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Plastic deformation in diacetylene (PTS) monomer single crystals

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The slip systems of diacetylene (PTS) monomer crystals which were deformed with a shear deformation and a micro indentation were determined. The (1 0 0) [0 0 1], (1 0 0) [0 1 0] and (1 0 2) [0 1 0] slip systems eventually were identified as the main slip systems from the stress–strain curves, slip lines and etch-pit arrangements.

1. Introduction

The study of crystal defects in diacetylene (PTS) polymer and monomer crystals which belong to crystal structure with $P2_1/C$ space group (polymer $a = 1.4493$ nm, $b = 0.4910$ nm, $c = 1.4936$ nm and $\beta = 118.14°$ at 300 K [1] and monomer $a = 1.4668$ nm, $b = 0.5174$ nm, $c = 1.4938$ nm and $\beta = 118.85°$ at 300 K [2]), has progressed further. The dislocation images in PTS polymer single crystals were observed by means of transmission electron microscopy [3–6] and also X-ray topography [7–10]. Recently, the images of an isolated dislocation in PTS monomer single crystals using X-ray topography were observed and its Burgers vector was determined [11]. The etch-pit measurement indicated that the (1 0 2) [0 1 0] slip system was found to be present in both monomer and polymer crystals but the (0 1 0) [0 0 1] slip system was observed only in monomer crystals [12]. In addition, research of the macroscopic deformation in polymer crystals shows that the deformation was mainly due to twinning deformation [13–15]. However, the deformation behaviour of monomer crystals has not yet been observed. Therefore, an investigation of the plastic deformation in the monomer crystals was undertaken and the relationship between the macroscopic slip systems and dislocation behaviour is discussed here.

2. Experimental procedure

Single crystals of PTS monomer were grown from slow, controlled saturated acetone solutions of purified monomers in the dark. The resulting monomer crystals were pale pink in colour and exhibited a morphology as shown schematically in Fig. 1. The deformation of monomer crystals was carried out by shear testing in an Instron-type machine (for further details see [16]). The specimens were deformed at a crosshead speed of 0.005 mm min^{-1} at 295 K. The (1 0 0) and (1 0 2) planes were selected to be shear planes and shear stresses were applied along predetermined crystallographic directions. The indentation was made using a micro-hardness machine at 295 K. To estimate the dislocation distribution, the etch-pits patterns of PTS crystals on the (1 0 0) and (1 0 2) planes were performed using methanol.

3. Results and discussion

The main slip systems in PTS monomer single crystals have not yet been decided using deformation tests. Two cleavage planes, both the (1 0 0) and (1 0 2) planes, were chosen as slip planes. The [0 1 0], [0 1 1] and [0 0 1] directions on (1 0 0) and also the [0 1 0] and [2 0 1] directions on (1 0 2) plane were selected as the shear directions.

Typical stress–strain curves are shown in Fig. 2, when the shear axes are parallel to the [0 1 0], [0 1 1] and [0 0 1] on the (1 0 0) plane. The small plastic deformation of both slip systems occurred before fracture. The yield stresses were about 300 kPa for (1 0 0) [0 1 0] and about 550 kPa for (1 0 0) [0 0 1]. In addition to these directions, when the [0 1 1] direction is taken to be the shear axis, almost all the specimens were fractured before plastic deformation. The slip lines on

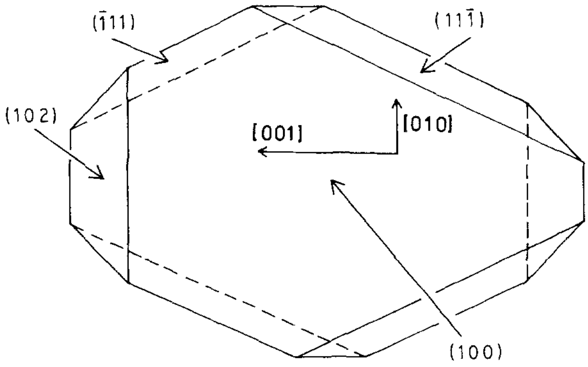

Figure 1 Schematic drawing of specimens and crystallographic habit planes of PTS monomer crystal.

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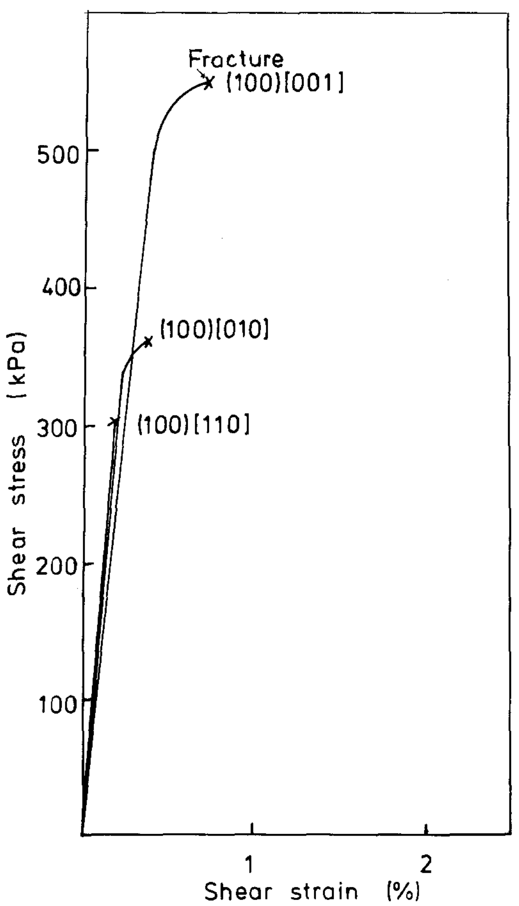

Figure 2 Typical stress–strain curves obtained on shearing with the (1 0 0) slip plane parallel to the shear plane.

the specimen surface can be locally observed on the {1 1 1} plane. This shows that the plastic deformation took place locally.

In addition, either the [0 1 0] or [2 0 1] directions were chosen as shear directions on the (1 0 2) plane. The stress–strain curves represent a much larger plastic deformation than that on the (1 0 0) plane, as shown in Fig. 3. On the other hand, when the shear axis is parallel to the [2 0 1] direction, the fracture occurred before plastic deformation. The yield stress was about 300 kPa for the (1 0 2) [0 1 0] slip system. To confirm these results, an indentation test was carried out with a micro-Vickers and micro-Knoop indentation machine. The indentations were made on the (1 0 0) plane as shown in Fig. 4a. After the indentation, no slip lines were observed on the (1 0 0) plane. However, the dislocation etch-pits emerged after etching (Fig. 4a). These etch-pits were distributed along the trace of (1 0 2) on the (1 0 0) plane and developed to be parallel to the [0 1 0] direction. The fact that the slip lines were not observed on the (1 0 0) surface indicates that the Burgers vector of these dislocations would be parallel to the [0 1 0] direction. Therefore, it seems that the emerged dislocations near the (1 0 0) surface have an edge character, as schematically shown in Fig. 4b.

According to X-ray topography [11], three kinds of dislocation structure are observed; one is the dislocation with Burgers vector [0 0 1] on the (1 0 0) plane. The second is the dislocation with Burgers vector [2 1 1], but the slip plane cannot be determined. The third is the bundles of pure screw dislocations with Burgers vector [0 1 0]. Comparing this with our results, the (1 0 0) [0 1 0] slip systems coincide with the X-ray experiment. In addition, it seems that the bundles of [0 1 0] screw dislocations correspond to either

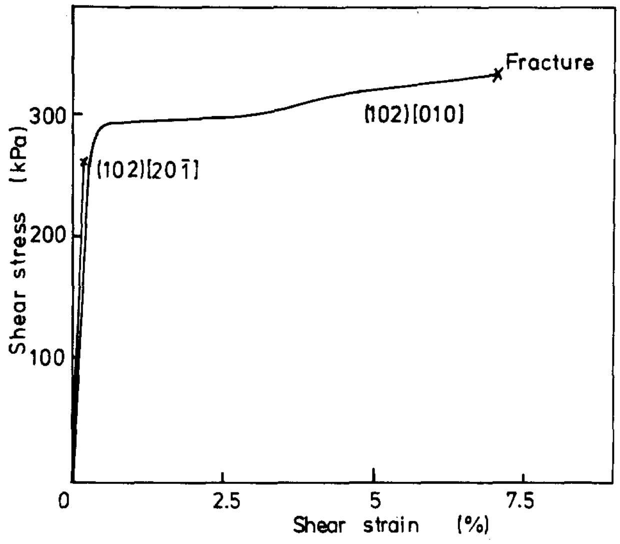

Figure 3 Typical stress–strain curves obtained by shearing with the (1 0 2) slip plane parallel to the shear plane.

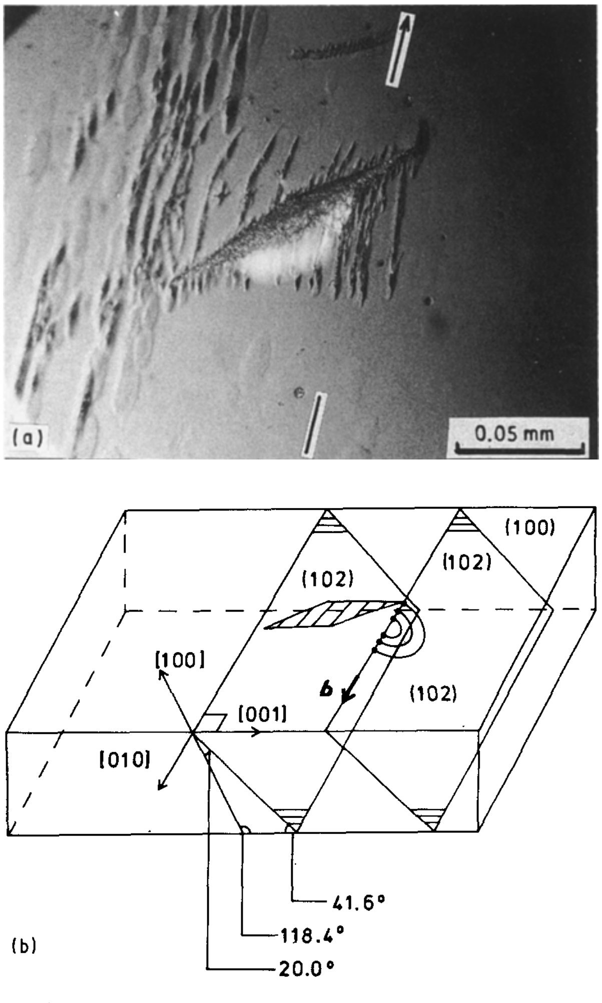

Figure 4 (a) Etch-pit pattern around an indentation on the (1 0 0) surface of PTS crystals at 295 K with a 20 g load using a Knoop indentation. The arrow shows the direction of the trace of the (1 0 2) plane. (b) Schematic illustration of a dislocation configuration and Knoop indentation pattern on the (1 0 0) surface.

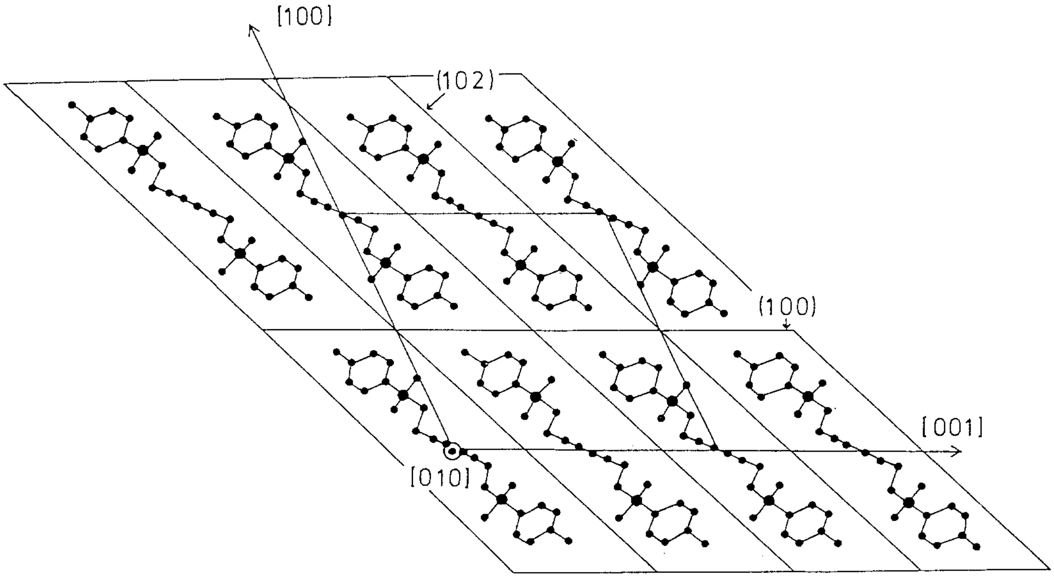

Figure 5 Molecular projection of the PTS monomer structure on the (0 1 0) plane. It should be noticed that both the (1 0 0) and (1 0 2) planes can act as slip planes from the molecular arrangement.

the (1 0 0) [0 1 0] or (1 0 2) [0 1 0] slip systems. The dislocation theory predicts that the shortest of possible perfect dislocation Burgers vectors should correspond to the slip direction based on Frank's energy criterion and the Peierls energy criterion, while the slip plane should be either the plane with the lowest Peierls energy or stacking fault plane [17]. The (1 0 0) [0 1 0] slip system clearly corresponds to these general rules. On the other hand, the (1 0 0) [0 0 1] slip system does not coincide with these criteria because of the larger unit vector in the [0 0 1] direction ($c = 1.4668$ nm). Therefore, the [0 0 1] dislocation would be dissociated by small partial dislocations with low-energy stacking faults. Both the (0 1 0) [0 0 1] and (1 1 0) [0 0 1] slip systems have been proposed as possible slip systems [12] but we cannot observe any these kinds of slip system in the shearing deformation. Thus, it seems that these dislocations would not be introduced due by the plastic deformation but during crystal growth. Comparing the spacing of the lattice planes of the (1 0 0) and (1 0 2) planes, the former is 1.494 nm and the latter is 0.402 nm. The simple Peierls's energy of this (1 0 2) [0 1 0] slip system will be very high because of the low spacing of the lattice planes. Therefore, although the (1 0 2) plane does not satisfy Peierls energy criterion of a slip plane, it seems that the crystal structure and the arrangement of molecules of PTS crystals clearly show that not only the (1 0 0) plane but also the (1 0 2) plane can act as a slip plane in Fig. 5. Thus, it should be noticed that slip systems in organic molecular crystals are determined due to the molecular arrangement of the crystals. It was not clear whether the degree of polymerization has any affect on the magnitude of the yield stress and the identification of slip systems.

4. Conclusion

A stress–strain curve on PTS monomer crystals was observed at 295 K by shear testing. The observation of slip line and etch-pit arrangements was carried out after deformation and indentation. The (1 0 0) [0 0 1], (1 0 0) [0 1 0] and (1 0 2) [0 1 0] slip systems were determined as the main slip systems.

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