

High-temperature nanoindentation testing of fused silica and other materials

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ABSTRACT

This paper describes a new high-temperature stage for small-scale mechanical property testing. This allows the determination of the load–penetration curve of a diamond tip in a temperature range extending from room temperature to 400°C. Both sample and indenter can be heated separately. Indentation curves show that very low thermal drift can be achieved. Nanoindentation results are presented for gold, soda–lime glass, fused silica and a polyimide and compared with existing microscale and bulk mechanical property data where available. Results from fused silica show that its mechanical properties exhibit a completely different temperature dependence from those of soda–lime glass, as expected since fused silica is an anomalous glass.

§1. INTRODUCTION

There is now a substantial body of literature based on depth-sensing indentation (Doerner and Nix 1986, Oliver and Pharr 1992, Pollock 1992, Hermann *et al.* 2000). However, to date, most nanoindentation measurements have been limited to room temperature since instruments for slowly measuring nanoscale displacements are highly sensitive to thermal expansion (Suzuki and Ohmura 1996, Smith and Zheng 2000). Since all mechanical properties are temperature dependent, small-scale measurements at elevated temperatures would open up significant new possibilities for the materials scientist. For example, the temperature of a wear-resistant coating usually increases in service, which will invariably result in changes in the hardness and modulus values of both the film and the substrate material. Clearly, it is necessary to make measurements at the service temperature rather than at room temperature for the surface engineering to be optimized. Although a prototype in-temperature ultramicroindentation instrument has been developed previously by Suzuki and Ohmura (1996), it has lower sensitivity and is susceptible to thermal drift and was used only for very rapid indentations.

This paper describes a new high-temperature stage for small-scale mechanical property testing which allows the determination of the load–penetration curve of a diamond tip in a temperature range extending from room temperature to 400°C with very low thermal drift. Nanoindentation results are presented for gold, soda–lime

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glass, fused silica and a polyimide and compared with existing microscale and bulk mechanical property data where available.

§2. EXPERIMENTAL DETAILS

2.1. High-temperature indentation configuration

The indentation instrument (NanoTest system) operates with a horizontal loading configuration which enables large samples and stages to be accommodated easily. Patents on the hot-stage design have been applied for (Micro Materials Ltd 2001). One configuration of the heating stage is shown schematically in figure 1. In this configuration, the displacement transducer is placed below the heated area, thus minimizing the influence of convection currents. A thermal shield is interposed between the loading head and the hot stage to preclude any significant radiant heating of the capacitor. A small heater and a miniature thermocouple have been added to the diamond stub to prevent heat flow upon diamond-specimen contact. The hot stage itself includes a highly effective, thermally insulating ceramic block. The temperature increase of the plate which supports the block is less than 1°C when the stage is operating at 500°C. For reactive specimens, the environmental cabinet must be purged with an inert gas. Specimens are attached by means of a magnesium silicate ceramic cement.

2.2. Calibration of the instrument

A Berkovich diamond indenter was used for all measurements. The instrument depth calibration was performed at each indentation temperature using a calibrated

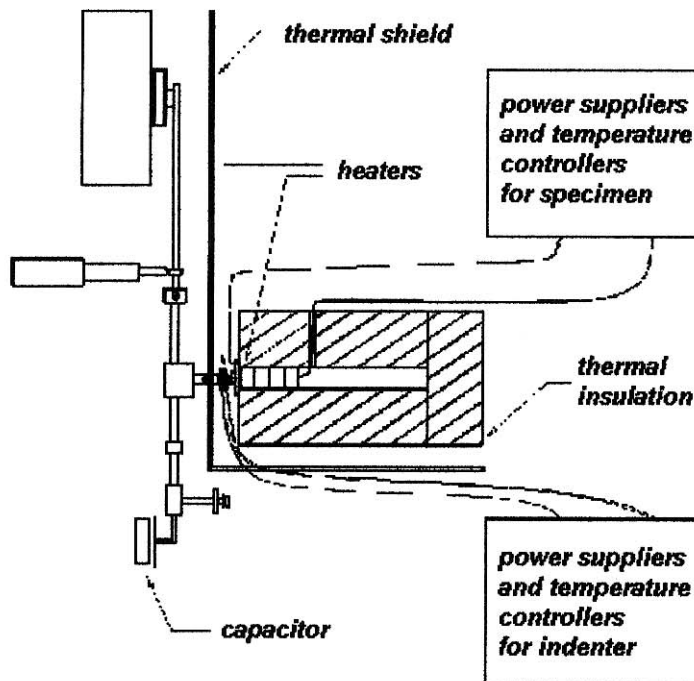


Figure 1. Heating stage configuration and instrumented indentation implementation.

Table 1. Indentation parameters.

Specimen	Glass transition temperature (°C)	Test temperatures (°C)	Maximum load (mN)	Loading rate (mN s ⁻¹)	Dwell time at maximum load (s)	Number of repeat tests for averaging
Gold	–	25, 200, 400	50	2.38	10	3–10
Soda–lime glass	≈520	25, 200	50	2.38	10	3–10
Polyimide	≈250	25, 100	10	0.25	30	5
Fused silica ^a	≈1050	25, 100, 200, 300, 400	150–200	3.53	10	15

^aThermal drift correction on fused silica; hold for 60 s at 90% unloading.

titanium nitride step on silicon wafer. The depth calibration varied by 2% over the range 25–400°C.

2.3. Indentation procedure and data analysis method

The indentation procedures for each specimen are summarized in table 1. For the glasses and polymer, the indentation temperatures were far below their glass transition temperatures. A longer holding time at maximum load was used on the polyimide specimen to minimize the effect of continuing plastic deformation during unloading on the shape of the unloading curve. This procedure leads to more accurate values of the modulus (Flores and Balta Calleja 1998). After correction for instrument compliance and thermal drift data were analysed by a power-law fitting procedure similar to that described by Oliver and Pharr (1992). The hardness H is determined from the peak load P_{\max} and the projected area A of contact. To obtain the elastic modulus, the unloading portion of the depth–load curve was analysed according to a relation which depends on the contact area:

$$C = \frac{\pi^{0.5}}{2E_r A^{0.5}}, \quad (1)$$

where C is the contact compliance and E_r is the reduced modulus defined by

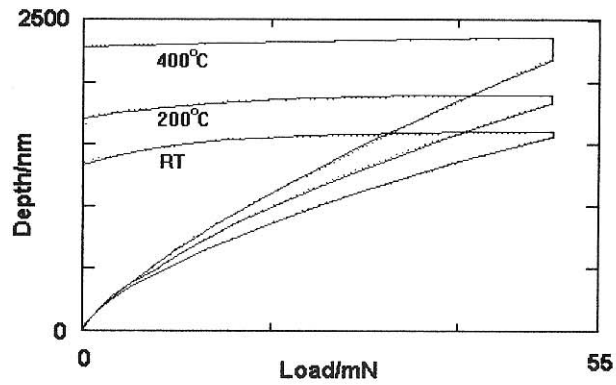
$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \quad (2)$$

where ν_s is Poisson's ratio for the specimen, ν_i is Poisson's ratio for the indenter (equal to 0.07), E_s is Young's modulus for the specimen and E_i is Young's modulus for the indenter (equal to 1141 GPa).

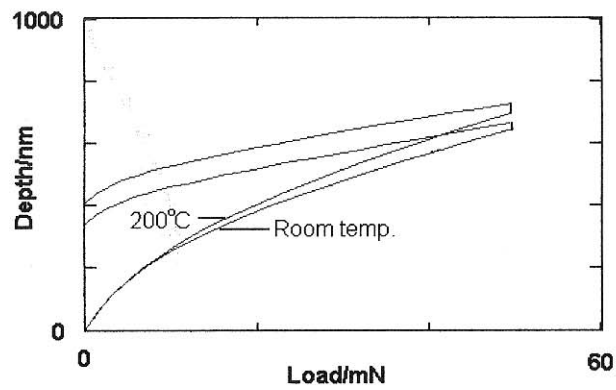
§3. RESULTS AND DISCUSSION

3.1. Gold, soda–lime glass and polyimide

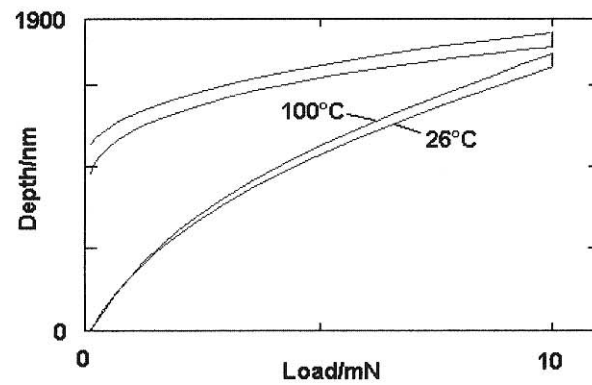
The hardness and modulus values of the gold, soda–lime glass and polyimide specimens decreased as the indentation temperature was increased (figure 2 and table 2). For these samples, appreciable creep was observed during the dwell period at maximum load. The amount of creep increased with increasing temperature, as expected. The results for gold were probably influenced by a change from pile-up to sink-in when the surface changed from a work-hardened condition to an annealed



(a)

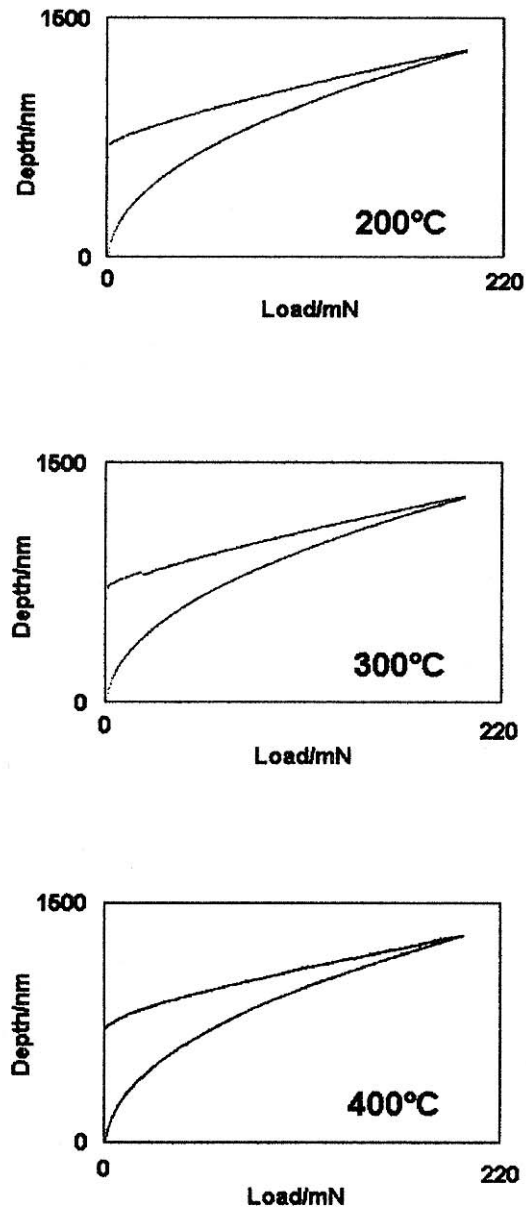


(b)



(c)

Figure 2. Indentation curves into (a) gold at 25°C (RT, room temperature), 200°C and 400°C, (b) soda-lime glass at 25 and 200°C, (c) polyimide at 25 and 100°C and (d) fused silica at 200, 300 and 400°C. Creep is observed under maximum load; thermal drift is determined under 90% unloading.



(d)

Figure 2. (continued)

condition. Notwithstanding this, the substantial decrease in hardness was probably due largely to annealing, which would be confirmed by repeating the measurements after cooling the heated specimen back to room temperature. The relatively small decrease in the hardness of the polyimide was expected owing to the high T_g for this sample. From the decrease in hardness for the soda-lime glass a temperature coefficient of the hardness of $-7.9 \times 10^{-3} \text{ GPa K}^{-1}$ can be estimated. This compares

Table 2. Temperature dependence of hardness and reduced modulus of polyimide, gold and soda-lime glass.

Specimen	T (°C)	H (GPa)	E_r (GPa)
Gold	25	0.84	86.3
Gold	200	0.59	74.1
Gold	400	0.38	68.8
Soda-lime glass	25	7.09	75.1
Soda-lime glass	200	5.76	73.3
Polyimide	25	0.186	3.526
Polyimide	100	0.169	3.055

reasonably with measurements of the variation in the microhardness of soda-lime glass using Vickers indenters, although it should be noted that there is some variability between the values reported in the literature. For example, a value of $-6.6 \times 10^{-3} \text{ GPa K}^{-1}$ has recently been reported (Watanabe *et al.* 1999). In comparison, Westbrook (1960) determined a much greater drop in hardness over the range 25–250°C whereas, interestingly, Le Bourhis and Metayer (2000) found little variation in microhardness below 300°C.

3.2. Fused silica

The data on fused silica are summarized in figure 3 and table 3. It is clear from the depth-load curves shown in figure 2 (*d*) that indentations can be performed at elevated temperatures with insignificant thermal drift. This is an important result, since reliable quantification is possible only in the absence of a load-dependent thermal drift. In all the experiments, there was a 60 s hold period after 90% unload-

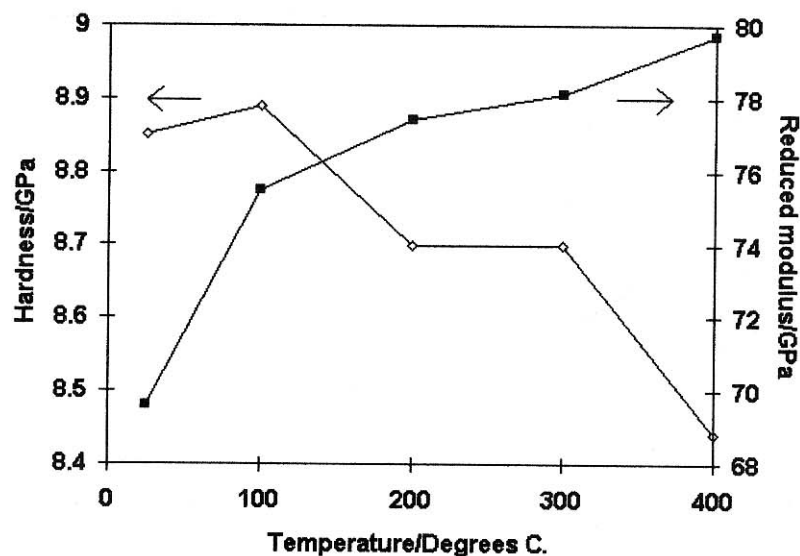


Figure 3. Temperature dependence of the hardness and modulus of fused silica.

Table 3. Hardness and reduced modulus data from indentations into fused silica at 25–400°C.

Temperature (°C)	H (GPa)	E_r (GPa)
25	8.85 ± 0.05	69.6 ± 0.35
100	8.89 ± 0.13	75.5 ± 0.38
200	8.70 ± 0.07	77.4 ± 0.42
300	8.70 ± 0.03	78.1 ± 0.30
400	8.44 ± 0.19	79.7 ± 0.66

ing to permit thermal drift correction; in figure 2 (*d*), only the 300°C data showed any evidence of drift.

Significant creep at maximum load did not occur in fused silica, even at loads and temperatures considerably higher than those used for the soda–lime glass indentations. Fused silica exhibited some softening at higher temperatures, but this was much less than that for other common glasses over the same temperature range (Watanabe *et al.* 1999, 2001), including the soda–lime glass used in the present work. Microhardness measurements by Westbrook (1960) also showed a smaller decrease in hardness with temperature for fused silica than for soda–lime glass. A linear regression fit to the hardness data in figure 3 yields a temperature coefficient of hardness of $-1.1 \times 10^{-3} \text{ GPa K}^{-1}$. Comparison of the results on the viscoelastic materials does not reveal a clear correlation between the temperature coefficient of the hardness and T_g . Similarly, in microhardness measurements on a range of TeO₂-based, Bi₂O₃-based and soda–lime silicate glasses at 25–600°C by Watanabe *et al.* (1999, 2001), no correlation was observed.

A difference in deformation mechanism is likely to be responsible for the differences between fused silica and soda–lime glass. Fused silica is known to densify relatively easily during indentation owing to its open three-dimensionally coordinated structure (Kurkjian *et al.* 1995, Watanabe *et al.* 1999). In contrast, the network modifiers (Na₂O) in soda–lime glass provide weak points for flow and fill interstices, thereby reducing the compressibility, and hence shear flow rather than volume flow is the dominant mechanism for this glass (Kurkjian *et al.* 1995).

It has been well established that the modulus of fused silica exhibits an anomalous temperature dependence, that is it increases with increasing temperature (Marx and Sivertsen 1953, McSkimin 1953, Spinner and Cleek 1960, Bucaro and Dardy 1974, Mazurin *et al.* 1983, Heraeus Quartztech 1994, Willems and Sannibale 2000). This type of behaviour was also observed in the present work. However, the indentation technique indicated a stronger temperature dependence than that previously reported in the literature. In this study the modulus was found to increase by over 14% between 25 and 400°C, whereas the literature data indicate a 5–10% rise in modulus. The difference may be due to densification; the alternative techniques for measuring the modulus usually use beam bending (Willems and Sannibale 2000), where structural change will not be a factor until temperatures of the order of 1000°C are reached. The fused silica results indicate that caution should be exercised when using fused silica as a nanoindentation reference material at elevated temperatures, even though the glass transition temperature of fused silica is over 1000°C.

§4. CONCLUSIONS

A new indentation hot stage has been developed for in-temperature tests up to 500°C and allows $P(h)$ curve determination. Results on soda–lime glass, gold, polyimide and fused silica have shown the great potential of our new hot stage. Indentations can be performed with insignificant thermal drift up to 400°C. Reliable quantification of high-temperature mechanical properties is therefore possible in the absence of any load-dependent thermal drift. Where comparison was possible with literature, good agreement was found. Fused silica exhibited a different behaviour from soda–lime glass, softening only slightly at higher temperatures. A difference in deformation mechanism is likely to be responsible since fused silica is known to densify relatively easily during indentation owing to its open structure (Ernsberger 1968, Kurkjian *et al.* 1995, Le Bourhis and Metayer 2000). The anomalous behaviour of fused silica (modulus increasing with increasing temperature) recently shown by beam-bending methods (Willems and Sannibale 2000) was also observed by indentation. The fused silica results indicate that caution should be exercised when using fused silica as an indentation reference material at elevated temperatures. This technique will be very helpful in the following: testing tribological and protective coatings, which are used at elevated temperatures, and microelectronic thin films, which are processed at temperatures up to 500°C; determining contact creep, particularly in small samples and in single phases in multiphase systems; studying the temperature-dependent complex modulus of polymer coatings; investigating fibre composites where the bonding strength between the fibre and matrix is temperature dependent; examining phase change phenomena, for example shape-memory alloys.

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