

Endothermic Decompositions of Inorganic Monocrystalline Thin Plates. I. Shape of Polycrystalline Product Domains versus Constraints and Time

G. BERTRAND, M. COMPERAT, M. LALLEMANT, AND G. WATELLE

Laboratoire de Recherches sur la Réactivité des Solides, Associé au CNRS, Faculté des Sciences Mirande, B.P. 138, 21004 Dijon Cedex, France

Received January 2, 1979; in revised form June 6, 1979

Copper sulfate pentahydrate dehydration into trihydrate was investigated using monocrystalline platelets with varying crystallographic orientations. The morphological and kinetic features of the trihydrate domains were examined. Different shapes were observed: polygons (parallelograms, hexagons) and ellipses; their conditions of occurrence are reported in the (P, T) diagram. At first (for about 2 min), the ratio of the long to the short axes of elliptical domains changes with time; these subsequently develop homothetically and the rate ratio is then only pressure dependent. Temperature influence is inferred from that of pressure. Polygonal shapes are time dependent and result in ellipses. So far, no model can be put forward. Yet, qualitatively, the polygonal shape of a domain may be explained by the prevalence of the crystal arrangement and the elliptical shape by that of the solid tensorial properties. The influence of those factors might be modulated versus pressure, temperature, interface extent, and, thus, time.

Introduction

A large variety of domain shapes has been reported in the literature dealing with the observation of, whether natural or not, crystalline planes of hydrated salts partially decomposed into anhydrous salt or lower hydrate. All the shapes observed, however, can be divided into the following three categories.

(a) Polygonal shapes as illustrated in Fig. 1a. It is a hexagonal domain of $\text{Ba}(\text{HC}_2\text{O}_4)_2$, BaC_2O_4 , $2\text{H}_2\text{O}$ occurring on the plane (100) of BaC_2O_4 , $\text{H}_2\text{C}_2\text{O}_4$, $2\text{H}_2\text{O}$ (1). Parallelograms (2), squares (3), hexagons, and rhombi have also been reported for various decompositions.

(b) Elliptical shapes, where the transformed domain is enclosed within a curve. In general, they are either ellipses or circles.

Figure 1b illustrates such a domain: it is that of copper sulfate trihydrate on one plane of a copper sulfate pentahydrate crystal (4-6). Figure 1c also shows circular domains of copper sulfate monohydrate, which occurred on one face of a pentahydrate crystal (5, 6).

(c) Ill-defined shapes which might be intermediates between both above groups and corresponding to an evolving domain. Figure 1d illustrates such an example involving the same transformation as in Fig. 1b.

So far, no study has entirely explained the observations made. A number of authors, however, have tried to explain the occurrence of polygonal shapes in terms of the part played by the initial structure, e.g., Garner (4) who observed polygonal domains during the decomposition, under low water vapor pressure, of cubic crystals of aluminium alum, regarded them as attack figures.

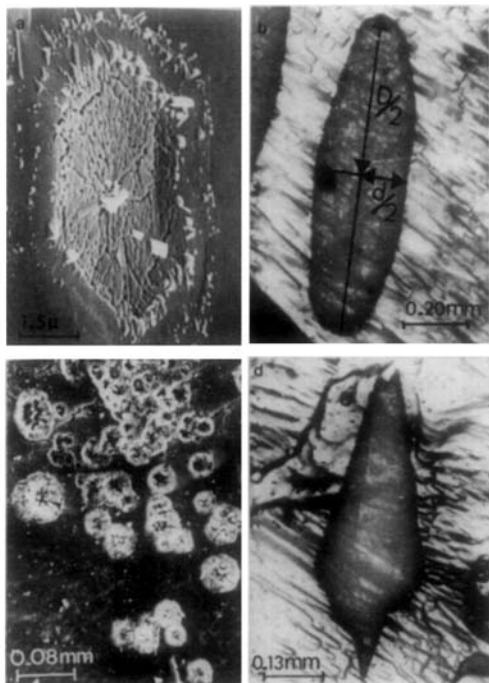


FIG. 1. Different forms of dehydrated domains on monocrystalline platelets. (a) Dehydration of barium dihydrate monoacid oxalate into monohydrated salt; (b) copper sulfate pentahydrate dehydration into trihydrate; (c) copper sulfate pentahydrate dehydration into monohydrate; (d) ill-defined, star-like domain of copper sulfate trihydrate.

Thomas and Renshaw (3) made similar remarks about domains occurring on the (100) face of crystals of nickel sulfate hexahydrate partially decomposed in vacuum.

The transformation reported in this paper is that of copper sulfate pentahydrate into trihydrate, which has already been largely investigated as to the shape of the transformed domains. Let us mention citations in the literature (4–7) reporting the existence of various shapes, the influence of the natural plane orientation upon these shapes, and the deformation of the latter with respect to out-of-equilibrium conditions of the initial crystal (mainly pressure). These observations, however, are isolated and do not yield any general rules. Hence, a systematic study has been undertaken on platelets cut from

monocrystalline pentahydrate to determine the influence of the following factors on the shape of trihydrate domains:

- crystalline orientation of platelets;
- factors of action: temperature and pressure;
- time.

I. Experimental

I.1. Material—Decomposition—Observation

Monocrystals of copper sulfate pentahydrate, grown in an aqueous solution, were cut by dissolution into platelets with given crystallographic orientations using a multi-wire cutter. The object of this technique is to obtain platelets with many crystallographic orientations which can be different from those of natural planes, thus extending the range of observations.

The results reported here refer to three types of platelets termed M_{\parallel} , a_{\parallel} , and C_{\perp} , respectively, parallel to plane M and to plane a and perpendicular to axis C of the crystal (8) (Fig. 2a).

These platelets weighing from 20 to 25 mg were put out of equilibrium in a thermo-balance coupled with an observation cell under temperature and pressure conditions yielding trihydrate identified radiocrystallographically.

Water vapor pressures were obtained using the static method of the dew point. The reaction was continuously followed, *in situ*, with binocular magnifying glasses fitted with a photographic device. In some cases, the reaction was stopped and the platelets were taken out of the reactor and observed in optical microscopy.

I.2. Experimental Results

I.2.1. Role of the crystallographic orientation of platelets on the shape of the transformed domains. The various platelets were submitted to similar pressure and temperature conditions to isolate this parameter

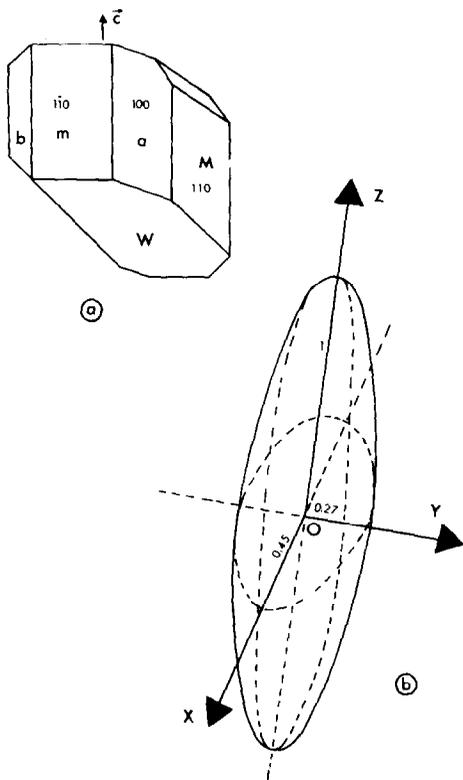


FIG. 2. (a) Schematic view of a copper sulfate pentahydrate crystal. (b) Reaction ellipsoid as envelope of elliptical domains. Example of the dehydration of a copper sulfate pentahydrate crystal into trihydrate.

(2.45 Torr, 45°C). Under these conditions, the dehydrated domains were all elliptical and, for each orientation, the specific ratio D/d of the long axis (D) to the short axis (d) could be determined (Table I), given the homothety of the domains from a certain extent; this point will be referred to in Section I.2.3.

TABLE I

	Orientation of platelets		
	M_{\parallel}	a_{\parallel}	C_{\perp}
D/d	3.44	2.20	1.67
Orientation of ellipses	C_{\parallel}	C_{\parallel}	\perp plane a

In addition, if the ellipses obtained from the three types of platelets are grouped around a point A, assuming that was where the reaction had begun, it was observed that they have a single envelope termed reaction ellipsoid shown in Fig. 2b. This volume built up from the shapes observed at the surface of the platelets is perfectly defined. Indeed, once equated and its main axes oriented with respect to the structure of the initial compound for a platelet with any orientation, we can predict the elliptical shape of the transformed domains and the value of the D/d ratio as well (6, 9).

Now, when the three orientation platelets were put out of equilibrium, under a pressure of 8 Torr at a temperature of 62°C, polygonal domains were observed. Either parallelograms or hexagons occurred on the C_{\perp} platelets (Fig. 3a). These shapes have a center of symmetry like the initial crystal (point-group $\bar{1}$). It should be noticed that the hexagon outline is irregular and Fig. 3b shows that the direction of the parallelogram sides are found again either in the sides or the indents of the hexagons. As will be shown below, a hexagonal domain results from the evolution of an initially parallelogram domain.

In conditions similar to those of the C_{\perp} platelets, the M_{\parallel} platelets show trihydrate rod-like domains (Fig. 3c). We have seen before that from elliptical domains an ellipsoid could be reconstituted. In the case of polygonal domains the work being done so far is not advanced enough to assert the existence of a defined geometrical domain which would be the envelope of the polyhedra occurring on the various planes.

However, comparing the parallelograms observed on C_{\perp} and the rods on M_{\parallel} allows such a volume to be expected although its shape cannot be accurately defined yet. The hexagonal domains also observed on C_{\perp} would then correspond to this volume deformation as it grows, which will now be explained.

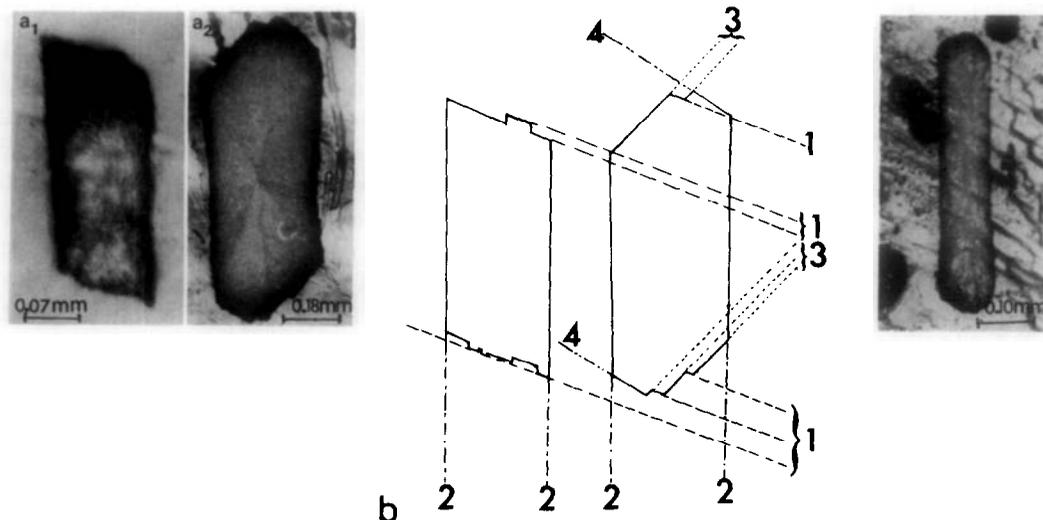


FIG. 3. Polyagonal domains resulting from the dehydration of copper sulfate pentahydrate into trihydrate. (a) parallelogram and hexagon on C_{\perp} platelets; (b) schematic representation of (a); (c) "rods" on M_{\parallel} platelets.

1.2.2. Role of pressure and temperature. Both influence the geometry of the transformed domain which may be, depending on the pressure-temperature constraint area, either polygonal or elliptical and they also influence the change in the ratio of the axes in the latter case.

The observations relating to platelets C_{\perp} are reported on the pressure-temperature diagram in Fig. 4.

When the transformation occurs with constraints corresponding to areas I and III, only elliptical forms were observed. We may then argue that either the transformed domains have this shape as soon as they occur, or that if initially they are polygonal, they are subsequently converted into an ellipse before the domain extent can be observed with the techniques used.

When the transformation occurs for constraints corresponding to the intermediate area II, only polygonal shapes were observed. Parallelograms were observed more often than hexagons in the area of lower pressures in area II.

Similar observations were made for platelets M_{\parallel} . In this case, however, it should be

noticed that the area where polygons were observed is narrower and close to 8 Torr for temperatures ranging from 50 to 62°C.

Let us now examine the role of pressure and temperature upon the axis ratio of ellip-

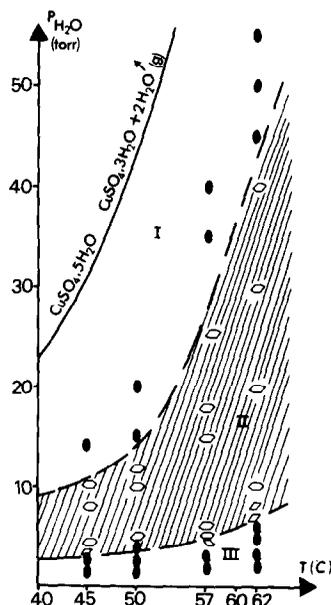


FIG. 4. Pressure-temperature diagram: shapes of the trihydrate domains observed on C_{\perp} platelets.

tical domains. Figures 5a and b show that the influence of pressure cannot escape from observation of the M_{\parallel} platelets and the C_{\perp} platelets as well. Such observations resulted in a systematic investigation vs pressure at constant temperature. Figure 6a shows the evolution in the D/d ratio of ellipses for M_{\parallel} platelets at 50°C. The curve shows a break corresponding to the observation of the polygonal shapes mentioned previously. On each side of this area (relatively near the curve maximum) the elliptical shape of the decomposed domains changes largely and in some cases the D/d ratio tends toward value

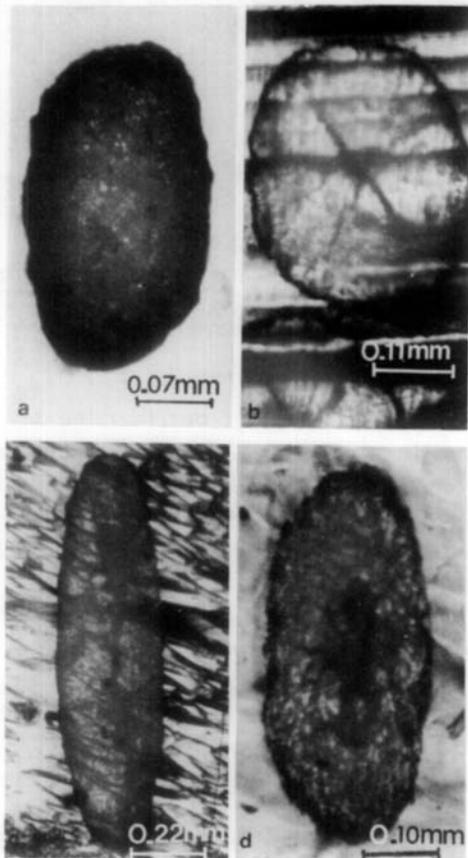


FIG. 5. Influence of water vapor pressure on the shape of decomposed domains: (a) platelet C_{\perp} , $T = 62^{\circ}\text{C}$, $P = 3$ Torr; (b) platelet C_{\perp} , $T = 62^{\circ}\text{C}$, $P = 55$ Torr; (c) platelet M_{\parallel} , $T = 57^{\circ}\text{C}$, $P = 4.6$ Torr; (d) platelet M_{\parallel} , $T = 57^{\circ}\text{C}$, $P = 32$ Torr.

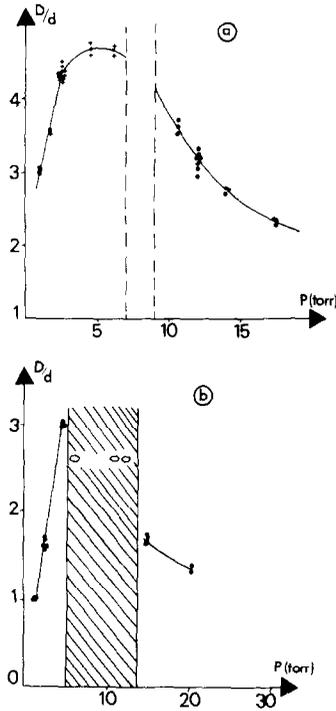


FIG. 6. Variation of the D/d ratio with water vapour pressure: (a) platelets M_{\parallel} ; (b) platelets C_{\perp} .

one when the pressure fixed approached the equilibrium pressure: identical remarks can be made for the C_{\perp} samples (Fig. 6b): the measurement of the D/d ratio increment from low pressures is interrupted by the occurrence area of polygonal shapes succeeded by a pressure range where the D/d ratio decreases.

The part played by temperature is similar to that of pressure as to its influence on the D/d ratio of the ellipses axes, as shown by values obtained for M_{\parallel} under 12 Torr (Table II).

TABLE II

	$T (^{\circ}\text{C})$		
D/d	53.5	57	62
	2.65	4.1	3.3

I.2.3. Influence of time on the evolution of the shape of decomposed domains. It must be made clear, first, that the evolution being observed using binoculars, the domains observed are macroscopic. As shown on the figures the domains correspond to actual sizes, 0.1 mm in magnitude. The time origin t_0 is noted, when the smallest domain is seen, i.e., about $2 \cdot 10^{-2}$ mm.

Let us first consider the evolution of a polygonal shape. The following observations were made on C_{\perp} platelets.

Figure 7 shows the existence, side by side, of a small parallelogram and a larger hexagon thus arousing attention on the time factor. The systematic study following such observations proceeded in this way: as soon as it occurs the evolution of a parallelogram is observed as shown in Figs. 8a to c. It is noticed that the domain initially represented by a parallelogram built on the straight lines whose directions are 1 and 2 (Figs. 9a and 3b) has evolved by the occurrence of two new directions 3 and 4 detected by examining the domain outline (Fig. 2b). An irregular hexagon occurs at a first place and evolves by multiplying its breaks into an indented ellipse as shown in the enlarged Fig. 9b. It

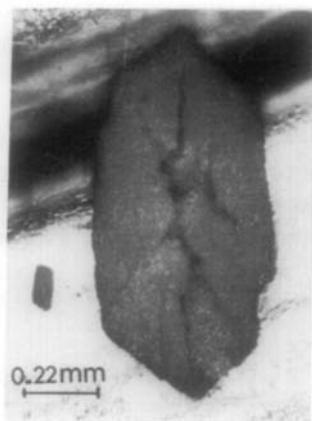


FIG. 7. Simultaneous observation of two domains. The part played by the progress rate upon morphology is shown (platelet C_{\perp} , $T = 62^{\circ}\text{C}$, $P = 10$ Torr).

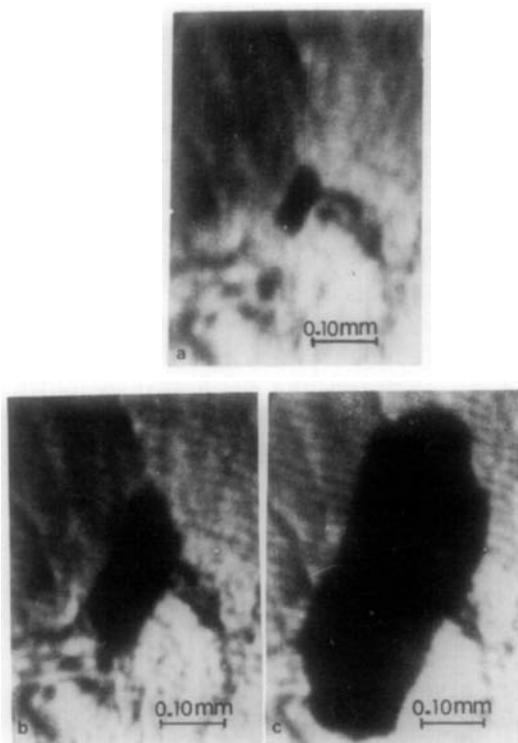


FIG. 8. Variation, versus time, in the morphology of a decomposed domain on a C_{\perp} platelet ($T = 62^{\circ}\text{C}$, $P = 15.5$ Torr): (a) t ; (b) $t + 5$ min; (c) $t + 13$ min.

is important to point out that the break directions of the matrix crystal identified by examining both the hexagon and the parallelogram are also found for the segments of the broken line outlining the macroscopic elliptical shape.

Numerous similar tests prove that this evolution is reproducible. They were, of course, made applying to the pentahydrate crystal constraints corresponding to the pressure and temperature values of area II (Fig. 4), the only area where polygonal shapes were observed.

Let us now consider the evolution of an elliptical form vs time. The growth homothety of such domains when they have reached a certain extent has been mentioned above. But, the elliptical shape eccentricity changes with time for a relatively short time

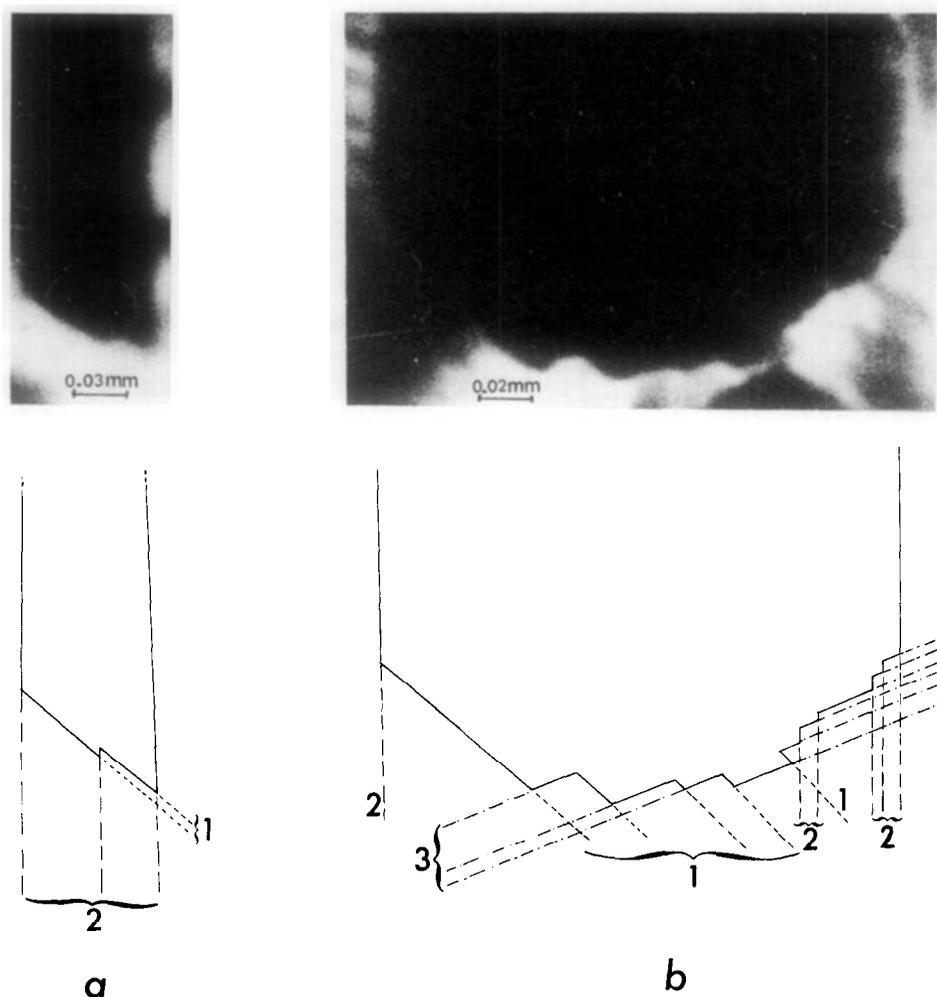


FIG. 9. Details of the polygonal domain outlines and schematic illustration (a) magnified part of domain 8a; (b) magnified part of domain 8c.

(a few minutes) as the domain occurs: eccentricity increases, decreases, and stabilizes. Figure 10 shows the change vs time of each D and d axis length (a and b) in the elliptical domain of trihydrate occurring under the conditions mentioned in the legend. From the beginning a growth rate increase toward D vs that measured toward d is noticed; the rate ratio listed in Fig. 10c reaches a maximum then declines and becomes appreciably constant. After 2 to 3 min the domains extend homothetically.

II. Discussion

Three main results are derived from the experiment study.

1. The existence of either polygonal or elliptical shapes in the transformed domain occurring in ranges of perfectly defined pressure-temperature constraints and sufficiently far from the pentahydrate crystal stability.

2. The transformation of polygonal into elliptical shapes.

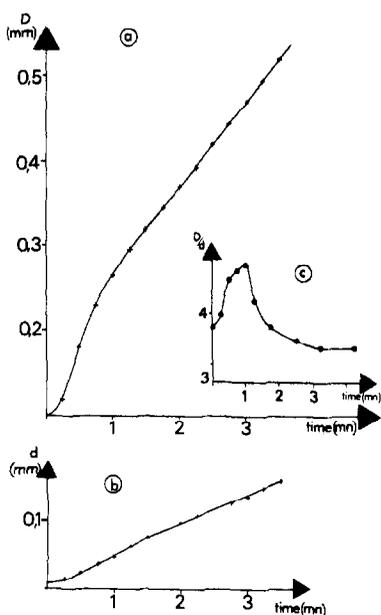


FIG. 10. Variation, versus tie, of the size of an elliptical domain ($T = 62^{\circ}\text{C}$, $P = 4.5$ Torr): (a) variation of D ; (b) variation of d ; (c) variation of D/d .

3. When only the latter are observed, the change in the ellipse eccentricity at the beginning of the reaction.

So far we cannot give an overall model explaining the occurrence and the development of these shapes but it seems of interest to debate a few qualitative explanations related to each result.

II.1. Influence of the Discontinuous Vectorial Properties of the Crystal on the Occurrence and Development of Polygonal Domains

It has been reported elsewhere (10, 11) that the transformation type considered involves water molecules removal then the rearrangement of the crystalline stacking of a shear type showed by moderate and collective movements of atoms. All these processes result in a fractionating of the matrix crystal which breaks into a finite number of planes (11). The crystallites in the new phase fill up the inside of the domain whose outline consists of the planes derived from the

breaks which occurred. Figure 11 is an illustration of one domain explaining the existence of a macroscopic, polygonal shape, which does not automatically mean that of the crystallites imagined.

It is, thus, the discontinuous, vectorial properties of the crystal which, by destabilizing successively parallel planes in a finite number of directions, explain that a polygonal domain may occur and develop homothetically, as is the case for attack figures and interpreted by some authors, among whom, Garner (4) and Osterheld and Bloom (13). Like us they argue the relationship between crystalline structure and existence of polygonal domains but they do not explain it by the type of crystalline restacking characterizing a dehydration.

II.2. Influence of Continuous Vectorial Properties on the Formation of Elliptical Domains

Our systematic study enables us to show that polyhedral shapes are only observed in a given range of constraints; in addition these



FIG. 11. Evolution of the polygon with reaction progress.

shapes evolve more or less rapidly toward an elliptical shape. In other pressure and temperature conditions, as soon as domains are visible, only elliptical shapes are observed. We also observed such shapes in the dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and they were reported in that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (12) and also in the decomposition of goethite into hematite (14).

The elliptical shapes cannot be correlated directly with the triperiodic structure of the hydrate but logically, however, the occurrence of one or several tensorial properties of order two in the crystal may be expected.

Given the following arguments we can more precisely think of the influence of thermal expansion and of the crystal thermal conductivity whose representative volumes are ellipsoids.

(1) The reaction is endothermic (24 000 cal per hydrate mole). Each active reacting site is a heat sink causing the occurrence of thermal gradients not only in the gas but also in the matrix crystal.

(2) We showed, in the solid, the existence of a thermal gradient using reaction ellipsoid and that of thermal conductivity, on the other, the relation between the reaction ellipsoid and that of thermal expansion (6, 9). The reaction proceeds most rapidly where heat flows more rapidly, i.e., where thermal expansion is lower. These results are sufficiently valid to continue in this way explaining the elliptical shape of the domains.

II.3. Influence of Various Factors on the Evolution of the Domain Shape

It is, thus, qualitatively possible to explain the polygonal shape of a domain by the prevailing role of the crystalline arrangement and the elliptical shape by that of the tensorial properties of the solid.

What remains is, on the one hand, the explanation of the shape evolution of the domains vs pressure and temperature, which comes to interpret the prevalence of the

stacking or thermal conductivity of the crystal in such or such constraint range, on the other, the explanation of the shape evolution of transformed domains vs time, i.e., conversion of polygonal into elliptical shape and the evolution of the ellipse eccentricity.

The occurrence of gradients in the reaction front environment and the existence of continuous vectorial properties such as expansion and thermal conductivity of the solid whose representative surfaces are ellipsoids, are enough to understand shape evolution with time.

Two types of observation can be made; the first shows the relation between deformation and gradient importance:

—the faster the progression rate of the polygon face considered the higher the gradient and the larger the deformation, e.g., in the case of C_\perp platelets the planes noted 2 (Fig. 9a) move about four times less rapidly than those noted 1 (0.05 mm min^{-1}). Indeed, experiments show that planes noted 1 are the first to be deformed (Figs. 2, 8, and 9).

—the larger the reaction front area, the greater the calorie consumption by the reaction (proportional to that area) and hence the interface thermal gradients. Now, for the given constraint conditions we do notice that the primary polygonal shapes reach a given size before deforming. Hexagons and then ellipses are always larger than parallelograms which are the primary shapes.

The second type of observation deals with the direction and geometrical characters of deformation.

It is noticed that the conversion of the polygon into the ellipse, indeed, occurs in the direction of faster heat flow and where thermal expansion is lower. In addition, the appearance of breaks or step sequences outlining the ellipse such as those illustrated in Fig. 11 clearly shows the simultaneous occurrence of discontinuous, vectorial properties responsible for the limited number of planes and of continuous vectorial properties

responsible for the macroscopic elliptical shape.

Finally, when the ellipse is the only shape observed, the change in its eccentricity at the beginning of the reaction may be explained by the interaction of thermal flows in the gas and the solid, given the different specific heat, media conductivity, and the fact that the gas is isotropic and the solid anisotropic. After a few minutes a stationary flow may be expected in the solid, which would correspond to the constant axis ratio of the ellipse vs time.

Conclusion

The above analysis attempting to interpret the geometrical shapes shown by transformed domains and the evolution of those shapes exhibits how complex the problem is.

The shape of a domain on a platelet of (*hkl*) orientation is defined by the module of the vector representing the displacement of the reaction, after a given time, in all directions (*uvw*) around a single site.

This displacement depends on the preferential directions fixed by the mode of crystalline restacking of shear type characterizing a dehydration, on the matter flow or water-removal rate, which itself depends on pressure and temperature constraints, on the tensorial properties of the solid, on mass flow-thermal flow coupling terms in the gas and the solid, and finally on time. It is, thus, obvious that so far a single model cannot be put forward to explain all the observations

and that further experimental data should be collected about the kinetics of the development of domains and the knowledge of flows.

References

1. J. C. MUTIN, Thèse de Doctorat d'Etat, Université de Dijon (1975).
2. G. BERTRAND, M. COMPERAT, M. LALLEMANT, AND G. WATELLE, *Ann. Chim. Fr.*, **4**, 77 (1979).
3. J. M. THOMAS AND G. D. RENSHAW, *J. Chem. Soc. A*, 2749 (1969).
4. W. E. GARNER, "Chemistry of the Solid State," Butterworths, London, (1955).
5. A. P. CHUPAKHIN, N. Z. LYAKHOV, AND V. V. BOLDYREV, *Kinet. Catal. (USSR)* **16**, 1092 (1975); N. Z. LYAKHOV, A. P. CHUPAKHIN, V. P. ISUPOV, AND V. V. BOLDYREV, *Kinet. Catal. (USSR)* **19**, 62 (1978).
6. G. BERTRAND, M. LALLEMANT, D. PINON, AND G. WATELLE, *Mater. Res. Bull.* **12**, 35 (1977).
7. M. G. WIEDEMANN, E. STURZENEGGER, AND G. BAYER, *Therm. Anal.* **1**, 227 (1975).
8. J. D. DANA *et al.* "System of Mineralogy," Vol. 2, p. 487, Wiley, New York, 1951.
9. G. BERTRAND, M. LALLEMANT, D. PINON, AND G. WATELLE, *Rev. Int. Hautes Temp. Refract.* **14**, 167 (1977).
10. J. C. NIEPCE, G. WATELLE, AND N. H. BRETT, *J. Chem. Soc. Faraday Trans. 1* **74**, 1530 (1978).
11. J. C. NIEPCE, M. T. MESNIER, AND D. LOUËR, *J. Solid. State Chem.* **22**, 341 (1977).
12. E. ENGBERG, *Acta Chem. Scand. A* **24**, 3510 (1970).
13. R. K. OSTERHELD AND P. R. BLOOM, *J. Phys. Chem.* **82**, 14, 1591 (1978).
14. F. WATARI, J. VAN LANDUYT, P. DELAVIGNETTE, AND S. AMELINCKX, *J. Solid State Chem.* **29**, 137 (1979).
15. G. BERTRAND, M. LALLEMANT, AND G. WATELLE, *Mater. Res. Bull.* **12**, 115 (1977).