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Microhardness and some fracture related problems in copper doped soda lime silica glass

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A wide range of practical problems requires the knowledge of the mechanical characteristics of doped oxide glasses. The main purpose of this study was to investigate the effect of ion exchange and a post-exchange thermal treatment upon Vickers microhardness of a multicomponent soda lime silica (SLS) glass in which the mobile sodium ions have been partially substituted by copper. It has been stated that in dependence of the indentation load, the indentation marks have been accompanied by traces of Palmqvist cracks. The deformation and fracture related phenomena are dependent on the temperature and time of the exchange and annealing processes.

Keywords: soda lime silica glass, ion exchange, mechanical properties.

1. Introduction

It is known in the glass technology that the strength of a glass object can be considerably increased by tempering or coating it with a thin foreign glass layer. In both cases, residual compression stresses are introduced into the near-surface layer [1]. Generally, these phenomena result in an increase in the material strength, fracture or a simultaneous increase in both these quantities. The pre-stressing of an object has, among others, a practical effect of providing a protection measure against the surface damage.

The purpose of the work reported was to investigate the effect of copper introduced by ion exchange and heat treatment in a hydrogen atmosphere upon the Vickers microhardness of a soda lime silica (SLS) glass. It should be emphasised that the monovalent copper used in the CuCl molten bath has an ion radius equal to that of the substituted sodium ion [2].

2. Experiments and results

2.1. Preparation and characterisation of the glass samples

A commercially available soda lime silica (SLS) glass, produced according to the Fourcault procedure, was used. The content of its main components (SiO_2 and Na_2O) corresponds to the miscibility gap in the system [3]. The glass samples were chemically treated in a CuCl molten bath at temperature below (723 K) and above (903 K) the glass transformation temperature ($T_G \cong 858$ K). Afterwards, the exchanged samples were hydrogenated typically at 773 K for 5 h. It has been found that due to the reaction with oxygen (from the surrounding air-atmosphere), some quantities of Cu_2O are formed.

Thermal annealing of the exchanged specimens in gaseous hydrogen reduces the valence state of the cuprous to cupric ions and leads to the formation of nanoparticles of the metallic copper. For more details of the technological procedures see our preliminary work [4]. Important for the present studies is also the previous statement that independently of the exchange conditions, copper is present in the SLS glass specimens as cupric and cuprous ions, the concentration of which depends on the exchange process. And so, for $T_{\text{exch}} < T_G$ the presence of monovalent copper prevails, while for $T_{\text{exch}} > T_G$ the divalent copper ions dominate. The oxidation of monovalent copper to the divalent form occurs due to the electron hopping, a process responsible for the electric conductivity of many oxide glasses doped with transition metal ions [5–7].

Figure 1 shows two microphotographs obtained by using a Philips CM 20 transmission electron microscope (TEM) for extracted replicas of the glass-surfaces of samples hydrogenated after exchange at 723 K (Fig. 1**a**) and 903 K (Fig. 1**b**). The TEM data are complemented by selected area electron diffraction (SAED) performances where the presence of crystalline Cu and Cu_2O have been detected. It has been evidenced that the quantities, size and distribution of the Cu and Cu_2O nanoparticles depend upon the technology parameters characteristic of the exchange and hydrogenation.

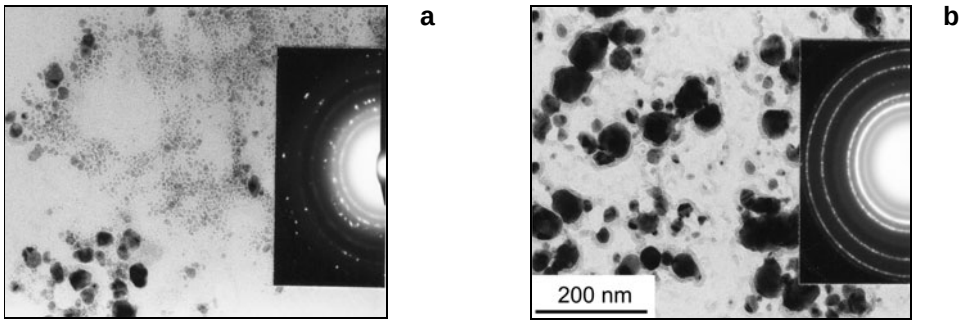

Fig. 1. TEM micrographs of SLS glass specimens exchanged at 723 K (**a**) and 903 K (**b**).

2.2. Microhardness evaluation and detection of cracks

To characterise the microhardness (VH), the Vickers diamond pyramid (Zwick 3212 tester) was used. The indentations have been made for loads ranging between 1 and 30 N, applied at a velocity of 1 mm s^{-1} and allowed to equilibrate for 15 s before measurement. The value of the diagonal lengths of the indentation marks ($2a = d$) was used to calculate the hardness according to the following relation $VH = F/A_S$, where F corresponds to the applied load and A_S, equal to $d^2/1.854368$ (in GPa), is the surface of the contact area [8]. The length of cracks c which develop after application of a given load, was determined using an optical microscope, approximately 15 s after each indentation. Figure 2 shows the idea of a sample-indentation (Fig. 2**a**) and the indentation-mark accompanied by cracks (Fig. 2**b**).

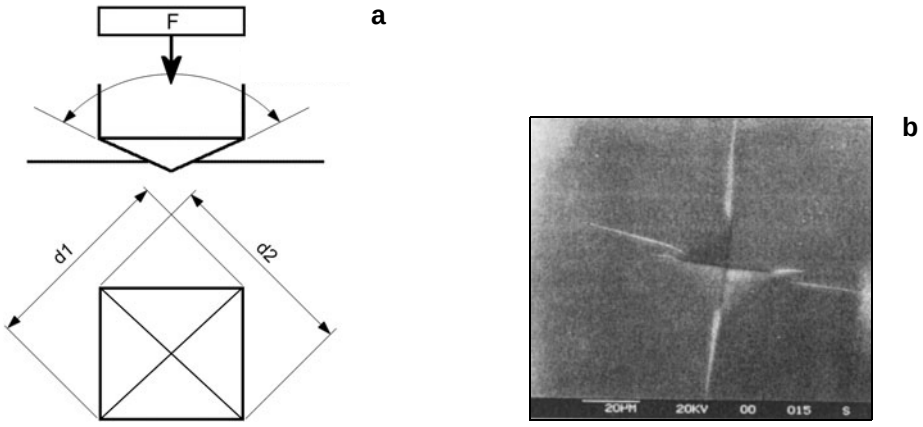

Fig. 2. Schematic presentation of the Vickers indentation (**a**) and the cracks appearing around (**b**).

The load dependence of the measured length of cracks appearing in samples exchanged for two and 72 h at the low and high temperature as well as hydrogenated afterwards has been shown in Fig. 3. With the exception of data which correspond to the longer exchange time at the higher exchange temperature, the results obtained are in good agreement with the fracture mechanics models according to which the applied load F should be proportional to $c^{3/2}$ [9–11]. Moreover, for a given load the cracks appear earlier and are longer in samples exchanged for shorter times at the lower exchange temperature (below T_G), suggesting larger brittleness of this material.

Figure 4 shows the effect of copper exchange at low and high temperatures for short and long times of exchange upon the microhardness of the SLS glass specimens. The strengthening effects induced by the presence of copper in the near-surface layer are more clear when compared with data obtained for not exchanged sodium and potassium containing SLS specimens, *cf.* Fig. 5. To understand the observed effects,

it should be also stressed that thermal treatment in air (for times and temperatures used for the copper exchange and/or hydrogenation) of not exchanged specimens induces only minor changes in the Vickers microhardness.

In general, during the Vickers indentation a complexity of phenomena occurs, *e.g.*, spontaneous elasticity and permanent deformation like plasticity, densification and elastic recovery effects, generation and propagation of cracks. These effects make hard any quantitative analysis of the results. It is also not straightforward to optimise the technology. Because the strengthening effect is distinctly larger for samples exchanged at the higher temperature, at which the formation of divalent copper and

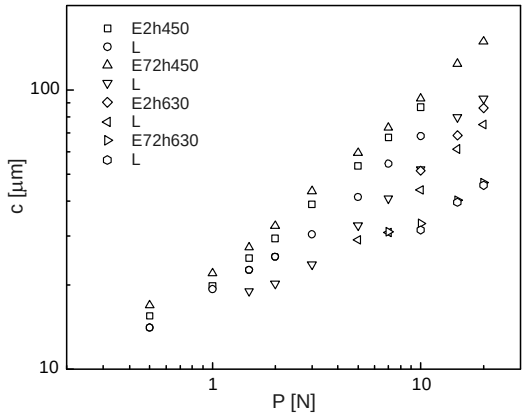

Fig. 3. Load dependence of the length of cracks (in a double logarithmic presentation) formed around the Vickers indentation mark in specimens exchanged with copper at high and low temperature for two and 72 h and for the afterwards hydrogenated samples.

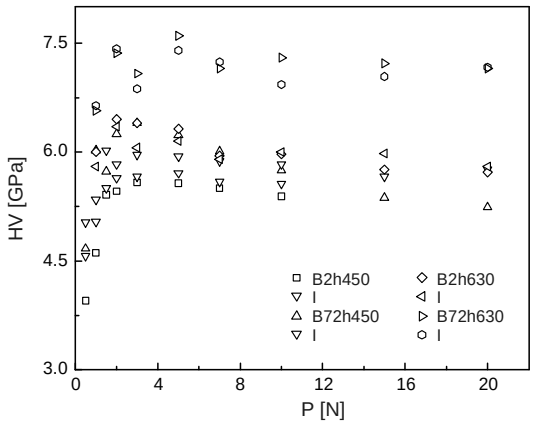

Fig. 4. Load dependence of microhardness of samples exchanged for two and 72 h at 723 K and 903 K as well as for those hydrogenated afterwards.

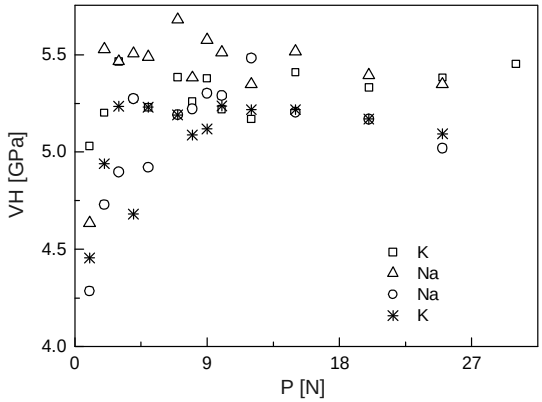

Fig. 5. Load dependence of microhardness of some SLS glasses containing different amounts of sodium and potassium oxide.

copper oxide prevails, the detected strengthening has been tentatively ascribed to the changes in the matrix morphology around these ions, *cf.* [12], and the formation of semiconducting Cu_2O nanoparticles, *cf.* [13].

3. Summary and concluding remarks

It has been stated that:

1. The copper valence state in the chemically and/or thermally treated SLS glass is very sensitive to the doping procedure and/or to the annealing atmosphere;
2. Ion exchange of soda lime silica glasses in the CuCl molten bath could be used for strengthening of the material;
3. The increase in hardness depends upon the exchange parameters, being larger for the higher temperatures and longer times at each exchange temperature;
4. The crack formation resistance of copper-doped SLS glass is comparable with values obtained for the potassium-doped samples [14] although the ionic radius of the cuprous ions is much smaller than that characteristic of potassium;
5. The simplified models of the fracture mechanics are not strictly applicable for all the investigated glass samples, and further experiments are necessary; *e.g.*, nanohardness measurements for the processes related to deformation and/or more thorough investigations into the formation and/or propagation of cracks for the processes related with fracture;
6. Regardless of the fact that microhardness is a complex property, it could serve as a valuable guide in many engineering applications of the investigated material.

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