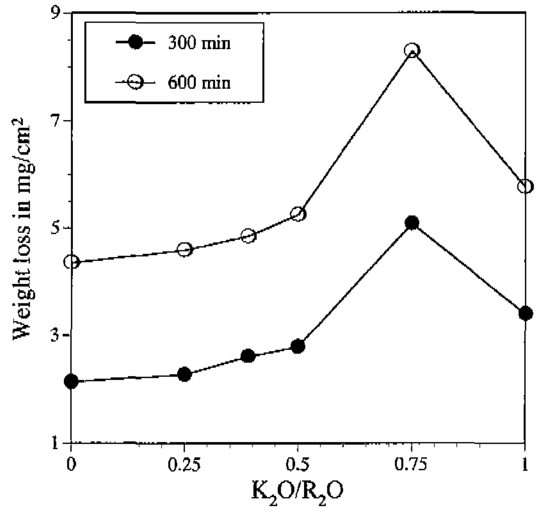

Fig. 3. Weight loss at 1400°C as function of K_2O/R_2O.

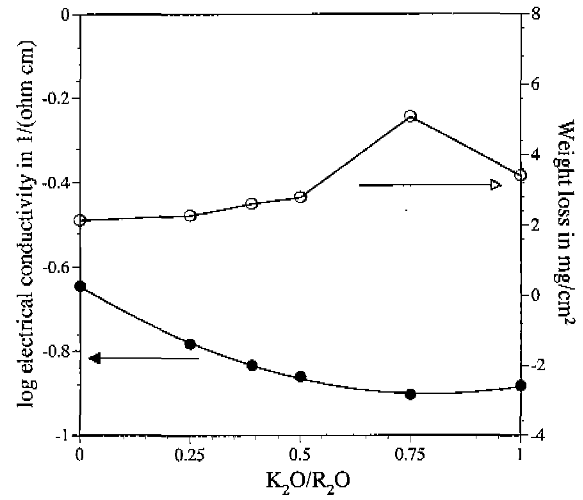

Fig. 4. Electrical conductivity (●) and weight loss (○) at 1400°C as function of K_2O/R_2O.

2. Correlation with electrical conductivity

In Fig. 4 the melt conductivity at 1400°C and the weight loss of melt at 300 min are presented as function of K_2O/R_2O. The melt conductivity shows minimum that usually is called the mixed alkali effect. The conductivity minimum is positioned between $K_2O/R_2O=0.65$ and 0.75. According to Nernst-Einstein equation, $\sigma=Ce^2D/\kappa T$ where C is the alkali ionic charge concentration, e the charge of ion under consideration, κ Boltzmanns constant and T absolute temperature, the electrical conductivity (σ) of melt is proportional to the diffusion coefficient (D) of alkali ion. It means that the diffusion of alkali ions in the melts between $K_2O/R_2O=0.65$ and 0.75 must be lowest, and thus the weight loss due to volatilization must show minimum if the diffusion in the melt is the rate determining step of the volatilization. Comparison of the conductivity results with those of volatilization in Fig. 4 indicates, however, that the role of alkali diffusion in the melt may be small for volatilization. It implies that at least in some instances, surface reaction and transport in the gaseous phase take a significant part in the volatilization kinetics of mixed alkali glass melts. This agrees with the suggestion of Conradt and Scholze[4] who studied on the volatilization from commercial glass melts extensively. It seems that the reaction at melt surface and the diffusion transport of reaction product into the atmosphere play more important role in the volatilization. However, the reason why the maximum in the weight loss occurs at K_2O/R_2O=0.75 can not be explained clearly. It is only suspected that this is also a kind of mixed alkali effect.

3. Correlation with commercial TV glass composition

From the foregoing, present commercial TV screen glass is a typical mixed alkali glass and its relative alkali concentration, K_2O/R_2O indicates 0.39. Vaporization of alkali from glass melts is important due to its influence on glass homogeneity and refractory corrosion. Especially, the reaction of the atmospheric water with the molten glass surface results in considerably higher concentration of alkali volatile species as ROH that corrodes the refractory materials and thus the service life of glass melting tank is decreased. For the commercial TV glasses it has been reported that KOH vapor concentrations in atmosphere exceed NaOH.[18] The present results for volatilization of Fig. 3 show that with replacement of Na_2O by K_2O the weight loss increases, its slope is changed steeply at K_2O/R_2O=0.5 and its maxima occurs at K_2O/R_2O=0.75. From the viewpoint of volatilization it seems to be better for TV glasses not to contain K_2O. However, in designing a glass composition it must be considered not only production technology but also application of glass product. Considering that TV glasses are used as an electronic component exposed to atmosphere, it is desirable that glass has a higher resistivity for good insulating and a better chemical durability. According to our recent work[19] in which some properties of TV glasses were investigated as function of K_2O/R_2O, the conductivity minimum occurred at K_2O/R_2O=0.5~0.65 and the chemical durability against water was the best at 0.35. Therefore, it is valuable that the mole fraction of K_2O/R_2O should lie between 0.35 and 0.5 to satisfy both production and application of TV glasses. The commercial TV screen glass with K_2O/R_2O=0.39 is in accord with this suggested range.

V. Summary

In the present work, the volatilization of TV screen glass melts with K_2O/R_2O=0, 0.25, 0.39, 0.5, 0.75 and 1 was studied. The dependence of weight loss on the square root of time for each glass melt showed no linearity and thus the rate determining process of the volatilization may be both the diffusion of alkalis in the melt and the surface evaporation reaction. The compositional dependence of weight loss showed a maximum value at K_2O/R_2O=0.75 where the melt conductivity is minimum approximately. From this opposite compositional dependence of both properties it is expected that in mixed alkali glass melts the surface reaction and the transport in the gaseous give more contribution to the volatilization than the alkali diffusion in the melt. According to the compositional dependence of the melt volatilization, it seems to be better that TV glasses do not contain K_2O. However, from the viewpoint of the application of TV glass product to electronic component used in atmosphere, it has been suggested that some amount of K_2O (K_2O/R_2O=0.35~0.5) is necessary to improve the glass properties, for example electrical resistivity and chemical durability.

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