Observations of crack healing in sodium chloride single crystals at low temperatures

The measured fracture surface energy of NaCl single crystals can be greater than the specific free energy by an order of magnitude. As discussed by Wiederhorn *et al.* [1] this difference arises from irreversible processes, mainly the multiplication of dislocations on planes adjacent to the cleavage crack plane. The relaxation of this stored energy can occur spontaneously upon removal of the applied fracture load and the resulting relaxation process makes low temperature crack healing possible [2]. Additional relaxation and crack closure occurs on annealing when thermal energy is supplied to the crystal.

Bandyopadhyay *et al.* [3] recognized crack pinching as an important healing process in uranium dioxide and Morgan [4] discussed the role of enhanced diffusion aided by dislocation motion in sintering studies of power compacts. High temperature crack healing mechanisms have been studied in ionic solids by several workers [3, 5, 6] based mostly on morphology changes at the crack tip. If after fracture an ionic solid was in a stress-free state, the role of crack-tip retreat as a healing mechanism, i.e. by continuous surface contact, would be augmented and crack surface pinch-off, i.e. by discontinuous surface contact, would be less pronounced. As discussed below, however, cracks in NaCl single crystals are usually associated with a residual stress field and crack healing takes place discontinuously by crack pinch-off.

Scanning electron microscopy (SEM), which is a powerful tool for characterizing the surface chemistry and structure of solids, has been employed in morphological observations of ⟨1 1 0⟩-type cracks in NaCl single crystals. Cracks were introduced on the surface of the specimen by impact with a sharp needle point. The cracks that developed were on {1 1 0} slip planes in four ⟨1 1 0⟩ directions in a cross-shaped pattern. Typical crack lengths measured from the impact point were about 250 μm, and the crack width near the tip ranged from 0.2 to 0.5 μm. In some instances, however, the crack width was less than 0.2 μm at the tip and the two surfaces spontaneously became pinched-off or came into smooth contact.

Observations of crack pinch-off were more common than crack tip retreat due to the non-uniform release of stored energy. Once crack pinching was initiated, crack healing occurred by a diffusion process during subsequent high temperature annealing. The healing of the pinched cracks progressed so rapidly during high temperature annealing that healing by uniform crack tip retreat could be neglected.

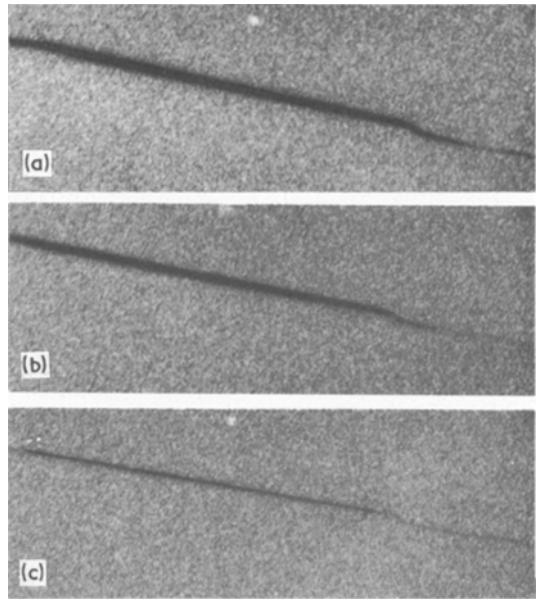

Figure 1 Hot stage scanning electron micrographs showing a decrease in crack width with increasing annealing temperature. Crack has propagated from left to right. Photographs were taken at (a) room temperature, (b) 200° C, and (c) 300° C, × 4400.

These experiments showed that at low temperatures (prior to diffusion becoming an important crack-healing process), as structural relaxation takes place the width of the crack is reduced. An observation of crack width changes in NaCl single crystals, shown by means of hot stage SEM, is illustrated in Fig. 1. The original gap width before annealing was 0.50 μm. After heating at a rate of 200° C h^{-1} in the hot stage, the measured crack width at 200° C had decreased to 0.37 μm. The crack width decreased further between 200 and 300° C, and at 300° C was 0.20 μm, i.e. about 40% of the original width.

The surface etching patterns* of samples annealed at low temperatures were found to be useful in showing the progress of structural relax-

* The etchant was CH_3OH with 2 mg cm^{-3} of $HgCl_2$.

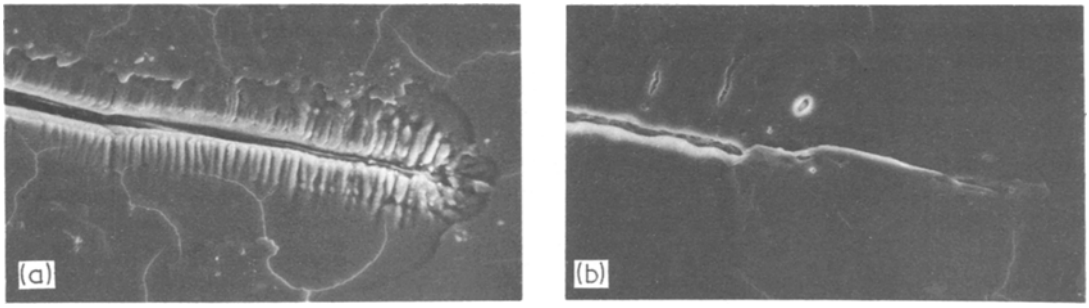

Figure 2 Scanning electron micrographs of etched surfaces of NaCl single crystals showing the effect of annealing on the deformed region near the crack. (a) An etch pattern showing the severity of the damage along the crack path (as cracked), (b) an etch pattern from a specimen annealed for 5 h at 200° C, × 230.

ation during heat-treatment. Fig. 2 shows the severity of structural damage near the crack plane at room temperature, and the progressive annihilation of dislocations and the resulting structural relaxation after annealing for 5 h at 200° C. The structural damage adjacent to the plane of the cleavage crack is greater near the crack tip. Since the severity of the structural damage is proportional to the amount of stored energy, the probability of crack pinching is highest near the tip of the crack. As the etch pattern in Fig. 2 demonstrates, the reduction in structural damage through a dislocation annihilation process is the main cause for the decrease in crack width in NaCl at 200° C. This evidence indicates that, although the exact healing mechanism depends on the annealing temperature, low temperature crack healing in NaCl single crystals is a continuous process aided by the relaxation of local strain in the deformed microvolume adjacent to the crack plane. At temperatures above 500° C diffusional processes play the dominant role in crack healing.

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Deterioration in air of silicon arsenide and silicon phosphide

Preparative and structural studies have for several years been conducted at this Institute on binary compounds of elements of the IV and V groups of the Periodic Table [1]. In this connection it has been observed that deterioration of SiP and SiAs crystals, when exposed to laboratory air for some time, takes place to such an extent to render X-ray investigations or studies of their physical properties difficult or impossible. The considerable interest in these materials shown by many research workers seemed to warrant an analysis of the character of the deterioration process.

The samples of SiP and SiAs used in this investigation were prepared from silicon, red phosphorus and arsenic in sealed evacuated silica tubes by direct combination of the elements or by transport reaction techniques. The products were characterized by their X-ray powder patterns, which have been reported previously [1]. It was observed that specimens which had been exposed to the laboratory atmosphere for about 1 year showed substantial increases in weight. A fresh