



# Stress induced grain boundary migration in very soluble brittle salt

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## Abstract

Grain boundary migration (GBM) was studied in-situ at room temperature, atmospheric pressure and an applied differential stress of  $\sim 9.5$  MPa under the optical microscope, in a wet aggregate of an elastic-brittle salt (sodium chlorate). The aggregate was previously deformed predominantly by a combination of grain boundary sliding, pressure solution and cataclastic solution creep. After deformation, but when the sample was still under differential stress, undeformed, fracture-free grains were observed to grow at the cost of deformed, intensely fractured grains. GBM rates typically fell in the range 2–10  $\mu\text{m}/\text{day}$ . GBM took place *only* as long as the sample was under stress. Boundaries stopped to migrate as soon as stress was taken off and started to migrate again as soon as the sample was stressed again. Our observations suggest that GBM in this material and under the prevailing experimental conditions is a stress-induced process, i.e. driven by differences in elastic strain between fractured and unfractured grains. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Recrystallisation by grain boundary migration (GBM) is an important process during ductile rock deformation. It may control the rate of deformation as well as texture and crystallographic fabric development. GBM is widely assumed to be driven by gradients in crystal plastic strain energy (e.g. Nicolas and Poirier, 1976; Urai et al., 1986; Drury and Urai, 1990; Shelley, 1993; Ranalli, 1995; Passchier and Trouw, 1996). GBM recrystallisation microstructures are therefore often considered conclusive evidence for dislocation creep.

We studied GBM under stress in a wet aggregate of a very soluble *brittle* salt (sodium chlorate) at room  $P$ – $T$  conditions. Sodium chlorate cannot deform plastically at room  $P$ – $T$  conditions. The aggregate deformed by stress-corrosion microcracking and solution transfer creep during the first days of the experiment, then stopped deforming while remaining under stress. Yet, GBM *did* occur in this material while the

aggregate was under stress. Undeformed, fracture-free grains grew at the cost of deformed, intensely fractured grains. However, GBM stopped soon after applied stress was reduced to zero, and started again immediately after the sample was put under stress again. This suggests that GBM was driven by gradients in fracture-related *elastic* strains. Care should be taken therefore, to use GBM microstructures as evidence for dislocation creep.

## 2. Materials and methods

Sodium chlorate ( $\text{NaClO}_3$ ) is a cubic, very soluble, brittle salt. Its solubility is comparable to that of  $\text{NaCl}$ , its hardness to that of calcite. At room  $P$ – $T$  conditions, dry single crystals of  $\text{NaClO}_3$  can sustain stresses up to about 20 MPa without measurable deformation. At higher stresses crystals fail catastrophically and fall apart into numerous fragments.  $\text{NaClO}_3$  has been used as a brittle end-member in studies into the effect of elastic strain on crystal growth rates (Ristic et al., 1988, 1997) and to study the effect of crystal plastic strain on pressure solution compaction rates (den Brok et al., submitted).

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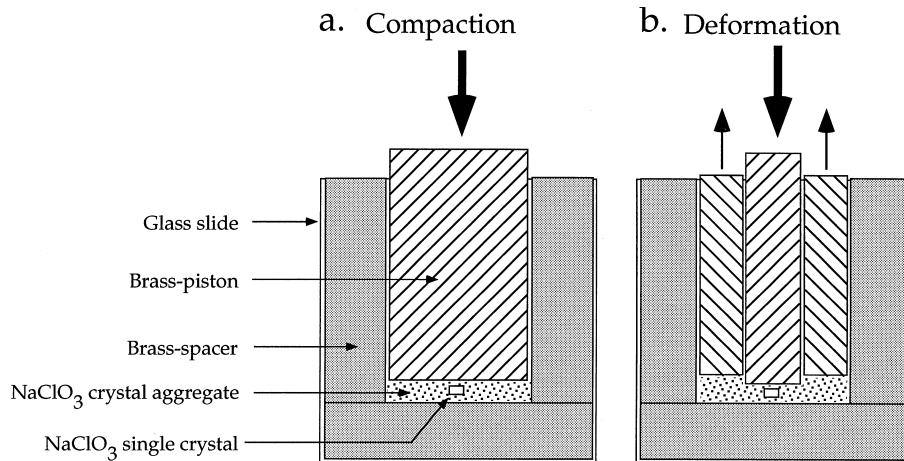


Fig. 1. Side view of experimental set-up used (real size). Set-up used for (a) compaction and (b) deformation. Brass pistons and spacers are  $\sim 0.32$  mm thin plates between  $\sim 1.3$  mm thin glass slides of  $50 \times 50$  mm<sup>2</sup> in size. The set-up was placed in vertical position with a weight resting on the moveable piston. During deformation, a weight rested on the central piston, whereas the two outer pistons were left without weight, thus being able to move outwards during deformation.

Observations reported here were made in a long term in-situ deformation experiment designed and carried out to study cataclastic creep of sodium chlorate single crystals. Experiments were carried out in a small transparent glass vessel, consisting of a 0.46 mm wide sleeve between two glass slides in which a brass piston could be slid to compact and/or differentially load crystal aggregates (Fig. 1). The vessel was closed on all sides except where the piston advanced. A single mm-size NaClO<sub>3</sub> crystal was put into the vessel and bedded in a matrix of smaller sodium chlorate crystals measuring 250–355  $\mu$ m in size. Aggregate plus single crystal was subjected to the following sequence of experimental conditions (all at room temperature): (i) dry compaction at  $\sim 2.5$  MPa for  $\sim 19$  min; (ii) addition of saturated NaClO<sub>3</sub> solution and subsequent wet compaction at  $\sim 2.5$  MPa for  $\sim 19$  h; (iii) application of differential stress of  $\sim 8.4$  MPa for 1.9 days; (iv) application of differential stress of  $\sim 9.5$  MPa during the following 69.6 days; (v) applied stress reduced to zero and kept zero for 119.5 days; (vi) application of differential stress of  $\sim 9.5$  MPa for 24.1 days; (vii) applied stress reduced to zero. Stress could not be measured in the sample, but was calculated by dividing load through sample section, without correcting for possible frictional effects. For more details about experimental procedures see den Brok et al. (1998).

### 3. Experimental observations

The experiment was originally designed to study stress corrosion microcracking in the single crystal and not to study GBM (results are reported by den Brok et al., 1998). No systematic observations were therefore

made in the surrounding aggregate during the first days of the experiment. Only after 7.5 days we observed (entirely unexpectedly) that GBM had taken place within the crystal aggregate in the area above and below the single crystal where the initially porous aggregate had been almost completely compacted. This compaction had taken place during first 1.9 days by cataclasis and solution transfer creep. As soon as we observed that GBM occurred, we started to systematically study selected areas by making photomicrographs within fixed time intervals. The areas did not measurably deform during the time that observations were made, i.e. strain was less than  $\sim 2\%$ . Grain boundaries could be seen as fine black lines due to dissolution-etching of the intersection of the boundaries at the surface of the glass slides.

#### 3.1. Description of deformed grains

Most of the old grains were intensely fractured and broken into numerous fragments (Figs. 2a, b and 3a). Both size and shape of the fragments was highly variable. Within single grains, fragments varied in size from 5 to 100  $\mu$ m. Length to width ratios of fragments within single grains fell in the range from 1:1 to 1:10. Some fragments were rounded, others had sharp angles, or were rounded on one and angular on the other side. Fragments were preferentially oriented at  $\sim 45^\circ$  to the loading direction. Some new fractures developed with time, and some old ones disappeared, but most were there from the beginning and remained unaltered until the end of the experiment. Some of the fractures changed position slightly during the experiment.

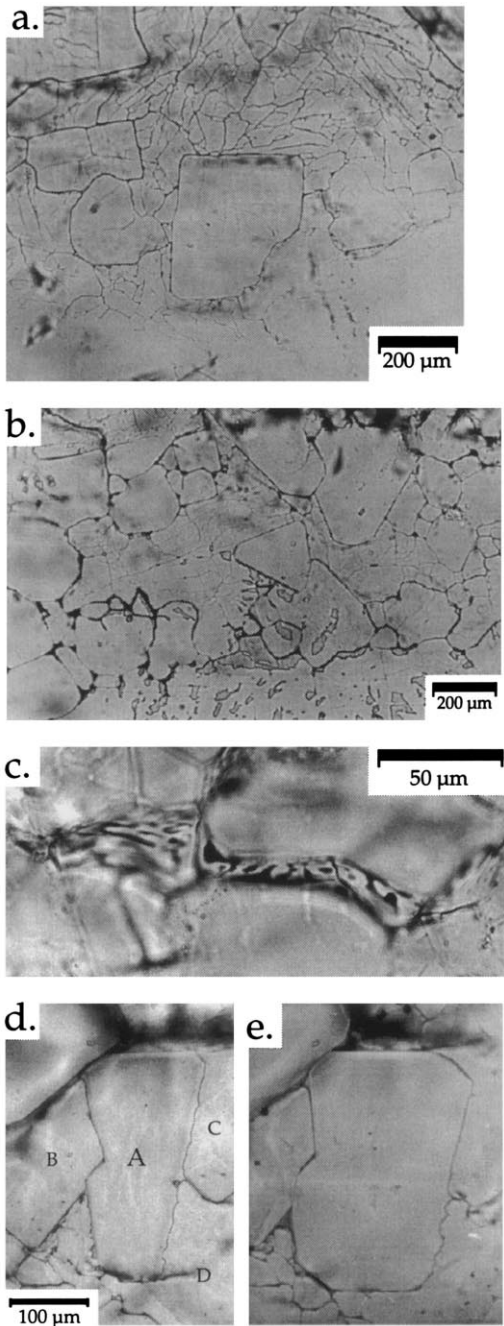


Fig. 2. (a) Optical micrograph showing new, subeuhedral grains growing in intensely fractured grains (cf. Fig. 3a). Picture was taken 30.6 days after beginning of the experiment. (b) Optical micrograph made after 119.5 days without stress, showing subeuhedral grains grown within intensely fractured grains. Microstructure had not changed during the last 106.5 days. Intensely fractured grains were still present. (c) Grain boundary oriented perpendicular to maximum compressive stress showing fluid inclusions (black). Picture was taken 5.1 days after beginning of second loading stage. (d) Characteristic lobate/cusped boundary structure between growing grain (A) and old, fractured grains (C and D). Boundary between A and unfractured grain B is smooth. Picture was taken 61.5 days after beginning of test. (e) Same grain as in (d) ~23 days later. Maximum compressive stress oriented north–south in all figures.

Not all old grains were fractured intensely. Grains with {100} at about 45° to the loading direction had numerous fractures. Grains with {100} oriented sub-parallel to the loading direction had relatively few or almost no fractures.

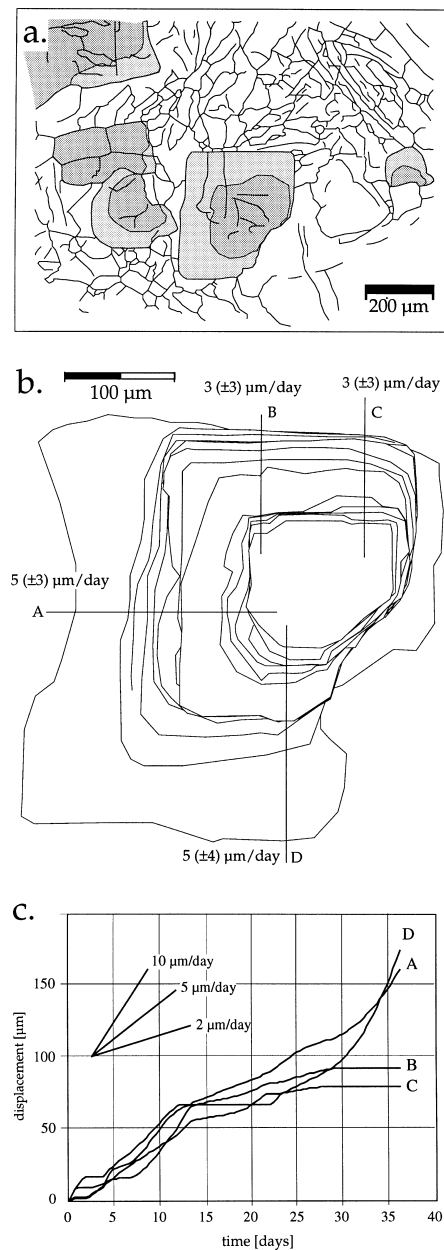


Fig. 3. (a) Drawing made from Fig. 2(a) (situation after 30.6 days) showing grain and fragment boundaries. Dark shading: growing grains after 14.0 days from the beginning. Light shading: new-growth during next 16.6 days. Note preferred orientation of fragment boundaries in large old grain, especially in upper right quadrant. Maximum compressive stress oriented N–S. (b) Drawing of growth stadia of grain in center of (a) between 7.5 and 61.5 days from the beginning. Along sections A, B, C and D growth velocity was determined. Average values are indicated. (c) Graph showing grain boundary position of (b) as a function of time along sections A–D.

### 3.2. Description of growing grains

Growing grains that were systematically studied during growth had initial sizes in the range 10–50  $\mu\text{m}$ . Some of these grains grew up to  $\sim 500$   $\mu\text{m}$  in diameter within  $\sim 71.5$  days. Their boundaries migrated at a relatively constant rate, typically falling in the range 2–10  $\mu\text{m}/\text{day}$  (Fig. 3). Boundaries always migrated into intensely fractured grains. Growth direction appeared not to be influenced by stress; growing grains had no preferred shape orientation. Their boundaries were mostly straight and parallel to  $\{100\}$ . The boundaries contained abundant fluid inclusions of spherical, ellipsoidal or tubular shape (Fig. 2c). They occurred isolated or in arrays with their long axes mostly oriented subparallel to  $\langle 100 \rangle$ . Size of the inclusions typically fell in the range 0.5–5  $\mu\text{m}$ . Migrating boundaries were commonly straight on the growth side and lobate/cusped on the fractured side (Fig. 2d and e). The grain boundary fluid seemed to dissolve its way into the fracture boundaries. Width of the grain boundaries was less than  $\sim 0.2$   $\mu\text{m}$ .

### 3.3. Observations made after unloading the aggregate

The sample was loaded and unloaded twice. The first time that the sample was unloaded, microscopic observations and pictures were made 10 days before and 13 days after unloading the aggregate, but not directly after unloading the sample. Considerable GBM had occurred within these 23 days. However, during the next 106.5 days that the sample was left stress-free, no further GBM could be detected, yet, intensely fractured grains were still present next to grains that had grown (Fig. 2b). As soon as the sample was loaded again GBM started at similar rates as during the first loading stage even though the sample did not measurably deform (strain  $< 0.2\%$  in this case). When the stress was taken off again (after 24.1 days) GBM stopped definitively within the next 4.3–7.0 days. Intensely fractured grains were still present next to grains that had been growing.

## 4. Discussion and conclusions

The experimental results show that: (i) GBM can occur in a brittle but very soluble material that cannot deform plastically; and (ii) GBM in sodium chlorate is a *stress-induced* process. Boundaries only migrate when samples are under stress. Furthermore, (iii) boundaries appear to migrate only into intensely fractured grains, and not into unfractured grains. This suggests that GBM is driven by differences in stress-induced (elastic) strain between fractured and unfractured grains. How can we explain these observations?

It is well known from crystal growth experience (among others on  $\text{NaClO}_3$  and other brittle salts) that small crystal fragments fractured from one single larger crystal and used as seed crystals, show a marked difference in growth rate under otherwise similar conditions. This effect, in crystal growth literature referred to as crystal growth dispersion, is most probably caused by differences in internal elastic strains, thought to be due to the fracture process (e.g. Ristic et al., 1988; Herden and Lacmann, 1997). Ristic et al. (1988) showed that in the case of growth rate dispersion of  $\text{NaClO}_3$  fragments the growth rate is roughly inversely proportional to the degree of internal elastic strain. That elastic strain has a strong effect on growth rate of sodium chlorate and other brittle salts has been demonstrated by Ristic et al. (1988, 1997). The application of a tensile stress of the order of  $\sim 0.5$  MPa on  $\text{NaClO}_3$  crystals held under supersaturation of a few percent resulted in an instantaneous reduction of growth rate to very low or even zero. On release of the stress, the growth rate returned to its original value.

Maybe elastic strain within the intensely and very irregularly fractured grains was on average higher than in the growing grains, thus providing a driving force for GBM. A simple GBM model assuming that diffusional material transport in solution across fluid-filled boundaries is driven by differences in elastic deformation (stress) and controlled by dissolution or growth rate (cf. Kamb, 1959) predicts that stress differences of 1–5 MPa may lead to GBM rates of the size observed in this study (see Appendix A). Further study of this mechanism is required. We are currently investigating the effect of elastic strain on dissolution/growth processes in saturated solution using different brittle salts as rock analogue materials.

The fact that GBM recrystallisation can occur in brittle materials and is probably driven by elastic distortions means that care should be taken to use GBM microstructures as evidence for dislocation creep. The present results suggest that GBM may also occur in wet cataclastically deforming rocks.

## Appendix A

Let GBM be driven by differences in elastic strain energy between two grains on either side of a grain boundary fluid film of thickness  $w$ . Assuming that elasticity is linear (Hookean), the difference in elastic strain energy  $\Delta U_{\text{el}}$  (J/mol) between the grains is given by:

$$\Delta U_{\text{el}} = \sigma^2 V_{\text{m}} / 2E \quad (\text{A1})$$

where  $\sigma$  is the difference in stress across the fluid film

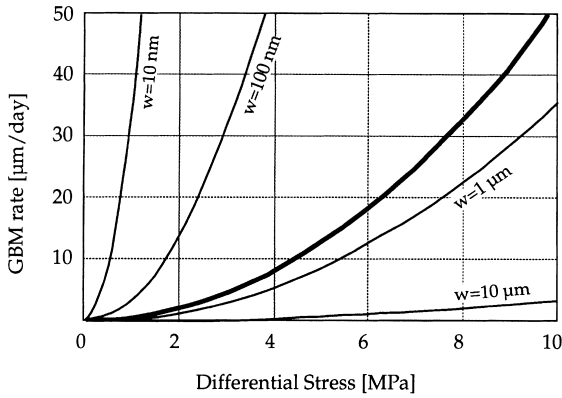


Fig. A1. Graph showing calculated GBM rate vs stress difference for simple stress-induced GBM rate model at room temperature (23°C). Thin lines are for *diffusion-controlled* stress-induced GBM (grain boundary width  $w$  is indicated for each line) and thick line for *dissolution/growth-controlled* stress-induced GBM. Reasonable fit is obtained between rates determined in experiment (2–10  $\mu\text{m}/\text{day}$ ) and rates predicted by dissolution/growth-controlled model for stress differences in the range 1–5 MPa.

( $\text{N}/\text{m}^2$ ),  $V_m$  the molar volume of the solid phase ( $\text{m}^3/\text{mol}$ ) and  $E$  the elasticity modulus ( $\text{N}/\text{m}^2$ ) of the solid phase. If the GBM rate  $v_{\text{GBM}}$  ( $\text{m}/\text{s}$ ) is controlled by diffusion across the boundary fluid film, then  $v_{\text{GBM}}$  may be related to driving force  $\nabla\mu$  ( $\text{J}/\text{mol}$ ) by Fick's law. The volumetric material flux vector  $j_v$  ( $\text{m}^3/\text{m}^2/\text{s}$ ) pointing down the stress gradient may then be written as:

$$j_v = -(DC/RT)\nabla\mu \quad (\text{A2})$$

where  $D$  is the diffusivity ( $\text{m}^2/\text{s}$ ),  $C$  is the solubility (mole fraction),  $R$  is the gas constant ( $\text{J}/\text{K}/\text{mol}$ ), and  $T$  is the absolute temperature (K). For a stress-induced driving force, i.e. for  $\nabla\mu = \Delta U_{\text{el}}/w$ ,  $v_{\text{GBM}}$  is then related to  $\sigma$  by the equation:

$$v_{\text{GBM}} = DCV_m\sigma^2/(2RTEw). \quad (\text{A3})$$

For sodium chlorate, with  $V_m = 4.3 \times 10^{-5} \text{ m}^3/\text{mol}$ ,  $C$  at  $23^\circ\text{C} = 0.16$  [mole fraction],  $D$  at  $30^\circ\text{C} = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$  and  $E = 43.67 \text{ GPa}$ , Eq. (A3) is plotted for different values for  $w$  in Fig. A1 (thin lines). For dissolution/growth controlled GBM,  $v_{\text{GBM}}$  is related to  $\sigma$  by the equation:

$$v_{\text{GBM}} = kV_m\sigma^2/(2RTE) \quad (\text{A4})$$

where  $k$  is the interface dissolution/growth velocity for a thermodynamic driving force of  $1RT/\text{mol}$ . For sodium chlorate,  $k \approx 30 \mu\text{m}/\text{s}$  for the  $\{100\}$  face at room  $P$ – $T$  conditions (e.g. Chen et al., 1979). The dissolution/growth controlled dependence of  $v_{\text{GBM}}$  on  $\sigma$  is plotted as a heavy line in Fig. A1. It appears that for fluid films with  $w$  roughly below  $0.5 \mu\text{m}$  the dissolution/growth process is rate controlling (observations indicate that  $w < 0.2 \mu\text{m}$  in the present study). Quite good agreement is obtained between measured (2–10  $\mu\text{m}/\text{day}$ ) and calculated GBM rates for dissolution/growth controlled GBM if stress differences driving GBM fall in the range 1–5 MPa (not unreasonable recalling that applied stress was about 9.5 MPa).

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