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Vickers microhardness indentation and fracture mechanics of chalcogenide arsenic–selenium glasses

M. HAMMAM,* J. J. SANTIAGO
Center of Chemical Electronics, Electrical Engineering Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

Measurements of Vickers microhardness have been carried out on As_xSe_{1-x} glass ($0.28 < x < 0.60$). The diamond pyramid hardness number as a function of composition revealed a maximum at 40% As, the stoichiometric composition, indicating that this composition is the most ordered and strongest of the alloys. Deviation from stoichiometry was found to increase the disorder and introduce weaker bonds. An attempt was made to use the indentation approach to determine the fracture toughness of the investigated glasses. Therefore, the extent of surface traces of well-developed penny-like (conchoidal) cracks extending from the corners of Vickers indents were measured and found to obey Lawn's relation $P/C^{3/2}$ = constant (where P is the indenter load and C is the characteristic crack dimension). An approximate value of the fracture toughness was inferred from these measurements.

1. Introduction

The Vickers hardness test method is one of the most common and reliable methods for hardness measurements. It provides useful information concerning the mechanical behaviour of brittle solids [1]. Moreover, the indentation microhardness is important for understanding the mechanisms of deformation and fracture of materials [2]. Studies on the indentation fracture in brittle materials have also shown that indentation testing is a simple technique for characterizing the fracture behaviour of glass and ceramics [3]. The indentation is generally carried out using sharp indenters such as a cone or pyramid, because of the geometrical similarity of the residual impressions. The contact pressure with such a geometry is independent of indent size and thus affords a convenient measure of hardness [1].

In particular, the hardness of glass is of direct practical importance since it is apparently related to bonding in these materials. It has often been used as an approximate measure of strength [4, 5]. Although hardness is extensively measured and many techniques are available for its measurement, there is still no satisfactory definition as far as glass is concerned [6].

A fracture mechanics analysis of the indentation fracture problem has been developed, and the microfracture patterns in brittle solids have been related to the contact load, in terms of standard material parameters. This has enabled fracture toughness data to be obtained by individual techniques [3]. Strength-related properties of ceramics and glasses were recently reviewed by Lawn [7]. He considered that indentation with a sharp, fixed-profile diamond pyramid (Vickers or Knoop) is the most practical way of introducing controlled flows for strength testing, requiring only access to a routine hardness-testing facility. Where the indenter in a contact system is considered to be sharp, indentation fracture mechanics has been shown to be characterized by lateral, median and radial components. During the course of propagation both the median and the radial components attain an equilibrium state. This has recently been analysed as growing primarily as a result of relief to residual stress surrounding the constrained plastic zones [8, 9], then tending to the well-developed configuration of stably propagating half-pennies with linear radial traces extending from the impression corners of the specimen surface. It is this stage of crack propagation which can be readily amenable to fracture mechanics analysis [3].

Based upon ideal "sharp indented" geometry, Lawn and Fuller [10] have provided a simple formulation for the well-developed stage of indentation fracture. The extent of surface traces of well-developed median cracks can be related to the contact load in terms of fracture toughness as follows:

$$P/C^{3/2} = \text{constant} = kK\pi^{3/2} \tan \psi \quad (1)$$

Here P is the indenter load, C is the characteristic crack dimension defined in Fig. 1, K is the fracture toughness, ψ is the half-angle of the indenter between opposing pyramid edges and k is a small correction factor.

A literature survey has revealed that there has been little study of micromechanical behaviour, hardness variation and crack patterns for chalcogenide glasses.

*Permanent address: Department of Physics, Faculty of Science, University of Mansoura, Mansoura, Egypt.

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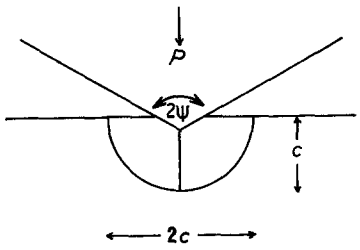


Figure 1 Median crack system associated with sharp indenter as proposed by Lawn and Fuller [10]. Shown is a section normal to the indented surface.

Therefore, a systematic study of the hardness characteristics of glasses in the system arsenic–selenium was undertaken. An attempt was made to use the Vickers indentation method to determine the fracture properties of these materials. In fact, the objective of the present investigation is to provide an understanding of the property known as hardness of chalcogenide glasses. We also established that the fully developed median cracks satisfy Equation 1, which is appropriate to centre-loaded penny cracks and has been amply utilized in the indentation fracture mechanics analysis. In addition, observations of the crack morphology exhibited by the various specimens are discussed.

2. Experimental details

Our arsenic–selenium compounds were synthesized by weighing out suitable proportions for the required composition in evacuated and sealed quartz ampoules. In order to ensure homogeneity and complete mixing of the elements, the sealed quartz ampoule was fitted into a horizontal motor shaft which was rotated around a tilted axis while in a tubular oven, and a final alloying step of 15 h at ~ 1100 K was used. The melt was subsequently quenched in air to obtain vitreous material. Our bulk samples were 0.8 mm thick slices cut from the quenched material. All the samples were finally polished to 0.05 μm finish. The samples exhibited a shiny faultless surface under a high-magnification microscope.

Indentations were performed using a Vickers Pyramid Diamond Indenter and a Tukon microhardness tester (Wilson Mechanical Instrument Division, New York, USA) with a 136° diamond indenter. Indentations were made at room temperature with loads varying from 100 to 800 g. The time of indentation was fixed to about 20 sec. At least six indentations per load were made on different locations on the sample surface. The diagonals of the resulting indentations and crack dimensions were measured on all specimens directly by using a filar eyepiece that was calibrated. This allowed an estimated accuracy of ± 0.1 μm.

The average diagonal length was then found and the diamond pyramid hardness (DPH) was calculated using the formula

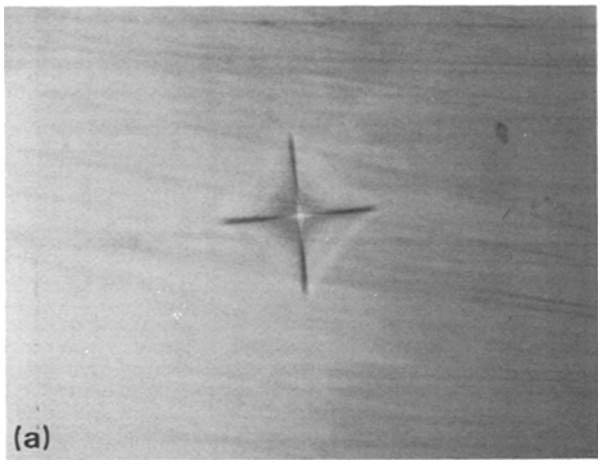
$$DPH = 1854.4P/d^2 \qquad (2)$$

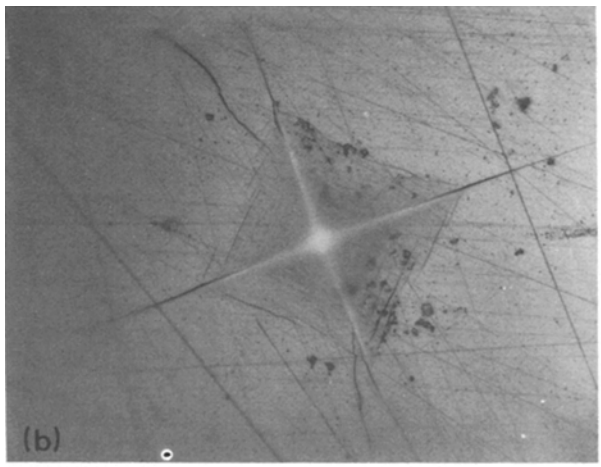
where P is the load in kg, d is the average diagonal length of the Vickers impression in mm and 1854.4 is a constant, the conversion factor of the tetragonal pyramid side-wall's surface to the perpendicular projection of the surface on the plane. The quantity proportional to this projection of the surface is the diagonal of the impression, d.

3. Results and discussion

3.1. Impression and crack morphology

During the measurements of microhardness using Vickers indentation on the surface of our glass samples some interesting microscopic observations concerning the impression and crack patterns were





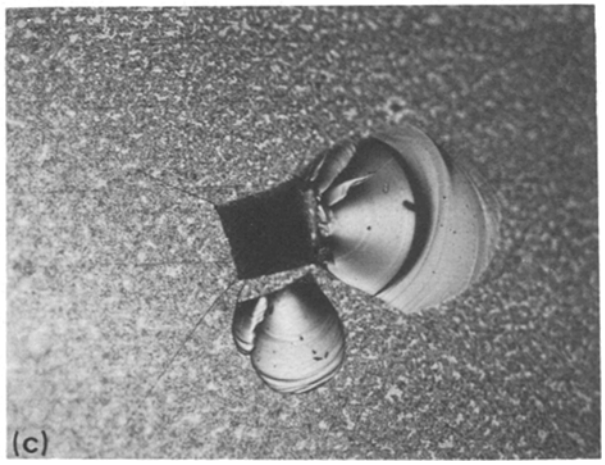


Figure 2 Typical photograph of Vickers indenter marks representing all the arsenic–selenium compositions studied: (a) load 100 g; (b) occasional formation of two cracks from the indenter diagonal (c) load 800 g.

made. It was found that, regardless of the composition, all our glassy materials showed about the same morphology at the same load. Typical photographs of Vickers indented marks, for different loads, representing all the compositions studies are shown in Fig. 2. These photographs represent almost all the different kinds of crack characteristics found for the different glass compositions.

When low-load Vickers indentations were examined (< 200 g), recognizable cracking occurred for off-stoichiometric samples, but the surface surrounding the indenter was always distorted for all the compositions at all the loads. This distortion increased in severity and a high damage was done to the surface at loads higher than 800 g. It is believed that as the Vickers indented load is increased, a transition from purely inelastic deformation to the formation of penny-shaped (conchoidal) cracks occurs beneath and across the major diagonals of the Vickers indent. Subsequent loading causes these cracks to extend and cut the free surface to yield the cracks as observed [1]. Occasionally, two cracks would form from the corner of the indenter diagonal (as shown in Fig. 2b) and surface traces of lateral vents were frequently visible in all the compositions.

Well-developed radial cracks were also visible. For some indentations, extra cracks that did not extend from the indent diagonal were observed. These may be shallow radial cracks which do not have the complete half-penny geometry but extend only a short distance beneath the surface. Similar cracks have been observed in a number of materials by Smith and Pletka [11] and Evans and Wilshaw [12]. These radial cracks along the major diagonals or the edges of the Vickers indent are probably the result of the unloading residual stresses [13, 14]. As mentioned before, these radial cracks emanate from the corners of the indentation and probably do not extend beneath the deformed zone [1].

From the thermodynamic point of view, Ghoneim and el Batal [2] reported that the interpretation of fracture strength is based on an analysis of the changes of electron density distribution of anions and cations under unaxial tensional stress. Regardless of the chemical composition, all glasses under mechanical stress develop a tendency to mobilize neutral molecules or ions as a means of increasing their thermal entropy through additional modes of vibration. Weyl [15] considered that composition complexity introduces disorder into the vibrational spectrum of a glass. It lowers the free energy of the system by increasing its configurational and vibrational entropy. The increase of entropy through complexity modifies all properties which involve deformation, flow or the motion of particles. When one component is substituted for another, both the enthalpy and entropy of the system are affected. So, composition studies can also be used to determine its effect on the dependent properties of microhardness.

3.2. *DPH* as a function of load

DPH was calculated from Equation 2. Fig. 3 shows the relation between the load P and the square of the

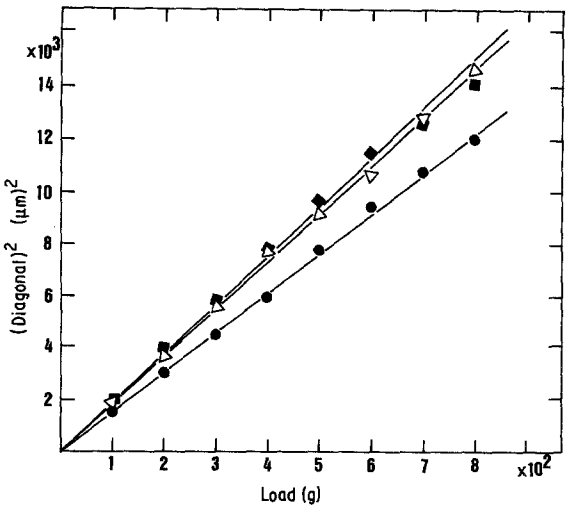


Figure 3 Relation between (diagonal)^2 and load for all the arsenic–selenium glasses studied. (■) $As_{33}Se_{67}$, (●) $As_{40}Se_{60}$, (△) $As_{50}Se_{50}$.

average length of the diagonal. It is clear that hardness is independent of load for all the compositions measured for loads from 100 to 800 g. Because hardness is independent of load, i.e. independent of penetration depth, it is likely that the displacement of glass is a bulk property rather than a surface-controlled phenomenon [6]. Neely and Mackenzie [6] found that the glass will be displaced towards a region below the indenter and the total surface of the sample does not change.

The slopes of the lines in Fig. 3, representing the hardness number for the different compositions studied, is plotted against the arsenic content in Fig. 4. A maximum is found at 40% As (the stoichiometric composition).

The behaviour of As–Se alloys in the 30 to 60% As region can be explicable in terms of structural units, as well as relative bond strength. According to Myuller [16], the bond strengths are

As–As	46 kcal mol^{-1}
Se–Se	49 kcal mol^{-1}
As–Se	52 kcal mol^{-1}

A maximum in density [17] and a minimum in compressibility [18] near or at 40%. As further illustrated

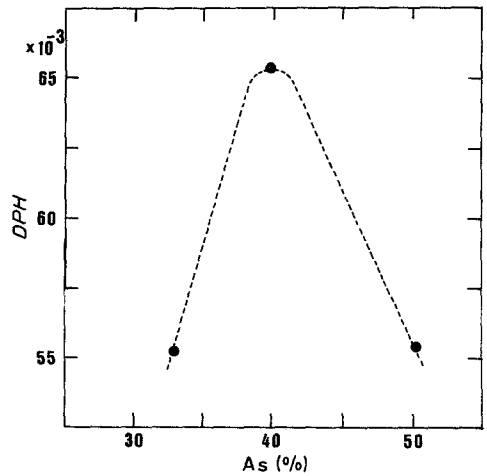


Figure 4 Compositional dependence of the hardness number of the arsenic–selenium glasses.

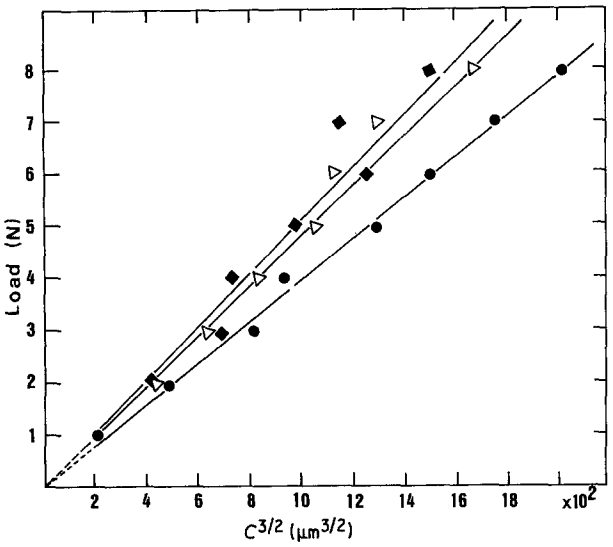


Figure 5 Relation between crack dimension C and indenter load P: (■) $As_{33}Se_{67}$, (●) $As_{40}Se_{60}$, (△) $As_{50}Se_{50}$.

the suggestion that $As_{40}Se_{60}$ represents the most ordered and strongest of the alloys, and that deviations from that composition increase the disorder in addition to introducing weaker bonds, as confirmed by our data in Fig. 4. On deviating from 40% As the disorder increases [19], the structure weakens and becomes more loosely packed. Near stoichiometry, the addition of excess arsenic is expected to increase the lateral extent of the layer-like units, whereas excess selenium tends to produce smaller units. Further support for this view is provided by Kolomiets *et al.* [20] in their study of the kinetics of dissolving As–Se alloys in dimethylamine and KOH. Kawamoto and Tschushihashi [21] observed a linear dependence of the DPH on the composition of Ge–S glasses. They explain the increase in the *DPH* with germanium content in the glass in terms of the increase of the number of Ge–S bonds.

3.3. Indentation fracture and fracture measurements

To characterize better the specimens measured, in so far as the micromechanical properties are concerned, a plot of the crack dimension, c, as a function of the indenter load, P, was established. This should yield a straight line in accordance with Equation 1. Fig. 5 shows this relation. From this figure it is clear that the relation $P \simeq C^{3/2}$ was found to hold satisfactorily in the case of the chalcogenide glasses studied. This relation has been used in deriving expressions for the stress intensity factor of the median/radial crack system in almost all of the indentation fracture models [11]. Although this relation has been confirmed on a number of materials [10, 11], it is necessary to verify it for a number of glasses in order to have confidence in the indentation fracture models.

To the knowledge of the authors, this relation has not yet been applied to any chalcogenide glasses. If the relation $P/C^{3/2}$ = constant obtains, a least-squares analysis of log P against log C should yield a value of the slope equal to 1.5.

Plots of log P against log C, for all the compositions

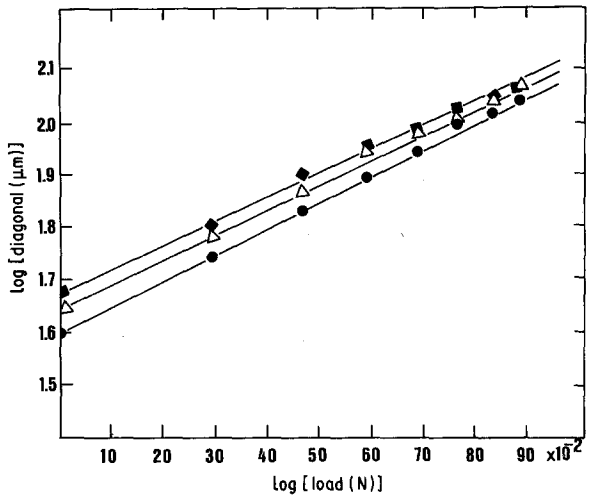


Figure 6 Plot of log P against log C for the investigated arsenic–selenium glasses. (■) $As_{33}Se_{67}$, (●) $As_{40}Se_{60}$, (△) $As_{50}Se_{50}$.

studied, are given in Fig. 6. The slopes were calculated using the average crack length of the well-developed median/radial cracks obtained at each indenter load and are listed in Table I.

All slopes are in reasonable agreement with the value 1.5. Therefore, it is concluded that the fully-developed median/radial cracks in As–Se glasses obey the relation for centre-loaded penny cracks of $P/C^{3/2}$ = constant. Furthermore, this result provides encouragement in using indentation experiments to evaluate the fracture toughness of brittle materials.

The average crack length at a particular indenter load for each specimen was used to get an idea about the indentation fracture toughness value K. The equation used is [11]

$$K = \psi_b(P/C^{3/2})$$

where

$$\psi_b = 1/\pi^{3/2} \tan \psi$$

The values obtained are approximate ones since no knowledge of the correction factor was available. Only a relative prediction of the fracture toughness values of indented As–Se materials is provided. Even in this case, Miyata and Jinno [3] reported that toughness values may be evaluated within a factor of two. Table I shows the variation of kK with the arsenic content. In our case, comparative data from microhardness testing of the anisotropy of K do not seem available in the open literature.

4. Conclusions

The microhardness of chalcogenide arsenic–selenium glasses as determined by Vickers indentation measurement was found to have a maximum at 40% As, the stoichiometric composition. This agrees well with

TABLE I Slopes of the log C against log P curves and the variations of kK with the arsenic content

Composition	Slope	kK (N $\mu m^{-3/2}$)
$As_{33}Se_{67}$	1.6	0.0758
$As_{40}Se_{60}$	1.4	0.0524
$As_{50}Se_{50}$	1.6	0.0689

other kinds of measurement, showing that the stoichiometric composition is the most ordered and strongest of the alloys. Deviation from that composition increases the disorder in addition to introducing weaker bonds.

Fully-developed median cracks for all the chalcogenide glasses studied were found to obey Lawn's relation $P/C^{3/2}$ = constant, from which an approximate idea of the fracture toughness values of indentation was found.

Our data on As–Se compounds from the microhardness test could not be compared with other chalcogenide glasses for lack of available data in the open literature.

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