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In-situ studies of the deformation and dynamic recrystallization of rhombohedral camphor

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Polycrystalline specimens of rhombohedral camphor have been deformed in compression in the temperature range 283 to 343 K and the deformation processes and the development of microstructure followed by transmission polarized light microscopy. Processes of slip, kinking and twinning have been observed, and in particular, the mechanisms of dynamic recrystallization and its effect on the development of zones of heterogeneous deformation have been investigated. The points of similarity between the behaviour of camphor and metals and minerals of low symmetry are discussed.

1. Introduction

The deformation processes which occur when crystalline materials are deformed to large strains at high temperatures are of importance in both the industrial hot-working of materials, and in the natural deformation of minerals as studied by the structural geologist. Although differing greatly in terms of the rates of strain and in the types of material involved, there is little doubt that many of the microstructural deformation processes which occur are common to both [1, 2].

These processes, the relationship between them, and the way in which inhomogeneous microstructures develop at high strains are not well understood. Work on minerals is hampered by the difficulties of laboratory deformation experiments, and the interpretation of the behaviour of metals, so far confined mainly to cubic materials, is restricted by the difficulties of preserving the unstable microstructures of rapidly hot-worked metals. The present work was undertaken to try and obtain some insight into the processes of high strain deformation and dynamic recrystallization by using polycrystalline specimens of a transparent organic compound as an analogue for either minerals or metals of low symmetry.

Similar materials have been used previously as analogues of metals in studies of solidification [3] and grain growth [4], and deformation cells viewed in transmitted light have been used to study the deformation of ice [5] and aggregates of granular minerals [6].

2. Materials

Materials known as "plastic organic crystals" have been studied for some time, and a historical review has been presented by Timmermans [7]. Many of these molecular crystals have, immediately below their melting point, a cubic structure in which the molecules are free to rotate (rotator phase). In this condition the materials are soft and ductile, and in a series of experiments, Hawthorne and Sherwood [8–10] have shown that the mechanical behaviour is controlled by similar deformation processes to those in metals. Although the transformations to phases of lower symmetry at lower temperatures are well documented, little attention has been paid to the mechanical behaviour of these phases.

Camphor ($C_{10}H_{16}O$) occurs in several forms, the actual transformation temperatures being dependent both on the purity of the material, and the proportions of D and L isomers present [11].

The phase transformations are as follows [11–13]:

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$$\text{liquid} \overset{452\,K}{\rightleftarrows} \text{fcc} \overset{370\,K}{\rightleftarrows} \text{rhombohedral I}$$

$$\overset{243\,K}{\rightleftarrows} \text{rhombohedral II (more birefringent).}$$

The details of the rhombohedral phases have not been reported. Rhombohedral I camphor was chosen for the present investigation because, being birefringent, changes in the microstructure during deformation and recrystallization could conveniently be followed in the polarizing optical microscope over a range of easily obtainable temperatures.

3. Experimental methods

3.1. Apparatus

Deformation experiments were carried out in the simple stage shown schematically in Fig. 1. The specimen was contained in a glass cell, 0.15 mm thick, and was deformed by driving a 0.15 mm thick piston into the cell at a constant rate. The temperature, monitored in the cell, could be varied by resistance heating, and was controlled to ± 2° C. Tests were carried out between 283 and 343 K. The deforming specimen was viewed in transmitted polarized light. Use of a quartz sensitive tint plate enabled orientation information to be obtained from the colours of the grains (see, for example, [14]). The dynamic events were recorded either on 35 mm film, or by using a time lapse camera, on 16 mm colour cine film [15].

3.2. Specimen preparation

Camphor of commercial purity was cold-pressed into sheets ~ 0.15 mm thick, and specimens ~ 7 mm x 7 mm were placed in the deformation cell. Preliminary experiments showed that, without affecting the nature of the deformation processes, silicon oil minimized friction between specimen and glass during the test, resulting in more homogeneous deformation of the specimen. The camphor was heated into the fcc phase field and slowly cooled. This produced grains of the rhombohedral phase which were generally elongated (Fig. 7a) and up to 1 mm long. At room temperature the grains tended to become equi-axed, but the process was slow, some elongation being apparent even after 500 h.

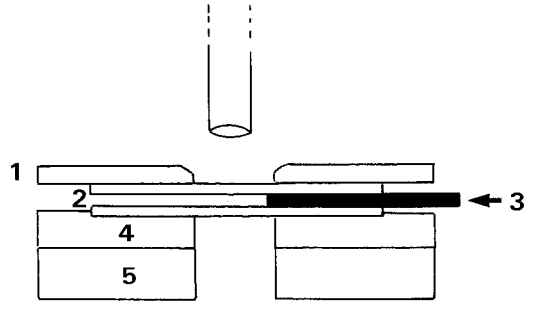


Figure 1 The deformation apparatus. 1, cover plate; 2, cell; 3, piston; 4, heated block; 5, insulation.

3.3. Reproducibility and validity of the tests

The reproducibility of the experiments was good, and, with experience, the various deformation processes in a particular specimen could generally be predicted. The deformation behaviour of a thin constrained specimen as used in the present work will clearly differ from that of a bulk specimen, and thus caution must be exercised in interpreting the results. Nevertheless, the behaviour is more likely to represent that of a bulk polycrystalline specimen, particularly at high strains, than *in situ* observations of free surfaces of either bulk or thin specimens. In order to investigate the effect of specimen thickness, some 0.5 mm thick samples were tested. These showed similar deformation processes to those observed in the thin specimens, and by focusing the microscope at points through the specimen it could be seen, for example, that dynamic recrystallization, producing grains of $\sim \frac{1}{10}$ specimen thickness, occurred in the middle of the specimen, and was not confined to the surface regions. However, the considerable overlap of information in such thick specimens was a bar to their wider use for tests.

Camphor from two sources was used, Hopkin and Williams, and BDH. Although the deformation mechanisms were similar in both, the transition, rhombohedral to cubic occurred at ~ 358 K for the H and W material, and ~ 373 K for the BDH. This could be due to either impurity effects, or to differences in the proportion of D and L isomers present.

4. Results and discussion

Some 40 tests were carried out as described above, generally at a strain rate of $\sim 10^{-4}\,\text{sec}^{-1}$. The mechanical behaviour was dependent on the temperature, and there was a marked change in the mode of dynamic recrystallization at ~ 310 K (H and W) or ~ 320 K (BDH). The results for the high- and low-temperature regimes will be presented separately.

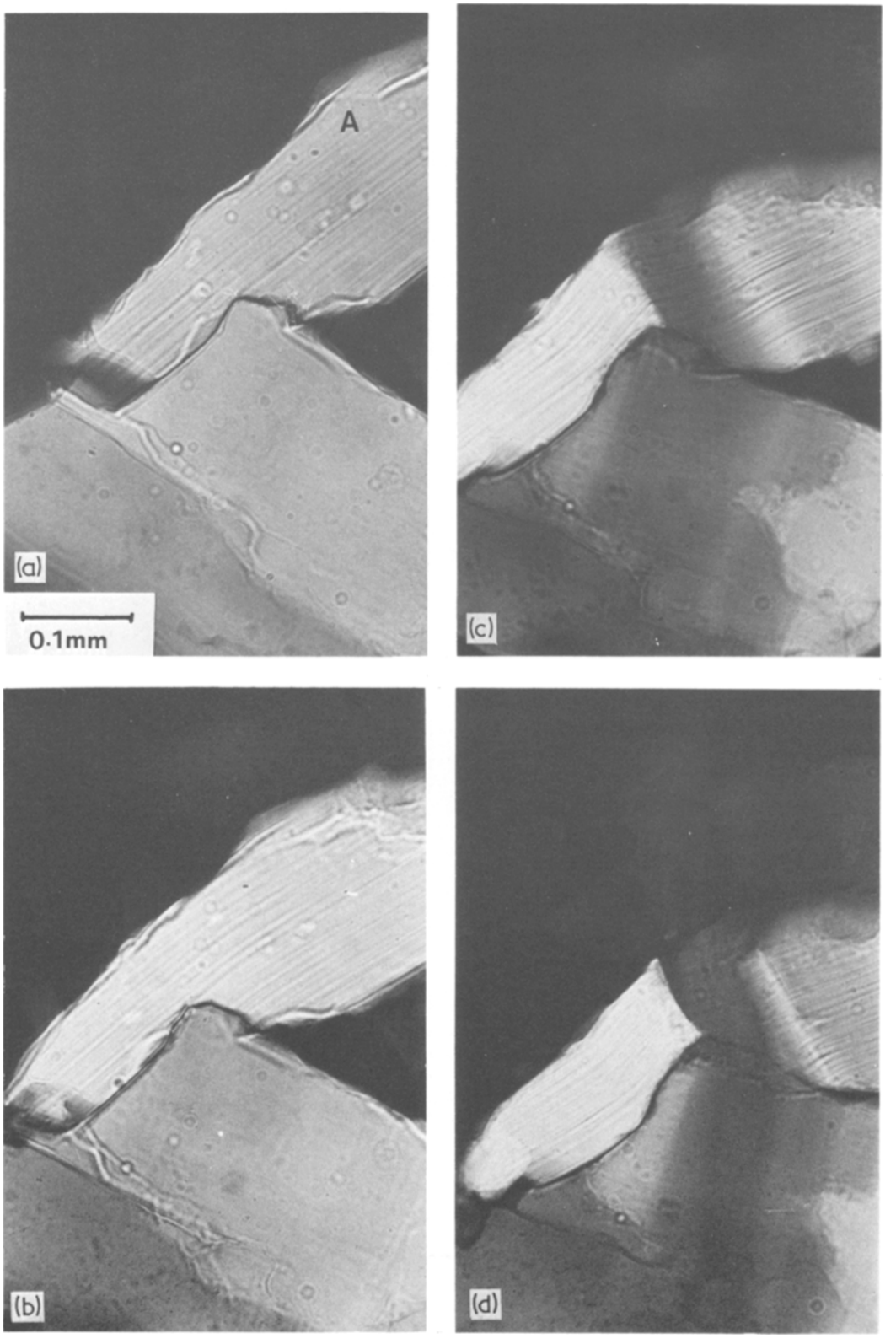


Figure 2 Deformation sequence at 320 K, showing slip, lattice bending, kinking and dynamic recrystallization in the kink bands (compression axis vertical).

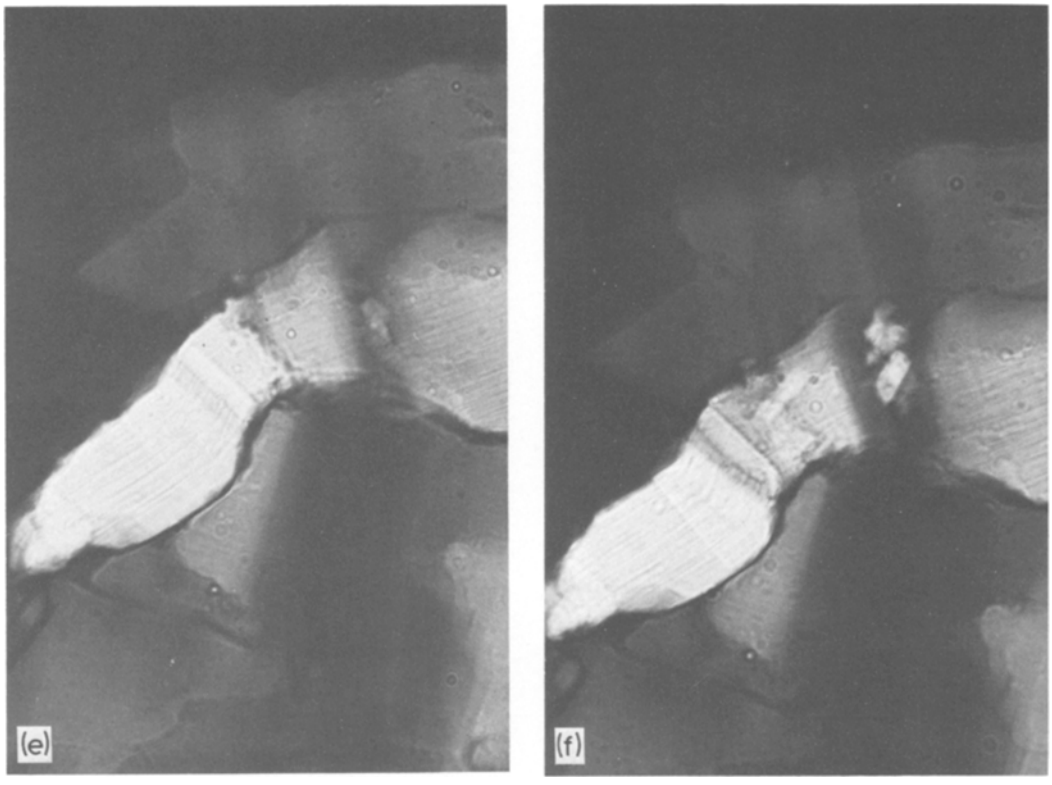


Figure 2 continued.

4.1. Low-temperature tests

4.1.1. Slip

Slip was found to occur easily on only one plane of the camphor grains, and this was generally the first indication of plastic deformation (Fig. 2a). Universal stage microscopy showed this to be the basal plane (0 0 0 1). Although the full crystal structure of camphor has yet to be determined, it is probable that the benzene rings are aligned parallel to this plane, thus making it a preferred slip plane. Support for this model was obtained by optical microscopy which showed the camphor to be uni-axial negative. Other materials of similar crystal structure which are optically negative also have their planar molecules aligned in this way ([14] p. 117).

4.1.2. Kinking

In grains oriented with the (0 0 0 1) plane perpendicular to the specimen plane, e.g. grain A in Fig. 2, if the local deformation was such as to cause bending of the slip planes (Fig. 2b), then slip was frequently followed by the development of kink bands as shown in Fig. 2. The process is gradual, lattice bending being followed by the formation of a sharp kink band (Fig. 2c) starting at one edge of the grain and propagating in a direction approximately normal to the slip plane. Migration of the kink bands was seen to occur (Fig. 2d) and continued deformation resulted in the formation of further kink bands (Fig. 2d to f) to accommodate the strain. Although kinking was more likely to occur in those grains whose slip planes were at small angles to the compression axis, because of the locally inhomogeneous strain as illustrated by Fig. 2, kinking occurred in grains of many orientations.

The above observations are similar to the results obtained for suitably oriented crystals of hexagonal metals [16] and are consistent with the proposed dislocation mechanism of kink formation, which is essentially one of glide polygonization.

4.1.3. Deformation twinning

Deformation twinning was frequently observed, particularly at high strain rates. It differed from kinking in that it was a rapid process. Part of a deformation sequence is shown in Fig. 3, where twins of two orientations can be seen. The instability of the deformed microstructure did

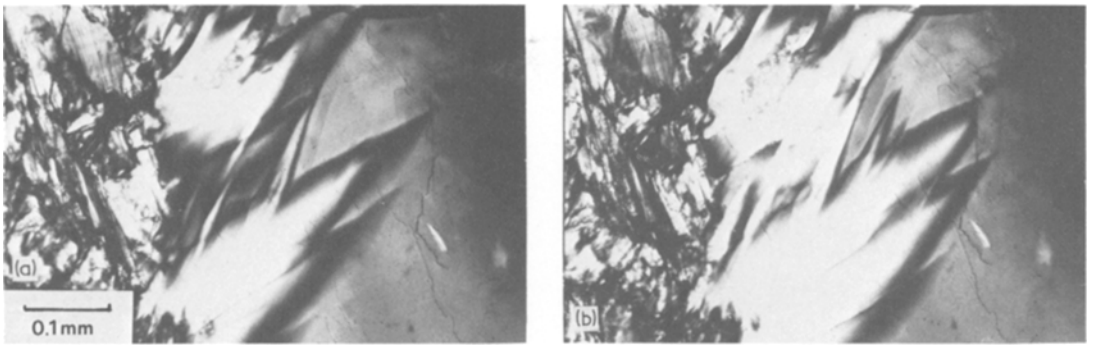


Figure 3 Deformation twinning at 293 K. (Compression axis horizontal.)

not allow the crystallography of the twins to be determined. Fig. 4 shows a characteristic twinned microstructure. The parallel twins are in grains with their basal planes almost parallel to the specimen plane, and the chevron twins are in a thin grain with the slip plane perpendicular to the specimen and parallel to the axis of compression. This grain is thus poorly oriented for slip or kinking.

4.1.4. Dynamic recrystallization

During the later stages of the deformation, dynamic recrystallization became increasingly important. The new grains were easily identifiable, being equi-axed, and much smaller than the original grains under all conditions of deformation. The grains originated at various sites in the specimen:

(a) *Kink band boundaries.* Although many kink bands remained stable and unchanged throughout the deformation, recrystallization occurred at kink bands in regions of severe lattice bending, and this is clearly shown in Fig. 2e, f.

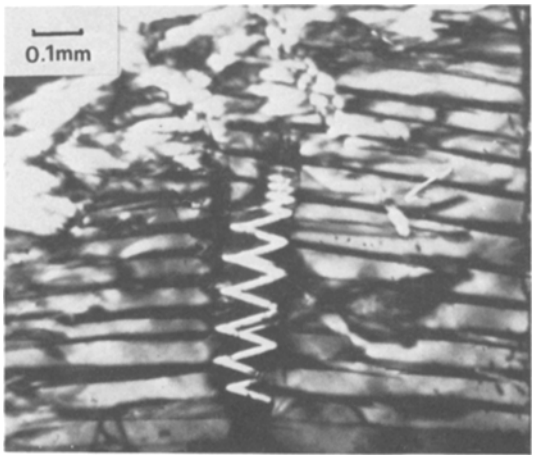


Figure 4 Twinned microstructure after deformation at 319 K. The "chevron" twins are in a narrow grain which runs from top to bottom in the micrograph. (Compression axis vertical.)

(b) *Twins.* Twinned regions invariably recrystallized, and an example is shown in Fig. 5. The twin boundaries developed irregularities (Fig. 5b) and eventually formed new grains (Fig. 5c).

(c) *Old grain boundaries.* Dynamic recrystallization frequently originated at the old grain boundaries, and this was most clearly seen in specimens which initially had an equi-axed grain structure. Such a microstructure could be achieved by stopping deformation after a small strain and allowing the newly recrystallized grains to grow for ~ 24 h. Fig. 6 shows the subsequent development of the microstructure on straining. Dynamic recrystallization at the grain boundaries results in a duplex microstructure similar to that found in metals or minerals undergoing dynamic recrystallization [17, 18].

In all the above cases, the mechanism of dynamic recrystallization appears to involve the migration of previously existing boundaries. This is most clearly seen in the time lapse cine sequences in which the action is speeded up by a factor of between 50 and 100. Regions near grain boundaries can be seen to develop misorientation, the boundary then bowing out to form a new grain, in the manner envisaged for static recrystallization of metals, see for example, [19].

The size of the dynamically recrystallized grains remained approximately constant during a test, and this was achieved by a process of continual recrystallization in the zone of dynamic recrystallization, the new grains regularly forming, and being consumed, the grain size being determined by the dynamic balance between the rates of nucleation and growth.

The size of the dynamically recrystallized grains

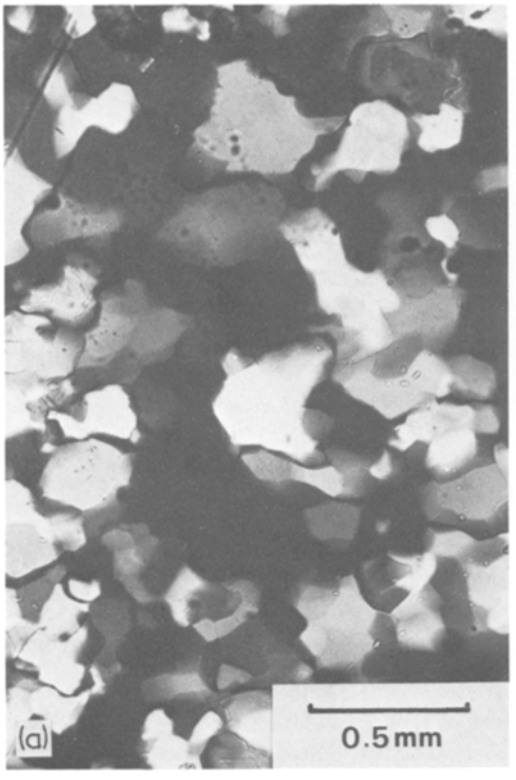
Figure 5 Dynamic recrystallization originating at deformation twins during deformation at 293 K. (Compression axis vertical.)

was found to be dependent on the strain rate and temperature of deformation, being smallest for low temperatures and rapid strain rates as is found for metals (see, for example, Sellars in [2]). Measurement of the grain size was difficult as the new grains were considerably smaller than the specimen thickness, thereby giving overlapping images. However, at room temperature the variation of grain size (d) with strain rate was found to be approximately as given below:

ϵ	10^{-2} sec^{-1}	10^{-3} sec^{-1}	10^{-4} sec^{-1}
d	20 μm	30 μm	50 μm.

4.1.5. The development of microstructure with strain

The overall microstructure which developed in a specimen during straining was a result both of the individual mechanisms discussed above, and their inter-relationship. This depended on the size, shape and orientation of the grains as well as on the strain rate. A good example of the development of structure is shown in Fig. 7. Grains A, B and C are oriented with the (0 0 0 1) planes parallel to their lengths and perpendicular to the specimen plane. Grains D and E have their (0 0 0 1) planes approximately parallel to the specimen plane. Although grain A is favourably oriented with respect to the compression axis for slip, this form of deformation is limited by contact with grain C, and kinks develop (Fig. 7b). At the same time, grain B is riding into grain A, causing high local deformation, resulting in dynamic recrystallization (Fig. 7b and c). At a later stage, grain E twins (Fig. 7c) and begins to recrystallize. It can be seen that grain D has undergone little deformation and survives almost intact (Fig. 7d). Similarly the



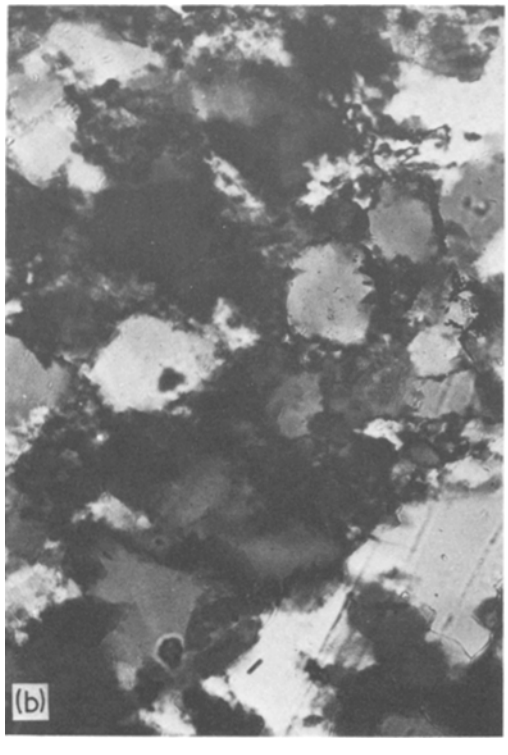


Figure 6 Dynamic recrystallization at the old grain boundaries during deformation at 310 K in a specimen with an initially equi-axed microstructure. (Compression axis vertical.)

regions of grain A which have undergone slip survive, whilst the inhomogeneously deformed parts of the grain recrystallize. The phenomenon of relict old grains remaining in a matrix of dynamically recrystallized grains even after high strains is commonly observed in minerals [1] and also in magnesium [20].

Thus, because of the anisotropic deformation of this material, an inhomogeneous microstructure is formed, particularly in specimens with a non-equi-axed initial grain structure. At high strains the deformation becomes concentrated in bands of dynamically recrystallized grains at angles of ~ 30 to 50° to the compression axis which spread across the specimen to form shear zones. These are discussed in more detail elsewhere [15].

4.2. High-temperature tests

As discussed earlier, above ~ 310 to 320 K there was a marked change in the mechanism of dynamic

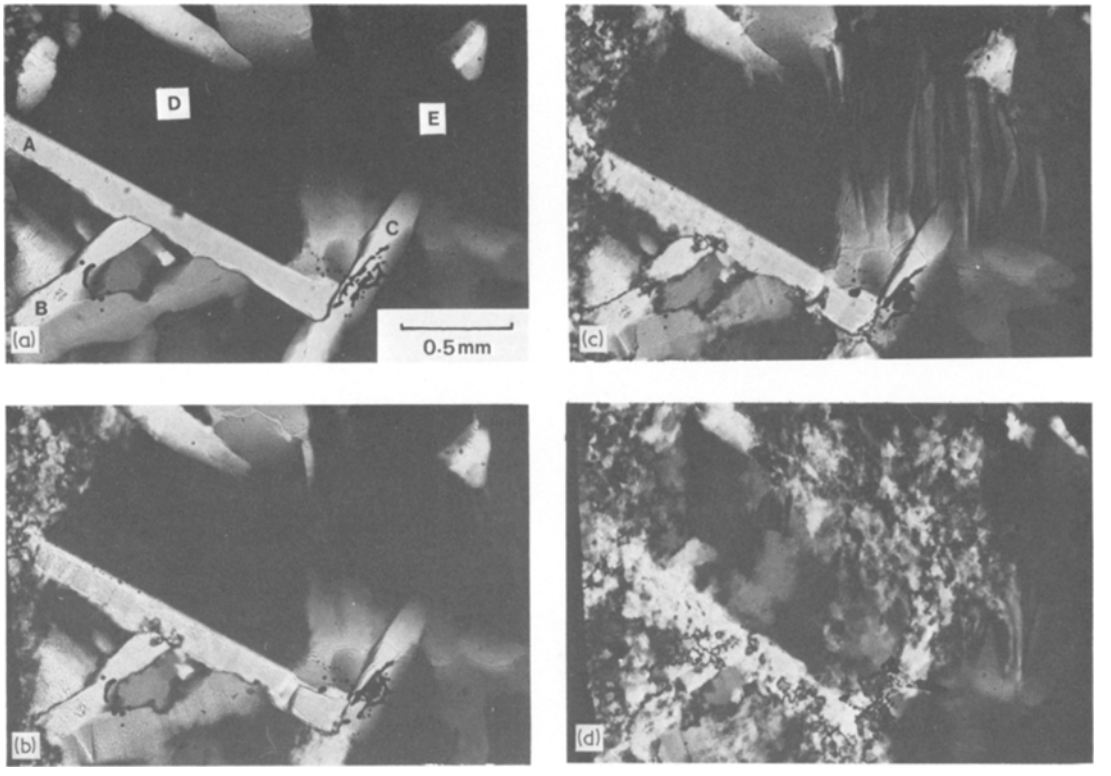


Figure 7 Development of microstructure with increasing strain at 310 K. (Compression axis horizontal.)

recrystallization, and the high-temperature behaviour is shown in Fig. 8. At an early stage of the deformation, certain grains, particularly those favourably oriented for slip (A and B) grew rapidly. In many cases the regions into which these grains grew appeared at least initially, to be undeformed, e.g. grain C. The driving force for this migration is not clear and would appear to be different to that of strain-induced boundary migration such as is found at lower temperatures. It is possible that elastic anisotropy in the material leads to stress-induced boundary migration. Kamb [21] proposed such a mechanism (piezocrystallization) to account for textural development in minerals, but as discussed by Nicolas and Poirier [1] there has been, as yet, no experimental support for this model. An alternative approach is to consider the effect of the anisotropy of plastic deformation as follows. Consider a grain with one slip plane, favourably oriented for slip with respect to the compression axis (Fig. 9), embedded in another grain unfavourably oriented for slip. On applying a compressive stress σ, the large grain will deform elastically, with stored energy/unit volume $\sim \sigma^2/2E$, whilst the small grain will deform plastically on one slip system storing negligible energy. Thus there will be a driving force for the small grain to grow, although this creates interfacial energy γ/unit area, and for the two-dimensional case of Fig. 9, growth will occur if

$$\sigma \gtrsim \sqrt{\left(\frac{4E\gamma}{w}\right)}.$$

This simple calculation neglects the strain incompatibility at the ends of the grain, but at elevated temperatures these can be accommodated by local diffusion. Thus, if the crystal has limited systems of easy slip, and has a low grain-boundary energy on at least one plane, as would seem to be the case for camphor, then this type of mechanism could account for the observed phenomenon.

The elongated grains formed as a result of this process, are seen to deform readily, and where two such sets of grains interact, e.g. Fig. 8d to f, smaller recrystallized grains form, and some of these may in turn elongate. In other regions of the specimen, recrystallization occurs by the same means as at lower temperatures, although there is a tendency for those new grains with favourable slip orientations to elongate as described above.

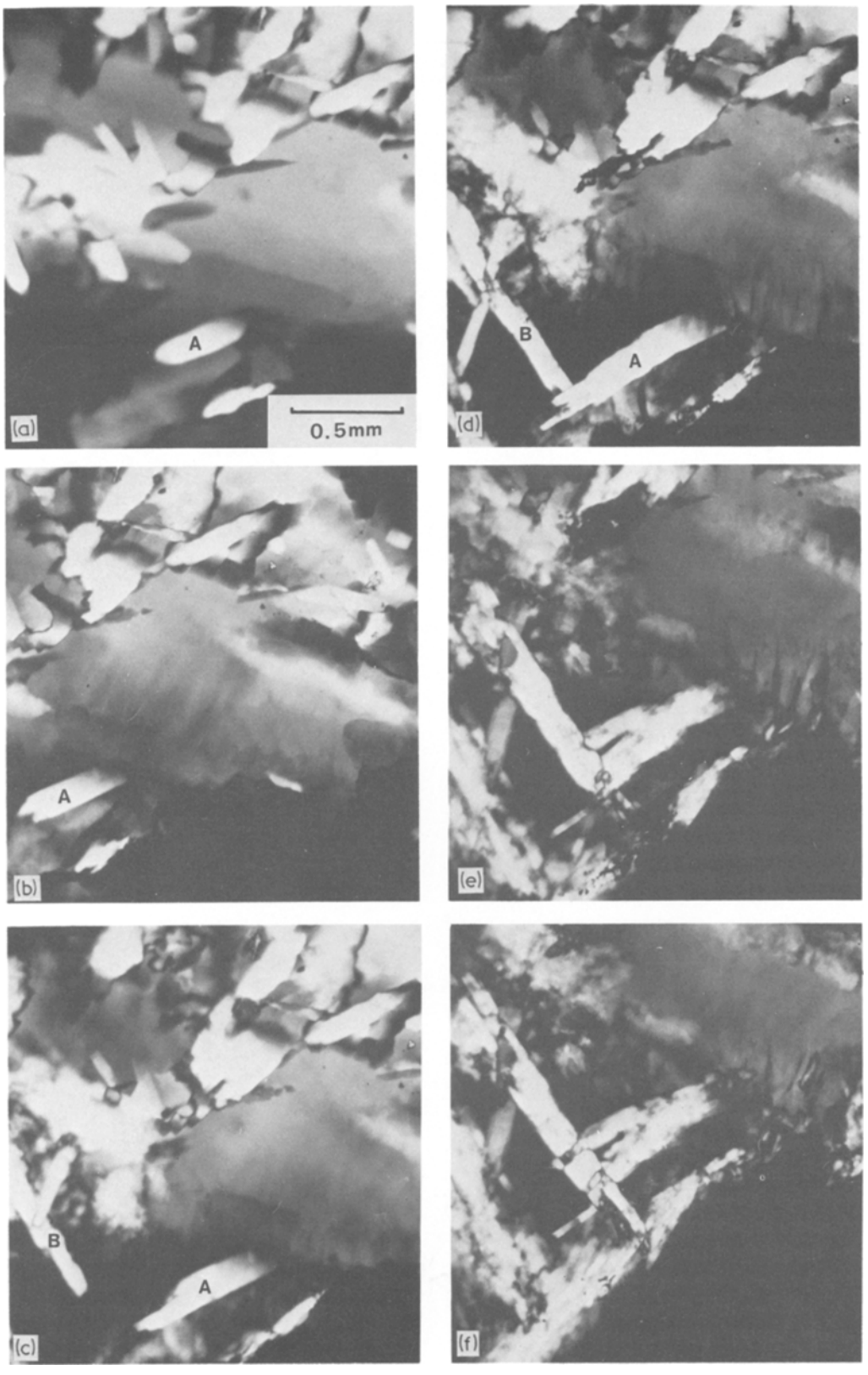


Figure 8 Deformation in the "high-temperature" range at 335 K, showing growth of elongated grains. (Compression axis horizontal.)

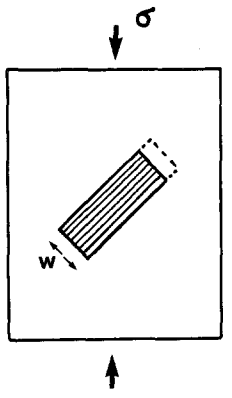


Figure 9 Diagram to show the growth during high temperature deformation of a grain favourably oriented for slip.

Thus, either by the growth of favourably oriented old grains, or by the selected growth of dynamically recrystallized grains, a crystallographic texture develops in the specimen, with the (0 0 0 1) planes being parallel to the planes of high shear stress. This is an example of the "oriented growth" method of texture formation long discussed by metallurgists (see, for example, [22]).

Further deformation is then confined to the textured regions which then form shear zones extending through the specimen. The formation of elongated grains during dynamic recrystallization has not been reported for metals, but there is evidence of somewhat similar microstructures in quartz mylonites (ribbon quartz) [23].

5. Conclusions

The deformation of polycrystalline specimens of rhombohedral camphor has been shown to involve processes of deformation and dynamic recrystallization such as are found in metals and minerals deformed at elevated temperatures. There are many points of similarity between the behaviour of camphor and metals and minerals of low symmetry, and although the use of such analogues must be treated with caution, the ability to study the deformation processes and the development of microstructure directly is valuable. Not only may events which would not be revealed by conventional post-deformation examinations (e.g. the continuous renewal of grains in regions of dynamic recrystallization) be detected, but also, direct observations, may, by providing clues, stimulate new ways of interpreting the very complex microstructure of naturally deformed minerals.

Acknowledgements

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