when a crack propagates evenly about the centre of the test piece. Zone II is characterized by strong, growing ridges which are oriented to the direction of tensile axis (Fig. 6). In the middle of the test piece, zone II abruptly changes to zone III (Fig. 7). The surface of zone III is macroscopically plain, but the examination of its fine structure reveals that it is scaley and clearly partly melted. Zone III is oriented parallel to the wide surfaces of test piece. Because the remaining zones (I and II on the other side of zone III) have identical struc-tures with the former zones I and II, we conclude that the fracture surface of an injection-moulded test piece is generated by two cracks which propa-gate similarly from both wide surfaces of the test piece. In the middle of the test piece, the longi-tudinal stress causes an abrupt crack formation between the bottoms of the cavities. Simul-taneously, a considerable amount of heat energy is liberated, which melts the surface of zone III. The existence of fracture zones I, II and III could possibly be explained by means of the different degrees of orientation in different parts of an injection-moulded test piece [10].

Acknowledgements

References

1. P. BEAHAN, M. BEVIS and D. HULL, *Phil. Mag.* **24** (1971) 1267.
2. R. P. KAMBOUR, *J. Polymer Sci. Makromol. Rev.* **7** (1973) 1.
3. T. E. BRADY and G. S. Y. YEH, *J. Mater. Sci.* **8** (1973) 1083.
4. T. L. PETERSON, D. G. AST and E. J. KRAMER, *J. Appl. Phys.* **45** (1974) 4220.
5. E. L. THOMAS and S. J. ISRAEL, *J. Mater. Sci.* **10** (1975) 1603.
6. K. V. GOTHAM, *Plast. Polym.* **37** (1969) 309.
7. P. L. CORNES and R. N. HAWARD, *Polymer* **15** (1974) 149.
8. R. P. KAMBOUR, *J. Polymer Sci. (A-2)* **4** (1966) 17.
9. A. PETERLIN, "Polymeric Materials", edited by E. Baer and S. V. Radcliffe (American Society for Metals, Metals Park, 1975) p. 175.
10. T. W. OWEN and D. HULL, *Plast. Polym.* **42** (1974) 19.

P. TORMALA
Institute of Materials Science,
Tampere University of Technology
SF-33101 Tampere 10,
Finland

S. LEHTINEN
J. J. LINDBERG
Department of Wood and Polymer Chemistry
University of Helsinki,
SF-00100 Helsinki 10,
Finland

Martensitic transformation cubic ⇌ rhombohedral in rubidium nitrate

The degree to which potentially martensitic mech-anisms are affected by orientational disorder and atomic mobility is an important aspect of crystal structural transformations [1, 2]. It is also of interest to examine a material which transforms from cubic NaCl-related to an intermediate rhom-bohedral structure, in order further to clarify details of the large change NaCl type → CsCl type in which the primitive rhombohedral angle alters from 60° to 90° and which was investigated in NH_4Br [3]. Two types of orientation relation were found, close to $(1\,0\,0)_{NaCl} \| (1\,1\,0)_{CsCl}$, $[0\,1\,0]_{NaCl} \| [\bar{1}\,1\,1]_{CsCl}$ (type A), and $(1\,0\,0)_{NaCl} \| (1\,0\,0)_{CsCl}$, $[0\,1\,0]_{NaCl} \| [1\,0\,1]_{CsCl}$ (type B). Dif-ferent authors have suggested new lattice corre-spondences [4, 5]. That of Hyde and O'Keefe [4] however, appears to be equivalent, for MX compounds, to the conventional contraction of $[1\,1\,1]$, leading to A type. Further data on B would be appropriate.

Rubidium nitrate provides the f c c parent lattice with marked orientational disorder in phase I [6, 7]; the rhombohedral structure in phase II, below 284°C [8]; and a CsCl-related cubic form III below 219°C. Phase III was earlier found to be in an orientation of type B with respect to I when the crystal was slowly cooled through II [9].

Although the volume change I → II is very slight, the lattice deformation is substantial, the 90° cell angle of I changing to 98° in the corresponding cell of II ([10] for lattice parameters). This cell is obtained by a 15.2% contraction along and a 6.4% expansion normal to [1 1 1]. It is the four-unit morphological cell of calcite-like structures.

Optical and X-ray measurements have been made on single crystal sheets of phase I freshly grown from the melt. A large microscope fitted with a transparent heating stage permitted observation in reflected and in transmitted polarized light. In the X-ray studies single crystals of I were grown on a transparent heater carried on the gonimeter head of a precession camera fitted with a polarizing microscope. Care was taken to record the Laue and precession diffraction patterns of phase II within 10 min of transformation I → II, in order to distinguish the effects of rapid detwinning or recrystallization. This limitation plus a paucity of reflections just after transformation limited the precision of ± 4°. The orientation relations quoted were reproduced in different crystals.

The orientation relation measured before relaxation effects were prominent was $(0\,1\,0)_I \| (0\,1\,0)_{II}$, $[0\,0\,1]_I \| [0\,0\,1]_{II}$ $(Z = 4) \pm 4°$. Restated in terms of the CsCl-related cell of II $(Z = 1)$, this becomes $(0\,1\,0)_I \| (0\,1\,1)_{II}$, $[0\,0\,1]_I \| [1\,\bar{1}\,1]_{II}$. This is the type A orientation found in the NaCl → CsCl type transformation. The rhombohedral structure permits planes and directions to be distinguished and shows that it is the $(0\,1\,0)_I = (0\,1\,1)_{II}$ plane which remains unrotated.

When crystals of II were allowed to anneal before measurement, a relation of type B was identified. Referred to the single unit cell of II this was $(2\,0\,\bar{1})_I \wedge (1\,\bar{1}\,1)_{II} = 3$; $[0\,1\,0]_I \wedge [0\,1\,\bar{1}]_{II} = 7°$, making $(1\,0\,0)_I \wedge (1\,0\,0)_{II} = 8°$, or, referring to the four-unit cell of II and idealizing, $(0\,0\,1)_I \| (0\,0\,1)_{II}$, $[0\,1\,0]_I \| [1\,1\,0]_{II}$ approximately. When a crystal was taken rapidly I(→ II) → III, both A and B type orientations were found in cubic III, relative to I.

In thermal cycles I → II → I, when the transformation was reversed promptly after full completion, it was fully reversible, surface effects being cancelled and the original orientation restored. In a cycle performed more slowly, an original $(1\,1\,1)_I$ plane was converted to a $(1\,0\,0)_I$ plane, the relation being $(0\,0\,1)_{Ic} \| (1\,1\,1)_I$, $[1\,\bar{1}\,0]_{Ic} \| [1\,\bar{1}\,0]_I$, ± 5°, where c denotes cycled. Whilst this suggests that B may be favoured by some relaxation effects, its presence in III in a quickly cooled crystal suggests that it is not entirely due to diffusive relaxation.

Optically, the shear nature of the transformations II → I → II has been demonstrated recently by Courtenay and Kennedy [11] whose photographs show the shape change from rhombohedral to cubic and the reverse across an interface $\| \langle 1\,0\,0 \rangle_I$, in individual rhombohedra of edge length 14 to 30 μm [8].

Our melt-grown crystals, after transformation to II, consisted of lamellae or "main bands", typically 0.4 to 2 μm thick, parallel to $\langle 1\,0\,0 \rangle_I$, and having tilted surfaces. In $\langle 0\,0\,1 \rangle$ projections two mutually perpendicular sets could appear in adjacent regions. Each main band was internally polysynthetically twinned, the twin traces being $\langle 1\,1\,0 \rangle_{II}$, and each adjacent pair of bands forming a herring-bone pattern (Fig. 1). The general appearance was reminiscent of In—Tl alloys. Within 15 min, the subtexture was removed by relaxation processes. The most common process, reminiscent of recrystallization, left the traces of the main bands (but not the twins) and was probably diffusive. However, there were other processes of sudden amalgamation of pairs of twins and of pairs of main bands, which will deserve further attention. Further results on the transformation are to be described later [11]. The various relaxation effects
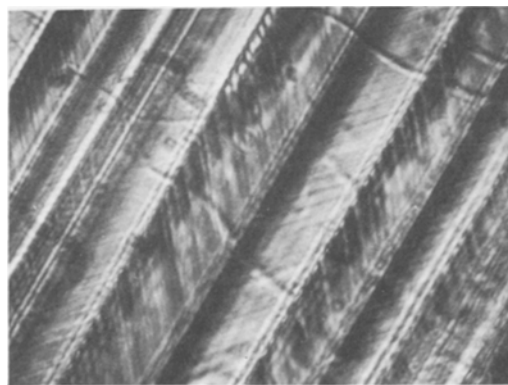

Figure 1 Rubidium nitrate II. Herring-bone pattern of main bands containing lamellar twins. Transmitted light, crossed polars, × 450, enlarged to 1200.

should be relevant to the loss of mobility of martensitic interfaces more generally.

Since the possible transformation twinning planes are $\{1\,0\,0\}_{II}$ and $\{1\,1\,0\}_{II}$, the twinned main bands are to be expected from a martensitic mechanism having a habit plane close to $\{0\,1\,0\}_{II}$, and a lattice-invariant shear $\{LIS\}$ provided by twinning on $\{1\,1\,0\}_{II}$.

To test whether martensite theory (using a single LIS) would apply, the relevant features were computed by use of the program MARTENS [3]. The habit plane provides a much more sensitive test of the operative LIS than do the orientation relations. With the reported l.p. the predicted habit plane (HP) is $4°$ from $\{1\,0\,2\}$ for $(1\,0\,0)$ $[0\,1\,1]$ LIS, and $9°$ from $\{0\,0\,1\}$ for the $(1\,1\,0)$ $[0\,0\,1]$ LIS. Although on the $[1\,0\,0]$ projection, the computed HP trace directions based on $(1\,0\,0)$ twinning agree with observation, whilst with $(1\,1\,0)$ twinning there is a discrepancy of $6°$, on the $[1\,1\,1]$ projection the traces observed can correspond only to the $(1\,1\,0)$ twinning. This is in accordance with the observed sub-texture in the main bands. The general agreement between theory and observations confirms that the transformation is martensitic.

The structural correspondence to produce B orientation is again that proposed [4]. The $(2\,0\,0)$ nets of NaCl type deform to become, for $RbNO_3$ II, $70°$ nets. The M atoms of the MX structure are consequently displaced from their positions at $\frac{1}{2}\,0\,0$ etc to positions between the $(2\,0\,0)$ X layers. With only moderate shuffle of the X layers along $[0\,0\,1]$, they become the faces of the primitive rhombohedron of II, in the required B type of orientation. If in the second part of the cycle, the crystal does not reverse this process, but the $70°$ nets continue to deform in the same sense to become $60°$ nets, without shuffles, this further deformation, with appropriate expansions, is simply the standard Shoji–Buerger correspondence (type A) [3] describable by expansion along $[1\,1\,1]$. The crystal is then f c c again. The faces of the primitive rhombohedron are the $\{1\,1\,\bar{1}\}$ of the cube. Thus when a crystal of I converts to II by correspondence B, then reverts to I by correspondence A, the $(1\,0\,0)_I$ becomes $(1\,1\,\bar{1})_I$, or conversely. The process can also be regarded as one continuous deformation similar to one shown in Fig. 4 of [12]. These considerations imply more generally that certain transformations might proceed according to two, or more, structural correspondences.

This demonstration of a martensitic mechanism in a structure having considerable thermal agitation, and for a transformation which appears not to be martensitic if the crystal is examined more than 15 min after transformation, shows that martensitic mechanisms are not necessarily precluded by the possibility of competing diffusive accommodation.

Acknowledgement

References

1. S. W. KENNEDY, *J. Mater. Sci.* **9** (1974) 1391.
2. YU. V. MNYUKH and N. A. PANFILOVA, *J. Phys. Chem. Solids* **34** (1973) 159.
3. W. L. FRASER and S. W. KENNEDY, *Acta. Cryst.* **A30** (1974) 13.
4. S. W. KENNEDY, *J. Mater. Sci.* **9** (1974) 1043.
5. B. G. HYDE and M. O'KEEFE, *Conference* on phase transitions and their application in materials science, edited by L. E. Cross (Pergamon, New York, 1973) p. 345.
6. S. W. KENNEDY, *Nature* **210** (1966) 936.
7. S. W. KENNEDY, *Phys. Stat. Sol. (a)* **2** (1970) 415.
8. E. W. COURTENAY and S. W. KENNEDY, *Austral. J. Chem.* **27** (1974) 209.
9. A. J. INVERSEN and S. W. KENNEDY, *Acta Cryst.* **B29** (1973) 1554.
10. P. P. SALHOTRA, E. C. SUBBARAO and P. VENKATESWARLU, *Phys. Stat. Sol.* **29** (1968) 859.
11. E. W. COURTENAY, S. W. KENNEDY and W. M. KRIVEN, to be published.
12. S. W. KENNEDY, *J. Mater. Sci.* **9** (1974) 2053.

S. W. KENNEDY
W. M. KRIVEN
*Department of Physical and Inorganic Chemistry,
University of Adelaide,
Adelaide, S.A. 5001,
Australia*