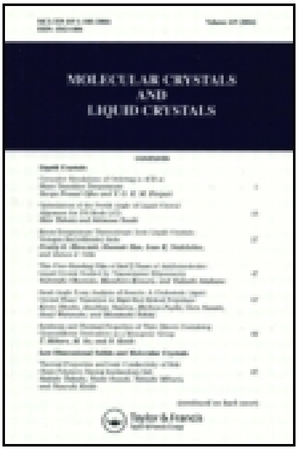

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst. 1994, Vol. 240, pp. 73–80
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Printed in the United States of America

STUDIES OF DEFECT BEHAVIOR IN LARGE-GRAIN, POLYCRYSTALLINE ICE USING SYNCHROTRON X-RAY TOPOGRAPHY

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Abstract Synchrotron White Beam X-ray Topography (SWBXT) has been used to conduct *in situ*, low temperature studies of the behavior of defects introduced into large-grain, polycrystalline ice of very low "as-grown" defect density. The generation of faulted and unfaulted interstitial dislocation loops as a function of imposed temperature changes was observed. Variations in the distribution of these loops in the vicinity of grain boundaries are discussed in the context of diffusion mobilities on the basal plane and the relative orientation between the basal plane and the grain boundary plane. Dislocation generation mechanisms under applied compressive stresses were also investigated *in situ* using a specially-designed compression stage. This has led to the novel observation of dislocation nucleation at stress concentrations on grain boundaries. The utility of SWBXT in dynamic studies of this general nature is demonstrated.

INTRODUCTION

Over the past twenty five years the determination of factors controlling the mechanical properties of ice has received considerable attention (for review see reference 1 and references therein). On a fundamental level, an understanding of dislocation generation mechanisms and dislocation dynamics both in the absence and presence of applied stresses are central to an understanding of mechanical properties. The use of etch pit analysis to reveal dislocation behavior suffers from severe limitations in that it can only ever reveal the surface intersections of dislocations, which may not be representative of dislocation behavior in the bulk. Similarly, transmission electron microscopy is limited by the necessity of utilizing thin samples which cannot represent the microstructure of bulk ice (see later). X-ray topography, on the other hand, has great potential in this area. Topography carried out using characteristic $K_{\alpha 1}$ radiation from conventional sources has been shown to be particularly useful for the study of dislocations in bulk single crystal ice.[1] However, the extension of the technique to the study of dislocation dynamics is limited by the fact that the time scale over which recovery (thermally-activated dislocation motion after the stress is removed) occurs has been shown to be short compared to the exposure times required in characteristic radiation topography.[2] This leads to blurred dislocation images which can be difficult to interpret, and can lead to erroneous measurement of dislocation velocities. Such difficulties are compounded in polycrystalline ice by the fact that the monochromatic nature of the radiation typically allows only a single grain to fulfil the Bragg condition for a given diffraction geometry. This makes it difficult to assess the role of grain boundaries in the deformation properties of ice in its natural, polycrystalline form.

The capability of X-ray topography for these kinds of studies has been greatly enhanced through the employment of area-filling, white X-ray beams from synchrotron radiation sources. The high brightness of such sources eliminates problems deriving from long exposure times, and the broad spectral range of the area-filling beam means that several grains in large grain polycrystals can be imaged simultaneously in a single, few second exposure. Short exposure times have been exploited by Whitworth and co-workers in studies of dislocation dynamics in single crystal ice.[2–6] In this paper, the use of Synchrotron White Beam X-ray Topography (SWBXT) for the study of the role of grain boundaries in both the generation of prismatic dislocation loops (along with their associated stacking faults) created by interstitial condensation in the absence of applied stress, and of dislocation generation under the action of an applied compressive stress in large-grain, polycrystalline ice is outlined.

EXPERIMENTAL

Columnar-grained ice with a very low initial dislocation density was grown using a seedless Czochralski method. The final specimens, typically measuring 25 x 15 x 2 mm^3, were transported to the Stony Brook Synchrotron Topography Station, beamline X-19C, at the National Synchrotron Light Source, Brookhaven National Laboratory, where the specimens were transferred to a specially-built cryostat incorporating a compression jig.[7] Topographs were obtained by allowing the highly collimated, area-filling (in this case stopped down to 6mm x 15mm) beam of synchrotron white X-rays to fall onto the large-grained polycrystalline ice samples while recording the area-filling diffracted beams on the detector. The detector, which consisted of a cassette containing 8"×10" sheets of Kodak SR5 X-ray film, was typically placed normal to the incident beam direction at a distance of 10cm from the crystal. A single few second exposure usually comprised several useful diffraction spots. *In situ* straining experiments were performed at -12°C, with compressive stresses, ranging from 0.4 to 2MPa, being sequentially applied for periods of about 5 minutes between exposures.

RESULTS AND DISCUSSION

Stacking Fault Depleted Zone near Grain Boundaries

It is well-known that stacking faults exist in freshly-grown ice single crystals.[8] Stacking faults in ice can be produced through condensation of interstitials, generated by cooling.[9] Although such faults produced by slow and moderate cooling have been studied extensively, no detailed studies of stacking faults formed by rapid cooling have been reported, presumably because of the high speed at which the microstructure changes. In particular, little effort has been made to study the stacking fault configuration near a large angle grain boundary. The short exposure times associated with the synchrotron radiation source enable observation of rapid changes in microstructure. Synchrotron topographic studies have shown that for polycrystalline ice specimens which had undergone thermal shock, regions located centrally in grains contained high densities of stacking faults, while regions located in the vicinity of both grain boundaries and free surfaces were usually fault-free.[10] These depleted zones can be understood by considering grain boundaries and free surfaces as sinks of water molecule interstitials. The existence of the depleted zone near the free surface implies that an ice sample as thin as a transmission electron microscopy sample cannot represent the microstructure of bulk ice.

In order to study the effect of a grain boundary on stacking fault configurations, a bicrystal sample was made, which had the large-angle grain boundary parallel to the largest surfaces. Each grain had a thickness of 1mm. The basal plane for grain 1 made an angle of about 30° with the boundary, while that for grain 2 was nearly perpendicular to the grain boundary. The fact that most dislocations in ice lie on the basal plane, means that one can discern the grain boundary orientation from the observed dislocation configurations, with long dislocation segments being visible in grain 1 and short dislocation segments in grain 2 (see Figure 1). The sample was initially cooled from -20°C to -60°C over a period of about thirty minutes. The developing microstructure was followed over thirteen steps as the crystal was slowly warmed back up to -20°C over a period of two hours. In grain 1, the rapid cooling produced individual unfaulted dislocation loops, individual faulted dislocation loops, and concentric dislocation loops connected by stacking faults. Examples of each of these dislocation loop configurations can be found on figure 1(a), which was recorded from grain 1 following the rapid cooling.

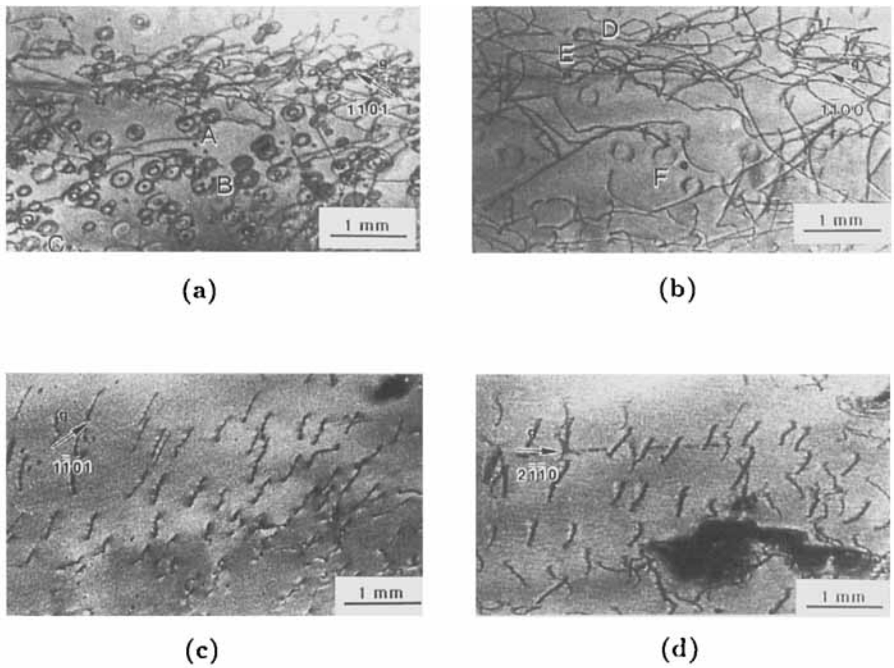

FIGURE 1. Details from X-ray topographs of ice. (a) $1\bar{1}01$ image of grain 1, recorded after rapid cooling (λ=0.84Å); (b) $1\bar{1}00$ image recorded after warming up to -20°C (λ=0.96Å); (c) $1\bar{1}01$ image recorded from grain 2 after rapid cooling (λ=0.65Å); (d) $2\bar{1}\bar{1}0$ image recorded from grain 2 after warming up to -20°C (λ=0.72Å).

All of these configurations are produced via a process of interstitial segregation on the basal plane that is similar to that proposed for hexagonal metals.[8,11] Initially a single layer disk of interstitials is formed between adjacent basal planes, i.e. a faulted dislocation loop with **b**=**R**=1/2[0001] (where **b** is the Burgers vector, and **R** is the fault vector). Then, this can be converted to a double-layer unfaulted loop, with **b**=[0001], via a mechanism involving the single layer loop being swept by partial dislocations.[8] As pointed out by Amelinckx,[11] it is energetically favored for the [0001] unfaulted dislocation loop to dissociate into two partial dislocations, on adjacent basal planes, which can climb conservatively to yield the kind of concentric dislocations loops connected by stacking faults observed in figure 1(a), recorded from grain 1. After annealing back up to -20°C, some of the concentric loops disappeared completely, such as those at **A**, **B** and **C** in figure 1(a), while others were transformed into the perfect prismatic dislocation loops observed at **D**, **E** and **F** in fig. 1(b), which was taken from the same area as fig. 1(a). In contrast, the same thermal shock did not produce any stacking faults in grain 2, as shown in fig. 1(c), which was taken at the same time as fig. 1(a), nor were any observed in the other images recorded simultaneously with fig. 1(c).

This suggests that the size of the depleted zone near a grain boundary is a function of the angle between the basal plane and the boundary, and implies that diffusion in ice occurs mainly on the basal plane.[10]. These observations are consistent with the measurement of the anisotropy of water molecule diffusion coefficient with crystallographic orientation in single crystal ice [12a,13,14] The diffusion coefficient was found to be larger perpendicular to the *c*-axis than parallel to the *c*-axis. Reliable relative magnitudes are not available because of the existence of surface layers and unknown dislocation structures (which can act as diffusion channels) in previous work.

Dislocation Sources at Grain Boundaries

In situ straining experiments were performed to examine the role of grain boundaries during plastic deformation.[15,16] Figure 2 shows enlarged portions of four topographs ($\mathbf{g}=10\bar{1}0$, $\lambda=1.07$Å), taken between intermittent loadings, in which three dislocation sources were observed in the same area of a grain. The loading direction, shown as **F** in Figure 2, makes an angle of about 80° with the grain boundary, while the basal planes are almost parallel to the sample surface. The shear stresses exerted on the grain boundary are of the order of 0.1MPa. After pre-stressing the sample, a build-up of stress becomes apparent on the boundary, as indicated by **X** on figure 2(a). The extent of the strained area is an indication of the amount of strain energy stored. Note that there were only a few dislocations in the grain prior to deformation. Upon further loading, semi-hexagonal dislocations with $[2\bar{1}\bar{1}0]$ Burgers vectors, lying on the basal plane, were pushed out of the stress concentration center on the grain boundary, as shown in figure 2(b). In figure 2(c), the main dislocation segment visible in figure 2(b) has glided about 0.8mm on the basal plane into the interior of the grain, while the dislocation generation process continues. The further the dislocations move from the source, the larger are their spacings. At the same time, several stress fields are generated, covering a large portion of the grain boundary.

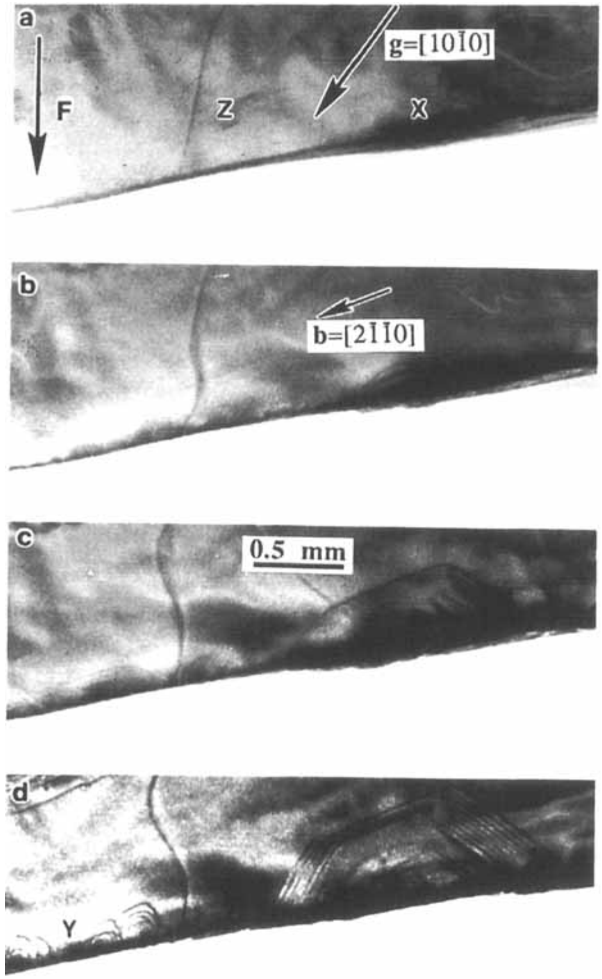

FIGURE 2. Four topographs (**g**=10$\bar{1}$0, λ=1.07Å) showing the operation of a dislocation source at a grain boundary at -12°C: (a) after pre-stressing; (b) following 11 minutes under a vertical compressive stress in the direction **F** of 0.5MPa; (c) after a further 10 minutes under 2MPa; and (d) after a further 15 minutes under 2MPa.

Near the dislocation source, individual dislocations can not be discerned because the spacing between the adjacent dislocations is below the resolution limit of X-ray topography (about 10μm). These dislocations glide on basal planes continuously as the compressive strain increases. That the strain field is relaxed by dislocation generation is indicated by the smaller scale of the stress field near the source in figure 2(d) compared with that in figure 2(c). The spacing between the first and the second dislocations, shown in figure 2(d) is 28μm, while the source is still centrally located. The closer spacing of the screw than the 60° segments is fully in accord with dislocation velocity measurements.[5] Further stressing activates another two similar sources, marked **Y** in figure 2(d).

On a microscopic scale a possible explanation for the dislocation generation mechanism at a large-angle grain boundary is as follows. Most grain boundaries in columnar ice are non-planar. A non-planar grain boundary is composed of low-energy planes and steps formed by intrinsic grain boundary dislocations. When a compressive stress is applied to the ice sample, grain boundary sliding occurs, driven by the shear stress on the grain boundary. Stress fields are then generated and extend from the intersections of the grain boundary facets. In this case, the accumulation of extrinsic grain boundary dislocations gliding to the intersections may also contribute to the large stress concentration. Once the stored elastic energy reaches a critical value, lattice dislocations are generated, and then glide away from the facet intersection to release the stored energy.

Figure 2 also reveals motion of a pre-existing individual dislocation marked **Z** in (a). This dislocation appears as a nearly straight line in figure 2(a), a characteristic configuration of lattice dislocations in a well-annealed ice sample. It gradually glides on the basal plane under stress to approximately take up screw and 60° orientations. The end of this dislocation which terminates at the boundary does not move detectably during the operation. The motion of dislocation **Z** takes place simultaneously with the operation of the dislocation source, but with a much lower velocity. The slow glide of this dislocation is driven by a small local resolved-shear stress on the basal plane, resulting from the externally applied stress. However the internal stress near the grain boundary (i.e., the stress concentration around the facet intersection) is much higher than the external stress.

Based on our observations, dislocation generation and multiplication are expected to occur when the grain boundary is under a shear stress and a resolved stress on the basal plane is provided. Since these constitute the general geometrical conditions under which polycrystalline ice is deformed, and since basal glide has been proven to be the main plastic deformation mechanism,[12b] this dislocation generation mechanism should be dominant in the early stages of plastic deformation of polycrystalline ice.

CONCLUSIONS

(1) During thermal shock, faulted and unfaulted dislocation loops form in ice except

at depleted zones near grain boundaries and free surfaces. The size of the depleted zone near a grain boundary in a particular grain is a function of the angle between the basal plane and the boundary, being largest when this angle is close to 90°.
(2) Grain boundaries can generate lattice dislocations in the early stages of plastic deformation.
(3) Lattice dislocations once generated by stress concentrations at grain boundaries glide on the basal plane as semi-hexagonal loops.

ACKNOWLEDGEMENTS

Research supported by the U.S. Army Research Office through grants numbers DAAL03-92-G-0319 and DAAH04-93-G-006 and in part by the donors of the Petroleum Research Fund which is administered by the American Chemical Society (M.D. and I.B.). Professor E.M. Schulson is acknowledged for the use of the Ice Research Laboratory. Topography carried out at the Stony Brook Synchrotron Topography Station, Beamline X-19C at the NSLS, which is supported by DOE.

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