CRYSTAL DISLOCATIONS AND DISSOLUTION

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The effects of polymorphism, solvation and degree of crystallinity on dissolution are well documented but the effects of other properties of the solid state have received little attention. This work investigates the relationship between crystal dislocations and dissolution using potassium perchlorate as a model solid.

Crystals were grown in silica gel by reaction between perchloric acid in the gel and potassium chloride diffusing into the gel from a solution on the surface. The crystals were harvested at depths of 0-1, 2-3, 4-6 cm. X-ray diffraction and DSC thermograms showed that the crystals were identical. Crystals were cleaved to expose the (001) plane, etched with a mixture of sodium sulfite and sulfuric acid, and the dislocation etch pits counted under surface illumination using a differential interference contrast microscope. Dislocation densities were 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 that an approximately 3-fold increase in mean dislocation density produced a 21% increase in the observed dissolution rate constant, K_{obs}, Table 1.

Additional crystals from the 1-4 cm growth level were divided into three groups; one was retained for control experiments and the other two groups were subjected either to mechanical stress or thermal stress. Mechanical stress was applied in a punch and die assembly by compression of the parallel (210) faces of the crystal using a 1.5 Kg weight. The number of dislocations was increased by a factor of approximately 70 and was accompanied by a 40% increase in K_{obs}, Table 1. Thermal stress was effected by heating the crystals in a differential scanning calorimeter to 200°, holding the temperature for 15 minutes followed by rapid cooling. Despite a 6-fold increase in the number of dislocations there was no significant increase in dissolution rate, Table 1.

Table 1. Dislocation densities and dissolution rate constants

	Dislocation density (cm^{-2})	$K_{obs} \times 10^3$ at 10.5° ($cm.s^{-1}$)[a]	Increase in K_{obs} (percent)
Effect of growth rate[b]			
4-6 cm growth level	3,668±902[d]	2.19	control
0-1 cm growth level	12,371±3,785[d]	2.64	21
Effect of stress[c]			
none	≃3,500[e]	2.04	control
thermal	≃22,000[e]	2.20	7.8
mechanical	≃250,000[e]	2.86	40

[a] mean of 3 determinations; [b] grown at 30° x 7-10 days; [c] grown at 25° x 7 days; [d] mean of 12-17 determinations ± 1.S.D.; [e] mean of 6 determinations.

A correlation between enhanced reactivity and dislocation density shown by crystals grown at different growth rates and the mechanically stressed crystals, can be attributed to the lowering of the free energy of activation at emergent dislocations from their values at the ideal crystalline surface (Tompkins 1976). The absence of a significant increase in K_{obs} with the increase in dislocation density for the thermally stressed crystals may be attributed either to polygonization or to homogeneous redistribution of solute impurity atoms in the crystal. Both effects can occur on heating (Johnston 1962; Nembach 1975) and lead to a reduction in the energy per dislocation. The results show that dissolution rate depends on the number of dislocations incorporated into the crystal during growth and also illustrate some of the complex effects crystal treatment has on dislocation density and dissolution rate.

Johnston, W.F. (1962) Progress in Ceramic Science Vol.2, p.62, Pergamon, New York
Nembach, E. (1975) Treatise on Solid State Chemistry Vol.2, p.500, Plenum, New York
Tompkins, F.C. (1976) ibid, Vol.4, Reactivity of Solids, p.193.

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