

Review

Ion exchange for glass strengthening

René Gy

Saint-Gobain Recherche, F-93303 Aubervilliers, France

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Abstract

This paper presents a short overview of silicate glass strengthening by exchange of alkali ions in a molten salt, below the glass transition temperature (chemical tempering). The physics of alkali inter-diffusion is briefly explained and the main parameters of the process, which control the glass reinforcement, are reviewed. Methods for characterizing the obtained residual stress state and the strengthening are described, along with the simplified modelling of the stress build-up. The fragmentation of chemically tempered glass is discussed. The concept of engineered stress profile glass is presented, and finally, the effect of glass and salt compositions is overviewed.

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1. Introduction: principles and applications

Glass strengthening by ion exchange, or “chemical” tempering, is a process where the original glasses are immersed into a molten alkali salt at a temperature below the glass transition. During the time of immersion, the alkali ions from the glass that are close enough to the surface are exchanged for those from the molten salt. This is a thermally activated inter-diffusion process, which results in the strengthening of glass, provided that the ionic radius of the penetrating ions is larger

than that of the ions which are simultaneously leaving the glass.

As for conventional glass thermal tempering, the strengthening comes from the build up of a residual compressive stress state, up to a certain depth below the surface. It is equilibrated by a tensile stress state in the internal layers. The compressive stress is created by the “stuffing” or “crowding” effect due to the replacement of small alkali ions by larger ones, in the same molecular sites, i.e. without changing much the network structure formed by the silicon–oxygen bonds in the original silicate glass.

The main industrial application of chemical tempering of glass is the fabrication of cockpit windows for aircrafts. Other

E-mail address: rene.gy@saint-gobain.com.

applications worth mentioning are high speed train windshields, high-end ophthalmic glasses, glasses for copy machines, glass substrates used in the fabrication of hard disk drive for data storage in computers, and glass items for drug delivery (auto injector cartridge).

In the next section, the main features of chemical tempering are summarized and compared with those of thermal tempering. They are further explained in the following sections where the physics of the process and mechanics of the products are discussed. The effects of glass and molten salts composition are eventually briefly overviewed.

2. Comparison with conventional thermal tempering

Compared to conventional thermal tempering, chemical tempering features the following differences:

- A higher surface compression and hence a larger strengthening level can be obtained.
- The compression depth is smaller.
- The optical quality of the ion-exchanged glass is very good: it is kept the same as that of the original glass. This is not the case for thermal tempering, for which the manipulation of a somewhat softened glass is required. Also, there is no 'strain pattern' (or iridescence), which is an optical defect that is visible on thermally tempered glass when lightening is slightly polarized.
- Very thin glass can be strengthened by ion exchange, whereas it is very hard to provide reinforcement to glass thinner than 2 mm on an industrial thermal tempering installation (air cooling).
- Complex-shaped glass items can be reinforced (not feasible with thermal tempering).
- When broken, the fragmentation of chemically tempered glass is different from that of thermally tempered glass; this can be a drawback or an advantage, depending on the application.
- The upper limit to the temperature range in which chemically tempered glass can be held is different from that of thermally tempered glass.
- The main drawback of chemical tempering is the cost. Because of the large cost, compared to conventional thermal tempering, this reinforcement process can only be applied for high value applications. For instance, whereas an efficient thermal strengthening of glass bottles is very difficult to achieve because of their complex shape, a hardly breakable glass bottle can be obtained after immersion in molten potassium nitrate for long enough. There would be no market for such an expensive glass bottle, though.

3. Physics of the process and characterization of the products

3.1. Ions inter-diffusion

It is supposed in this section that sodium is the only exchangeable (alkali) ion in the glass and potassium the only exchangeable (alkali) ion in the molten salt. Since potassium is heavier than

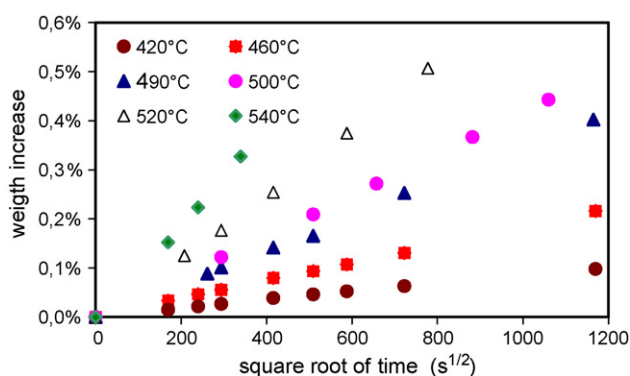


Fig. 1. Relative increase of weight of chemically tempered soda-lime silicate glass as function of square root of processing time for different temperatures.

sodium, an increase of weight is expected after ions inter-diffusion. Fig. 1 presents the increase of weight of flat glass test samples as a function of the square root of t (time of immersion in molten potassium nitrate) for different temperatures T . Let us assume that the glass thickness is larger than twice the inter-diffusion depth. The observed linear dependency is consistent with the normalized potassium concentration, or exchange rate, $C(x,t)$ in the glass being solution of a one-dimensional inter-diffusion equation, where x is the depth into the glass measured from the surface

$$\frac{\partial c}{\partial t} = \frac{D_K}{1-\alpha c} \left[\frac{\partial^2 c}{\partial x^2} + \frac{\alpha}{1-\alpha c} \left(\frac{\partial c}{\partial x} \right)^2 \right] \quad (1)$$

$$\alpha = 1 - \frac{D_K}{D_{Na}} \quad (2)$$

where D_K and D_{Na} are the self-diffusion coefficients of K and Na ions, respectively. The initial condition is $C(x,0)=0$; the boundary conditions read $C(0,t)=1$, $C(\infty, t)=0$. This equation is quite complex because the cation self-diffusion coefficients (and hence α) generally strongly depend on the local concentration of the cation in the glass.

Fig. 2 presents measured potassium concentration profiles (microprobe analysis) for different processing condition. At high temperature, and/or long processing time, the potassium penetration depth is larger than at lower temperature and/or shorter processing time but the concentration profile has a more complex

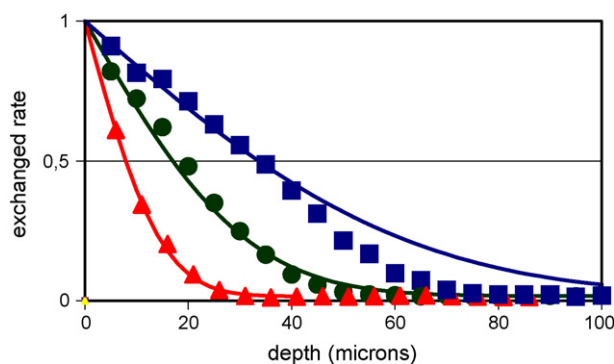


Fig. 2. Normalized Potassium concentration in soda-lime silicate glass for different chemical tempering conditions. Triangle: 420 °C for 72 h; Circle: 460 °C for 72 h; Square: 490 °C for 72 h. The lines are according to Eq. (3), where D is obtained from the weight increase measurements.

shape, reflecting the complexity of Eq. (1), whereas for lower temperature and shorter times the concentration profile shape is closer to that of the complementary error function

$$C(x, t) = \operatorname{erfc} \left(\frac{x}{2(Dt)^{1/2}} \right) \quad (3)$$

where D is a constant inter-diffusion coefficient. From Eqs. (1) and (2), this is expected only when the self-diffusion coefficient of both ions are close to each other ($\alpha = 0$) and independent of C . It is known that in single alkali glass obtained by cooling from a melt, the alkali self-diffusion coefficient strongly increases with the alkali concentration; therefore an *erfc*-shape profile after inter-diffusion would not be expected even at low temperature. A likely explanation may be that at high temperature and/or long processing time, the molecular network structure of the modified glass becomes closer to that of normal potassium glass obtained by cooling the melt, whereas at low temperature (short processing time) the glass network structure is not changed by the ion exchange process. The development of such a surface structural relaxation may also affects the residual stress profile after ion exchange and its measurement: this is further discussed in Section 3.

The exchanged depth $x_e(t)$ can be defined as $c(x_e) = 0.005$ or any other convended low value. If Eq. (3) holds, i.e. if a concentration independent inter-diffusion coefficient D can be considered, then $x_e(t)$ scales with $(Dt)^{1/2}$ and with the glass weight increase. The glass weight increase measurement provides a quick and convenient way for identifying a constant inter-diffusion coefficient, and its dependency on temperature. It is found to follow the Arrhenius law

$$D = D_0 \exp \left(\frac{-E}{RT} \right) \quad (4)$$

where the activation energy E is easily determined. It is of the order of 150 kJ/mol for soda-lime silicate glass.

These approximations are convenient for roughly estimating the exchanged depth for different temperatures and processing times, once a microprobe concentration profile has been determined after exchange in one given condition. This estimation tends to overestimate the exchange depth for high temperature and long process times, when the concentration profile strongly departs from the *erfc* shape. A more sophisticated approach would be to identify a concentration dependant inter-diffusion coefficient, and its temperature dependency, from several microprobe concentration profiles and the use of the Boltzman–Matano method. For a more accurate description, more complex models for ions inter-diffusion are proposed [1].

3.2. Residual stress

3.2.1. Residual stress measurements

In order to evaluate the thickness stress distribution after chemical tempering, photoelastic methods are generally used [2], where the birefringence due to the residual stress in glass is measured. It is supposed that the ion exchange does not significantly modify the photoelastic coefficient of glass. In the simplest amongst these methods, a small rectangular probe is

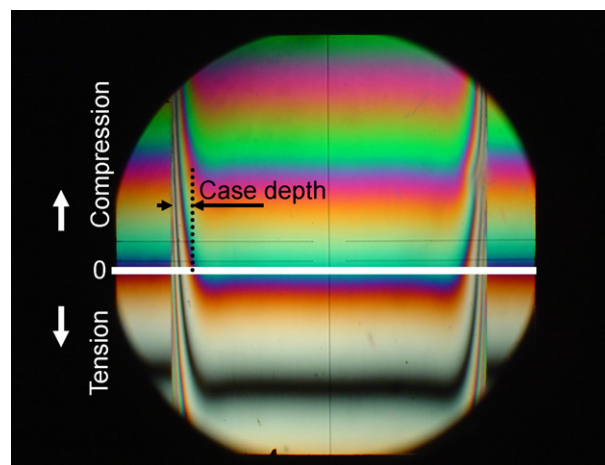


Fig. 3. Stress pattern in a chemically tempered glass: side view in a polariscope equipped with a Babinet compensator.

cut from the chemically tempered glass. The birefringence is measured in a polariscope, where the light path is parallel to the sample surface. When a Babinet compensator is used, the shape of the observed parallel fringes reproduces that of the residual stress profile (Fig. 3). The system is conveniently built into a microscope to enlarge the observation field close to the surface. The compression depth or “case depth” x_c , can be evaluated: it is the depth where a fringe crosses the zero birefringence line. The core stress is a uniform low tensile stress that can also be quite accurately evaluated. One observes sometimes a slight maximum of the tensile stress just below the compressive zone. The compressive stress profile and especially the high surface stress are hardly measurable with this method, because the birefringence ranges from very large to very small value on a short distance. This makes the parallel fringes sometimes hardly distinguishable from each other. The birefringence level can be reduced by cutting a sufficiently thin slice in the sample and this enables the distinction of the fringes close to the surface. For high process temperature, the compression maximum is not found at the surface but significantly below the surface (Fig. 4). This is attributed to the surface structural relaxation. As mentioned in Section 2, the exchanged glass tends to progressively change its structure, towards that of a lower density potassium glass – the same as that which would be obtained from a melt – releasing at the same time a part of the stress in the most outer layers. However, there may be doubts with the obtained stress profiles because, when the thickness of the slice is not large enough compared to the case depth, there is a significant modification of the residual stress state that is due to the slicing. In particular, a tensile maximum, not related to the ions exchange, may appear below the compression depth [4]. But it is not clear that this artefact is the unique cause for the observed tensile maximum. There might be other causes, may be related to the fact that, beside “stuffing”, the exchange of sodium for potassium results in gradients of many glass properties, thermoelastic and others, close to the surface [3]. This would require further investigation.

There is a steep refractive index decrease from the surface towards the internal layers. This effect enables the use of differ-

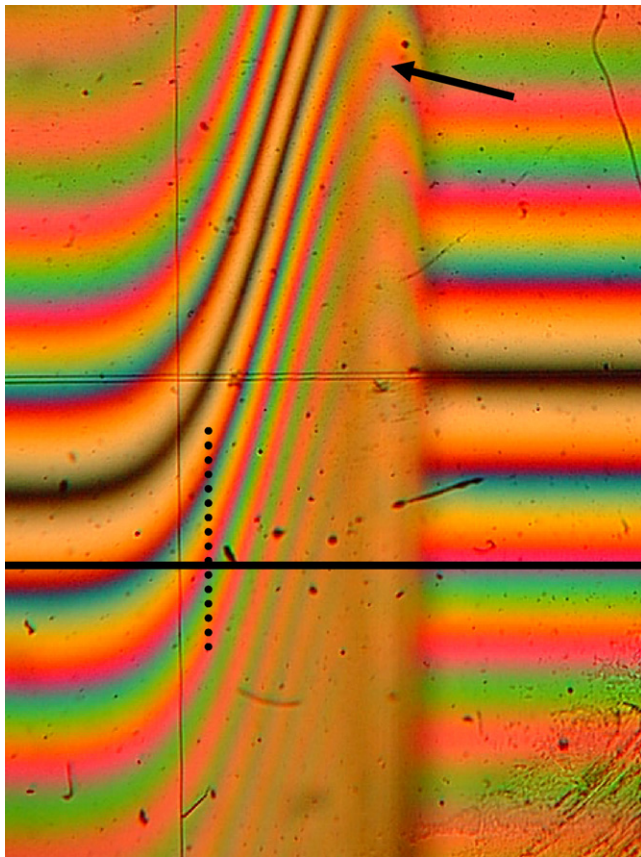


Fig. 4. Side view in polariscope for a chemical tempering stress profile showing a maximum compression stress below the surface (arrow). The processing temperature is higher than for the stress pattern shown in Fig. 3.

ential surface refractometry for the measurement of the stress profile in the exchanged layers. A double prism with an internal screen is used to guide an incident light through multiple curved paths in the glass layers close to the surface. The curved paths enable rays of light to emerge from the glass, after multiple reflections at the surface. These rays interfere with each other, and a set of bright fringes are observed (at infinity) corresponding to definite incidences, and definite depths probed by the light. Their analysis allows for the determination of the index profile as a function of depth, close to the surface. Two polarized incident lights are used, with planes of polarization parallel and perpendicular to the surface, hence two different index profiles are obtained, corresponding to the birefringence due to the stress profile in the glass layers close to the surface. The method, and the corresponding “Stratrefractometer” apparatus, is described with more details elsewhere [2]. An example of index profiles measurement for both polarizations is shown in Fig. 5, and the corresponding stress profile in Fig. 6. The method provides an accurate measurement of the case depth which is generally consistent with that obtained with the Babinet polariscope. There are also limits to the method: when there is significant surface structural relaxation, the surface glass molar volume tends to increase and the index profile may also show a maximum below the surface, instead of at the surface. Then surface differential refractometry does not work (no fringes) or provides fringes

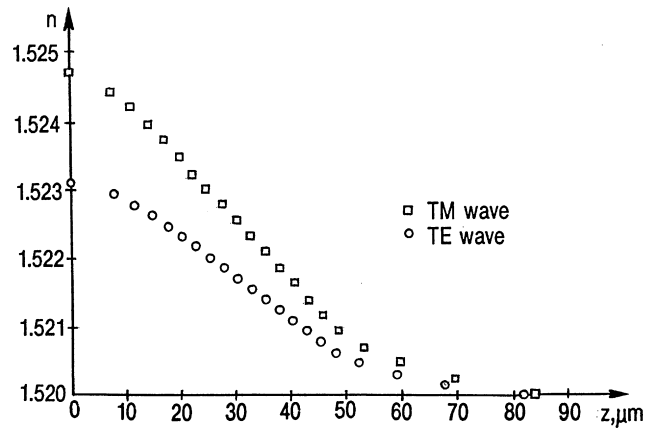


Fig. 5. Stratrefractometer: example of refractive index n profiles as a function of depth z in a chemically tempered soda-lime silicate glass for light polarized parallel (TM) and perpendicular (TE) to the glass surface (from Ref. [2]).

that are more difficult to interpret, because the standard analysis requires that the refractive index be monotonically decreasing from the surface.

There are non-photoelastic, but destructive methods for surface compressive stress measurement that work whatever the index profile and structural relaxation produced by chemical tempering. It is possible to measure accurately (optically) the slight curvature variation which is produced after etching in dilute hydrofluoric acid, of a very thin layer on one of the surface of a chemically tempered sample. Assuming that the glass thickness and elastic constants are known, and not modified by the ions exchange, the application of the Stoney formula readily leads to an estimate of the compression stress averaged over the small etched depth. The repetition of this procedure allows for the determination of the compression stress profile and confirms that when large surface relaxation takes place, the compression maximum is located below the surface.

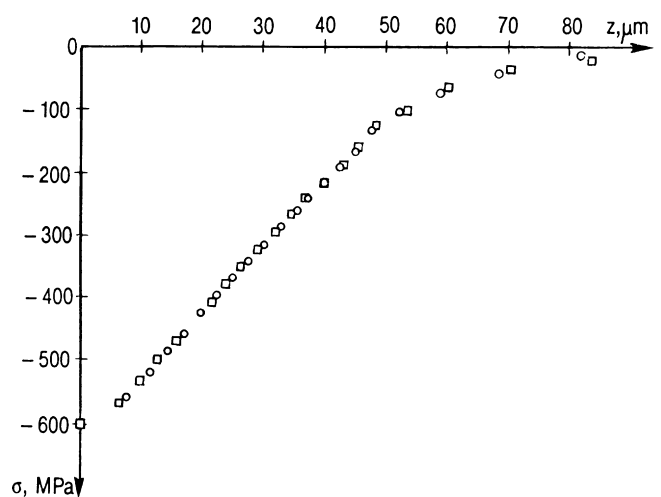


Fig. 6. Stratrefractometer: measured compression stress σ profile as a function of depth z in the chemically tempered glass sample corresponding to Fig. 5 (from Ref. [2]).

3.2.2. Residual stress build-up

It is supposed in this section that the unique stress-inducing effect of the ion exchange is the “stuffing” effect. The measured surface compressive stress for a soda-lime glass chemically tempered in potassium nitrate typically is of the order of 500 MPa. Theoretically, the “stuffing” effect would produce a surface stress of the order of $(1/3)(\Delta V/V)(E/(1-\nu))$, where E and ν are the glass elastic constants and $\Delta V/V$ the free volume expansion caused by the substitution of an alkali for the other. As the molar volume of usual soda-lime glass is roughly 8% less than that of the corresponding potassium glass, the expected surface stress after exchange with potassium would be of the order of 2000 MPa. This discrepancy may be explained by the fact, already mentioned, that the molecular structure of the exchanged glass is not that of a potassium glass cooled from the melt, but is closer to that of the original soda glass. So actually, would it be free from the core constraint, the expansion of the surface due the full alkali exchange would be less than 8%. Anyway, it is reasonable to assume that this free expansion is proportional to the normalized concentration C so that, by analogy to thermal stresses, the residual stress profile $\sigma(x, t)$ reads

$$\sigma(x, t) = \frac{kE}{1-\nu}([C](t) - C(x, t)) \quad (5)$$

where k is the free expansion due the full ion exchange and $[C](t)$ the rate of exchange averaged over the thickness. The form of Eq. (5) ensures that the residual stress state is self-equilibrated and also shows that the case depth is the depth where the actual exchange rate equals the average one, which is readily obtained from the relative increase of weight, the glass thickness and the atomic masses of the exchanged ions. This equation also allows showing that the case depth is always smaller than the diffusion depth, all the more that the exchanged depth is not small compared to the glass half thickness. As long as the exchanged depth is smaller than the glass half thickness, the core stress scales with $[C](t)$, so it also increases like the square root of the processing time t .

The viscoelasticity of glass tends to reduce the stress. Generally speaking, significant stress relaxation occurs in glass well below the glass transition temperature and Eq. (5) has to be modified to account for this [5]

$$\sigma(x, t) = \frac{kE}{1-\nu} \int_0^t \psi(t-t') \frac{\partial}{\partial t'} ([C](t') - C(x, t')) dt' \quad (6)$$

Eq. (6) involves the viscoelastic stress relaxation function ψ , which strongly depends on temperature, in the same way – i.e. with the same activation energy – as the glass viscosity.

After some manipulation of Eq. (6), it can be shown that the compressive surface stress $\sigma(0, t)$ and the tensile core stress $\sigma_{\text{core}}(t)$ are more simply related to ψ according to

$$\sigma(0, t) = \sigma_{\text{core}}(t) - \frac{kE}{1-\nu} \psi(t) \quad (7)$$

When the temperature increases, ψ tends towards zero more quickly, so does the stress profile. Actually, the core stress still increases like $t^{1/2}$ at the beginning, so that the viscoelastic relaxation mostly decreases the surface compression, quickly at high

processing temperature. On the other hand, the viscoelastic relaxation does not directly affect the concentration profile, nor much the case depth, which can be increased in a shorter time when the temperature is raised. So, there exists a best process temperature compromise, for a given maximal allowable processing time, which depends on whether the emphasis is on the maximum surface compression or on a large case depth. This is very important for strengthening optimization, as explained in the next section.

In addition to viscoelastic relaxation, surface structural relaxation also takes place for long processing times and/or high enough processing temperature. This also tends to reduce the surface stress, so that the maximum of compression is not at the surface but below the surface as shown in Fig. 5. Eq. (6) can hardly reproduce such a stress profile [5], unless k is let to depend on x . In order to account for the observed maximum compression below the surface, appropriate refinements of the viscoelastic model for stress genesis during glass chemical tempering, taking into account surface structural relaxation, are still needed.

When an originally chemically tempered glass is reheated, significant ionic inter-diffusion may resume. This tends to flatten the ion exchange concentration profile and the corresponding residual stress field. In practice, chemically tempered glass cannot withstand a temperature too close to the chemical tempering temperature, except for transients much shorter than the chemical tempering duration.

3.3. Strengthening

It is well known that glass strength is not an intrinsic property, with a definitely ascribed value. Generally speaking, there is a statistical distribution of strengths. It reflects the statistical distribution of the severity – i.e. of the depth – of the impairing surface flaws (cracks). This makes the strength to depend on the size of the test-samples. The measurement of strength is usually done by flexural tests. Many such tests exist and some are standardized. For the characterization of the high strengthening provided to the glass surface by chemical tempering, ring-on-ring tests [6] are preferred because they do not put a large tensile stress on the machined edges of the test-sample. The calculation of the strengthening effect of chemical tempering would require the calculation of the stress intensity factor for a surface crack with a given depth c , in the complex-shape ion exchange stress field, taking into account the crack closure effect [7]. This is a rather complicated calculation. An insight into the main effect can more readily be obtained by the simplifying assumption that the surface compression linearly decreases from σ_s down to zero at the depth x_c . After chemical tempering, the strength σ of a glass whose most severe surface crack has a depth c , then reads

$$\sigma = Y \frac{K_{IC}}{\sqrt{\pi c}} + \sigma_s \left(1 - \frac{2c}{\pi x_c} \right) \quad (8)$$

The first term in Eq. (8) is the strength of the original glass involving the glass toughness K_{IC} and a non-dimensional crack shape factor Y , and the second term is the reinforcement. Eq. (8)

which holds for $c < x_c$, shows that the reinforcement decreases with the strength of the original glass. Glasses with initial surface cracks deeper than the case depth are hardly reinforced.

In practice, typical surface cracks of industrial “as-float” flat glass have a depth of the order of 10 μm , and a case depth of the same order provides significant reinforcement, measured in a ring-on-ring flexural test. But actually, such a small case depth is not of great practical value for the applications where glass is subjected to contact damage. This problem is illustrated in Fig. 7, where the flexure strength of damaged soda-lime float glass test-samples is presented. Prior to strength measurement, the damage is done with a Vickers diamond indenter that comes in contact with the glass surface at a given contact load P . In Fig. 7, the strength is plotted as a function of the load on the diamond for (i) non-treated glass, (ii) thermally tempered, 3 mm thick (surface compression stress around 100 MPa) (iii) chemically tempered glass (surface compression stress around 250 MPa, case depth around 90 μm). The depth of a contact damage cracks generally scales with $P^{2/3}$, so the strength is expected to scale with $P^{-1/3}$ and this explains the shape of curve (i) [8]. In thermally tempered glass the case depth is around 20% of the glass thickness: it is much larger than the deepest Vickers damage crack, so that the obtained reinforcement is constant, and curve (ii) is vertically shifted from curve (i) by the amount of the constant reinforcement. The strongest reinforcement is, as expected, obtained with chemical tempering, but for up to a limited damaging load. Beyond that limit, the damage depth is larger than the case depth and the strength of the chemically tempered glass falls down to the level of the untreated glass. This is below that of the thermally tempered glass, which will provide the best strengthening when very large contact damaging loads have to be taken into consideration.

So again, as mentioned in the previous section, there are two opposite effects that have to be taken into account when one seeks to optimize the chemical tempering process, from the strengthening point of view. If one aims at a very high strength for glasses that can otherwise benefit from some surface protection against contact damage during service, one will favour low temperature chemical tempering, whereas, if the glass surface can be subjected to severe contact damage during service, then a large case depth has to be favoured and this generally comes

at the price of a lesser undamaged strength because of a lower compressive stress on the surface.

4. Fragmentation of chemically tempered glass

When a thermally tempered glass, with thickness larger than 2 mm, is broken, a very small fragmentation is obtained. In addition to strengthening, this property contributes to the safety provided by thermal tempering, as small blunt glass fragments are less dangerous than the large and sharp pieces which are produced when non-reinforced glass is broken. When chemically strengthened glass is broken there is no such fine dicing of the glass, except when the glass is very thin, with thickness of the order of few hundreds of microns [9]. On the other hand, thermal tempering of such a very thin glass is not feasible, because of the very high heat exchange coefficient that would be required to produce a large enough core-surface temperature difference upon cooling. Let us consider a through-thickness crack running in a direction belonging to the glass plane. The side length of a glass fragment is the length at which such a crack bifurcates. This bifurcation is supposed to take place when the corresponding stress intensity factor reaches a given critical value. Assuming that the crack front is a straight line perpendicular to the plate, the stress intensity factor can be computed numerically for both thermal and chemical tempering stress distributions. It is shown [9] that the stress intensity factor is larger – i.e. for given glass thickness and bifurcation length, the core tensile stress necessary for bifurcation is less – in the chemical tempering case compared to thermal tempering. However, this is not enough to bring any fine fragmentation to thick chemically tempered glass because of the very low tensile core stress. For chemically strengthened glass, the surface compression does not depend on the thickness and the core stress decreases when the glass thickness increases: Eq. (5) shows that when the exchanged depth is small compared to the glass thickness $[C]$ is small and so is the tensile core stress, whereas when the exchanged depth is a significant part of the glass thickness, then $[C]$ is large and so is the tensile core stress. In very thin glass, the tensile core stress level may become comparable to the surface compression and the bifurcation length becomes small enough to produce a very fine dicing.

5. Engineered stress profile (ESP) glasses

This concept has been proposed quite recently [10,11]. The principle is to design the ion exchange stress profile so that the stress intensity factor for a surface crack is a decreasing function of the crack depth. Upon loading, this particular shape of the stress intensity factor will make the smaller cracks become critical first, but they will grow in a stable way, whilst the larger one are still arrested, until they all reach the same critical depth and become unstable almost simultaneously, when the glass is eventually broken. Such an engineered stress profile is characterized by a steep increase of the compression stress from the surface, up to a definite depth where it reaches a maximum. It can be produced in a double ion-exchange process. The first step is a normal but long (up to several days) chemical tempering aiming at a rather large case depth and the second step is a

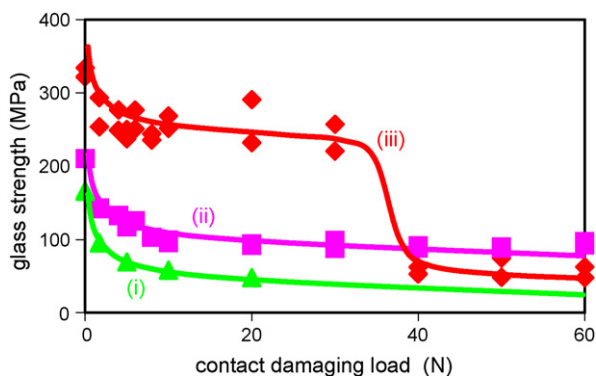


Fig. 7. Strength of soda-lime silicate glass as a function of damaging load, after contact damage with a Vickers diamond: (i) as-float glass; (ii) after thermal tempering; (iii) after chemical tempering. The lines are guides for the eye.

short inverse ion-exchange carried out for a much shorter time at lower temperature.

The main characteristics of ESP glass is a strong reduction of the scatter in the obtained strengths distribution, compared to that which is observed after the first step only. There is no increase of strengthening on average. ESP glass features other interesting properties: visible multiple surface cracking becomes apparent upon loading, long enough before the eventual failure, providing initial warning before complete destruction of the glass. This could be interesting from the safety point of view or in order to keep memory of any prior loading. It is also reported that ESP glass are not sensitive to static fatigue: contrary to most silicate glasses, their strength in ambient (humid) environment does not depend on the stressing rate [12]. This is likely related to the stable growth of cracks. It is not completely clear yet and further investigations are required on that aspect. Finally, the possibility that such a double ion-exchange process brings better strength after contact damage, compared to the conventional one-step chemical tempering, remains to be evidenced.

6. Glasses and salts for chemical strengthening

All silicate glasses can be strengthened with the ion exchange process, provided that they have enough alkalis in their composition. Low alkali glasses, like low thermal expansion borosilicate or alkali-free alumino-borosilicate glasses (like the one used for active matrix liquid crystal displays) cannot be chemically strengthened, though this might be desirable for some applications, since their low thermal expansion also makes them unfit to thermal tempering. Increasing the alkali content tends to lower the temperature at which viscoelastic relaxation occurs, which is not wanted, but soda glasses which are better suited to chemical tempering than standard soda-lime glass exist. They include glasses with large amount of alumina and mixed alkali glasses. High alumina content is beneficial, when associated with alkali, because it tends to reduce the number of non-bridging oxygen atoms in the silicate network, which makes the alkali diffusion coefficients larger. The alkali inter-diffusion coefficient is also increased when the two alkalis are already presents in the original glass. Large divalent cations, but zinc and magnesium, generally are considered as detrimental to the mobility of the alkali, hence to the chemical tempering. Many glass formulations for chemical strengthening have been patented. Saint-Gobain makes such a special soda glass. It is used, under the registered trademark Solidion, in the fabrication of cockpit windows for aircrafts. For large passenger aircrafts, a typical cockpit window is a complex laminated glazing, including at least two thick chemically reinforced special glasses of that kind. Such a window typically has to survive a collision with a 1.8 kg bird at a 180 m/s impacting speed and conventional soda-lime float glass cannot be strengthened to the required level in a reasonable processing time in molten potassium nitrate.

Generally speaking lithium-containing glass can be more easily chemically strengthened in sodium nitrate, than sodium containing glass in potassium nitrate. Because the lithium–sodium inter-diffusion coefficient is much larger, a larger case depth can be obtained at lower temperature and in a

shorter processing time, so that the surface compression is not attenuated much by viscoelasticity, neither by structural relaxation. Chemically strengthened lithium glasses have a lower temperature capability, though, because, for the same reason, the concentration profile is more quickly flattened by further inter-diffusion upon reheating.

Potassium or sodium – in case of lithium containing glass – nitrates are the most widely used salts for chemical tempering. They have low enough melting temperature, slightly above 300 °C, and can be used safely in austenitic stainless steel tanks up to around 500 °C, where the rate of decomposition of the nitrate becomes a difficult concern. Nitrogen oxides are formed already from 400 °C and must be released from the environment. Anyway, because of the viscoelastic relaxation, the chemical tempering of standard soda-lime silicate glass would not take advantage from a more stable anion. Only some special glasses with high Strain Point may benefit from higher processing temperature and require special salts, like sulphates and other mixtures. More importantly, as the salt is continuously used, it is progressively enriched with the original alkali from the glass. The surface exchange rate tends to decrease, and so does the compression stress and hence the reinforcement. At some point, the salt must be renewed. There is also a disposal/recycling issue with used salts. Finally, a key point in salts for chemical tempering is the control of the very low concentration of some elements which are shown to strongly affect the strength of the chemically tempered glasses [13].

7. Conclusion

In conclusion, glass chemical tempering in molten nitrate enables the fabrication of the strongest glass products, but they are also amongst the most expensive. An improvement of this situation should come from a better understanding of the process. There are many fields still to explore, or to re-visit, on both the scientific and the technological aspects of the strengthening of glass by ions exchange. Not all of them have been discussed or even mentioned in this short overview. Just to mention two: the possibilities and difficulties in using an electric field or ultrasonic waves as assistance to the process.

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