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The influence of mechanical stress on the growth of crystals

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ABSTRACT

A review is presented of the author's recent work on the influence of mechanical stress on the growth rate of materials. On the basis of the results, it is proposed that growth rate dispersion of secondary nuclei arises as a result of competition between stress reduction and dislocation enhancement of growth rates in the developing particles, with the former being the major influence at low particle sizes. The results are shown to account for the particle size and material dependence of the dispersion. Mechanistic studies suggest that the principal mechanism of stress reduction in growth rate is the influence of the applied stress on the surface free energy of the crystal. This effects both nucleation at the growth centre and the migration of growth steps across the crystal surface.

Keywords: Solution growth, growth inhibition, secondary nucleation, dislocations, lattice strain.

1. INTRODUCTION

The phenomenon of growth rate dispersion in crystals formed following secondary nucleation by attrition fragment in industrial crystallisers, causes considerable difficulties in the specification of operating parameters and the prediction of the size distribution of the product particles[1]. Why such crystals should exhibit a wide range of growth rates from zero to some maximum value is not fully understood[2].

Studies of the problem suggest that the cause lies in the structure of the growing particle, all other parameters such as supersaturation, agitation, temperature, etc being controllable[3-5].

Attrition can be regarded as a fracture process preceded by deformation. The nature of the deformation process will vary depending on the nature of the material. A brittle solid will deform elastically to fracture possibly retaining some degree of elastic strain. A plastic solid will undergo successively; elastic deformation, plastic deformation and finally fracture to yield a particle with an increased mechanically induced dislocation content compared with the original particle and possibly some residual strain. Additionally, as has been proposed previously[6], the fracture particles may also contain varying numbers of dislocations due to the non-uniform distribution of growth dislocations in the original particle. In order to assess whether or not these varying properties do influence the growth process, we have examined the influence of stress on the growth of brittle and ductile materials in the macro- and micro-crystalline forms[7-12].

A suitable starting point for this review is the data obtained from our preliminary study of secondary nucleation in sodium chlorate[7]. This is presented in Figure 1 in a form that encapsulates some of the various features of growth rate dispersion. From this, we note that:

a)   growth rate dispersion is greatest at small sizes;

b)   it is at the lower end of the size range that zero growth rates are encountered; and

c)   the data points appear to converge to a more constant value at sizes approaching some critical size (in this case 100 – 150 μm)

A further consideration in the interpretation of Figure 1 is that examination of the growth of larger sized crystals of sodium chlorate (200-20.000 μm) has revealed an average growth rate of 3.5×10^{-8} ms^{-1} which provides an approximate convergence limit to the spread of points on Figure 1. This result is consistent with the general observations of a decrease in the range of growth rate dispersion with increasing particle size.

The obvious conclusion that can be derived from the data presented in Figure 1 is that we require to define the nature of processes that cause:

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- growth rate enhancement to yield the growth rates in the upper part of the range, and
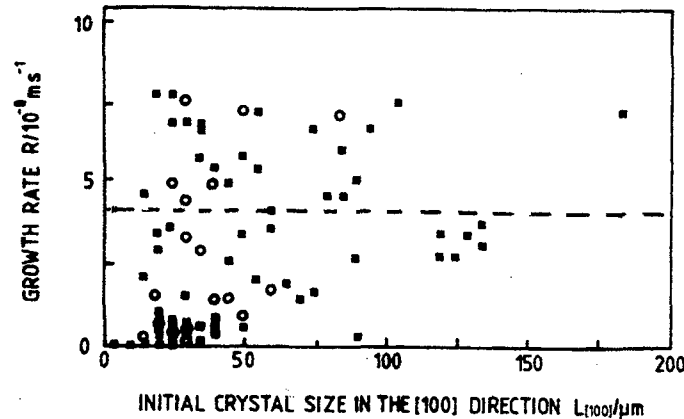- growth rate suppression for growth rates below this level.

Fig. 1.The variation with initial crystal diameter of the rate of growth of sodium chlorate microcrystals in the [100] direction at supersaturation $\sigma = 0.35\%$. The dotted line represents the average growth rate (3.5×10^{-8} ms^{-1}) of larger crystals in the size range 200-20000 μm.

The latter should be capable of yielding zero growth rates under extreme conditions. The combination of the two effects should lead to a decrease in dispersion with increasing particle size to yield the average growth rate for the larger particles.

2. DISLOCATION ENHANCEMENT OF GROWTH RATES

The role of dislocations as growth sources is well defined through both the original theoretical work of Burton, Cabrera and Frank[13] and those who followed them, also from the multitude of subsequent experimental examinations devised to test these theories. There are three potential sources of the growth dislocations that might influence the subsequent growth of an attrition particle.

a) from the attrition nucleus and which develop into the new crystal;
b) from the area of refacetting of the fractured interface. This area is always heavily strained and dislocations could form readily and propagate from this volume into the growing sector;
c) by contact of the particle with other particles in solution during growth;
d) by plastic deformation of the particle during the attrition process.

The first process has been defined to occur[14,15] but we find that, all too often, dislocations in the seed terminate in the strain that is located at the newly developing interface[9]. Only under conditions of most careful regeneration can they be encouraged to persist. Even then, the numbers that do propagate are too low to make a major influence on the eventual growth rate of the developing crystal. We feel therefore that this potential source can be eliminated as a major contributor.

From our own work[10], Fig. 2 defines the second process. Fig 2a shows an X-ray topograph16 of a ($0\overline{1}1$)slice of a potash alum crystal which has been grown following cutting to show the development of both the interface and the lateral (100) growth sectors. The seed was immersed in a stirred, saturated solution following which the supersaturation was developed by lowering the temperature. Growth took place at the dark volumes XX' which represent the strain developed in the vicinity of the {100} interfaces during the refacetting process. Dislocations generate from this volume and propagate into the {100} sectors. Studies of the subsequent growth rates as a function of the number of dislocations developed yielded the variation shown in Fig. 2b. This confirms that variable numbers of growth dislocations can be generated on refacetting a fractured interface and that these lead to variation in growth rates.
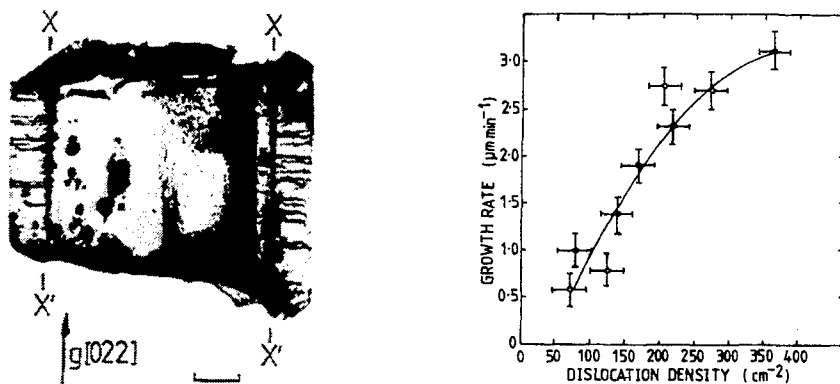
Fig. 2. X-ray topograph of a thin ($0\bar{1}1$) slice of a potash alum crystal regrown to show the development of dislocations in the{100} sectors. The dark line XX' represents the strain developed at the refacetted interface. Dislocations can be seen to develop from this volume. Some of these become refracted into adjacent sectors as growth proceeds. Others continue to propagate towards the growing interface .The relationship between growth rate at constant supersaturation, σ = 6.4%, and dislocation density for the {100}sectors of potash alum .

Equally important to dislocation enhancement is the consequence of collisions between the particles in solution. This process is particularly effective when smaller colliding particles adhere to the surface of a principal particle. The subsequent overgrowth can result in the formation of additional mismatch dislocations and lead to an overall enhancement of growth rates[17]. Alternatively, variable numbers of mechanical dislocations can be produced as a consequence of the degree of plastic deformation that results in the impacted and fractured crystal. In some circumstances, these can develop as growth dislocations and influence the growth rate[12].

It is obvious that the noted variations in growth rate could result from any of these sources and that they could yield a range of growth rates sufficiently variable to yield a wide dispersion. What we cannot assume, however, is that their absence would yield a zero growth rate. There are well – defined mechanisms of crystal growth which allow growth on dislocation-free crystals[18,19]. Thus we can only expect that dislocation based processes will provide a dispersion which will range from some minimum to a maximum value. For the suppression of growth, and particularly zero growth we must look to the influence of lattice strain on the growth process.

3. STRAIN REDUCTION OF GROWTH RATES

3.1 Large Crystals (~ 1cm dimension)
In order to assess the influence of strain on crystal growth, large specimens were mounted in a growth cell furnished with a means of straining the crystal during the growth process[12]. The result of this procedure is shown for the{100} habit faces of potash alum in Fig. 3.

This confirms that the growth rate decreases on straining and is recoverable on removing the stress. It can be also restored to the original growth rate by an increase in supersaturation. Hence the process is reversible provided that plastic deformation does not occur. Application of a high tensile stress resulted in a decrease I growth rate to zero.

Extension of the experiments to other materials showed, as might be expected, that the magnitude of the effect depended on the mechanical nature of the material[8]. Potash alum is a brittle material of low plasticity and tensile extension of this material yields the formation of only small numbers of mechanical dislocations. In contrast, and under similar conditions, sodium chlorate, which is even more brittle fractures before plastic deformation occurs, undergoes a more significant reduction in growth rate when the stress is applied[20].

This progression was underscored by further studies of sodium nitrate. On extension, this ductile material does not show the sudden changes in growth rate of the two previous materials. A more gradual change occurred which was followed by partial recovery as the material plastically deformed (Fig. 4).
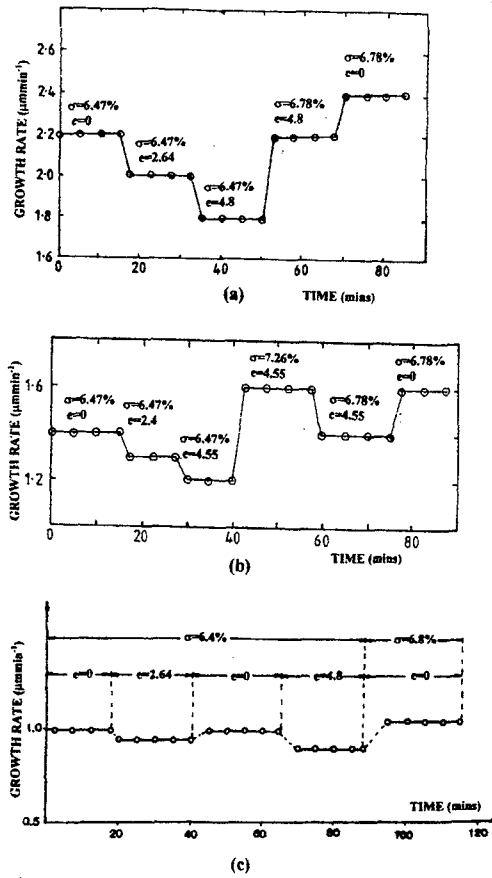
Fig. 3. The influence of tensile microstrain (e) and supersaturation (σ) on the growth rates of the (a) {100}, (b) {110}, (c) {111} faces of potash alum single crystals as a function of time.
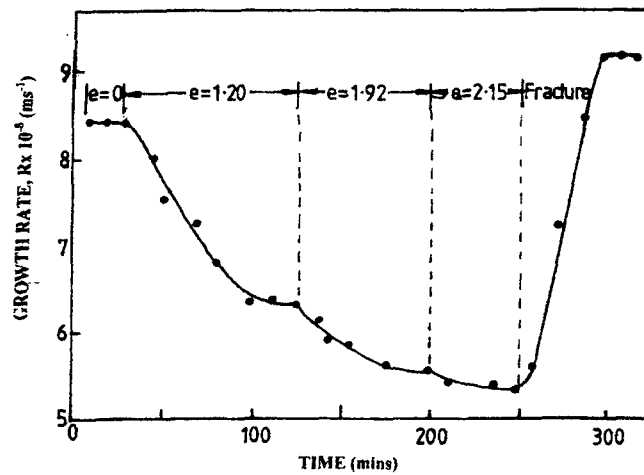

Fig. 4. The influence of successive applications of tensile microstrain (e) on the growth rate of sodium nitrate single crystals (σ = 0.4%)
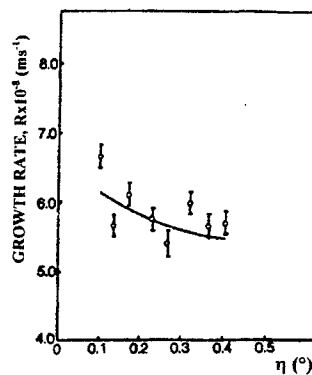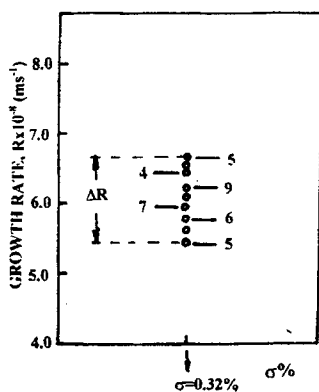
In summary, our studies of the influence of tensile strain on the growth rates of large crystals show a reduction of growth rate with increasing strain and zero growth under high strain conditions. They also indicate that the degree to which the reduction occurs is highly dependent on the brittle/plastic nature of the material.
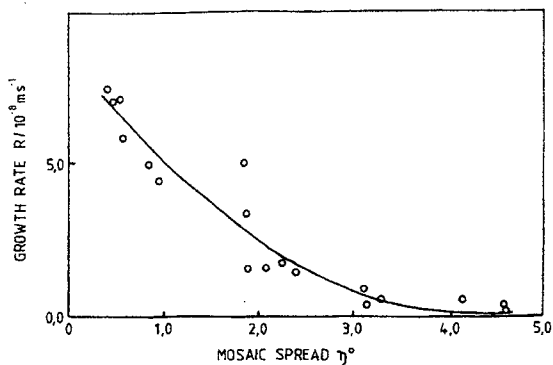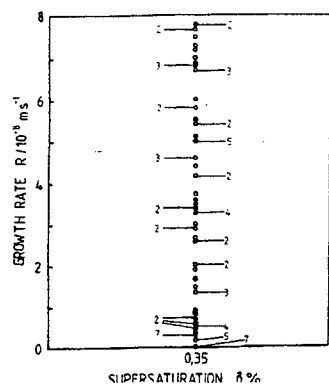
(a)
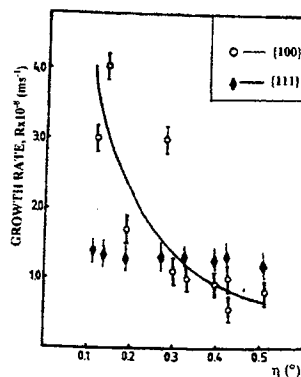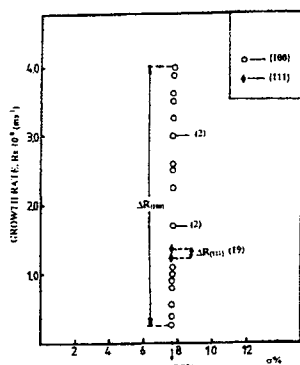
(b)

(c)

Fig. 5.Graphs showing the growth rate dispersion of microcrystals of Sodium chlorate, {100} faces, (b) Potash alum, {100} and {111} faces and (c) Sodium nitrate {104} faces at constant supersaturation (left hand column) together with graphs showing the relationship between the growth rates and integral strain in the particles (right hand column). The strain is expressed as mosaic spread η.

3.2 Microcrystals (~ 50-100 μm dimension)

The above variations refer to the behaviour of crystals some 200 times larger than those usually formed in industrial crystallisers. The question that must be answered is whether or not the same philosophy can be applied over the smaller size range more characteristic of the industrial product. Whilst there is no problem in assessing the growth rates of such crystals, it might be anticipated that the measurement of strain could present some difficulties. Happily, with the advent of large synchrotron sources producing polychromatic X-ray beams of high intensity, low divergence and high collimation, methods are now available[4,21] for the assessment of the integral strain in very small crystals (>100 μm) from the asterism which induced strain causes in Laue diffraction patterns[22].

Measurements of growth rate dispersion on our three chosen materials are presented in Fig. 5, together with the relationships in each case between the growth rate and the mosaic spread of the crystal. There is a distinct correlation between the growth rates and the mosaic spread (induced strain). Immediately noticeable from these data is the fact that over the range, the degree of growth rate dispersion and the amount of induced strain varies in the order, sodium chlorate > potash alum > sodium nitrate. This reflects the increasing plasticity of the materials.

These distinctions mirror the experiments which were carried out on the larger crystals and serve to confirm that, although the size difference is large, the results of experiments on large crystals can be used to speculate on the behaviour of small crystals of these materials.

Thus, we confirm a significant influence of mechanical and growth induced lattice strain on the growth rates of crystals. That this is dependent on the mechanical characteristics of these materials is not surprising. When combined with the present and previous studies of the influence of dislocations on crystal growth, it offers an explanation of the range of growth rate dispersion including zero growth. It remains, however, to define the mechanistic basis of the process and to explain such factors as the size dependence of the effect.

4. MECHANISTIC STUDIES

In order to determine the mechanistic basis for the effect, it is necessary to have some means of defining in-situ a specific stress and, at the same time, to observe the nature and behaviour of growth sources on the crystal surface.

We have used two methods to develop such strain - radiation damage and the direct application of tensile stress to the crystal[23-25]. Simultaneously with the application of the stress, we have observed the form and development of the growth sources using an interferometric technique[26].

Both techniques for the introduction of strain to the samples show that the principle influence of strain is to slow the movement of the growth steps across the surface of the crystal. Within the space allotted it is not possible to present the detail of all experiments. The results of a typical tensile experiment are show in Fig. 6. Using a more sophisticated version of the simple tensile stress system used in our earlier experiments[27] we have performed simultaneously stress/strain experiments during growth and interferometric examination of the crystal surface.

In Fig. 7 we present interferograms taken at various points during the straining of a paracetamol crystal[28]. In Fig. 7 we show the overall dependence of growth rate on stress. The curvature observed fits well with the nature of the material. Paracetamol shows a well-defined plastic behaviour that has been shown to take place by slip of dislocation of the types {110} [001] and {111}[001][31]. Thus we would expect that the initial rapid development of elastic strain would give way to a slower relaxation in this factor as the plasticity develops. In parallel, there would be noted a fall off in the inhibition of the growth rate.

From the interferograms, it will be detected readily that here is an increase in the spacing of the interference fringes as the stress is increased. This corresponds to a decrease in the tangential velocity of the underlying growth steps. Similar results were obtained with both types of experiment; radiation induced strain and tensile induced strain and we can confidently claim that the principal influence of strain on the growth process is its influence on the initiation and development of the growth sources.
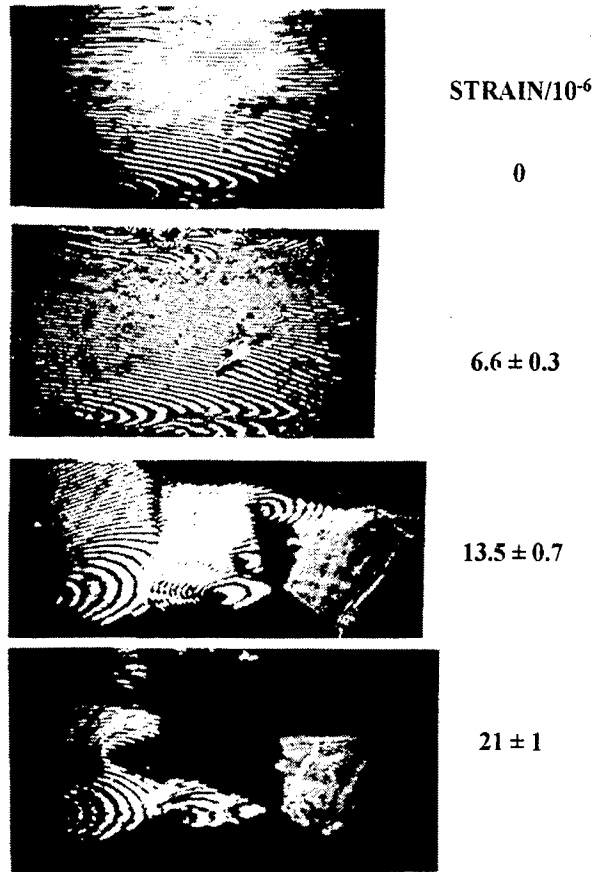
Fig. 6. Interferograms of the growth of a (001) surface of paracetamol as a function of applied tensile strain.
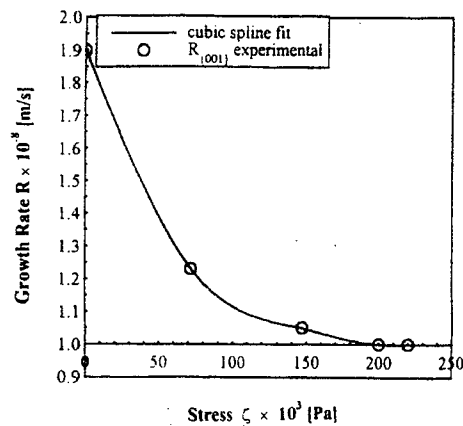

Fig. 7. The dependence of the growth rate of paracetamol (001) surfaces on applied tensile strain.

5. THEORETICAL BASIS

The development of the strain at the crystal surface could influence growth processes in two ways. Firstly, the surface-free

energy will increase, which can effect the nucleation of growth steps and their propagation over the surface. Secondly, the chemical potential of the surface (μ_s) will increase thus decreasing the driving force for crystallisation $\delta\mu = \mu_1 - \mu_s$ (μ_1 is the chemical potential of the liquid phase).

Let us consider first an active dislocation that emerges on the unstrained crystal surface. The dislocation core is surrounded by an elastically distorted (stressed) region of energy $\varepsilon_{disl} \approx Gb^2/8\pi^2$ [29], where G is the shear modulus, b is the modulus of the Burgers vector and r is the distance from the dislocation core to the point of observation. The elastic energy of one molecule is then $\Omega\varepsilon_{disl}$, where Ω is the specific molecular volume. Chernov has shown[5] that this elastic energy could be sufficient to increase significantly the chemical potential of the crystal over distances of the order of the radius of the critical nucleus. As a consequence, the local solubility around a dislocation, will increase by an amount defined as $\sigma_{disl} = \varepsilon_{disl}\Omega/kT$. It follows from this expression that a necessary condition for keeping the dislocation active, in terms of nucleating growth steps, is that the absolute value of supersaturation acting in reality upon the central part of the spiral must be higher by $\Omega\varepsilon_{disl}$ relative to the equilibrium state. In other words, the elastic energy hinders the nucleation of steps and helps dissolution at the dislocation core.

Applying the same philosophy to the more generally strained crystals, it is reasonable to assume that the elastic energy around the dislocations will be increased by a certain amount compared with that of the unstrained crystal. The greater the elastic strain, the higher the supersaturation required to render the dislocations active. This explains the passive role of dislocation sources in the strained crystals in the region of low supersaturation below the critical supersaturation. Instead, dissolution takes place, accompanied by the growth of unstrained portions of the crystals.

The second factor that defines the growth kinetics of strained crystals is the velocity of migration of steps over the crystal surface. This factor assumes an important role as soon as the face starts growing. Thus, the current evidence points to the influence of strain on growth step propagation as the principal cause of growth rate dispersion

More work requires to be done to define the mechanistic basis for the influence of strain on growth. The present results do however point to the need for more detailed, direct studies of the influence of strain on both nucleation and growth step velocities. These can only come from the close examination of the influence of strain on the development of the growth centres on the crystal surface. To this end, in-situ atomic force microscopy studies of selected materials are proposed and will be reported in due course.

6. CONCLUSIONS

In conclusion, we feel confident that growth rate dispersion is primarily a consequence of stress reduction of the growth rate of small particles following fracture and refacetting. Effectively, we envisage a series of particles propagating at a narrow range of growth rates dependant on the dislocation density at the surfaces. These growth rates are then reduced by the inhibiting factor of any integral strain. At the smallest particle sizes the strain contribution is dominant with the result that zero (or very small) growth rates can be observed in highly strained crystals. Gradual increase in crystal size leads to the strained material being covered with unstrained material resulting in an increasing dominance of the dislocation contribution. As a result the lower limit to the growth rate dispersion rises with increasing particle size until the average growth rate is reached.

The upper boundary of the range of dispersion represents dominantly dislocation controlled growth. However the increase in particle size leads to a rapid decrease in dislocation density (the controlling factor) with a parallel fall-off in the growth rate to the average. Beyond the limit of convergence the strained core of the crystal is completely covered with unstrained material and the strain becomes ineffective. Within the upper size range of the small particles which form in industrial crystallizers and in crystals bigger than these the dislocation density remains fairly constant, as does the average growth rate.

The influence of stress is very much dependent on the mechanical properties of the material which defines the size range over which this model will operate. This concept offers the potential for the development of empirical models for the prediction of growth rate dispersion in a wider range of materials.

A more extended review of this work can be found in a recent article by the author and his principal co-worker Dr R. I. Ristic[30].

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