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Crystal defects and dissolution

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Summary

Potassium perchlorate crystals were grown in silica gel by reaction between perchloric acid in the gel and potassium chloride diffusing into the gel from a layer of solution on the gel surface. The crystals were harvested at depths from the surface of 0-1, 2-3, 4-6 cm. X-Ray diffraction and DSC thermograms showed that the crystals were identical and no impurities were detected by X-ray energy analysis. Octahedral crystals were selected, cleaved to expose the (001) plane and etched with a mixture of sodium sulfite and sulfuric acid. The dislocation etch pits were counted under surface illumination using a differential interference contrast microscope. Dislocation densities were approximately normally distributed with the mean densities being greatest at the 0-1 cm level where the growth rate was fastest and lowest at the 4-6 cm growth level where the growth rate was slowest. Bulk dissolution measurements, carried out under sink conditions in 95% ethanol using the USP rotating basket method, showed a positive correlation between the observed dissolution rate constant, K'_{obs}, and the dislocation density. Dissolution rates increased with the number of dislocations such that an approximately 3-fold increase in mean dislocation density produced a 21% increase in K'_{obs}.

Introduction

Crystals are always imperfect in some sense and these imperfections or defects can confer some important chemical and mechanical properties on crystalline materials. Crystal defects can be broadly classified into point and lattice defects. Points defects are localized imperfections and are, in general, thermodynamically stable. They include vacancies (vacant sites in the crystal lattice caused by the absence of atoms) and extra atoms (foreign or of the same species) occupying interstitial or substitutional positions in the crystal lattice. Lattice defects include

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line defects or dislocations and grain boundaries, which are arrays of dislocations. Dislocations are regions within the solid at which the regularly repeating lattice array shows a discontinuity or a distortion from the ideal alignment of units within the crystal. The atoms in this region are therefore not properly surrounded by neighbours. Since the imperfection is contained within a few atomic diameters of a line, it is called a line defect or dislocation (Read, 1953). There are two types of dislocation, the edge dislocation and the screw dislocation which represent, not discrete types, but special orientations. Dislocations have a localized energy associated with them made up of an elastic strain energy and a core energy (Johnston, 1962) and are therefore thermodynamically unstable. The greater chemical potential (or unsaturation) at the dislocation core and the localized energy of dislocations are responsible for enhanced reactivity at dislocation sites over "ideal" sites on the crystal surface.

Many studies have shown a relationship between dislocation content and properties such as dehydration, decomposition, catalytic activity, etc. (see Table 1). Tawashi (1968) suggested that the nature and extent of deviation from perfection can probably explain the anomalies in the observed dissolution rates of certain crystals but no attempt has been made to demonstrate a direct correlation between dislocation content and overall dissolution rates.

The surface layer on a crystal face consists of a set of steps interrupted by kinks and separated by planar portions. Frank (1958) developed an extensive theory whereby dissolution is treated as a process of kink movement along the steps and the progression of unit steps across a face of a crystal. When a receding step reaches the edge of the crystal, it is eliminated. However, where a step terminates at a screw dislocation, it will not be eliminated as the screw dislocation is a source of steps. On a perfect surface, new steps may only by formed by a two-dimensional nucleation process (i.e. the formation of a hole in the crystal surface) and this only occurs if the undersaturation is sufficiently large. If two-dimensional nucleation can occur more rapidly at a dislocation site than elsewhere, an etch pit may form. An etch pit is a steep-sided pit formed by successive nucleation at dislocation sites. The profile of an etch pit depends on the rate at which it deepens by nucleation of steps at the dislocation and the velocity of the steps across the surface. The latter process may be considerably reduced, or even prevented, by crystal "poisons", or etchants, which adsorb onto the surface steps and retard their movement across the surface. The use of etching solutions provides a direct, simple technique for detecting the emergent dislocations on an exposed crystal plane. Several workers have studied the crystal poisoning and subsequent inhibition of dissolution rate by impurities (or poisons) added to the dissolution medium (Piccolo and Tawashi, 1970; Bisaillon and Tawashi, 1976; Magrill, 1975). They suggested that impurities were adsorbed onto the "primary sources" or "active sites" of the crystal surface thus retarding the rate of solute removal from kinks and steps.

The interrelationships between impurities present in the crystal (point defects), dislocations and dissolution kinetics are complex but may be summarized as follows. (i) Impurities can enter into solution and act as a poison thereby decreasing the dissolution rate (self-poisoning) (Sears, 1960; Bundgaard, 1973). (ii) Impurities in

Table 1

Effects of crystal defects on various properties

Property	Crystal	Effect	Reference
Hardness	KBr	Increased growth rate, decreased hardness due to greater number of dislocations [a]	Ridgway and Aulton (1971)
Catalytic activity	LiF	Increased number of dislocations, increased catalytic activity	Hall and Rase (1964)
Phase transitions	Dichlorobenzene	Transition from α to β nucleates at defects	Kitargorodskii et al. (1965)
	Polymorphic changes	Transformation are nucleated at defects [a]	Bryn (1976)
Dehydration	$NiSO_4 \cdot 6H_2O$	Preferential dehydration at emergent dislocations	Thomas and Renshaw (1969)
Decomposition	$CaCO_3$	Preferential decomposition at emergent dislocations	Thomas and Renshaw (1967)
Dissolution	Hydroxyapatite	Preferential dissolution at emergent dislocations	Jongebloed et al. (1974)
	LiF	„	Ives and Hirth (1960)
	$NiSO_4 \cdot 6H_2O$	„	Thomas et al. (1971)
	Aspirin	Variations in overall dissolution due to defects [a]	Pfeiffer (1971); Mitchell et al., (1967, 1971)
	Digoxin	„	Chiou and Kyle (1979)
Electrical properties	Silicon	Defects result in enhanced number of conduction electrons in semiconductors	Moore (1967)
Fluorescence	Anthracene	Defects play a significant role in fluorescence	Helfrich and Lipsett (1965)
Photolysis	Anthracene	Preferential photodimerization at dislocations	Williams and Thomas (1967)
Polymerization	Trioxane	Defects play a significant role in polymerization	Bassett (1967)

[a] Suggested; no direct experimental evidence.

crystals tend to segregate at dislocations and inhibit dissolution (Gilman et al., 1958). Occasionally, impurity atoms enhance dissolution (Johnson, 1962; Ives and Plews, 1965). (iii) Dislocations are thermodynamically unstable, having an associated localized energy which results in an increase in free energy and a reduction in the activation energy for dissolution at points where they emerge on the crystal face. Hence, it may be speculated that a crystal with a higher dislocation density should have a higher thermodynamic activity (i.e. metastable with respect to a crystal with a lower dislocation density) which may result in a greater overall dissolution rate when the process is under surface control. (iv) Crystal defects play an important role in determining the strength of the cohesive forces between the atoms, molecules, etc. The nature and strength of the cohesive forces should therefore affect the crystal dissolution rate.

Studies of the interrelationships between dislocations and dissolution rate may be divided into: (a) those where the importance of defects in the dissolution process has been shown experimentally; and (b) those where the role of defects is suggested but there is no direct experimental evidence (see Table 1).

In the former category, the dissolution kinetics at dislocation sites has been the subject of much research (Gilman et al., 1958; Ives, 1963; Sears, 1960; Ives and Hirth, 1960; Gallily and Friedlander, 1965; Thomas et al., 1971) but there has been no attempt to relate these to the overall dissolution rate of the crystal.

In the latter category, significant differences have been reported in the dissolution rates of various commercial samples of drugs such as aspirin and digoxin (Mitchell and Saville, 1967, 1969; Florence et al., 1976; Florence and Salole, 1976; Chiou and Kyle, 1979). These observations have not, as yet, been fully explained. However, crystal defects have been proposed as a possible cause (see Table 1).

There is evidence that the number of dislocations (or dislocation density) depends on the crystal growth rate. In a general discussion on crystal growth, Garner (1949) and Frank (1949) stated that crystals grow more regularly, the lower the supersaturation (and hence, lower growth rates). A correspondence between growth rate and dislocation density has been shown for crystals of triglycine sulfate (Izrael et al., 1972), calcium tartrate (Henisch et al., 1965), and potassium perchlorate (Patel and Rao, 1979).

Lieu et al. (1976) prepared 3 sets of barium sulfate crystals under differing conditions for dissolution studies. They found that there was a 3-fold difference in surface area between two sets of crystals but a corresponding 12-fold difference in the surface reaction rate constant. They concluded that the different crystals may contain quite different numbers of "active sites" per unit area for growth or dissolution. If it can be assumed that "active sites" are crystal defects, then the observed differences in the rate of the surface reaction may be due to different numbers of defects present in the two sets of crystals. However, the authors made no attempt to quantify the number of "active sites".

Although the relationship between growth rate and defect content of crystals is well established, studies are required to correlate defect content with overall dissolution rates.

The approach in this work was to grow crystals at different rates, determine the number of dislocations at each growth rate and then correlate the dislocation density with subsequent dissolution rates.

Potassium perchlorate ($KClO_4$) was chosen as a model crystalline material since large, well-formed crystals could be grown in silica gel with relatively low dislocation densities, the crystals could be easily cleaved along the (001) cleavage plane, and a suitable etching solution has been reported (Patel and Rao, 1979).

Materials and methods

Gel growth of potassium perchlorate crystals

Single crystals of $KClO_4$ were grown in a silica gel medium according to a method described by Patel and Rao (1977, 1978, 1979).

A solution containing 13 g sodium metasilicate (certified A.C.S., Fisher Scientific) in 100 ml distilled water was filtered through Whatman's No. 1 filter paper and 20 ml placed in glass tubes 20 cm in length and 2.5 cm internal diameter. Two drops of glacial acetic acid (reagent A.C.S., Allied Chemicals, Canada) were added to the gelling solutions from a Pasteur pipette, 10 ml 1 N perchloric acid (Analytical reagent, Mallinckrodt) was added and the solutions were mixed on a vortex mixer. The addition of the acetic acid decreased the final pH of the gelling solutions from about 6.9–4.5 and increased the transparency of the gels. The tubes were kept at 30°C in a constant temperature water-bath (Magni Whirl Blue M Electric) for 24–48 h which allowed the solutions to gel. Approximately 30 ml of 1 N potassium chloride (Analytical reagent, British Drug Houses) was carefully placed on the surface of the gels which were kept at 30°C for a further 7–10 days during which time well-formed single crystals of $KClO_4$ grew throughout the length of the tube.

Harvesting of crystals

The tubes were marked off from the gel-solution interface in 1 cm increments down the length of the gel columns. Crystals from each growth level (i.e. 0–1 cm, 1–2 cm, 2–3 cm, etc.) were removed and placed in beakers. The crystals were separated from the gel by repeated washings in water. After air-drying at room temperature the crystals at each growth level were stored in tightly stoppered glass jars.

Crystal characterization

Crystal defects

(a) Cleaving and etching

Crystals with the octahedral habit shown in Fig. 1 were cleaved by placing a scalpel blade perpendicular to the (210) face and tapping sharply on the upper edge of the blade. This exposed the (001) plane of the crystal. The crystals were etched by swirling gently in a mixture of 5 ml 0.25 M sodium sulfite (Baker analyzed, J.T. Baker Chemicals) and 5 ml concentrated sulphuric acid (reagent grade, American Scientific and Chemicals). The crystals were etched for 3 min followed by washing in ether for 1 min.

(b) Microscopy

A net graticule marked off in 100 squares was placed in the eyepiece of a surface illumination, differential interference contrast microscope (Model R, Nikon). The etched (001) plane of the crystal was viewed and the number of dislocation etch pits noted in the squared graticule. The dislocation etch pits over the whole area of the (001) plane were counted. The etch pits on 12–17 crystals from 3 different growth

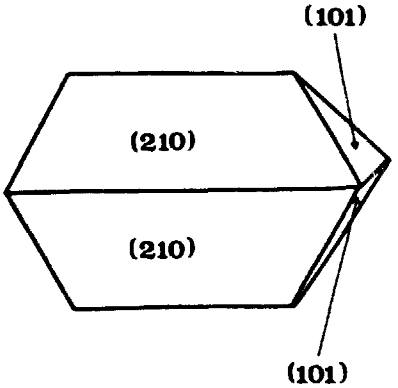


Fig. 1. Diagram of a single $KClO_4$ crystal showing the geometry and position of crystal faces, characterized by their Miller indices.

levels (0–1, 2–3 and 4–6 cm) were counted. The lengths of the edges of the exposed (001) plane were measured using a travelling microscope and the area of the plane calculated. Hence the dislocation density (number of dislocations per cm^2) was determined.

X-Ray diffraction

Approximately 300 mg of the ground samples of $KClO_4$ from growth layers 0–1, 2–3 and 4–6 cm was exposed to CuKα radiation in a wide-angle X-ray diffractometer (Philips). The location and intensity of the peaks at different values of 2θ were studied.

X-Ray energy analysis

Octahedral crystals of $KClO_4$ from the 0–1 and 4–6 cm growth levels were coated with spectrographic graphite. The crystals were placed in the specimen holder of a scanning electron microscope (ETEC, Autoscan) connected to an X-ray energy analyzer (ORTEC, Model 6200). X-Rays in the 0–20 keV energy range were analyzed.

Thermal analysis

Thermal analysis was performed using a differential scanning calorimeter equipped for effluent gas analysis (Perkin Elmer DSC-1B). Crystals were ground in a glass pestle and mortar and 1–5 mg samples were weighed using a Cahn Gram electrobalance directly into aluminum sample pans. The scanning rate was varied and open pans and volatile sample pans with a pinhole were used.

Solubility determination

After grinding, excess amounts of potassium perchlorate from the three different growth levels were equilibrated with 95% v/v ethanol by rotation in a water bath thermostatically controlled at 10.5°C. Samples were filtered using a syringe fitted with a Millipore filter and after appropriate dilution, were analyzed for potassium content using atomic absorption spectrophotometry.

Surface area

The octahedral habit of $KClO_4$ has regular, well-defined crystal faces. The dimensions of each face were measured using a travelling microscope (Swift and Son) reading to $\pm 5.0 \times 10^{-4}$ cm and used to calculate the total surface area.

Bulk dissolution of potassium perchlorate crystals

The bulk dissolution rate of crystals grown at the 0–1, 2–3 and 4–6 cm growth levels was determined using the U.S.P. dissolution apparatus as described previously (Burt and Mitchell, 1980). For each dissolution experiment between 7 and 11 crystals were taken to give approximately constant weights and surface areas. Before each dissolution experiment, the crystals were washed in 5 ml of 95% v/v ethanol for 30–60 s to remove surface particulate matter and then dried and weighed. 800 ml of 95% v/v ethanol was placed in the 1000 ml glass vessel and equilibrated at 10.5°C in a constant temperature bath.

The crystals were placed in the wire basket, lowered into the dissolution medium and rotated by means of a constant speed motor (Fisher Stedispeed Stirrer). The rotating velocity (in rpm) was measured using an electronic stroboscope (Flash Tac, Electronic Applications) and constant checks on the rotating velocity were made throughout the dissolution trial.

2.5 ml samples of the dissolution medium were removed from a point 4–5 cm below the surface of the dissolution medium at suitable time intervals, made up to 5 ml with a solution of $2\ \mathrm{mg \cdot ml^{-1}}$ cesium in water and stored in airtight, borosilicate glass vials prior to analysis. At the end of each experiment, the crystals were reweighed and the weight loss during dissolution used as a mass belance check. Dissolution was followed at a rotation speed of 500 rpm for 120 min during which time there was negligible change in surface area.

Analysis of dissolution medium

Samples were analyzed for their potassium content using a K-hollow cathode lamp (Cathodeon Ltd.) and an atomic absorption spectrophotometer (Varian Techtron, Model 4).

Potassium is partially ionized in the air–ethyne flame and to suppress ionization an excess of cesium chloride (to give a final concentration of $1\ \mathrm{mg \cdot ml^{-1}}$ Cs) was added to all solutions. The samples were vaporized in an air–ethyne mixture flame and absorbances measured at a wavelength of 766.4 nm with a slit width of 100 μm and lamp current of 5 mA.

Results and discussion

X-Ray diffraction patterns for the octahedral crystals grown at the 0–1, 2–3 and 4–6 cm growth levels were identical with each other; all d values were characteristic of $KClO_4$ (Selected Powder Diffraction data, 1974).

Thermal analysis results are given in Table 2. On heating the samples, only one endothermic peak was observed at 311°C or 306°C depending on whether a closed pan with pinhole or an open pan was used. $KClO_4$ does not form hydrates (Whaley,

Table 2

Thermal analysis of $KClO_4$ crystals

Habit	Gel growth level (cm)	Endothermic peak maximum °C (scanning rate °C/min) [a]	Exothermic peak maximum °C (scanning rate °C/min) [b]
Mixed P	0–1	311 (20)	
Cubic P	0–1	311 (20)	
Cubic O	0–1	306 (20)	
Octahedral O	0–1	306 (20)	
Octahedral O	4–6	306 (20)	281 (20)
Octahedral O	4–6	306 (20)	284 (10)
Octahedral O	4–6	306 (20)	286 (5)

P, closed pan with pinhole; O, open pan

[a] Increasing temperature; [b] decreasing temperature.

1973) and this was confirmed experimentally as no weight loss occurred on heating the samples to 500°C. All samples showed identical thermograms. The endothermic peak corresponds to an enantiotropic, polymorphic phase transition from the orthorhombic form to a cubic, high temperature form (Donnay and Ondik, 1973; Barin and Knacke, 1973). Cooling the samples from 320°C resulted in an exothermic peak between 281–286° depending on the cooling rate, demonstrating the reversibility of the phase transition.

Impurities incorporated into the crystal during growth can exert a profound influence on the dissolution kinetics. Therefore the octahedral crystals were analyzed for possible impurity content by X-ray energy analysis. X-Ray energy spectra for crystals from the 0–1 and 4–6 cm growth levels showed only energy peaks characteristic of $KClO_4$.

The etchant mixture of concentrated sulphuric acid and 0.25 M sodium sulfite was developed for $KClO_4$ crystals by Patel and Rao (1979). They demonstrated the reliability of the etchant for revealing dislocations in the following ways: (a) there was a one-to-one correspondence between the etch pits on the opposite halves of a cleaved crystal, showing that the etch pits corresponded to line defects that were present in the crystal prior to cleavage; and (b) the etch pits grew bigger and deeper on successive etching implying that the etching was proceeding along line defects.

A further experiment was carried out to verify the findings of Patel and Rao (1979). The etch pit distributions on the cleaved, etched surfaces of $KClO_4$ crystals were noted. The surfaces were then polished by exposure to water for 2–3 min, to produce a smooth surface free of etch pits. After re-etching, the etch pit distribution on each crystal plane closely resembled the distribution previously noted for the plane.

The etch pits were typically of a hexagonal shape, and were pointed or flattened at the apex (see Fig. 2).

It is possible to estimate the maximum dislocation density that can be resolved with the various detection methods. For the etch pit method (using an optical

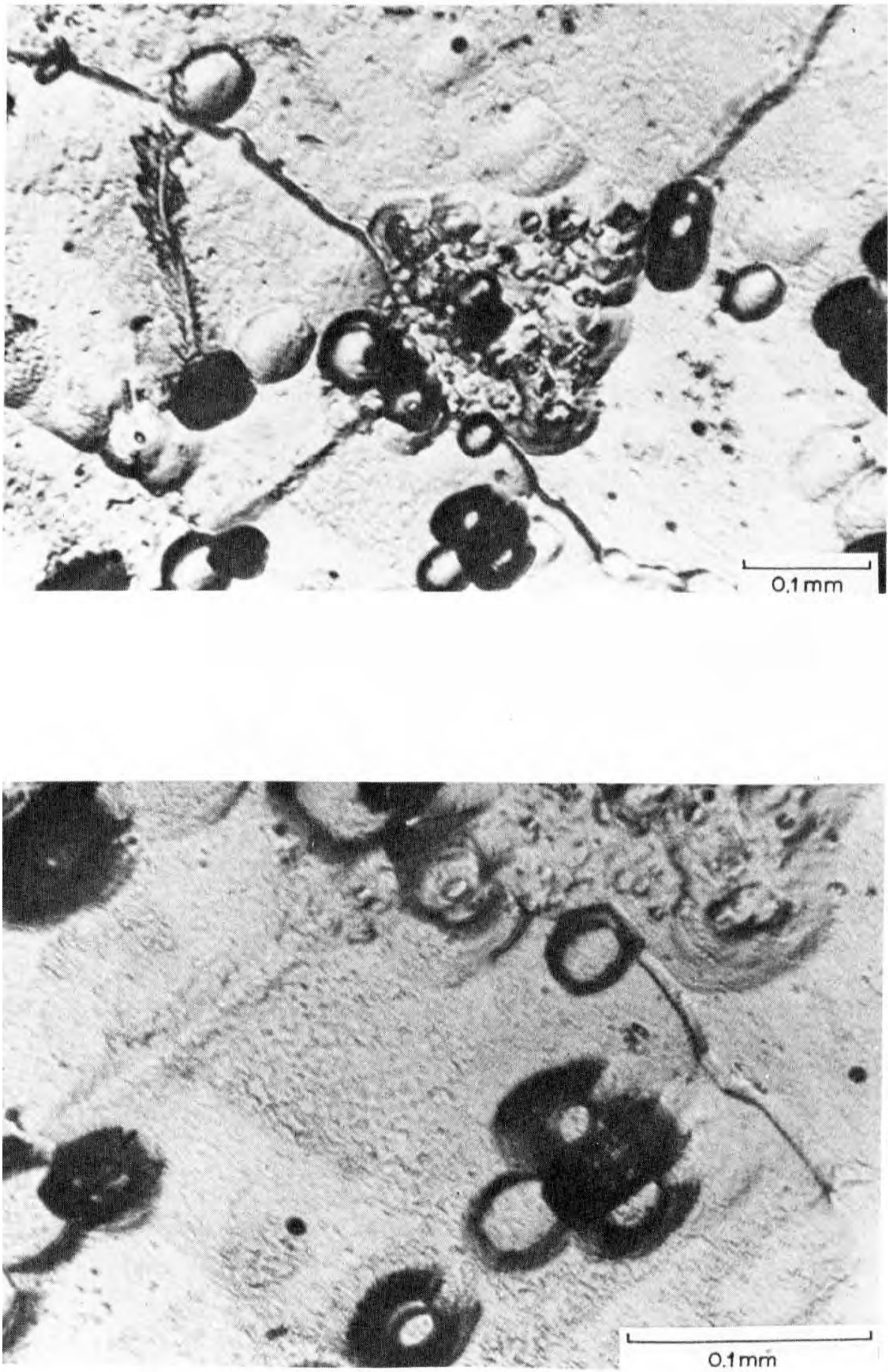


Fig. 2. Dislocation etch pits on the cleaved and etched (001) plane of $KClO_4$.

microscope) the maximum dislocation density is approximately 4×10^8 cm^{-2}. The dislocation densities of the gel-grown $KClO_4$ crystals were several orders of magnitude below this value.

It was observed on all cleaved and etched crystals that at the point at which pressure from the scalpel blade had been applied during cleavage, a small cluster of densely packed dislocation etch pits was present. Since these etch pits were largely a result of the cleaving process, they were not included in the count of dislocation density.

Fig. 3 shows the number of $KClO_4$ crystals falling within a given dislocation density range for the 0–1, 2–3 and 4–6 cm growth levels. The average crystal growth rate is greatest near the top of the gel column where the concentration gradients are high (0–1 cm growth level) and smallest near the bottom where the concentration gradients are low (4–6 cm growth level). The dislocation densities are approximately normally distributed, the mean density being shifted to lower values, the lower the rate of growth (see also Table 3). The range of the distribution of dislocation densities at each growth level also decreases as the growth rate is decreased. All crystals had a dislocation density of between $10^3 - 2 \times 10^4$ cm^{-2}. This density range is relatively low, since the as-grown density for non-metallic crystals is usually in the range of $10^4 - 10^6$ cm^{-2} (Johnston, 1962). However, growth in gels enables a high degree of structural perfection to be achieved. From observations of the growth process, it has been tentatively concluded that there exists in the immediate neighbourhood of the crystal surface, a supersaturation which remains

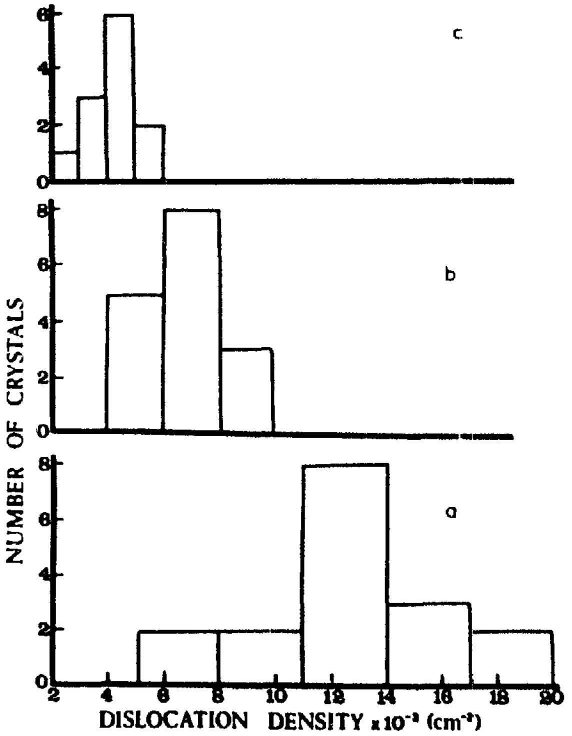


Fig. 3. Number of $KClO_4$ crystals with a given dislocation density range from the (a) 0–1 cm, (b) 2–3 cm and (c) 4–6 cm growth levels.

Table 3

Dislocation densities, solubility, surface areas and dissolution rate constants for $KClO_4$ crystals

Growth level (cm)	Dislocation density (cm^{-2}) Mean[a] ± 1 S.D.	C_s (10.5°) ($mg \cdot cm^{-3}$)	S[b] (cm^2)	$K'_{obs} \times 10^3$ ($cm \cdot s^{-1}$)	
					Mean
0–1	12,371 ± 3,785	0.203	1.4–1.7	2.77	
				2.66	2.64
				2.50	
2–3	6,633 ± 1,476	0.203	1.0–1.6	2.62	
				2.44	2.47
				2.34	
4–6	3,668 ± 902	0.203	1.4–1.6	2.41	
				2.21	2.19
				2.11	
				2.04	

[a] Mean of 12–17 determinations.

[b] Between 8–11 crystals for each experiment.

constant during growth. The gel also supports the crystal and, at the same time, yields to its growth without exerting major forces upon it. This relative freedom from constraint and the stable pattern of concentration gradients are important factors in the achievement of high structural perfection in the crystals. Another important function of the gel is that of suppressing nucleation thereby reducing the competitive nature of growth.

Several workers have shown that the dislocation density increases as the supersaturation (and hence the growth rate) is increased, for a variety of crystalline materials. However, the validity of the conclusions reached in a number of these studies is questionable. Patel and Rao (1979) reported that the dislocation density of $KClO_4$ crystals grown in silica gels decreased with the depth below the gel-solution interface (i.e. decreasing growth rate). Their observation was based on a single density measurement at depths in the gel only 0.4 cm apart. This study shows there to be a considerable range in dislocation density, e.g. between 5000 and 20,000 cm^{-2} for crystals grown at a depth of 0–1 cm. Henisch et al. (1965) counted the number of etch pits on crystal faces of calcium tartrate. No details of the etchant used were given and no experiments to establish its reliability for revealing dislocations were carried out. In addition, etching techniques are usually done on clean, cleavage planes and not on crystal faces.

The overall bulk dissolution rate of the octahedral crystals may be described by Eqn. 1:

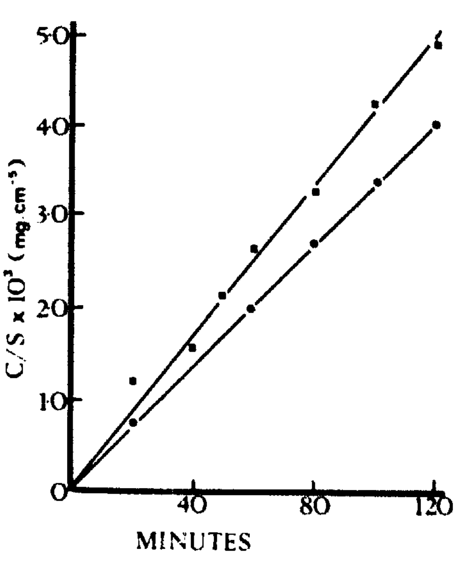
$$\text{rate} = S \cdot K'_{obs}(C_s - C) \qquad (1)$$

where S is the total surface area of the crystals, C_s is the equilibrium solubility in the diffusion layer at the solid–liquid interface, C is the concentration in the bulk solution at time t and K'_{obs} is an observed rate constant. Dissolution occurred under sink conditions since at no time did the concentration of $KClO_4$ exceed 3.9% of its saturation solubility. When $C_s \gg C$ and S is constant, the overall dissolution rate is proportional to an observed rate constant, K'_{obs}. Fig. 4 shows typical plots of concentration change/S with time for the octahedral crystals at different growth levels. The slopes ($mg \cdot cm^{-3} \cdot s^{-1}$) were determined using linear regression analysis and were used to calculate K'_{obs} ($cm \cdot s^{-1}$) from the relationship:

$$K'_{obs} = \frac{\text{slope} \cdot V}{C_s} \tag{2}$$

where V is the volume of dissolution medium. Values of C_s and S for the crystals grown at three growth levels are given in Table 3. Due to the size differences between crystals, the total surface area for different dissolution experiments varied between the ranges given in Table 3.

Values of K'_{obs} determined at the 3 growth levels, 0–1 cm, 2–3 cm and 4–6 cm are given in Table 3. Fig. 5 shows a plot of the mean and the range of K'_{obs} as a function of the mean dislocation density ± one standard deviation. K'_{obs} increases with increasing dislocation density, such that an approximately 3-fold increase in mean dislocation density produces a 21% increase in K'_{obs}, between crystals grown at the lowest and highest growth rates. An analysis of variance of the data is shown in Table 4. The two sources of variation are between K'_{obs} at each growth level and between K'_{obs} at different growth levels. Since there are 3 values of K'_{obs} at the 0–1 cm and 2–3 cm growth levels and 4 at the 4–5 cm growth level, one observation was dropped from the latter group for the analysis of variance. The exclusion of the K'_{obs} value of 2.21×10^{-3} $cm \cdot s^{-1}$ did not change the mean and the range of the K'_{obs} data at the 4–6 cm growth level. The ratio of the two variances, *F*, equal to 5.99, was



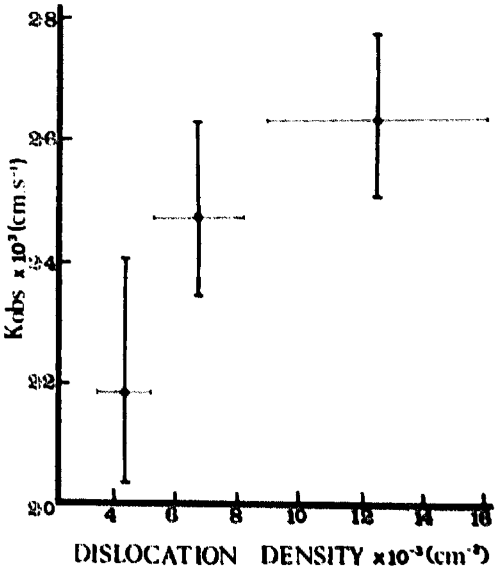


Fig. 4. Plot of concentration in the bulk/surface area versus time for $KClO_4$ crystals at 10.5°C and a rotation speed of 500 rpm. Growth levels: ■, 0–1 cm; ●, 4–6 cm. Lines fitted by linear regression analysis.

Fig. 5. Plot of mean K'_{obs} as a function of the mean dislocation density for $KClO_4$ crystals. Horizontal bars indicate ± 1 S.D. of dislocation densities. Vertical bars indicate the range of K'_{obs}.

Table 4

Analysis of variance of K'_{obs} data for $KClO_4$ crystals grown at different growth levels

Source of variation	Sums of squares	Degrees of freedom	Mean square (variance)
Between growth levels	3.2×10^{-7}	2	1.6×10^{-7}
Between K'_{obs}	1.6×10^{-7}	6	2.67×10^{-8}
Total	4.8×10^{-7}	8	-

tested against the $F(2,6)$ ($P = 0.05$) distribution. This gave a significant result at $P = 0.05$, i.e. the mean K'_{obs} for the different growth levels are different. The least significant difference (LSD) at a 5% level of significance was obtained to determine where these differences lie. Two means are significantly different if the absolute difference between the two means is greater than the LSD. The calculated LSD (0.05) was 3.25×10^{-4} and the following conclusions may be drawn: (a) there is no significant difference between mean K'_{obs} at the 0–1 cm and 2–3 cm growth levels; (b) there is no significant difference between mean K'_{obs} at the 2–3 cm and 4–6 cm growth levels; and (c) the mean K'_{obs} at the 0–1 cm and 4–6 cm growth levels are significantly different ($P = 0.05$).

It is well known that impurities (point defects) and differences in the crystalline characteristics of a solid, e.g. its polymorphic form (Milosovich, 1964), degree of solvation (Shefter and Higuchi, 1963) and degree of crystallinity (Florence and Salole, 1976) may exert a significant effect on the dissolution rate. X-Ray diffraction and thermal analysis showed that the crystals from the different growth levels were identifical in their chemical and crystalline characteristics. No impurity peaks were observed from X-ray energy analysis, although this technique would not detect trace amounts of impurities. Nevertheless, it is unlikely that impurities were responsible for the observed differences in K'_{obs} for crystals grown at different levels. Since crystals grown at faster rates incorporate more impurity atoms than crystals grown at slower rates, crystals from the 0–1 cm level might be expected to contain a higher concentration of impurities than crystals from the 4–6 cm level (Malicsko and Szomor, 1971; Izrael et al., 1972; Brooks et al., 1968). This would most likely result in inhibition of the dissolution rate for the crystals from the 0–1 cm growth level and K'_{obs} for the 0–1 cm level crystals would be lower than K'_{obs} for the crystals from the 4–6 cm growth level. The results indicate that this is not the case.

Crystals with a higher dislocation density will have a higher thermodynamic activity relative to crystals with a lower dislocation density, due to the localized energy associated with dislocations. This results in a greater overall dissolution rate as shown by the data in Table 3 and Fig. 5. Although no attempt was made to determine the rate-controlling step in the dissolution reaction, the very low solubility of the $KClO_4$ crystals in the dissolution medium and the high rotation speed would indicate a surface-controlled process. It is unlikely that differences in K'_{obs} would be observed where dissolution was transport controlled. Although the difference in mean dislocation densities in crystals grown at the 0–1 cm level and the 4–6 cm levels is relatively small, it has a significant effect on dissolution rate.

Conclusions

(1) $KClO_4$ crystals grown at different rates in silica gel showed identical X-ray diffraction patterns and DSC thermograms and therefore have the same crystal structure.

(2) X-Ray energy spectra showed only energy peaks characteristic of $KClO_4$, no impurities being detected.

(3) Crystals grown at the highest growth rate (0–1 cm level) had the highest mean dislocation density and those grown at the slowest rate (4–6 cm level) showed the smallest mean dislocation density.

(4) The observed dissolution rate constant for crystals from the 0–1 cm level was greater than for crystals from the 4–6 cm level.

(5) In this simple, inorganic model system, the incorporation of a greater number of crystal defects during growth, has a significant effect on the bulk dissolution rate measured under conditions where the surface reaction contributes to the overall dissolution process.

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