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Load dependence of hardness of the doped soda-lime silicate glasses

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The aim of the work described was to study the load dependence of micro- and nano-hardness for soda-lime silicate glass doped with some univalent cations. The Fourcault-type glass samples were chemically treated by dipping them in melted baths of KNO_3, $AgNO_3$ and CuCl. The nano- and micro-hardness were determined by using the Vickers diamond indenters for applied loads ranging between 0.1 and 500 mN (registered loading and unloading mode), and between 0.2 and 30 N (conventional application of the load), respectively. For the behavior of hardness and Young's modulus (registered nano-indentation) the normal indentation size effect has been observed, but in the low load range of conventionally indented specimens the reverse indentation size effect has been found. The detected size effects were discussed in terms of some empirical models proposed in the literature for crystalline materials. It has been shown that: 1) the Meyer's law is only suitable for describing the nano-indentation characteristics measured in a narrow range of indentation load; 2) the classical Meyer's law and the energy balance model are insufficient for describing the reverse indentation size effect; 3) the difficulties in acquiring accurate and precise micro-hardness readings in the range of low loads can result in the inconformity of experimental data with the empirical models.

Keywords: silicate glass, ion exchange, nano- and micro-hardness, analysis of the indentation size effect.

1. Introduction

Metallic nano-particles embedded in a dielectric matrix are well-known for their attractive properties, strong optical resonance and fast non-linear optical polarizability associated with the plasmon frequency of the conduction electrons in the particles [1]. For a wide range of potential applications of these materials the knowledge of their mechanical characteristics could be very useful, and the hardness is one of the most proper one exploited for brittle materials. A renewed interest in these studies relates with development of both new materials, like coatings, composites *etc*., and new techniques, *cf*. the registered hardness, for characterizing the mechanical behavior of composite materials.

It has been found that the indentation hardness, which is defined as the ratio of the indentation load to the contact area of the resultant indentation impression, decreases as the test load increases [2, 3]. This behavior is referred to as the normal indentation size effect (ISE). Sometimes, the reverse type of ISE (RISE) where

the apparent micro-hardness increases with increasing applied load, was also detected [4]. A load-independent range usually follows the load range of hardness in which the indentation size effects appear. Several empirical models have been elaborated for description of these effects in crystalline materials [5, 6].

To our knowledge, there are only a few studies of these phenomena in silica-based composite glasses. Hence, the aim of the work described was to reexamine and analyze the load-dependences of micro- and nano-hardness for the soda-lime silicate (SLS) glass doped with potassium, silver and copper, with particular emphasis to the low loading range.

2. Samples and measurements

The content of the used commercially available glass was as follows (in wt%): 72.9 of SiO_2, 12.6 of Na_2O, 6.5 of CaO, 4.5 of MgO, 1.8 of Al_2O_3 and 1.7 of other compounds, among them of Fe_3O_4. This corresponds to the miscibility gap in the (Na_2O–SiO_2)-system [7]. Indeed, the presence of a phase separation yet in the original SLS glass specimens has been evidenced by the transmission electron microscopy [8]. Samples in the shape of plates about 1 mm thick were subjected to chemical treatment in a molten bath of CuCl, KNO_3 and $AgNO_3$ mixed with $NaNO_3$ at different temperatures for different periods of time. More details concerning the ion exchange procedures could be find in some previous papers [9, 10]. As far as potassium and silver enter the glass structure in the form of univalent cations, copper has been detected in the glass matrix as cupric and cuprous ions. The concentration of both copper valence states depends on the exchange time and temperature. It is worth to remind that for the exchange temperature (T_{ex}) lower than the glass transition temperature ($T_g \cong 823$ K), the presence of univalent copper prevails, while for $T_{ex} \geq T_g$, the divalent copper ions are dominating. Air annealing of the exchanged specimens at about 673 K for times up to four hours induces effective reduction of the silver ions to atoms and the formation of colloidal nano-particles. For the reduction of copper ions more efficient agents are necessary, and the annealing in gaseous hydrogen at 773 K for 5 h was sufficiently effective.

For indentation tests the Vickers-pyramid was used for the conventional and registered application of the testing load. In the first case, the loads ranged between 0.2 and 30 N. After indentation, the lengths of both diagonals of the indentation mark were measured by optical microscopy and the Vickers hardness (VH) number was calculated from

$$\mathrm{VH} = 1.8544\frac{P}{d^2} \tag{1}$$

where P is the test-load in newton, d – the average length of the diagonals in micrometer, and 1.8544 is a constant geometrical factor for the Vickers pyramid. In the case of the registered measurement mode, the application of a testing load, from the range of 0.1–500 mN, was followed during the cycles of loading and unloading. The appli-

cation of each individual load results in a full load dependence of the indentation depth h. The corresponding nano-hardness is determined from

$$\mathrm{VH} = 1.8544\frac{P}{49h^2} \tag{2}$$

The relation $d \cong 7h$, valid for the Vickers indenter [11], was exploited for the presentation of data obtained by the conventional indentation. All measurements have been performed in air at the room temperature.

3. Micro- and nano-hardness data

Figures 1**a**–1**c** show typical load dependences of the conventionally measured microhardness for potassium, silver and copper doped SLS glass specimens, respectively.

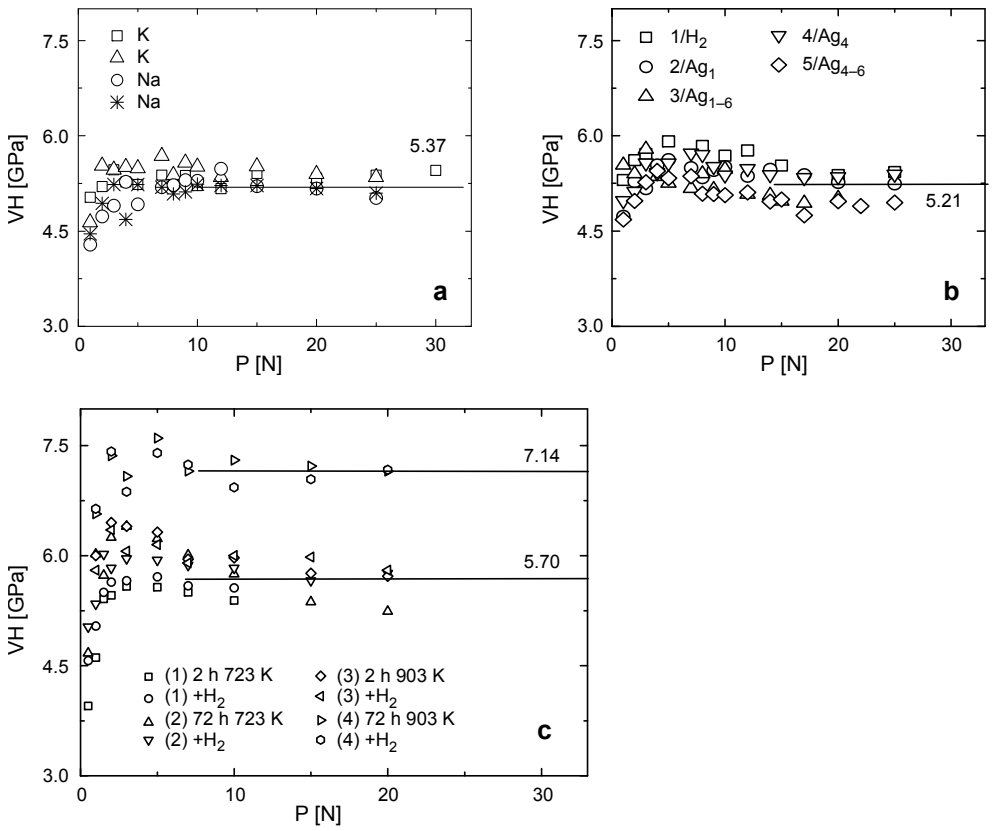

Fig. 1. Load-dependences of the conventionally measured hardness for the soda-lime silicate glasses doped with: two potassium quantities, where points □ correspond to samples containing more potassium ions than △ (**a**), two quantities of silver; the data correspond to ions with $Ag_4 > Ag_1$ (after exchange), and colloids (Ag_{1-6} and Ag_{4-6}) obtained after hydrogenation for 4 h at 673 K (**b**), copper – four samples after exchange (for 2 and 72 h at 723 and 903 K) and their H_2-treatment afterwards (**c**).

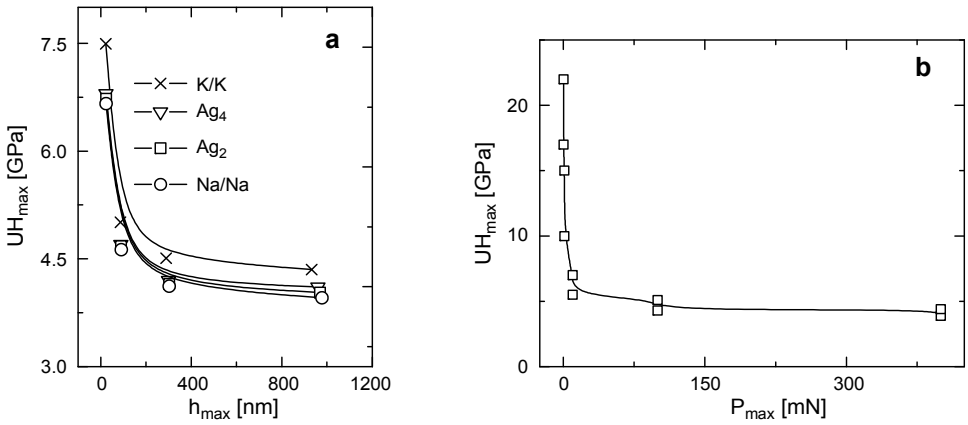

Fig. 2. Dependence of the nano-hardness upon the indentation depth, h_{max}, for Ag- and K-doped samples (**a**), and upon the applied load, P_{max}, for the Cu-doped SLS glass (**b**).

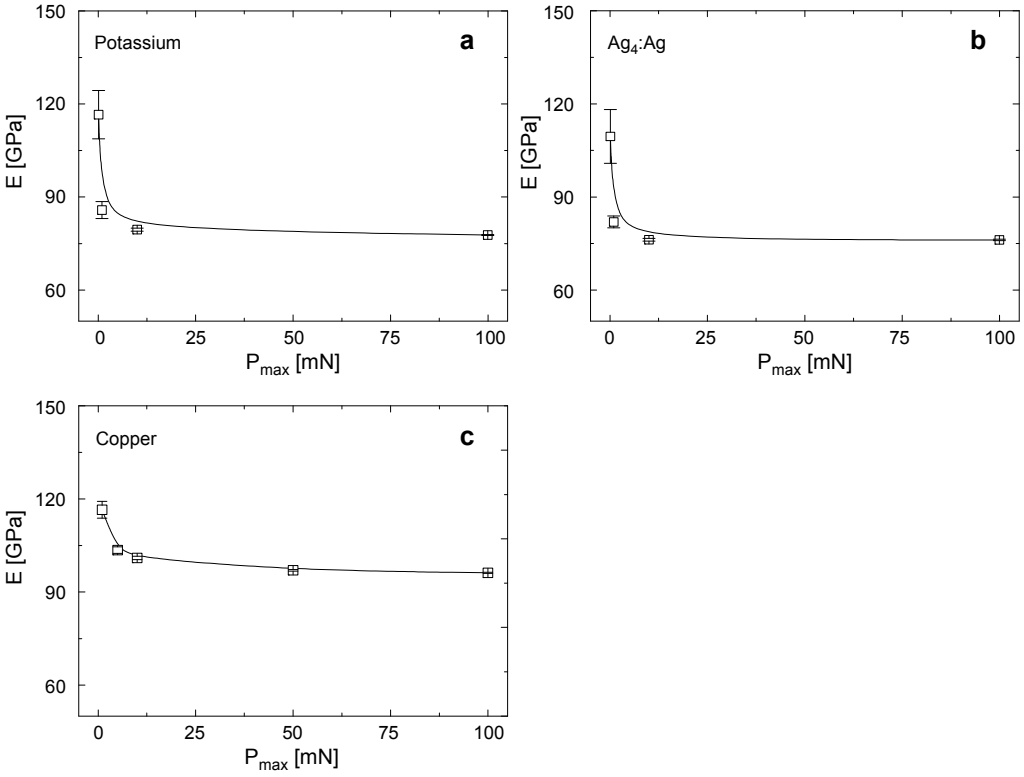

Fig. 3. The load dependence of the Young modulus for potassium (**a**), silver (**b**) and copper (**c**) exchanged soda-lime silicate glass determined from data obtained during the unloading–indentation cycle.

As can be seen, in the lowest load region, the measured hardness of all samples increases more or less significantly with the indentation load. After attaining a maximum value, the micro-hardness tends to attain a constant value with further increasing indentation load. Such a behavior differs from that reported for many brittle ceramics whose hardness in the low application-load range was found to decrease with the increasing load [2, 3].

Figures 2**a**, 2**b** and 3**a**–3**c** show examples of the results obtained by the registered indentation measurements. In this case, the hardness values (*cf*. Fig. 2) in the lowest load-range, which corresponds to the smallest penetration depth values, behave in a way different from those detected for the conventionally measured hardness; namely, they decrease with the increasing load and penetration depth. This behavior corresponds to the normal ISE. For larger testing-loads the nano-indentation hardness attains nearly constant values similar to the case of micro-hardness.

Also the Young's modulus of the doped SLS samples decreased with the increase of the testing load (*cf*. Fig. 3). This characteristic has been calculated from the sample's stiffness determined as $S = \mathrm{d}P/\mathrm{d}h$ at the upper part of the unloading P vs. h curve [12].

On the basis of the presented results, one has to conclude that the apparent hardness of the doped SLS glass specimens is a function of the test load at low indentation loads, this function is different for different loading modes, and the hardness becomes nearly load-independent for large indentation-loads.

4. Analysis of the results

It has been shown that the mechanical characteristics of the doped SLS glass are size dependent, and this dependence is clearly observed when the size becomes sufficiently small.

Several approaches have been proposed in the literature to describe the relationship between the indentation load P and the indentation diagonal length d detected for crystalline materials [5, 6]. We tried to exploit some of them to describe the results obtained for the soda-lime silicate glass doped with copper.

4.1. Analysis according to the Meyer relationship

Usually, the detected ISE in hardness testing is described in terms of the classical Meyer's law, which correlates the applied load P with the resulting indentation size d:

$$P = A d^n \tag{3}$$

where the exponent n is the Meyer's index, and A is a constant; for reference *cf*. for instance [13]. Both parameters can be derived from the log–log presentation of the experimental data. According to ONITSCH, $n < 2$ indicates the normal ISE behavior, for RISE $n > 2$ is expected, while for $n = 2$, the hardness should be independent of the applied load [14].

Our nano-indentation data yield for n the values between 1.74 and 1.87, dependent on the sample, to be indicative of the normal indentation size effect. On the other hand, the load dependence of micro-hardness gives for the Meyer's index n a value nearly equal to two (1.98), which is not suitable for the observed RISE. One has to remember, however, that the classical Meyer-law is an empirical expression, and the criteria given for n by ONITSCH have been suggested for crystalline materials [14].

4.2. A polynomial series presentation and the energy-balance considerations

To improve the description of the indentation size effects detected in crystalline materials, the proposal of BUECKLE is frequently used [15]. Accordingly, the relationship between the indentation load P and the indentation diagonal d is:

$$P = a_0 + a_1 d + a_2 d^2 + ... + a_n d^n \tag{4}$$

where a_i ($i = 0, 1, ..., n$) are fitting parameters. It is supposed that the term a_0 corresponds to a load threshold for an indenter to make a permanent indentation but it is so small that it can be omitted in most situations. Moreover, it has been shown that a good fit of the experimental data can be obtained by using only two terms of the above polynomial series presentation. The expression:

$$P = a_1 d + a_2 d^2 \tag{5}$$

has been, for instance, successfully used for description of the load-dependence of micro-hardness for the NaCl:Ca^{2+} crystals [16].

A physical meaning of the last equation was proposed by FRÖHLICH *et al*. based on some energy balance considerations [17]. Multiplying both sides of this equation by the penetration depth h, one obtains:

$$Ph = a_1 dh + a_2 d^2 h \tag{6}$$

The term Ph is considered as a measure of the work done by the applied indentation load during indentation while the first and second terms on the right-hand side correspond to the energies consumed for producing the new free-surfaces (proportional to dh) and the permanent deformation (proportional to d^2h). But also this proposal can be verified only in a formal way.

Transforming the simplified Bueckle equation to the form:

$$P/d = a_1 + a_2 d \tag{7}$$

the applicability of the energy-balance model has been used to analyze the micro-hardness behavior for our SLS samples exchanged at 903 K with copper. The relationship between P/d and d reveals that two straight lines with different slopes are fitting the experimental data well. FRÖHLICH *et al*. [17] detected a similar behavior of a soda-lime glass and suggested that the first, steeper, slope of the $P/d(d)$ dependence is related to

the behavior of the chemically strengthened glass surface. This suggestion could in principle be accepted for the explanation of our results.

JIANGHONG GONG *et al*. [18] detected similar behavior of the $P(d)$ relation for a variety of ceramics and attributed the results to indentation-induced micro-cracking. Because of the radial cracks that arise at the corners of indentation marks a smaller indentation size results and the indentation test yields a higher apparent micro-hardness for a given applied test load. The question whether our RISE originates from a contribution of some cracks to the micro-hardness values cannot be positively answered. At present, it seems more correct to suppose that the RISE shown in Fig. 1 is a consequence of some experimental errors related to the testing arrangement and the differences between the stress state characteristic of the surface and the internal layers of the exchanged SLS glass specimens.

5. Summary and conclusions

In the described studies, the load-dependence of Vickers micro- and nano-hardness of soda-lime silicate glass doped with potassium, silver and copper was measured. The following conclusions may be drawn:

– Nano-indentation yields, among others, a reasonable estimate of the Young's modulus of doped SLS glass specimens. The modulus is load-dependent, similar to the nano-hardness;

– Both characteristics of the samples exhibit in the lowest loading-range the normal indentation size effect that can be described by the classical Meyer's-law;

– Unlike many other brittle materials, the micro-hardness of these specimens exhibits a reverse indentation size effect. This means that in the low test-load range the measured hardness increases with increasing indentation load. The Meyer's $P(d)$-relation and the energy balance model are insufficient for describing the detected reverse indentation size effect;

– More careful experimental technique is necessary to precisely measure the diagonal lengths of the indentation marks obtained in the conventional loading mode. The indentations should be as large as possible without inducing excessive cracking that can interfere with the measurement of the diagonals;

– Further experiments are in progress to analyze, in a quantitative way, the effect of micro-cracking on the hardness measurements.

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