JOURNAL OF MATERIALS SCIENCE **39** (2004) 2883–2885

Method for viscosity measurements of glasses and glass pastes

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An indentation test has been developed to measure the apparent viscosity of industrial glasses and glass pastes in an intermediate temperature range (700–900 °C). This kind of investigation on glasses has already been the subject of previous papers [1–4] but the test was performed at a constant indentation load. A new approach is proposed, based on a constant penetration speed. From the recording of the load-displacement curves, it is possible to calculate the viscosity value.

In the present study, measurements were conducted on oxides glasses and glass pastes containing calcium fluorides. The quantity of fluorine and calcium is higher in the glass pastes. In the vitreous matrix of these pastes, scanning electron microscope observations coupled to energy dispersive X-ray spectrometry microanalyses (SEM-EDX) reveal the presence of calcium fluoride (CaF_2) but also quartz (SiO_2) dispersed microcrystals (Fig. 1). The fluoride crystals precipitate because the amount of fluorine present in the glass is too high [5].

A schematic representation of the setting is given in the Fig. 2. The main parts of the apparatus are:

– The cylindrical mold in stainless steel (diameter 56 mm and height 70 mm). Thermic losses are controlled by the use of an alumina tube and an insulating ring below the mold.

– The furnace to provide a constant temperature which is automatically regulated.

– A stainless steel needle (length 200 mm) which ends with a hemispherical indenter (diameter 6 mm). Its position is eccentred in order to carry out, by rotation of the needle, new measurements on areas not disturbed by previous tests. A thermocouple is introduced into the needle up to the tip indenter. After each measurement, the surface state of the indenter is controlled and cleaned by quenching if necessary.

– The tests are performed on a traction–compression hydraulic machine (Instron 1341). The indentation force is measured by a force cell of 0–2.5 kN or 0–100 N.

The indentation tests were carried out at a constant penetration speed (6 mm·s^{-1}).

Specimens required for this study are made of melting glass and glass paste flowing in cylindrical molds on the industrial site. They are then cooled at ambient temperatures. Before indentation measurements, the samples are reheated to the desired range in the furnace (Fig. 2) and maintained to this temperature during at least 30 min to reach equilibrium. No problem of bubbling at the surface is noticed. The temperature of the sample surface is controlled by a thermocouple before each measurement (uncertainty ±2.5 °C).

The theoretical interpretation of the results in terms of viscosity (η) is deduced from the Johnson relation [6], defined for Newtonian fluids:

$$F = \frac{16}{3}\eta \dot{h}\sqrt{hR} \tag{1}$$

where F is the applied force, h the penetration depth, $\dot{h}$ the constant penetration speed and R the radius of the indenter. This relation (1) is true only in the case where $h \ll R$.

The parameters $\dot{h}$ and R being known, the viscosity can be determined from the slope of the straight line F^2 according to h.

First the experimental setting was calibrated with a well-known rheology alkali-silica glass (supplied by Saint Gobain). The temperature corresponding to its "Littleton point" ($\eta = 10^{6.6}$ Pa.s) is 730 ± 10 °C.

Fig. 3 shows a typical experimental force-indentation curve recorded on this reference glass at 730 °C and the predicted evolution calculated by the Johnson formulation. It may be noted that three domains exist, corresponding respectively to penetration depths of (0–0.1 mm), (0.1–0.4 mm) and (0.4–1 mm). In the first domain, the experimental load is underestimated compared to the theory of Johnson. This fact is due to the glass superficial softening caused by the indenter tip which is slightly warmer (±2 °C). In the second domain, the experimental data vary in very

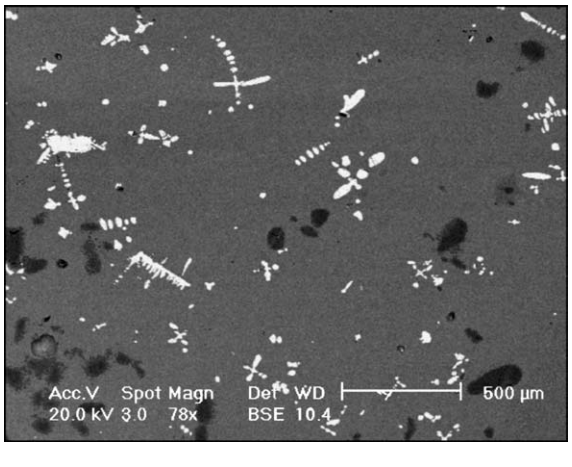

Figure 1 Scanning electron micrograph of the glass paste in cross section showing the CaF_2 (white) and SiO_2 (dark grey) microcrystals.

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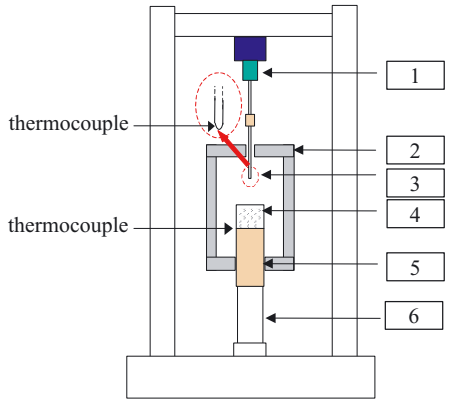

Figure 2 Schematic picture of the indentation test setting: (1) force cell, (2) furnace, (3) needle in stainless steel with indenter at the front, (4) mold for the sample, (5) insulating element with alumina tube and (6) hydraulic jack.

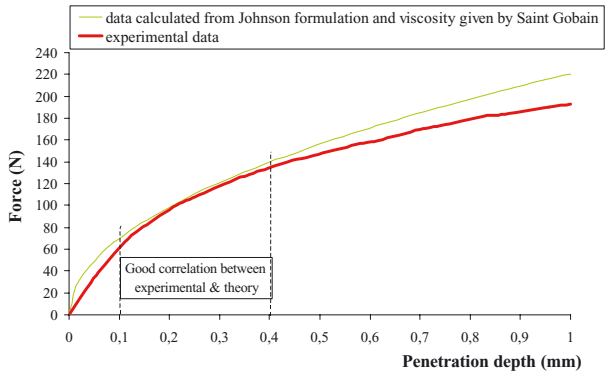

Figure 3 Force vs. penetration curves for the reference glass (Saint Gobain) at 730 °C.

good correlation with theoretical results (discrepancy of 13.8% at 0.1 mm and 3.2% at 0.4 mm). However, it is not true in the last domain because the geometrical condition $h \ll R$ is no longer valid.

Therefore, the viscosity is determined from the slope of F^2 versus h, for h contained between (0.1–0.4 mm) (Fig. 4).

Finally, the agreement with the viscosity expected is very close and confirms the validity of this indentation test.

Afterwards indentation tests were carried out on both vitreous materials at five temperatures: 700, 750, 800, 850 and 900 °C. As the glass paste contains rigid particles in the matrix but in little quantity (less that 5 vol%

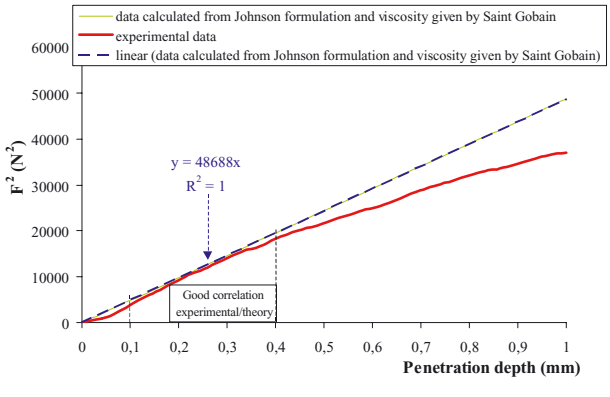

Figure 4 Force squared vs. penetration curves for the reference glass (Saint Gobain) at 730 °C.

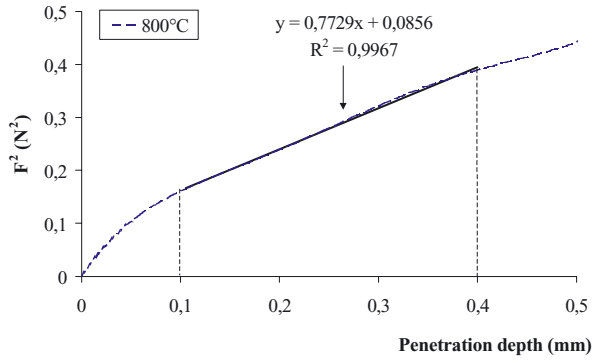

Figure 5 Force squared vs. penetration curves for the glass *G* at 800 °C.

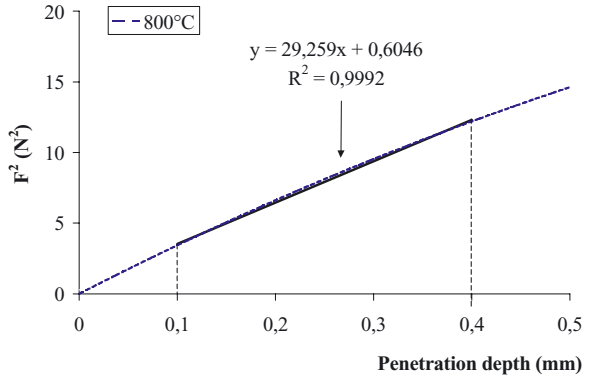

Figure 6 Force squared vs. penetration curves for the glass paste *GP* at 800 °C.

measured by microscopic image treatment), its behavior is assumed Newtonian. Figs 5 and 6 show typical force squared-penetration curves recorded at 800 °C respectively on the glass (*G*) and the glass paste (*GP*).

Applying the procedure previously described, the values of viscosities obtained are shown in Fig. 7 where the logarithm of the viscosity η is plotted against the temperature.

The glass paste exhibits a higher viscosity than glass as we would expect it, because of the existence of unmelted CaF_2 crystals in the glass paste (fusion temperature equal to 1360 °C). To compare with viscosities measured on classical soda-lime glasses, values found in the literature [7] and given by Saint Gobain are plotted in Fig. 6. It appears that, for the same temperature, the viscosity of glass and glass paste investigated is lower than this of a classical soda-lime glass. It is not surprising because calcium fluorides are known to act

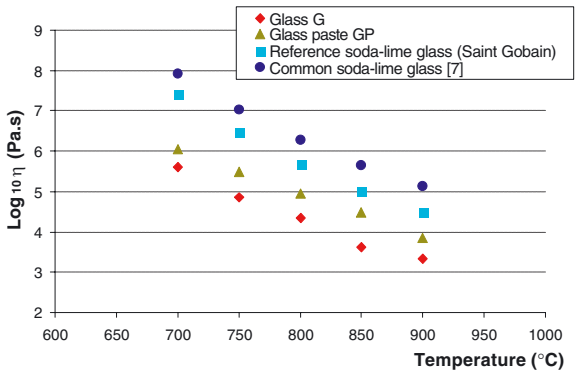

Figure 7 Viscosity vs. temperature curves for the glass *G*, the glass paste *GP*, the reference glass and a common soda-lime silica glass.

as a flux agent [8]. This effect is caused by the replacement of strong chemical linkages of ≡Si–O–Si≡ by lower links of ≡Si–F. The result is that the glass structure is weakened [5].

The viscosity increase of the glass paste compared to this of the glass has been studied according to the Einstein relation [9]:

$$\eta_{GP} = \eta_G(1 + 2.5\varphi)$$

where φ represents the volumic proportion of rigid particles (5 vol%).

This shows that the value of the glass paste viscosity should increase at all temperatures as:

$$\eta_{GP} = 1.125\eta_G$$

but, depending on the temperatures considered, $\eta_{GP} = 2.7$ to $6\eta_G$. This difference may be linked to a modification of the glass structure around the particles. To check this point, it is necessary to make other measurements: new indentation tests in the region of the particles (nanoindentation) and chemical analyses around the particles to evaluate the possible diffusion of elements (fluorine, calcium. . .).

Acknowledgment

The authors wish to acknowledge Gilbert Fiorucci for his continual assistance in the setting of the apparatus and during the measurements.

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Received 17 July
and accepted 5 November 2003