SPONTANEOUS MIGRATION OF ALKALIS IN GLASS IRRADIATED BY THE ELECTRON BEAM

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If the glass is exposed by fast electrons the ionized alkali cations can be released from their original sites and are driven by the electric field deeper inside to the glass. The decay curves were measured and two migration regimes have been revealed for alkali ions in the glass. The first regime, the incubation period, is characterised by the individual ion migration, and by the linear-like decay in the decay curve. If the number of released alkali ions achieves the percolation point the first regime bursts into the regime of spontaneous migration that is characterised by the cooperative transport of alkalis and by the rapid exponential decay in the decay curve.

INTRODUCTION

The alkali glass irradiated by the electron beam undergoes changes in the glass structure. These changes manifest in the microanalysis as the decay of alkali X-ray intensities [1]. The same effects are observed in other analytical methods using electron beam with lower primary energies as a probe [2]. The X-ray intensity decay was interpreted as caused by a temperature change [3] or as an effect of the electric field created by the incident electron beam [1] based on the model used to explain oxygen outgassing from glass during electron bombardment [4]. However, the temperature and electric field effects cannot be separated in most cases and have to be taken into account together. Interpretations backed only by arguments of either the rise in temperature or the influence of the electric field were found to be insufficient and unable to explain all findings.

The glass can also be irradiated by other probes. It was found that if the glass was irradiated by gamma rays [5], the electrical conductivity initially increases. This increase is attributed to defects induced by gamma rays that enable easier motion of mobile ions. The introduction of disorder is also observed by irradiating quartz with neutrons [6]. In general, it appears that irradiation of glass causes significant changes in the glass structure. The changes can be larger for an electron probe due to the creation of an electric field inside the irradiated volume. The field eases moving of ions from their original sites, creating new defects in this way.

The shapes of the observed alkali X-ray decay curves depend on the conditions of electron bombardment, mainly on the current density of the beam. The decay curves display two distinct regions under normal conditions (not too high current density so that the temperature is not too high [7]). Instantaneously after the exposure, the decay curve displays a slow, linear decrease (figure 1). The linear decrease is a result of both an increased temperature and electric field establishment that enable the alkali ions to move faster along the lines of force of the electric field. After some time, denoted as the incubation period, the decay curve changes into an exponential decay. Only linear part of the exponential decay is displayed in Fig. 1 to preserve reasonable proportions for the incubation period. The incubation time can vary in the range from seconds to hours depending on the particular conditions.

The change of the primary electron energy influences the incubation period. It has been shown for a K_2O-CaO-SiO_2 ternary glass that the change of primary electron energy in the range between 30 keV and 50 keV can be fully explained by the different temperature increase in the irradiated volume [8].

Primary electrons injected into an insulator create an electric field within the exposed volume. The field exists even if the specimen surface is coated by a conductive layer due to charged particles deposited inside the volume. The intensity of the field depends on the sample, the current density and the primary electron energy. The electric field intensity is mainly determined by the

density of trapped electrons inside the sample, except at extreme conditions of well-focused electron beams of high intensities, where the primary electrons are able to create a significant electric field. The number of trapped electrons is determined by the electronic structure of the solid, namely, by the number of defects in the structure and by the energetic depth of traps.
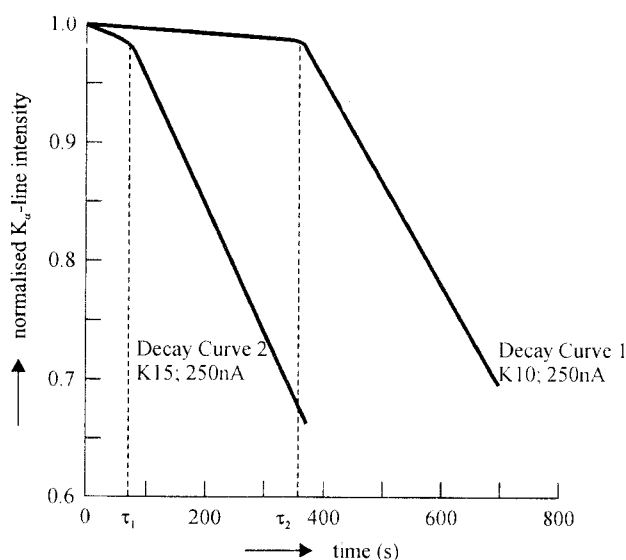

Figure 1. Typical X-ray intensity decay curves. The displayed $K\alpha$ lines of X-ray intensities of potassium are normalised to the initial X-ray intensities. The first decay curve was measured for 0.1 K_2O + 0.9 SiO_2 glass and the second one for the 0.15 K_2O + 0.85 SiO_2 glass. Primary electron energies were 50 keV and the diameters of the electron beams were 100 μm for both cases. Corresponding incubation times τ_1 and τ_2 are displayed for both curves.

In the case of an electron probe we assume an insulator target coated with a conductive thin layer set at the ground potential. We also neglect the influence of the thin positively charged layer at the surface, created by secondary electron emission, which is much thinner than the electron range [9]. The steady charge distribution forming the electric field is achieved in a time much shorter (a fraction of a second) than that required for analysis so that we do not need to take into account the dynamics of the electric field creation. The overall charge distribution will be assumed homogeneous inside the irradiated volume. This assumption implies the following relationship [9] for the electric field E_E at a depth z below the surface:

$$E(z) = \frac{\rho}{\varepsilon} (z - R) . \qquad (1)$$

where ρ is the charge density of trapped electrons, ε is the dielectric constant of the sample and R is the electron

range. Under these assumptions the electric field is maximum at the surface and decreases linearly to zero at the electron range.

MODEL

The binary alkali glass structure can be described by the modified random network (MRN) model [10] that suggests that the alkali modifier (M) enters into the silica network not only as a bridging oxygen breaker but the modifier forms its own coordination polyhedron. The glass $(M_2O)_x(SiO_2)_{1-x}$ is then formed by two types of polyhedra connected at the vertices. This model is valid if the modifier can be taken as an impurity in the rigid silica network. For higher concentrations of M ions, M-O-M dimmers must be present, and for even higher concentration, M clusters will develop.

If the glass is irradiated by an electron probe, the electric field is created by trapped electrons instantly. However, the field itself is not strong enough to release the alkali ions from their positions instantly. This idea is supported by experiments where an alkali-ion--containing glass was subjected to a strong electric field near the electric breakdown limit. The alkali migration lasted hours in those experiments [11].

Another effect of the primary beam is an energy deposition inside the exposed volume that results in a rise in temperature. The temperature distribution is set to its equilibrium instantly after the electron exposure [12]. Maximum temperatures inside the irradiated volume were calculated according to an algorithm published in Ref. [13] and were taken to be constant in the irradiadiated volume for sake of simplicity.

The alkali atoms are largely bonded by the ionic bond in the glass and their activation energy is E_u. As soon as an alkali cation is ionized by a primary electron, it can move from its position (as doubly ionized) and is driven by the electric field until it recombines with a free or trapped electron or until its path is blocked by a high energy barrier. The recombined or blocked alkali ion is no longer bonded to the structure by the same bond but by a rather weaker one which results in the lowering of its activation energy to E_r. The activation energy is also lowered for alkalis in the vicinity of the migration paths of the released alkali ions due to a reduction in their displacement energy.

The number of alkalis with lower activation energy increases with time because the number of released alkalis increases. As soon as the fraction of released alkalis reaches a critical value p, corresponding to a percolation threshold, p, a spontaneous cooperative migration of released alkalis takes place in the irradiated volume. The percolation idea is supported by microphotographs of cross sections of exposed volume etched by diluted 1% HF where increasing density of

channels with time was observed [7]. The incubation time corresponds to the situation of totally interconnected channels in these photographs. The channels can correspond to the paths of corrupted bonds along which the released alkalis can move preferably.

Assuming $E_r \ll E_u$ the following equation is valid [8]

$$\ln i\tau = \ln\frac{pe}{\sigma} + \frac{T_r}{T} \quad . \tag{2}$$

where τ is the incubation period, i is the current density, $T_r = E_r/k_B$ is the temperature corresponding to the energy E_r, k_B is the Boltzmann constant, σ is the effective ionization cross section, e is the electron charge and T is the temperature in the irradiated volume.

Reaching the percolation point, ionized unreleased alkali cation can easily hop from its original site into the previously formed network of paths and take part in the cooperative migration. If one assumes that all ionised alkali ions hop into the network of path and contribute to the migration, then the rate of migration at time t is [8]

$$\frac{dc}{dt}(\tau) = -c_0\sigma\frac{i}{e} \quad , \tag{3}$$

where c_0 is the initial alkali concentration.

EXPERIMENTAL PART

The binary alkali glasses were melted in Pt crucible from pure batch and quenched some time near T_g. The following glasses were prepared Na10 (10% Na_2O + + 90% SiO_2), Na15 (15% Na_2O + 85% SiO_2), Na20 (20% Na_2O + 80% SiO_2), K10 (10% K_2O + 90% SiO_2), K15 (15% K_2O + 85% SiO_2), Rb15 (15% Rb_2O + + 85% SiO_2) and Cs15 (15% Cs_2O + 85% SiO_2), all in molar concentrations. Blocks of glasses were polished and coated with a 20 nm carbon layer. Specimens were exposed in an electron microprobe analyser; the diameter of the beam was measured at the fluorescent screen using an optical microscope and set to 100 μm. The accelerating voltage of the used electron beam was 50 kV. The absorption coefficients of the measured lines were calculated from the tabulated absorption coefficients [14] for particular atoms. It was found that the information depth for potassium $K\alpha$ line is slightly lower than the electron range, that is approximately about 6 mg cm^{-2} [15] for 50 keV electrons.

RESULTS

It was found that the incubation period decreases with the increasing electron beam current density. This shortening of the incubation period is partly due to the temperature increase (temperature influence), partly due

to the increase of the electric field created inside the sample (electric field influence) and partly due to the higher ionization rate of alkali ions (beam influence).

The incubation period for the binary sodium glass was found to be zero even for very low current densities. The result is in agreement with previous findings [3]. Figure 2 shows $\ln(it)$ versus $1/T$ plot for the exposed binary silica glasses. Due to the equation (2) slopes of the least square fits are directly proportional to the E_r.

The activation energy of potassium ion in the potassium glass increases with the alkali content (figure 2). Keeping constant alkali content in the glass the activation energy at the percolation point is the highest for the caesium glass and the lowest for the potassium glass.
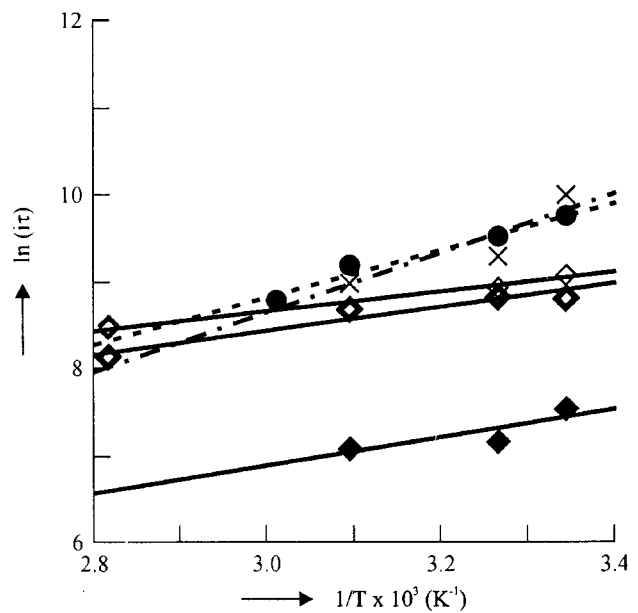

Figure 2. Plots of $\ln(i\tau)$ versus $1/T$. The rhombi mark binary potassium glasses and the corresponding least square fits are drawn by the solid lines. The circles mark binary rubidium glass and the corresponding least square fit is drawn by the dashed line. The crosses mark binary caesium glass and the corresponding least square fit is drawn by the dash-doted solid line. The primary electron beam used was 50 keV of energy and 100 μm of a diameter.

◇ - K10, ◆ - K15, ◆ - K20, ● - Rb15, × - Cs15

The normalised migration rate at the percolation point is according to the equation (3) directly proportional to the σ of alkali ions. The effective ionization cross section is the highest for the lowest alkali content (figure 3 for the sodium glass and figure 4 for the potassium glass) and decreases as other alkali ions enter into the glass. However, the migration rates of sodium ions are about an order higher than migration rates of other alkali ions.
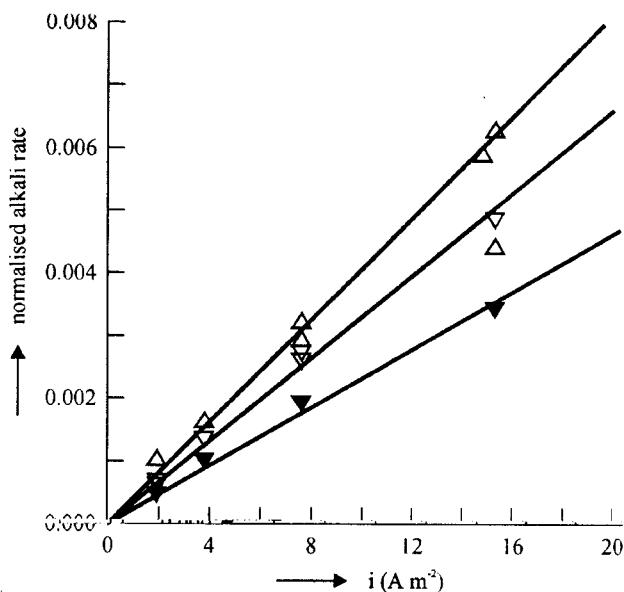
Figure 3. Sodium migration rate in the exposed glass. The primary electron beam used was 50 keV of energy and diameter of 100 μm. The triangles mark binary sodium glasses and corresponding least square fits are drawn by the solid lines.
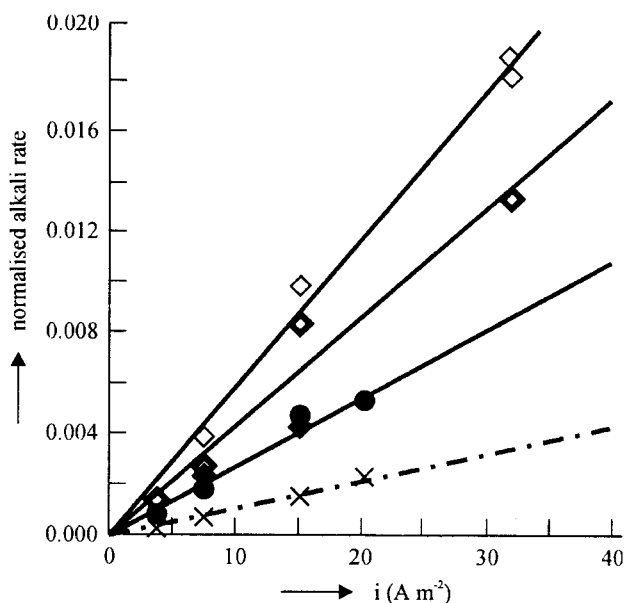Δ - Na10, ∇ - Na15, ▼ - Na20.

Figure 4. Alkali migration rate in the exposed glass. The rhombi mark binary potassium glasses and the corresponding least square fits are drawn by the solid lines. The circles mark binary rubidium glass and the corresponding least square fit is drawn by the dashed line (nearly coincides with the solid line for K20 glass). The crosses mark binary caesium glass and the corresponding least square fit is drawn by the dash-dotted line. The primary electron beam used was 50 keV of energy and diameter of 100 μm.

◇ - K10, ◆ - K15, ◆ - K20, ● - Rb15, × - Cs15.

Keeping constant an alkali content in the glass, the σ is the highest for the sodium glass and decreases as an atom number of the ion increases (figure 4).

DISCUSSION

At the first sight it is a surprising fact that the activation energy E_r increases with the content of alkali concentration in the potassium glass, but it can be explained by the following. The incubation period decreases with the increasing content of alkali ions in the glass because the formed network of paths is thinner and the displacement energy, that is a dominated component in the activation energy, is higher.

The activation energy of released alkali ions decreases with decreasing alkali ion size in binary glass, and for sodium ions is nearly zero. This is in an agreement with the idea that the released alkali ion is bonded very weakly and that its activation energy is predominantly determined by its displacement energy, that increases with its ion size.

The normalised migration rate at the percolation point is according to the equation 3 directly proportional to the σ of alkali ions. The network formed by the released alkali ions is thinner as the number of alkali ions in the glass increases, due to the decrease of the incubation period. The effective ionization rate at the percolation point is the highest for the lowest alkali content, as the network is the thinnest and the probability of the ionised alkali cation hop into the network is the lowest. The migration rates of sodium ions are about one order higher than migration rates of other alkali ions due to the small ion size.

Not all ionized alkali ions are released. Some of them are being relaxed to the original sites and do not contribute to the overall number of released alkali ions. The probability of releasing will increase with decreasing ion size due to the lowering in the displacement energy. In this way the increase of σ with decreasing atom number can be explained.

Due to the considerable decrease in the activation energy of released alkali ions, one can expect a significant rise in the conductivity of the irradiated volume after the percolation point is achieved. At this point paths are open and released alkali ions are mobile. However, the conductivity can be decreased by the longer bombardment because relaxation processes begin to close the paths in the glass. Moreover, the alkali ions reaching approximately half of the electron range group into aggregates that are not very mobile in the relaxed glass. The high conductivity is therefore expected in the short time range after the percolation point is achieved.

CONCLUSIONS

Binary alkali glasses irradiated by electron probes show an incubation period except for the binary sodium glass where no incubation period can be observed even ·for very low current density of an electron beam. During the incubation period the migration rate of alkali ions is very low. The alkali ions are released from their original sites by the ionization process and are subsequently driven by the electric field, formed by the electron probe, into new sites. As soon as the concentration of such alkali ions achieves a critical point, the percolation threshold, the incubation period ends and fast spontaneous migration begins.

The incubation period decreases with the current density of an electron beam. The activation energy increases with both the increasing alkali concentration in the glass and the increasing alkali ion size. The normalised rate of migration after the incubation period increases with the decreasing alkali concentration and with the decreasing ion size.

Acknowledgement

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SPONTÁNNÍ MIGRACE ALKÁLIÍ VE SKLE OZÁŘENÉM ELEKTRONOVÝM SVAZKEM

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Sklo ozářené rychlými elektrony mění svoji strukturu. Na rozdíl od ozáření neutrálními částicemi, elektrony vytvářejí v ozářeném objemu dielektrického vzorku elektrické pole. Alkalické ionty ionizované dopadajícími elektrony mohou být uvolněny ze svých původních pozic a díky elektrickému poli budou migrovat dovnitř vzorku. Pohyb alkálií byl pozorován pomocí mikroanalýzy, to jest pomocí detekce charakteristického rtg. záření. Byly měřeny těkací křivky (časová změna intenzity rtg. záření), které odhalily dva migrační režimy. První režim, označovaný jako inkubační perioda, je charakterizován individuální migraci iontů a pomalým lineárním poklesem rtg. záření. Uvolněné ionty migrují podél cest, které lze zobrazit pomocí elektronové mikroskopie a jejichž hustota roste s časem. Jakmile počet uvolněných alkálií dosáhne perkolačního bodu, první migrační režim přejde do režimu spontánní migrace, jenž je charakterizován kooperativním transportem alkálií a rychlým exponenciálním poklesem charakteristického rtg. záření.

Bylo zjištěno, že inkubační perioda roste s rostoucí proudovou hustotou dopadajícího elektronového svazku a že inkubační perioda neexistuje pro binární sodno-křemičité sklo, a to i pro extrémně nízké proudové hustoty.

Aktivační energie uvolněných alkálií klesá s velikostí alkalického iontu a pro sodík je nulová. Tato skutečnost je ve shodě s představou, že uvolněný iont je vázán velmi slabě a že jeho aktivační energie je dominantně určena jeho transportní energií, která roste s velikostí iontu.