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The influence of the composition on (the load-dependence of) the microhardness of Y—Si—Al—O—N glasses as measured by Vickers indentation

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The hardness of multiple glasses in the Y—Si—Al—O—N system has been determined as a function of the indentation load. The measured hardness significantly depends on the load, which implies a substantial influence of the indentation size effect (ISE). The measured hardness has been deconvoluted in a load-dependent part and a load-independent hardness using the method of Bull *et al.* The influence of the overall composition on the hardness of these glasses has been investigated. It is shown that, by increasing the nitrogen content, a load-independent hardness of over 9 GPa can be achieved, which is far higher than most common glass systems. © *2004 Kluwer Academic Publishers*

1. Introduction

Y—Si—Al—O—N glasses are formed as intergranular phases during the liquid-phase sintering of Si_3N_4-based ceramics using sintering additives such as Al_2O_3 and Y_2O_3 [1, 2]. In these ceramics they have a pronounced influence on the high-temperature properties due to softening of these intergranular phases. Investigation of glasses of different Si–Al–O–N systems shows the existence of Si–N bonds [3]. Nitrogen coordinates preferably with three silicon atoms (NSi_3) whereas oxygen coordinates with two silicon atoms at maximum (OSi_2). Because nitrogen has a higher coordination than oxygen, replacement of oxygen for nitrogen will result in a higher degree of network formation. This increase of the network connectivity leads to an improvement of the mechanical properties [4]. It has e.g., been observed that Y—Si—Al—O—N glasses generally show a high stiffness, hardness and fracture toughness, which makes these glasses interesting for a number of applications such as fibers and scratch-resistant glass for wristwatches [4]. For that reason the interest in these glass systems is gradually shifting from the influence that they have in engineering ceramics towards their applicability as bulk materials or coatings.

In the literature, a few Vickers hardness values have been reported for Y—Si—Al—O—N glasses. These values indicate that the hardness can be as high as 10–13 GPa [2, 4–6], which is more than twice as high as for vitreous silica and soda-lime glass. Despite these encouraging results, the authors feel that two matters have to be resolved in order to estimate their performance in real applications. Firstly the effect of the overall composition of the glass on the hardness is not clear yet and secondly, the hardness measurements have so far been performed at a single (low) load (1–3 N). In order to make a good comparison between two materials the effect of the load on the measured hardness has also to be taken into account [7]. For a Vickers indentation the

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microhardness (H_v) is defined as the ratio between the applied load (P) and the squared length of indentation diagonal (d_i) multiplied by a geometrical factor:

$$H_v = \frac{1.854P}{d_i^2}, \tag{1}$$

This relation does not account for elastic recovery, which implies that the measured hardness is still a function of the load. When the indenter is removed from the surface, the material will partially elastically recover. Due to this process the indentation size will decrease somewhat. This results in an apparent indentation diagonal (d_m). Substitution of d_m for d_i in Equation 1 leads to the apparent hardness (H_v^{app}). Since $d_m < d_i$ the apparent hardness will be always higher than the load-independent hardness (H_v^0). This effect is referred to as the indentation size effect (ISE) [8, 9]. There are a number of ways to describe the indentation size effect, e.g., the model of Bull, the proportional specimen resistance (PSR) model, or Meyer's Law [10]. Of these methods the approach of Bull *et al.* is chosen because, for most materials it fits the effect very well and gives an output in the form of a load independent hardness which can be used to directly compare different materials. The authors are aware that in some cases Bull's equation can lead to a slight underestimation of the load-independent hardness due a transition from load-dependent to load-independent behaviour at high loads [11]. The error introduced by such a transition would be very small for these materials as compared to the obtained load-dependent and load-independent hardness.

The method of Bull *et al.* separates the apparent hardness into a load dependent and a load independent part, described by:

$$\begin{aligned} H_v^{app} = \frac{1.854P}{d_m^2} &= H_v^0\left(1 + \frac{d_i - d_m}{d_m}\right)^2 \\ &= H_v^0\left(1 + \frac{\delta}{d_m}\right)^2 \end{aligned} \tag{2}$$

The elastic recovery parameter ($\delta(\mu m)$) is used to describe the susceptibility of the material to ISE. It is defined as the difference between the length of the indentation diagonal before and after relaxation. In this description δ is assumed to be independent of the load and can be considered to be material specific. Since δ for most materials is 1–2 μm the difference between the apparent and load-independent hardness will be substantial for small indents while the apparent hardness will approach the load-independent hardness with increasing indent size [7]. This means one has to be especially careful when measuring harder materials since smaller indents are generated.

In order to make a well-defined comparison between the hardness of different materials one has to correct for the ISE by determining the load-independent hardness from load dependent measurements or by minimizing the ISE by taking a sufficiently high load. The goal of this investigation is to obtain load-independent hardness data for Y—Si—Al—O—N glasses and to study the load-dependence of the hardness. Moreover the effect of the chemical composition of the glass on the hardness is studied. This kind of data is needed to evaluate and optimise the performance of these materials in different types of applications.

2. Experimental

The size and position of the Y—Si—Al—O—N glass-forming region was estimated from available data in the literature and a matrix of compositions was drawn up to cover a large part of this region [6]. Weighed-out compositions are listed in Table I. Starting materials were: Y_2O_3 (Shin Etsu Y-474), SiO_2 (aerosil OX50), Al_2O_3 (Taimei >99.99% pure) and Si_3N_4 (Akzo Nobel, P95H). The starting powders were dispersed in isopropanol and mixed in a ball mill using Si_3N_4 balls. The resulting mixture was dried and pressed into pellets of 1–2 gram. These pellets were fired in an induction furnace for a short period (8–15 min) under flowing nitrogen. Rapid cooling was achieved by switching-off the power supply to the coil, whilst maintaining a

TABLE I Weighed-out compositions of the investigated Y—Si—Al—O—N glasses, load-independent hardness (H_v^0) and elastic recovery parameter (δ) as calculated from experimental data

	Equivalent percent (Eq%)					Molar percent (mol%)				Hardness	
Sample	Y	Si	Al	O	N	Y_2O_3	SiO_2	Al_2O_3	Si_3N_4	H_v^0 (GPa)	δ (μm)
K1	35	45	20	83	17	33.2	39.8	19.0	8.1	9.3	1.5
K2	35	45	20	90	10	31.1	46.7	17.8	4.4	8.7	1.0
K3	35	45	20	95	5	29.8	51.1	17.0	2.1	8.3	1.0
K4	35	32.5	32.5	83	17	35.3	23.4	32.7	8.6	9.3	1.2
K5	35	32.5	32.5	90	10	32.9	31.8	30.6	4.7	9.2	1.5
K6	35	32.5	32.5	95	5	31.5	37.1	29.2	2.2	–	–
K7	35	56	9	83	17	31.5	52.7	8.1	7.7	9.0	1.3
K8	35	56	9	90	10	29.7	58.5	7.6	4.2	8.5	1.2
K9	35	56	9	95	5	28.5	62.2	7.3	2.0	8.2	1.6
K10	41	42	17	83	17	39.4	36.1	16.3	8.2	9.3	1.7
K11	41	42	17	90	10	36.9	43.2	15.3	4.5	8.9	1.7
K12	41	42	17	95	5	35.3	47.8	14.7	2.2	8.8	1.4
K13	25	52	23	83	17	22.9	48.2	21.1	7.8	8.9	1.5
K14	25	52	23	90	10	21.6	54.3	19.8	4.3	8.5	1.1
K15	25	52	23	95	5	20.7	58.3	19.0	2.1	7.7	1.4

nitrogen atmosphere in the furnace. The crucible consisted of a molybdenum melting pot and lid, which was powder-lined on the inside with hexagonal-BN powder to prevent sticking. Melting temperature and time were adjusted per sample in order to obtain thoroughly molten, transparent, X-ray amorphous, glass droplets. The microhardness tests were carried out on polished (10 μm diamond polishing wheel) glass samples using a Leitz Miniload 2 microhardness tester with a Vickers diamond. Since tip blunting has a pronounced effect on the measured hardness [12] a new diamond was used. The top angles (136°) of the diamond were measured with confocal microscopy (Nanofocus μSurf). At the same time the contact area and ridges were determined to be free of any imperfections that could interfere with the measurements. The samples were cleaned with ethanol and dried prior to measuring. Loads from 1 to 20 N were applied to the samples for 30 s. Both indentation diagonals were measured and averaged. Per load a total of six indents were made.

3. Results and discussion

Except for composition K6, homogeneous glasses were obtained. Composition K6 repetitively formed a milk-white translucent material, which was excluded from further investigation. The other glasses were completely transparent. They were smoke-grey of colour as has been reported by other authors [2, 13]. With increasing nitrogen content they became darker in appearance.

3.1. Determination of the load-independent hardness (H_v^0)

The measurements show a substantial decrease of the apparent hardness with increasing load (Fig. 1). At higher loads these curves are expected to level off, although this does not occur in the measured range. Over the whole load range these curves show that the loads, which have been used in literature (0.1 to 0.3 kg) lead to a severe overestimation of the load-independent hardness of the glasses, which can lead to an error of up to 25%. The hardness values, which have been reported in literature, have to be interpreted with this effect in mind.

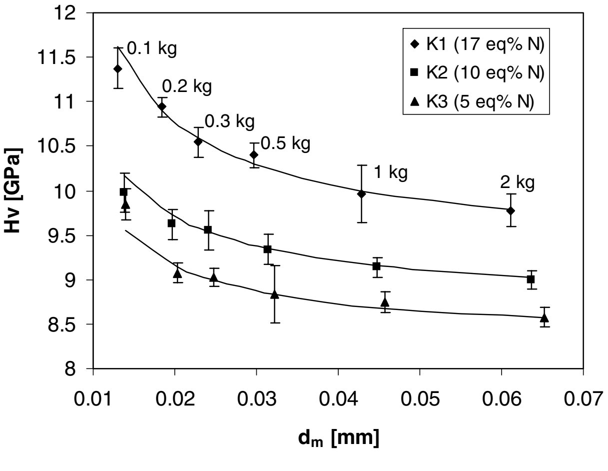

Figure 1 Apparent hardness (H_v^{app}) versus the measured indentation diagonal (d_m) for glasses K1, K2 and K3. Error bars represent the 95% confidence interval. The measurements are fitted to the Bull's equation (Equation 2).

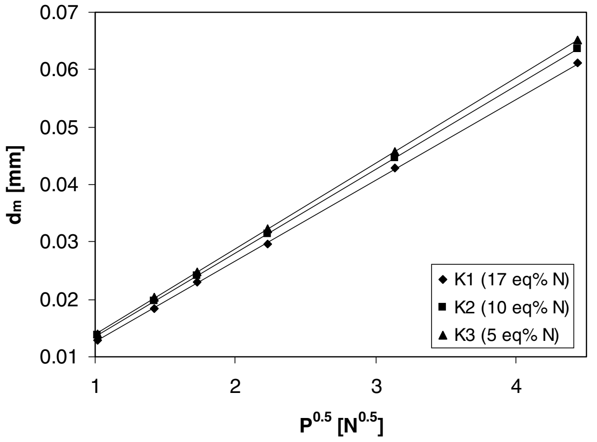

Figure 2 Plot of the measured indentation diagonal (d_m) versus the square root of the load ($P^{0.5}$) . Lines represent the linear least-squares estimate (glasses K1, K2 and K3).

In order to obtain the load-independent hardness (H_v^0) from the measured indentation size (d_m) Equation 2 is rearranged to the linear equation [10]:

$$d_m = \left(\frac{1.854}{H_v^0}\right)^{\frac{1}{2}} P^{\frac{1}{2}} - \delta, \qquad (3)$$

Thus a plot of d_m versus $P^{1/2}$ should yield a straight line with interceptδ and slope $(1.854/H_v^0)^{1/2}$.

Applying the method as described above to the raw data results in a good fit (Fig. 2). This indicates that Bull's equation is adequate to describe hardness-load curves for these systems. The parameters H_v^0 and δ as derived from the slope and the intercept of the fit are listed in Table I. The load-independent hardness (H_v^0) ranges from 7.7 to 9.3 GPa, which is significantly lower (~30%) than apparent hardness values thus far reported for Y—Si—Al—O—N glasses [1, 2, 5, 6] but is still higher than values known for conventional glass systems (e.g., vitreous silica = 5.3 GPa [10]).

3.2. The dependence of the load-independent hardness (H_v^0) on the chemical composition

There are no correlations readily available to link the hardness of this complex system directly to the chemical composition. A great complication is the presence of both four- and higher coordinated aluminium which prevents accurate estimation of the amount of the non-bridging oxygen (NBO) in the glasses [14]. Furthermore, most theories, which are designed for relatively simple oxide glasses fail to describe the influence of nitrogen in the glass network.

A simple solution would be to assume that the load-independent hardness is linearly dependent on the composition. An additive type equation can then be written

TABLE II Additive parameters (a_i) of Y_2O_3,Al_2O_3, SiO_2, and Si_3N_4

i	a_i (GPa)
Y_2O_3	10.7
SiO_2	6.8
Al_2O_3	7.9
Si_3N_4	17.9

down:

$$H_v^{0,\text{calc}} = \sum_{i=1}^{n} a_i x_i \tag{4}$$

This means that the load-independent hardness (H_v^0) can be expressed as the sum of the molar fractions (x_i) of its individual components (i) times a 'partial hardness' (a_i). The values for a_i have been calculated for H_v^0 and are given in Table II. Comparison of all the measured hardness values with the calculated ones shows that this crude model provides a fair description of the influence of the individual components on the load-independent hardness.

It shows that the addition of silicon nitride clearly enhances the hardness of the glasses, which can be attributed to the formation of NSi_3 links in the glass network. From a structural point of view we can understand these changes. The Si—N bond is not much stronger than the Si—O bond, but the bending resistance of the NSi_3 unit is much greater than that of the OSi_2 unit (bending force constants: $OSi_2 = 9.6$ N m^{-1}, $NSi_3 = 97.3$ N m^{-1} [15]). This explains why the introduction of a limited amount of nitrogen results in a relatively strong enhancement of the network rigidity. It is also interesting to notice that the incorporation of nitrogen leads to a substantial deviation from existing relations between the hardness and glass-transition temperatures [16]. For instance for composition K1 with a glass transition temperature of 953°C [17] a hardness around 7.5 GPa is expected whereas it turns out to be much higher (9.3 GPa). This relation is based on the assumption that the mean difference between the specific heat capacities of a substance in the melt and in the glassy state ($c_{p,\text{melt}} - c_{p,\text{glass}}$) is equal for different glasses, which is viable for most oxide glasses [16]. It describes the amount of energy involved in transforming a ridgid glass in a plastic pseudo-melt at the measurement temperature. In the oxynitride glasses this energy increases upon nitrogen incorporation [18], which offers a plausible explanation for the unusually high hardness.

It can also be noted that the replacement of SiO_2 by Y_2O_3 leads to an increase of the hardness. This increase suggest the formation of very strong covalent O—Y—O cross-linking bonds, as has been previously noted by Becher *et al.* [5].

In practice the observed trends imply that the addition of silicon nitride to the system is in two ways beneficial. Firstly, there is a direct influence of the NSi_3groups on the hardness. Secondly, the addition of nitrogen shifts the glass-forming region more to the alumina- and yttria-rich side of the system, which allows a further increase of the hardness by addition of a greater quantity of yttria and alumina [6]. In that respect there is room for improvement of the hardness of these glasses.

3.3. The elastic recovery parameter (δ)

In crystalline systems a substantial amount of effort has been dedicated to explaining the various parameters that are used to describe the ISE in terms of materials characteristics. It is assumed that the elasticity as well as the viscosity of the material influences the extent of the ISE [19]. Other processes like fracture and (in crystals) slip are also known to contribute to the indentation process and the ISE [9, 11]. A distinct influence of the environment (e.g., the presence of water) has also been noted for vitreous silica [10, 20]. Based on the notorious susceptibility of this material to subcritical crack growth we believe that this behaviour might be related to fracture related processes although this was not explicitly stated in the original paper of Hirao *et al.* [20].

Although there is only a limited amount of data available for other glass systems the ISE appears to be present in most glasses [10, 21]. The absolute decrease of the hardness with the load is lower than in most ceramics, due to the relatively low hardness, which is probably the reason that the effect has not received as much attention in glasses as in ceramics. Nevertheless this investigation shows similar δ-values as can be found as in ceramics, indicating that similar mechanisms are active in glasses. The current tests show only a limited effect of the composition on the δ-values, if any at all. It appears that the δ-values increase towards the borders of the glass forming region, whereas the lowest values can be found in the centre. However, in order to interpret these results more information on the ISE in a wider range of glass systems is needed, since only a relatively small variation in e.g., the viscosity and Young's modulus can be achieved in a single system. Moreover we need a better understanding of the relevant mechanisms that contribute to the plasticity of the material.

4. Conclusions

It has clearly been shown that the ISE has to be taken into account when measuring the load-independent hardness of Y—Si—Al—O—N glasses. Measurements at relatively low loads will lead to an apparent hardness, which is significantly higher than the load-independent hardness and renders comparison with other measurements at different loads unreliable. Measuring the hardness of materials with different compositions or at comparable low loads can lead to a misinterpretation of trends since the ISE may vary with the composition or material. In our load-dependent studies it is shown that the addition of nitrogen increases the hardness of Y—Si—Al—O—N glasses over the whole load range and thus the load-independent hardness. Compositional variations have shown a clear hardness increase by the incorporation of nitrogen. Nitrogen not only increases the load-independent hardness, but also allows greater quantities of yttria and alumina to be incorporated in the glass matrix, which has an additional hardness increasing effect.

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