Slow crack growth in proton- and deuteron-irradiated quartz

It is well known that cracks in silicates can grow subcritically in the presence of a chemically reactive external environment [1, 2]. In principle, there is no reason why analogous crack growth behaviour should not arise from migration of an active chemical species *within* the material, although bulk diffusion might be expected to slow down the process [3]. Thus, for instance, large cracks in soda-lime glass grow noticeably at constant load in vacuum, whereas in pure fused silica no such effect is observed [4]: the network-modifier component in the glass clearly plays an active role in the crack extension.

In this note, we present observations of slow crack growth in irradiated quartz as evidence for the above phenomenon. Single crystal slabs of (0001) α-quartz were pre-abraded to introduce a uniform layer of surface microcracks some 10 μm in depth. A selected area of surface was then exposed to a uniform beam of protons or deuterons (accelerated through 0.9 and 1.0 MV respectively) such that the mean ion penetration depth [5] extended just below the abrasion microcracks. The total irradiation dose was $\simeq$ 1-2 $\times$ 10^{22} ions m^{-2} in all cases. To avoid surface fragmentation arising from charging effects, beam currents were maintained well below 5 $\times$ 10^{18} ions m^{-2} sec^{-1}. Hertzian fracture tests were then carried out on both irradiated and unirradiated portions of the specimen surface in an evacuated chamber [6, 2].

In the Hertzian test, a spherical indenter is loaded onto the crystal surface at a constant rate until a "cone crack" propagates from a particularly favourable flaw just outside the contact

TABLE I Critical loads to cone fracture (N) at three temperatures and at "fast" (75 N sec^{-1}) and "slow" (2.5 N sec^{-1}) load rates

Temperature (°C)	Load rate	Unirradiated	Proton-irradiated	Deuteron-irradiated
25	fast	650 ± 38	712 ± 55	864 ± 82
225	fast	565 ± 32	663 ± 40	690 ± 59
	slow	558 ± 18	665 ± 55	714 ± 70
500	fast	287 ± 19	260 ± 29	271 ± 31
	slow	282 ± 23	186 ± 17	179 ± 21

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circle. Within unirradiated areas, the development of the cone was abrupt, at all load rates and temperatures. Within irradiated areas, a stage of slow subcritical growth in the form of a surface ring preceded the formation of the cone, this stage becoming visibly apparent at high temperatures and slow load rates. (A similar "embryo" stage is observed for tests in an external environment [2, 7].) Some further high-temperature tests were made with the indenter straddling the border between unirradiated and irradiated areas; in all such cases the cone was observed to initiate in the irradiated zone.

These observations are quantified by the critical load at cone formation (Table I). Measurements have been made at three temperatures, and at fast and slow load rates. The unirradiated areas show an intrinsic, time-independent decrease in Hertzian strength with rising temperature [2]. The irradiated areas show similar temperature trends, but with an additional strength reduction at slower load rate in the high-temperature tests; this time-dependent effect correlates directly with the initial subcritical growth stage. A secondary "radiation-toughening" effect is evident in the room-temperature data, but this appears to anneal out as the temperature is raised.

The above behaviour is consistent with a damage model in which the radiation treatment "stuffs" a layer below the crystal surface with active defect centres and attendant lattice disordering [8-10]. A state of surface compression is thereby induced in the crystal; hence the toughening effect noted in Table I. At elevated temperatures the defects become mobile: the surface compression thus relaxes, and the active centres interact in a rate-dependent manner with the crack tip to give subcritical extension.

It is the nature of the rate-dependent interaction which is of prime interest here. We are led to propose the following sequence of events.

(i) *Dissociation of hydrogen atoms from the irradiated lattice.* The beam implants the lattice with atomic hydrogen (or deuterium) with a concentration of H/SiO_2 up to 0.03. Since the data in Table I show negligible load-rate effects until high temperatures are attained, it seems probable that the decelerating beam particles interact with, and become bound to, the crystal lattice (very likely by means of the first stage of the bond-breaking reaction discussed below). On heating the crystal the hydrogen dissociates from the lattice and tends to liberate at a free surface. Evidence in favour of this step comes from observations of hydrogen evolution and bubble formation in "wet" ($H_2O/SiO_2 > 0.001$) fused silica heated above 350°C [11].

(ii) *Stress-enhanced diffusion of hydrogen atoms to crack tip.* With the crystal surface outside the indenter contact circle in a state of tension, the tips of the microcracks provide preferential "sinks" for the diffusing hydrogen. Of course, some of the dissociated hydrogen may combine into H_2 molecules before reaching the microcracks, but a reasonable amount might be expected to survive the diffusion stage in atomic form.

(iii) *Reaction of atomic hydrogen with stressed crack-tip bonds.* Upon reaching the crack tip the hydrogen reacts with the highly stressed siloxane bonds [11]:

$$\text{(-Si-O-Si-)} + \text{H} + \text{H} \rightarrow \text{(-Si-OH . -Si-)} + \text{H} \rightarrow \text{(-Si-OH . H-Si-)}\,.$$

In the first stage the siloxane bond is broken, forming a terminal hydroxyl group and a "dangling" silicon bond. In the second stage the dangling bond readily captures a second hydrogen, leaving a weakly-coupled (hydrogen) bond across the crack plane. The crack then advances at subcritical load. It is to be noted that reaction with atomic rather than molecular hydrogen is strongly favoured by energy considerations; in the latter case extra work would be required to dissociate the molecule to achieve the final reaction products. A manifestation of this effect has been clearly demonstrated in the hydrogen embrittlement of ferrous alloys [12]; a hot filament positioned at the mouth of a subcritical crack in a gaseous hydrogen environment causes molecular dissociation, and thereby enhances the crack velocity by several orders of magnitude.

We may conclude by suggesting that the subcritical growth effects observed here relate to the kinetics of the slowest of the three steps enumerated above. More detailed studies of fracture kinetics may accordingly be of value in providing information on the mechanics of radiation damage and crack propagation.

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