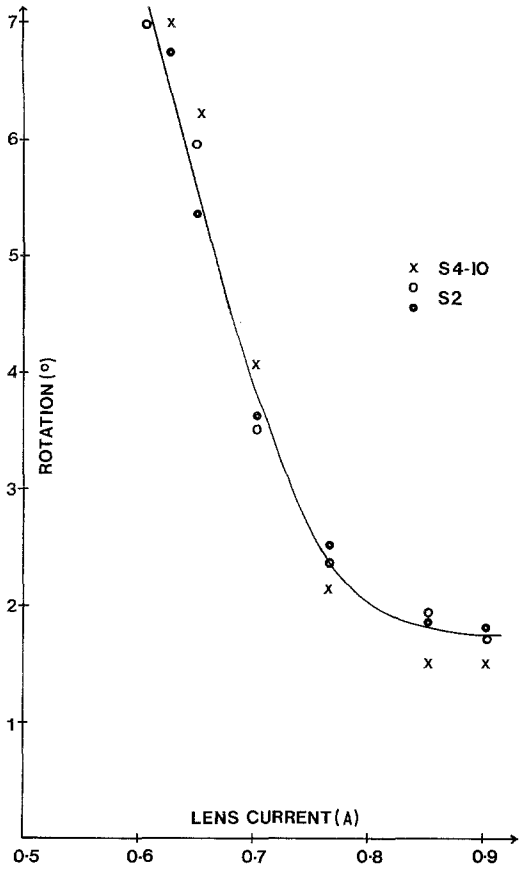

Figure 1 Experimental measurement of rotation between SACP and micrograph for S2 and S4-10 Stereoscans at 30 kV.

The net rotation through the lens will, therefore, be slightly changed, by an amount depending on the form of the field distribution. This might be expected to differ from one instrument to another, but measurements made on three "Stereoscans" (two mark 2 and one S4-10) gave similar results at 30 kV.

When two orientations are being compared (as for example across a grain boundary) these rotations are of no significance. But when accurate absolute determinations of orientations are being made, or when crystallographic directions in the specimen surface are being found, the rotations must be taken into account.

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DAVID C. JOY*
Department of Metallurgy and Science of Materials, University of Oxford, UK
CAMILLA M. MARUSZEWSKI,
Department of Neurology, University of Maryland Medical School, Baltimore, USA

*Present address: Materials Science Division, Bell Telephone Laboratories, Murray Hill, New Jersey 07974, USA.

Hertzian fracture of glass ceramics

Whereas many studies have been made of the formation and structure of a vast range of glass ceramics in recent years, comparatively little attention has been devoted to the fracture properties. Nevertheless, it has become clear [1-3] that microstructural parameters can assume a controlling role in the fracture of this type of solid. Basically, the microstructure can affect the material strength in two ways: first, it can determine the size of incipient surface flaws from which catastrophic cracks may initiate; second, it can provide "obstacles" to the passage of a "well developed" crack, thereby influencing the fracture surface energy. Of these two factors, it is the second which characterizes more the underlying fracture processes of a given material.

Studies of the mechanics of Hertzian fracture [4, 5] show that the "critical load" (the load at which a cone-shaped crack suddenly forms just outside the circle of elastic contact between spherical indenter and flat specimen) provides a measure of the fracture surface energy under conditions of crack equilibrium. Moreover, the test is reasonably insensitive to any variations in the elastic properties of the material (as long as the stiffness of the specimen remains small in comparison to that of the indenter) or in the state of microstructural flaws. The need to

consider the flaw distribution may in fact be avoided altogether by subjecting the test surface to an appropriate pre-abrasion treatment [6] to introduce a uniform density of controlling nucleation centres for the cone cracks (and thereby to ensure a high degree of reproducibility in results). The versatility of the Hertzian technique, with the capability of rapid data accumulation from relatively small specimens, has been adequately demonstrated in a comprehensive study of the fracture properties of various structural modifications of silica [7]. Detection of the critical fracture event is made straightforward in all brittle solids, transparent or opaque, with the incorporation of suitable acoustic sensors [8].

In this work we demonstrate the application of the Hertzian fracture test to the study of the effect of heat treatment on a specific glass ceramic system [9]. The glass ceramic was prepared from a batch of molecular composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, with 3.72 wt% TiO_2 included to induce fine grain crystallization. The raw materials were lithium carbonate (analytical grade), alumina (British Aluminium Co, Cera grade), crushed crystalline quartz (Thermal Syndicate Ltd) and titania (Laporte, Tiona VC grade). The batch material was twice melted with intermediate crushing and cast into bars which, after cooling as a glass, were subdivided into smaller specimen slabs about 50 mm × 35 mm × 10 mm. The specimens were then given individual heat-treatments comprising 25 to 710°C at 4°C min^{-1}, 710 to 755°C at 0.23°C min^{-1}, then at 4°C min^{-1} to a specified temperature with a hold of 1 h. This treatment produced controlled nucleation and growth of crystals, as evidenced by an increasing opacity at higher temperatures; the resultant microstructure in each case is of a submicron scale. Finally, the specimens were machined flat and parallel faced, and were then abraded with a slurry of grade 1000 silicon carbide grit to produce surface flaws $\approx$ 3 μm in length.

The Hertzian tests were performed on an Instron testing machine, with a tungsten carbide sphere of radius 4 mm as indenter. Preliminary runs showed the critical fracture load to be reasonably insensitive to rate effects. For instance, changes in Instron cross-head speed from 0.05 to 2.5 mm min^{-1}, and the test environment from water to a dry nitrogen atmosphere, produced a maximum variation of less than 10% in the results (the corresponding variation for soda-lime glass under the same conditions is greater than a factor of two [10]). The system is, therefore, not far from equilibrium prior to cone fracture, as is necessary for any fracture surface energy investigation. Accordingly, a cross-head speed of 0.05 mm min^{-1} and laboratory atmosphere were chosen as the most convenient test conditions for all subsequent runs.

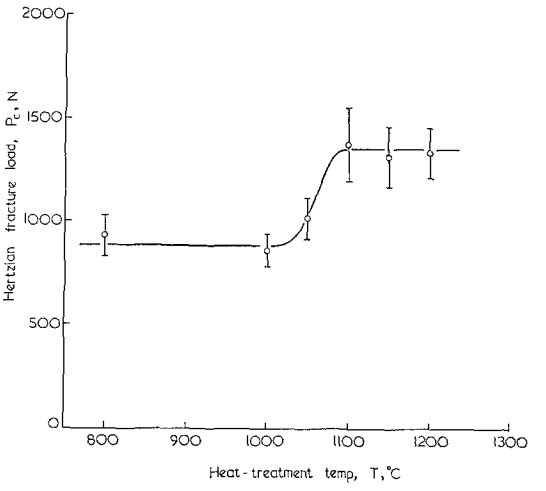

Figure 1 Hertzian fracture load as a function of maximum temperature of heat treatment of a lithia–alumina–silica glass ceramic. Bars indicate 0.25 to 0.75 load probability limits.

Fig. 1 shows the critical fracture load as a function of the heat-treatment temperature for the glass ceramic. The data points represent 0.50 ± 0.25 probability values from cumulative distribution plots of the fracture loads for at least thirty tests per specimen. A strengthening effect is evident above about 1000°C, which correlates with the major change in microstructure in the material occurring between 1000 and 1100°C.

The effects of heat-treatment on the microstructure of lithia–alumina–silica glass ceramics have been studied by transmission electron microscopy [9, 11]. The treatment at 800°C leads to the development of a dense growth of equi-axed 0.1 μm grains of β-quartz solid solution (ss) with no sign of residual glass phase. The specimen heated at 1000°C has a similar β-quartz structure but in addition 0.01 μm particles of anatase are observed, especially at grain boundaries. The structure is considerably coarser after the 1100°C treatment, when the major phase grains are found to have grown to 0.5 to 1.0 μm and to have transformed from

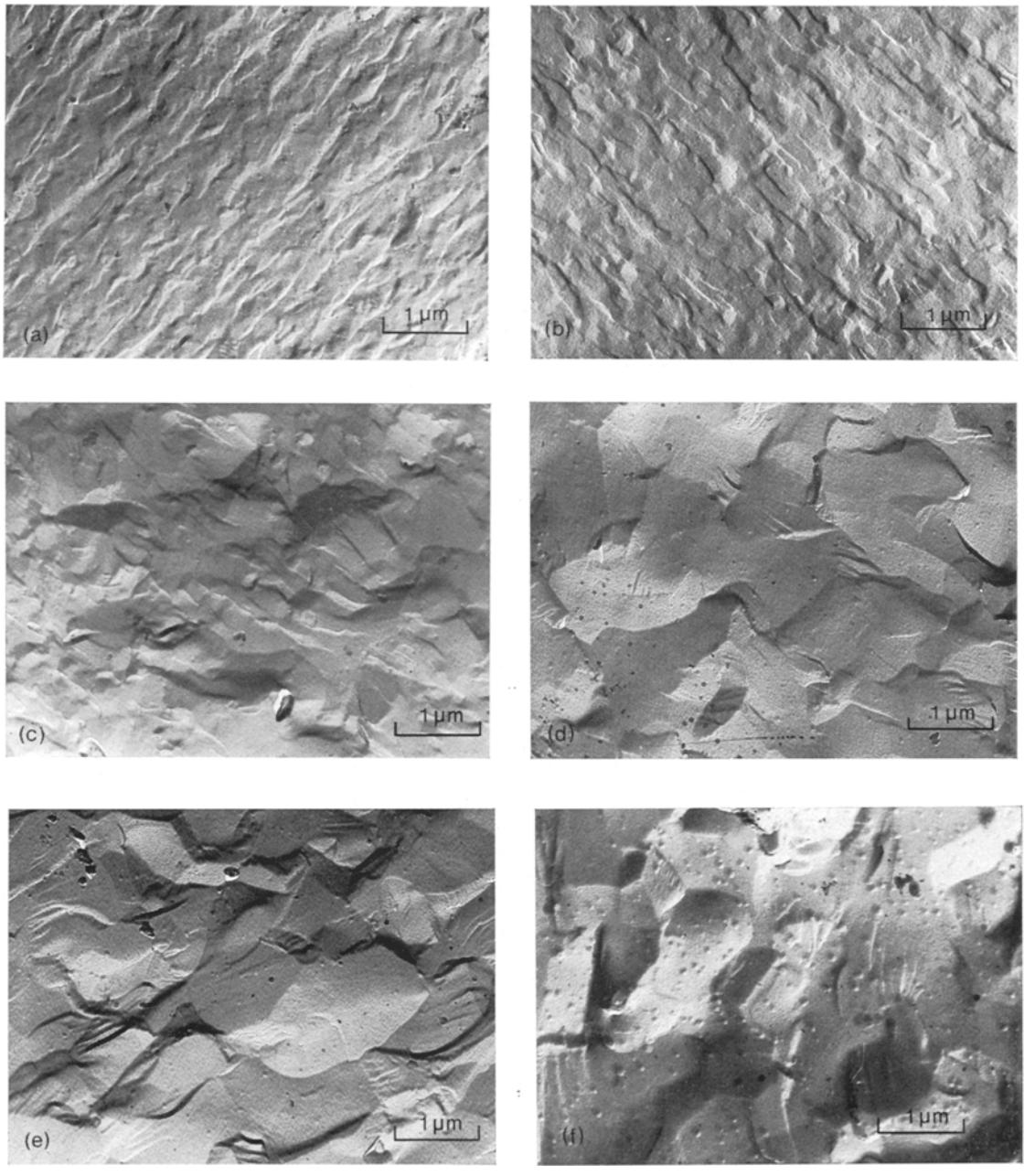

Figure 2 Vacuum-fracture carbon replicas of a lithia–alumina–silica glass ceramic after heat-treatment with 1 h hold at maximum temperatures of (a) 800, (b) 1000, (c) 1050, (d) 1100, (e) 1150, and (f) 1200°C.

β-quartz ss to a keatite ss known as β-spodumene. The structure after the 1050°C treatment is intermediate, consisting of small crystals of β-quartz ss and a roughly equal proportion of larger grain keatite ss. Heat-treatment above 1100°C leads to progressive elimination of the smallest keatite grains and to slight coarsening of those anatase crystals which lie at grain boundaries.

Electron micrographs of carbon replicas of surfaces produced by fracture of specimens in vacuo are illustrated in Fig. 2. For the specimen heated at 1000°C (Fig. 2b) the fracture path is deflected by individual β-quartz ss grains, but

only a proportion of the grains are apparently effective in this regard. This is shown by the fact that the fracture steps (produced when the crack front divides in passing around effective obstacles and subsequently rejoins) have lengths of the order five times the grain diameter. However, for specimens heated to above 1100°C (Fig. 2d to f) almost all the keatite grains cause a change in fracture direction, and the roughness of the surface is greater. Part of the fracture is certainly transgranular, as evidenced by the surface markings, and part is probably intergranular.

The abrupt change of fracture surface pattern between 1000 and 1100°C correlates with grain growth that occurs when the phase transformation takes place, and the 1050°C specimen shows both types of pattern. A coarsening of the grain size is known to have a significant influence on the path of fracture and hence on the effective fracture surface energy [12]. Indeed, in the present case, the increase in fracture surface area alone with heat-treatment temperature is sufficient to account for the increase in fracture energy. Because the crystallographic structures of β-quartz and keatite solid solutions are closely related, it may be anticipated that the intrinsic work required to create new surfaces is similar for both phases and therefore of secondary importance in determining the origin of the fracture energy change. Further factors, such as anisotropy of mechanical and thermal properties, may also influence the fracture energy, but these are felt to be insignificant in comparison with the grain-size effect in the present case.

The presence of the anatase crystals is revealed in Fig. 2f by hollows in the fracture surface, clearly indicating that circumferential cracking has taken place due to the radial tension produced from the heat-treatment temperature. Because of the small size of the anatase crystals we do not consider them to have a great influence on the fracture. However, the apparent slight drop in fracture load between 1100 and 1200°C in Fig. 1 may, if significant, be due to the coarsening of the anatase crystals which occurs in this temperature interval.

In summary, we conclude that the Hertzian fracture test is a convenient means of studying the relation between the fracture characteristics and microstructure of fine-grained ceramic materials. In particular, in the lithia–alumina–silica system studied a coarsening of the grain microstructure within the phase-transition temperature range 1000 to 1100°C manifests itself in the processes which deflect a crack from its planar path, with an attendant increase in the fracture surface energy.

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B. R. LAWN*
T. R. WILSHAW
Applied Sciences Laboratory,
University of Sussex,
Brighton, UK
T. I. BARRY
R. MORRELL
Division of Inorganic and Metallic Structure,
National Physical Laboratory,
Teddington, Middlesex, UK

*On leave from University of New South Wales, Australia.