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Full Length Research Paper

Effect of storage and thermochemical treatments on glass indentation cracks and residual stresses

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In this work, the effect of storage, annealing and chemical strengthening on indentation radial cracks of a sodalime glass is presented. During the storage of an indented glass with a Vickers indenter, the induced radial cracks propagate under the combined effect of the residual stresses and the environmental humidity (stress corrosion). The cracks length achieves a threshold of stability after 6 to 24 h. The threshold level and the necessary time to reach it depend both on crack dimensions (length and aperture) which are directly related to the indentation load. The annealing glass treatment leads to a crack healing phenomenon caused by viscous flow. A maximal healing effect corresponding to 20% crack length decrease is reached after annealing at 620°C during 90 min. The strength value of this healed state corresponds to that of a non indented glass (90 MPa). The probable causes of this strengthening are the crack shortening and the indentation residual stresses relaxation demonstrated by photoelasticimetry measurements. The chemical treatment (ion exchange by KNO_3 salt melt) generates residual compressive stresses on the glass surface as shown by photoelsticimetry investigations.

Key words: Glass, indentation, cracks, annealing, ion exchange, residual stress.

INTRODUCTION

Glass is a brittle material showing a very sensibility to surface flaws. The measured strength is very low, rarely greater than 100 MPa. This is because the surface micro cracks act as stress concentrator's that is for very low applied stresses; the induced local stresses are very high exceeding the theoretical value (Donald, 1989). To overcome this problem, there are many methods proposed in literature. Among these methods, we can cite the thermal annealing the thermal tempering and the ion exchange. Annealing involves heating the glass to a uniform temperature near the transformation temperature range for a time sufficient to permit removal (relaxation) of stresses initially present in the material (Kreidl, 1986). The glass is then cooled at a sufficiently low rate avoiding any cooling stresses introduction (Zarzycki, 1982).

Modern methods of chemical tempering are based on ion exchange occurring by diffusion (Zarzycki, 1982). Glass articles are immersed in an alkaline salt melt at a temperature below the glass transition temperature. During immersion, the glass alkali ions near the surface are exchanged with those of the molten salt. In a KNO_3 melt bath, we have a replacement of sodium ions Na^+ (r = 0.98 Å) of glass by a potassium ions K^+ (r = 1.33 Å). The more voluminous sodium ions K^+ result in a high surface compressive stresses (Rene, 2008). Since the fracture of glass products is usually caused by extensive stresses initiating at the surface, the introduction of these high surface compressive stresses leads to a strengthening effect (Arun, 2010). The ion exchange treatment is not only useful for mechanical strengthening but also for other reasons such as the production of optical waveguides (Manfred et al., 2003).

Vickers indentation technique is widely adopted for intrinsic mechanical properties characterization of glass and other brittle materials (Chuchai et al., 2009). The

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Table 1. Chemical composition of the used glass.

Oxides	SiO_2	Na_2O	CaO	MgO	Al_2O_3	K_2O	TiO_2	F_2O_3	SO_3
% molar	63.11	19.44	6.06	10.34	0.46	0.23	0.07	0.01	0.27

Table 2. Some physical characteristics of the used glass.

Characteristic	Value and unity
Elastic modulus	72 GPa
Poisson's ratio	0.22
Vickers hardness	4.7 GPa
Toughness	0.74 MPa$\sqrt{m}$
Thermal expansion coefficient	8.5 x 10^{-6} K^{-1}
Transition temperature	502,8 °C
Density	2.51 g/cm^3
Optical transmission	92%
Refractive index	1.511

generated surface cracks are used as a model of natural surface defects for understanding fracture of ceramics and glasses (Gong et al., 2002). In addition to the elastic stress field induced during loading, there is a residual stress field around the indentation after the load was removed (Kaiyang and David, 1994). These residual stresses play an important role in determining the toughness and subcritical crack growth (Kaiyang and David, 1994).

To quantify the residual stresses in materials, several methods can be used. Each method has its advantages and limitations. The X-ray diffraction method, for example, can only be applied to crystalline materials. Electrical methods are limited in their ability to distinguish residual stresses from total stresses (Chuchai et al., 2009). Optical methods (photoelasticimetry) are limited to transparent materials. The photoelastic technique based on the physics of light waves and the induced birefringence in materials has been widely used to determine the stress state in real situations (Ayatollahi and Nejati, 2011).

The birefringence can be studied by analyzing the polarization transformation of optical waves after passing through the stressed material. For example, a linearly polarized light wave may become elliptically polarized. This phenomenon is explained by the fact that one component of the wave is delayed relative to the other. The delay between the two components of the wave corresponds to the phase retardation which depends on the incident light wavelength (light color) (Ayatollahi and Nejati, 2011). This delay is directly related to the stresses magnitude in the traversed material. Stresses in transparent materials can therefore be measured by following the change in the polarization state (Ayatollahi and Nejati, 2011). With the photoelasticimetry method, we can operate by transmission or by reflection. In both cases, the principle is the same: the material is placed between two polarizing filters and observed by transmission or by reflection. The relation between the stress level and the induced birefringence of the photoelastic model is given by Maxwell's law:

$$\delta = C\ e\ (\sigma_1 - \sigma_2) \quad (1)$$

where C is a photoelastic constant characterizing the tested material. It is expressed in Brewster (glass constant C = 2 Bw).

One Brewster corresponds to 10^{-12} m^2/N. δ is the path difference and e the sample thickness.

For a wavelength of the used monochromatic radiation λ, the path differences are expressed in number of wavelength (Ayatollahi and Nejati, 2011) in which case, Equation (1) becomes:

$$\sigma_1 - \sigma_2 = \frac{\lambda}{C\, e} \quad (2)$$

EXPERIMENTAL PROCEDURE

The used samples (50 × 12 × 3) mm^3 were cut from the same soda-lime glass sheet. This glass was made by the Algerian company named: Mediterranean float glass (MFG). The chemical composition in molar percent, provided by the supplier is given in Table 1 while the main physical characteristics are summarized in Table 2.

Samples were previously annealed to relax any residual

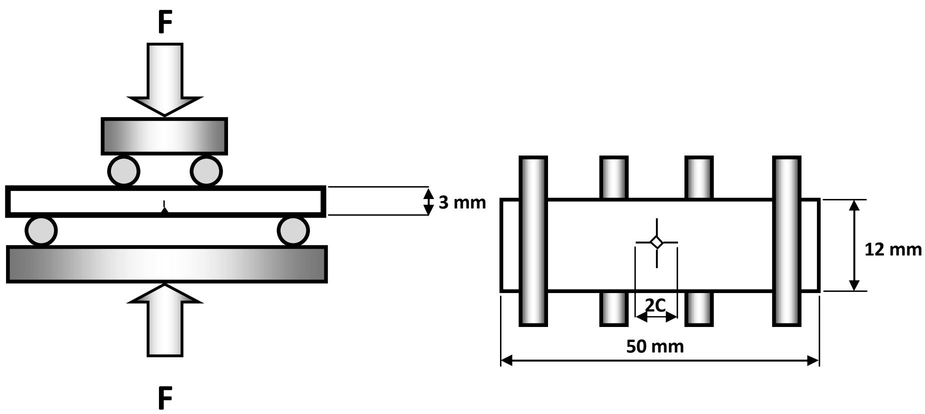


Figure 1. Front and bottom views of the loaded sample and the position of the indentation.

stresses. The annealing treatment was performed at 530°C for 30 min with a heating rate of 5°C/min and a cooling rate of 3°C/min to ambient temperature. We performed three indentations for each applied load: 5, 10, 15 and 20N. The dwell time at the maximum load is 15 s.

Effect of storage

The first set of tests concerns the study of the effect of storage in air on the propagation of Vickers indentation radial cracks. We followed the evolution of the radial cracks lengths (2C) as a function of storage time. Measurements were made after: 1.5, 6, 24, 30, 48, 54, 72, 78 and 96 h.

Effect of annealing and ion exchange

The Vickers indentations were made on these samples in the position and orientation shown in Figure 1. Indentation loads are ranging from 5 to 20 N with a step of 5 N and each sample has only one indentation. We followed the evolution of radial cracks as a function of the treatment:

- Annealing heat treatment: This treatment was performed at different temperatures (530, 560, 590 and 620°C) for different holding times (30, 60 and 90 min).
- Ion-exchange treatment in potassium nitrate KNO_3 melt: this treatment was carried out at T = 480°C for 2 h.

The strength of the indented samples is measured by 4 points bending tests (Figure 1) with a strain rate equal to 1 mm/min. The specimen is placed on two rollers separated by L = 40 mm. The load F is applied on the non-indented face by two other rollers separated by l = 20 mm. The indentation is located on the side of external supports between the inner rollers that is in the domain of maximal applied load. Thus, the radial cracks parallel to the axis rollers are loaded in tension by the maximal applied load. The strength (σr) is given by the following relationship:

$$\sigma_r = \frac{3F(L-l)}{2bw^2} \quad (3)$$

F: force à la rupture F.
b: width of used specimen (12 mm).
w: height of used specimen (3 mm).

The samples to be tested by 4 points bending tests were slightly chamfered to minimize the edge effect.

RESULTS AND DISCUSSION

Effect of storage

Figure 2 shows the evolution of the radial crack length (2C) with storage time on Vickers indentations obtained under different loads. We note that crack length increases with storage time regardless of the indentation load. Crack propagation occurs under the action of tensile residual stresses and also by the effect of humidity (stress corrosion or sub-critical crack growth) (Hamidouche et al., 1994; Madjoubi et al., 2007).

We note that the largest radial crack propagation (2C) is observed in the early hours of storage (6 to 24 h). In this stage, the slope of the curve which expresses the propagation speed is higher. After that, the propagation continues, but less significantly until the cracks reach a threshold of stabilization. It appears that both the reached threshold and the time needed to achieve it increase with the indentation load. For example, the crack corresponding to a 5 N load stabilizes in 30 h after a propagation of about 6.25% of the initial length, whereas that obtained with a 20 N load is stabilized after a storage time of 72 h and a propagation near 17% of its original length.

When the load increases, the residual stresses increase implying larger radial cracks and longer relaxation time.

Effect of annealing and ion exchange

Effect of annealing

a.) Effect on the radial crack length: The variation of the crack healing of radial cracks (Δ 2C), obtained with a

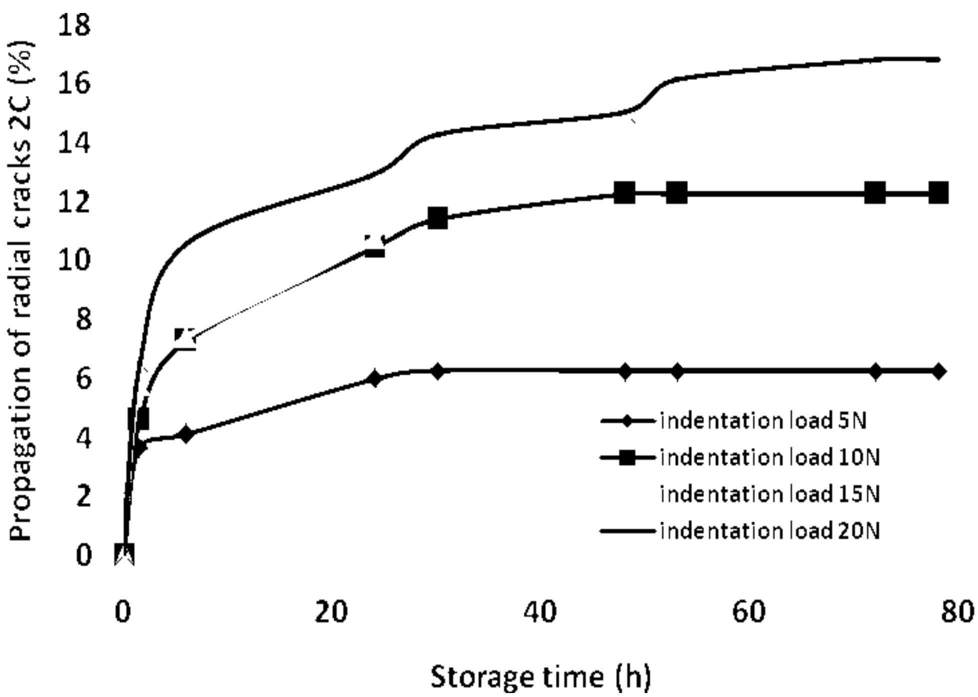


Figure 2. Propagation of Vickers indentation radial cracks (Δ 2C) as a function of storage time.

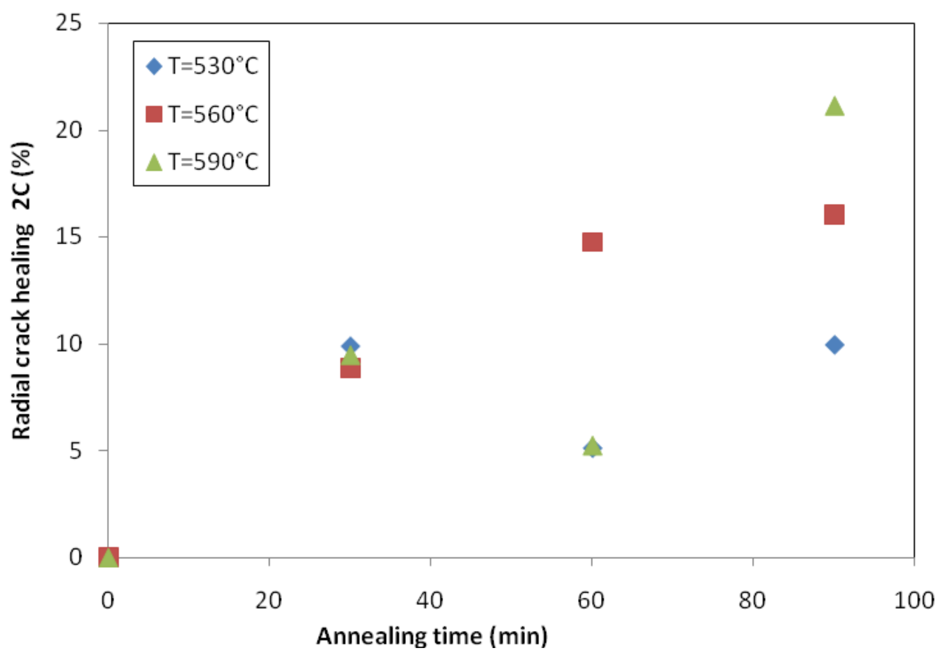


Figure 3. Radial crack healing at different temperatures and time treatment for an indentation load of 20N.

20 N indentation load as a function of the annealing time at different temperatures, is shown in Figure 3.

The curves show an increase of the healing rate with annealing temperature, except for the curve obtained with a treatment realized just at the transition temperature (Tg = 530°C). At this temperature, the crack healing is limited because of the solid state of glass and its important viscosity. Beyond the transition temperature, the glass viscosity decreases causing viscous flow that promotes cracks healing. During healing, morphological

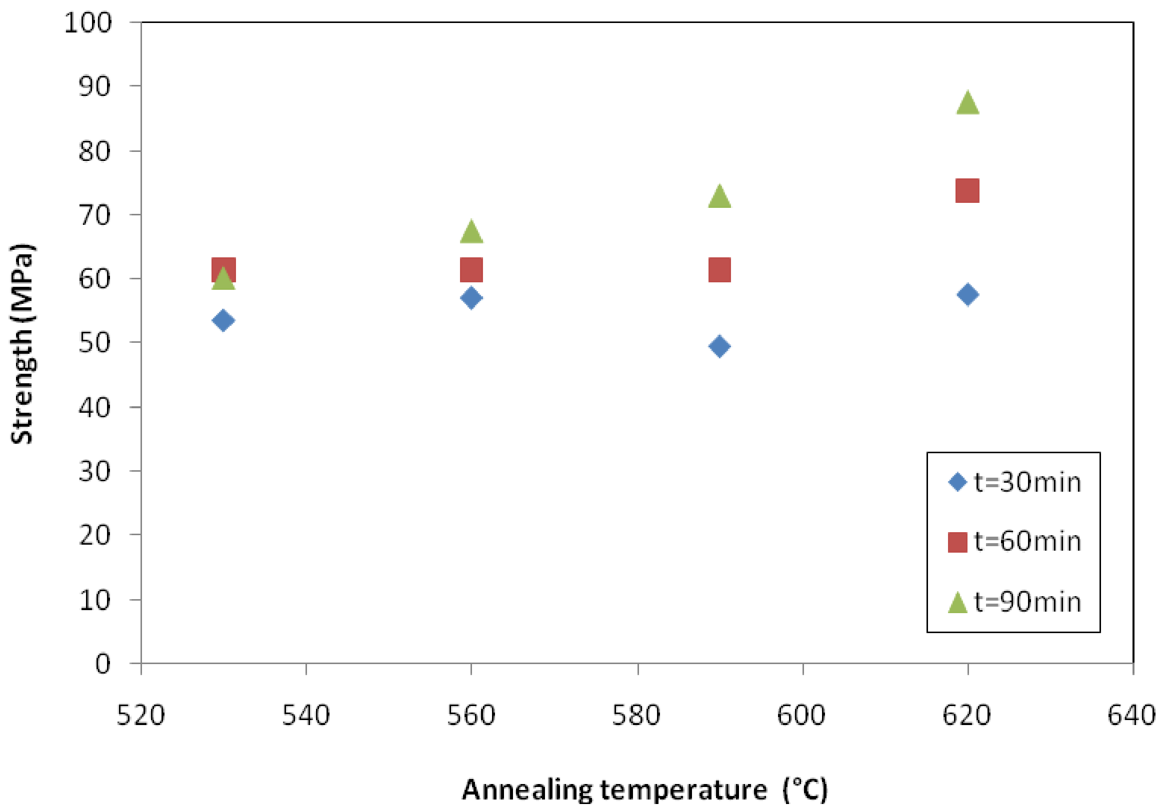


Figure 4. Evolution of the strength of samples indented with a load of 20N as a function of annealing temperature for different treatment time.

changes of the crack occurs. Indeed, there may be continuous regression of the crack from the tip, discontinuous narrowing along the crack, and crack tip blunting.

The decrease in the crack healing of radial cracks, which expresses the decrease in crack length was also observed by X. Carbonneau (1997), who treated at different temperatures zircon indented with a load (P = 98 N) and by Kolli [14] on annealed glass. The radial cracks healing rate versus time indicates that prolonged treatment can lead to a decrease in crack healing. First, the residual stresses induced by indentation are relaxed. The initially sharp cracks are also blunted by viscous flow, driven by capillarity. According to Hrma et al. (1998), the blunting effect can slow subcritical cracking.

b.) Effect on strength: Figure 4 shows the evolution of the strength of indented samples (20 N) after annealing at different temperatures and for different treatment times.

We note that the curves are almost identical: the strength increases continuously with temperature and annealing time, but not the curve obtained after an annealing time of 30 min. this period is insufficient to cause the vitreous flow and important crack healing. Strength of the order of 88 MPa is reached with a treatment at 620°C during 90 min. This is close to the non-indented glass strength (around 90 MPa). The mechanical reinforcement observed is attributed to the healing of median cracks.

The strength of the annealed indented samples increase substantially. This increase is related to the evolution of median cracks. After relaxation of indentation residual stress, these cracks shrink and blunt according to the temperature and the annealing time (Figure 5).

Effect of ion exchange on the crack lengths

In Figure 6, we presented the evolution of the radial crack length before and after an ion exchange treatment during 2 h with potassium nitrate (KNO_3) melted at 480°C. We note that ion exchange leads to radial cracks healing which depends on indentation load. For example, for an indentation load of 5 N, the initial length 2C is 199 µm and becomes 116 µm after treatment (about 42% recovery). For an indentation load of 20 N, healing corresponds only to 6% of the initial radial cracks length (397 µm).

When the indentation load increases, the increased residual tensile stresses lead to more open radial cracks which become difficult to heal during ion exchange treatment. The thermo-chemical treatment; realized at 480°C, allows only a partial stress relaxation. The ion

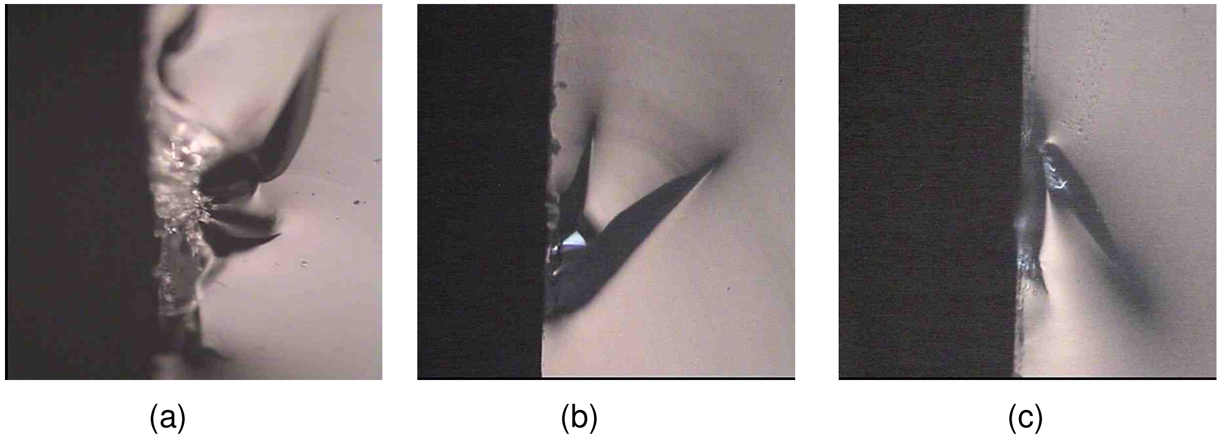


Figure 5. Fracture surfaces showing median cracks obtained using indentation load of 20N (median profile). (a) as-received glass, (b) glass annealed at 590℃ for 30 min, (c) glass annealed at 620℃ for 30 min.

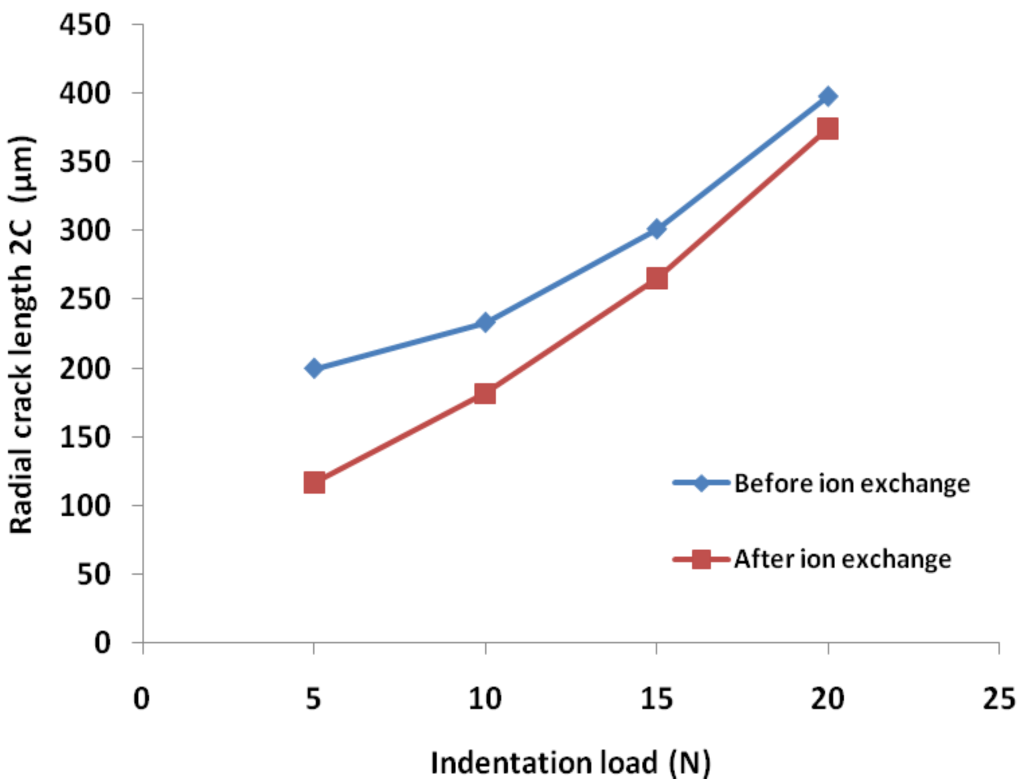


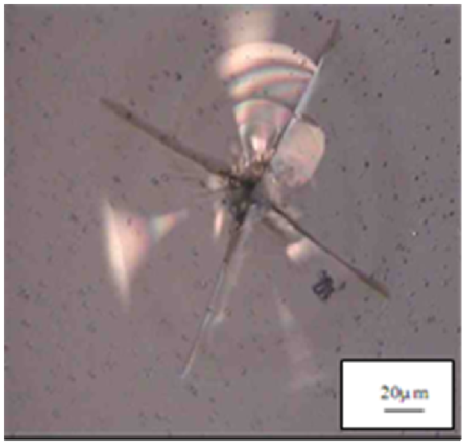
Figure 6. Radial crack length 2C before and after ion exchange.

exchange generates important compressive surface stresses causing the closure and then the healing of cracks particularly for low indentation loads. The residual stresses of these indentations can be relaxed at this temperature treatment favoring the effect of ion exchange.

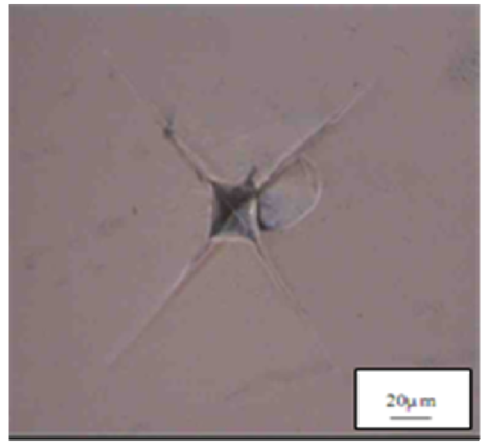
Figure 7 shows the effect of ion exchange treatment on Vickers indentation radial cracks obtained under 20 N.

Study of the indentation residual stresses by photoelasticimetry

The study of indentation residual stresses relaxation by photoelasticimetry was carried out on Vickers indentation realized under a load of 20 N. Indentations were performed on two glass state: annealed glass (30 min at 530℃) and the ion exchange treated glass (KNO_3 at



(a)



(b)

Figure 7. Vickers indentation obtained with a load of 20N before (a) and after (b) ion exchange.

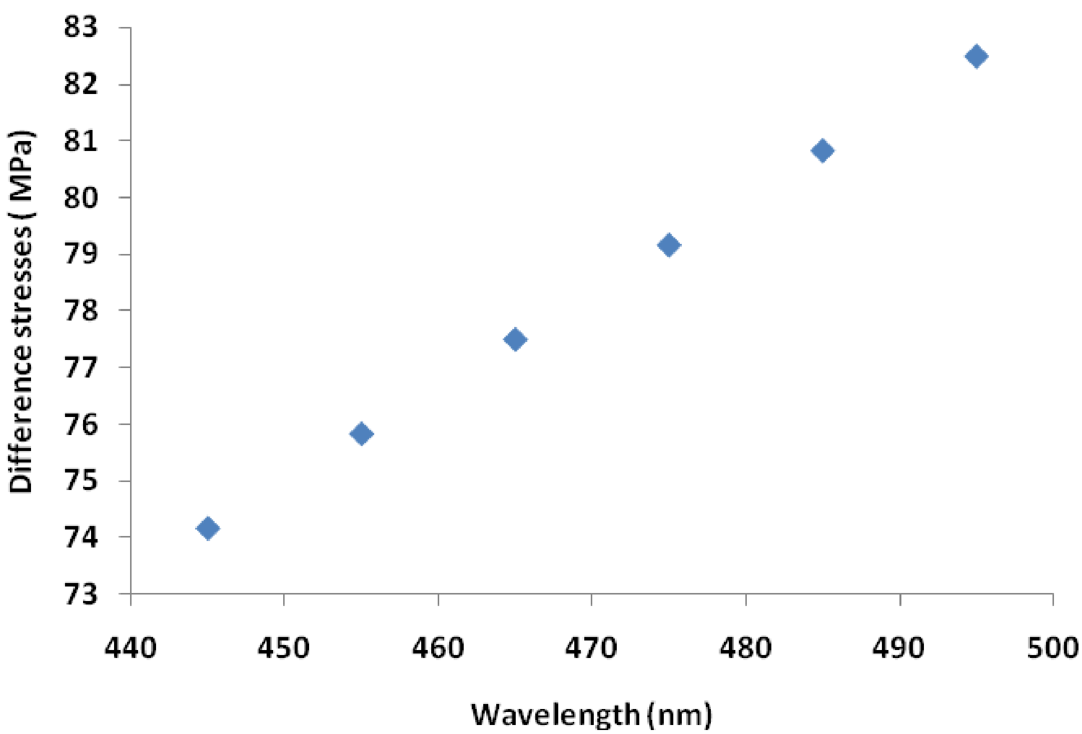


Figure 8. Evolution of differences stresses determined by photo-elasticity as a function of wavelength.

480°C for 2 h). Obtained prints were viewed with an optical microscope (Leica DM1000) and the correspondent photographs were taken with a digital camera. We followed the evolution of residual stresses over storing time up to 96h. Image processing was done using a special treatment program in a range of wavelengths between 445 nm and 500 nm according to the colors observed around the indentation and with a tolerance equal to 10 nm. The stress values are obtained by calculation from Equation (2). The values found are shown in Figure 8.

To simplify the study, we present only the effect of storage on indentation residual stress relaxation by choosing the wavelength λ = 475 nm.

Figure 9 shows an indentation realized with 20 N and observed by optical microscope equipped with a polarizer

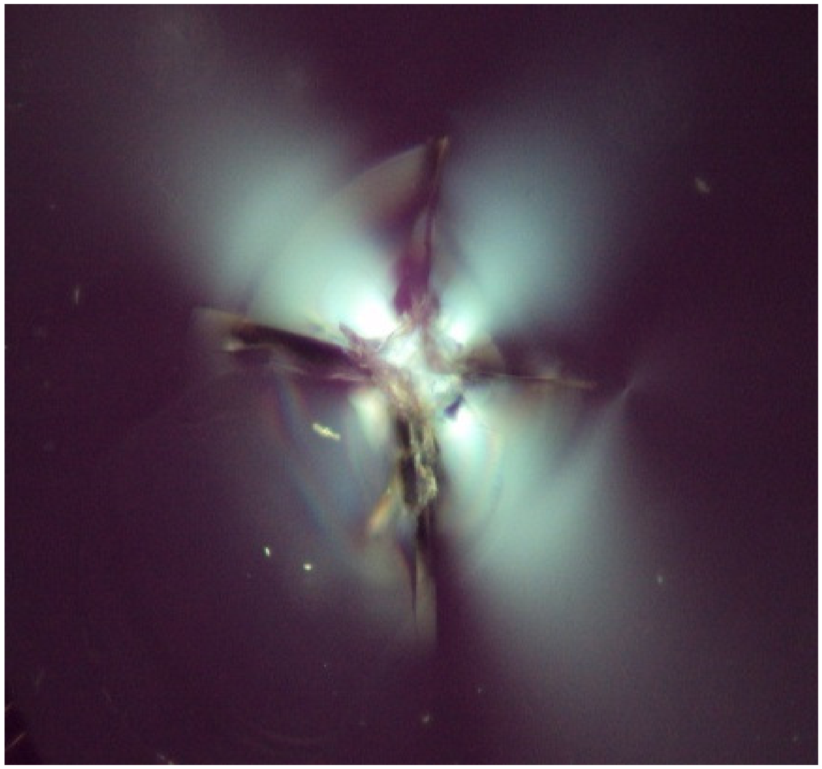


Figure 9. Indentation with a load of 20 N on a glass annealed at 530°C for 30 min.

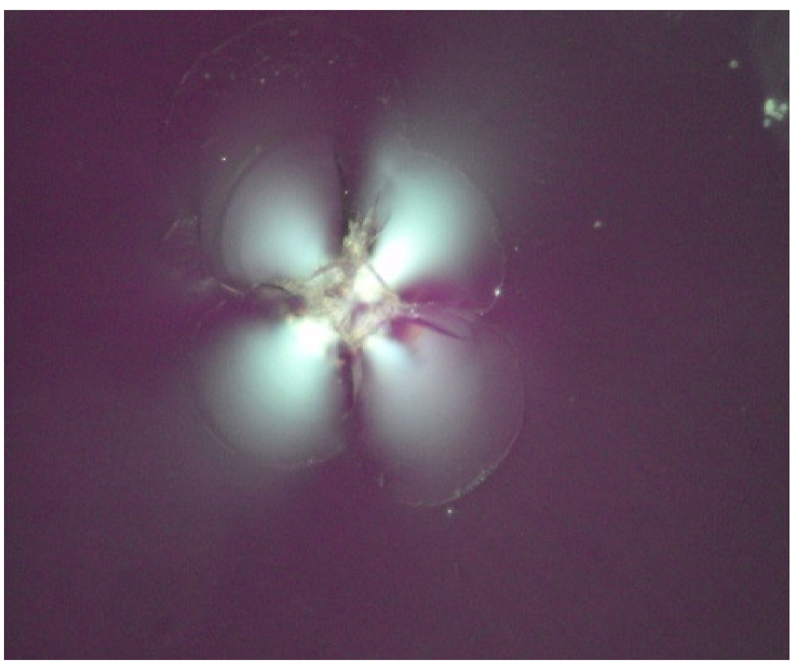


Figure 10. Indentation by a load of 20 N on a glass treated by ion exchange.

and an analyzer. The brightest parts represent the densest areas. Therefore the residual stresses are greater, leading to an optical path difference. Figure 10 shows that the superposition of the chemical treatment

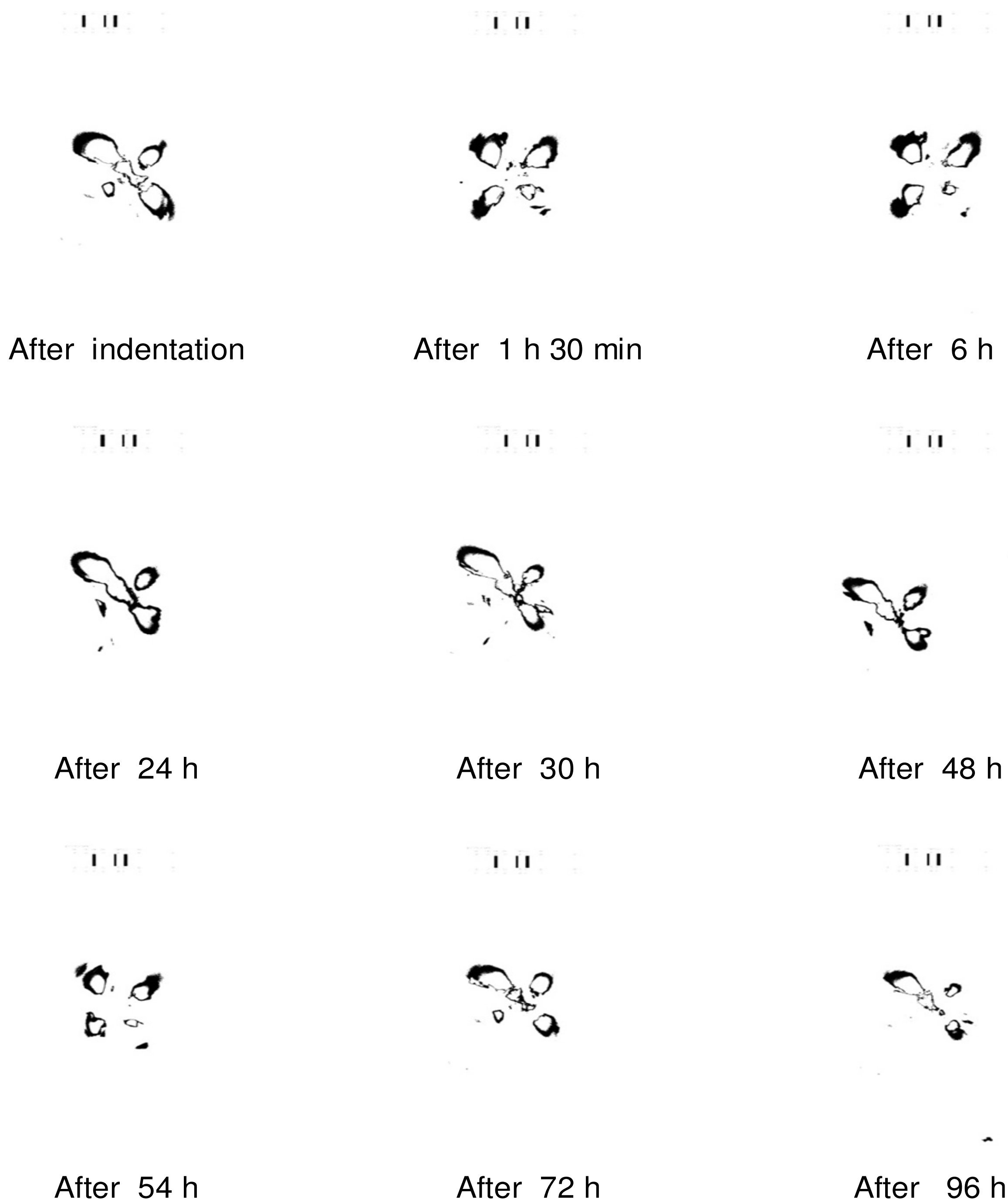


Figure 11. Iso-chromes for an indentation at 20 N (λ = 475 nm) versus storage time obtained on annealed glass.

compressive stresses with the indentation residual stresses results in stresses that are different from that observed on annealed glass.

Figure 11 shows the iso-chromes after images processing of the indentations. We note that the stresses relax over time. This is visible on the iso-chromes surface areas which decrease especially during the first two days of storage.

The Iso-chromes obtained for indentations performed on the glass treated by ion exchange are shown in Figure 12. It appears that the storage time does not influence significantly the iso-chrome area.

Tensile residual stresses of indentations performed on annealed glass can be relaxed over time by propagating cracks (creating a new fracture surfaces). In the case of ion exchanged glass, the established compressive residual stresses opposing to indentation residual stresses prevent any crack propagation. Consequently no

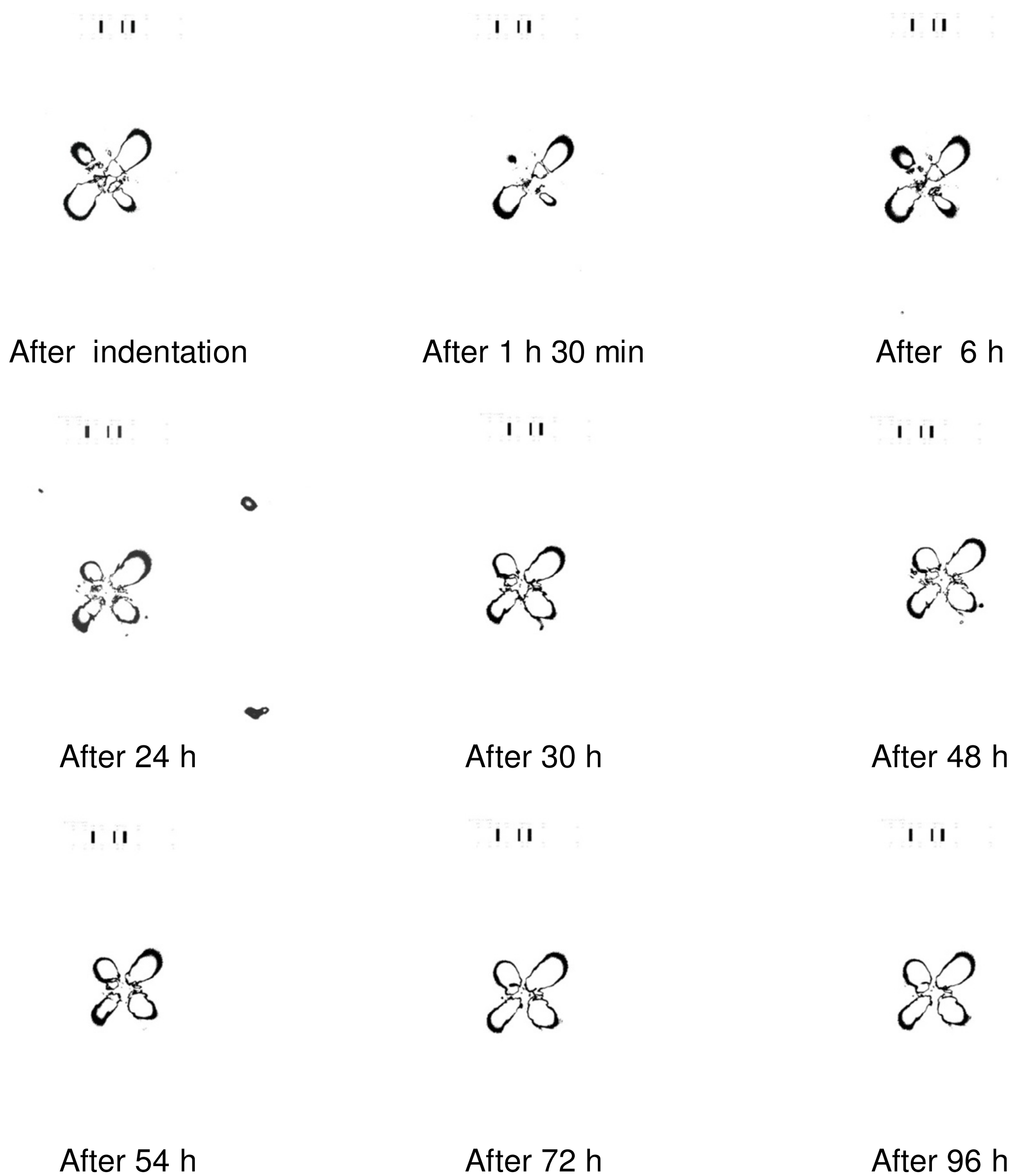


Figure 12. Isochrome, obtained for an indentation (20 N) with (λ = 475 nm) for a chemically treated glass, versus storage time.

stress relaxation can be noted.

If an indentation is made on an annealed glass and then treated chemically (after indentation), the stress state (Figure 13) is quite different from that shown in Figure 12. This means that the incorporation of the indentation residual stresses before or after chemical tempering significantly alters the resulting residual stress field.

Conclusion

Indentation radial crack length increases with storage time and reach a threshold of stabilization after 6 to 24 h. The reached threshold and the time needed to achieve it increase with the indentation load. Annealing Vickers indentations induced a radial and median crack healing. Consequently, the strength of indented glass is increased.

Ion exchange leads to radial crack healing which depends on indentation load. Tensile residual stresses of indentations performed on glass can be relaxed over time by propagating cracks. In the case of ion exchanged glass, the established compressive residual stresses opposing to indentation residual stresses prevent any crack propagation. Consequently no stress relaxation

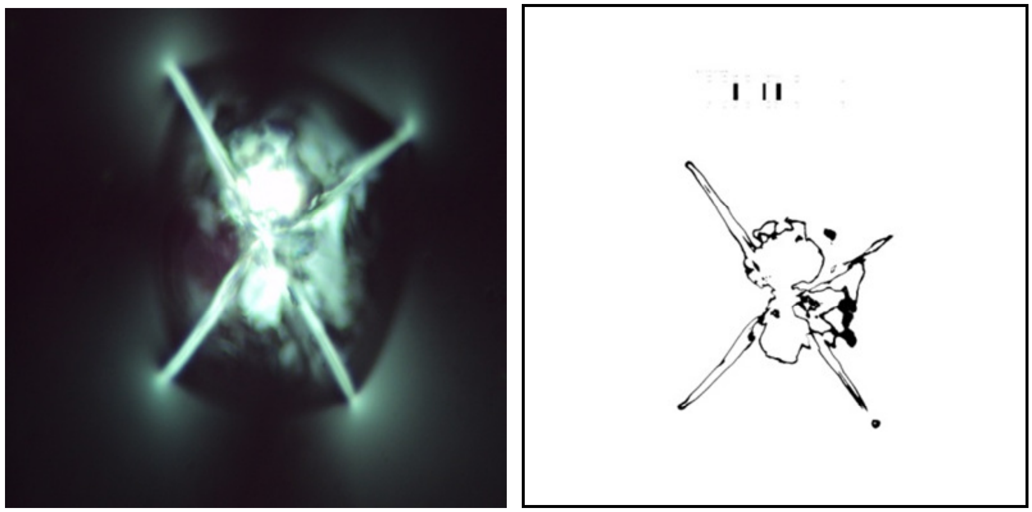


Figure 13. Indentation made by a load of 20N and then chemically treated (ion exchange) and the corresponding iso-chrome.

over time can be noted.

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