Structure of grain boundaries in wet, synthetic polycrystalline, statically recrystallizing halite – evidence from cryo-SEM observations

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ABSTRACT

It is well known from nature and experiments that the presence of brine strongly affects the microstructural evolution and the mechanical and transport properties of halite. Existing interpretations of the grain boundary structure in deformed, wet, salt samples annealed statically at room temperature are based on indirect evidence from reflected light microscopy and conventional scanning electron microscopy. This paper presents direct observations of fluid-filled grain boundaries using the cryogenic-scanning electron microscope (cryo-SEM) in which the grain boundary fluids were frozen before breaking the samples. The rapid cooling transforms the brine into two phases, i.e. ice and hydrohalite, which are easily recognized from characteristic segregation patterns. We studied samples of wet, synthetic, polycrystalline halite annealed under static conditions at room temperature. In coarse-grained samples, fine-scale segregation patterns were observed at the boundaries of the primary recrystallizing grains. These points indicate the existence of fluid films with a thickness in the range of 30 nm, but the finer scale structure of the fluid remains unknown. In fine-grained samples, the distribution and reorganization of fluids with annealing time is recorded by the combination of contact healing and successive accumulation of fluids in triple junction tubes. The contact healing is attributed to the small initial grain size, such that the fluid film necks down by accumulating the fluids into previously existing triple junctions via neck growth. Electron backscatter diffraction measurements of both primary and secondary recrystallized grains indicate that they are euhedral, i.e. the grain growth morphology is controlled by the anisotropy of the grain boundary energy of the growing grain, which results in planar growth faces.

Key words: cryo-SEM, fluids, grain boundary, halite, morphology, recrystallization.

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INTRODUCTION

The presence of fluids has major effects on the dynamics of geological processes in the Earth’s mantle and crust (e.g. Fyfe et al. 1978). In minerals, such as quartz (Griegs 1974; Hirth & Tullis 1992; Jaoul et al. 1984; Kronenberg & Tullis 1984; Post & Tullis 1998; Tullis & Yund 1982), feldspar (Dimanov et al. 1999; Tullis et al. 1996), olivine (Mei & Kohlstedt 2000a,b), bischofite (Urai 1983), carnallite (Urai 1985) and halite (e.g. Spiers et al. 1990; Urai et al. 1986a), water-rich fluids play a significant role in recrystallization, grain growth and development of texture (Evans et al. 2001; Urai et al. 1986a).

Halite has been investigated in detail because the interplay of fluid morphology and deformation can be studied at relatively low temperatures and pressures (e.g. Urai et al. 1986b), allowing systematic laboratory experiments of practical duration (Watanabe & Peach 2002). The results are also relevant to other fluid-bearing minerals, including partially molten rocks (Spiers et al. 1988).
The effect of fluids on grain boundary mass transfer in halite has been demonstrated by numerous examples from nature, and also by experiments during both fluid-phase diffusional creep (pressure solution) (de Meer et al. 2002; Hickman & Evans 1991; Martin et al. 1999; Peach 1991; Schutjens 1991; Spiers & Schutjens 1990; Spiers et al. 1990) and fluid-assisted grain boundary migration (Peach et al. 2001; Schenk & Urai 2004; Urai et al. 1986b; Watanabe & Peach 2002). However, the structure of the halite grain boundaries that contain water is still a matter of debate. Firstly, for pressure solution, three different, nonexclusive models have been proposed (den Brok et al. 2002): (i) the thin film model, (ii) the island-channel model and (iii) the island-crack model.

In the thin film boundary model (Hickman & Evans 1991; Renard & Orteleva 1997; Rutter 1976) the grains are separated by a thin, structured water film with a thickness of a few nanometres. This film is proposed to transmit the contact stress, and dissolution followed by diffusion is the process of transport of material. The island-channel boundary model (Lehner 1990; Spiers & Schutjens 1990) is based on the assumption that, during pressure solution, the fluids residing in thin films are squeezed out between the grains, resulting in solid–solid contact (islands) through which the contact stresses are transmitted, together with water-filled channels through which the material transport takes place by diffusion. This microscopically rough island-channel structure is dynamically stable. The island-crack boundary model (den Brok 1998; Dysthe et al. 2003; Gratz 1991) proposes static islands that are separated by microfracture-controlled fluid channels. In contrast to the solid–solid contact of the island-channel model, the islands in this model contain thin films comparable to the earlier proposed thin film boundary model. However, compared to the thin film model, the total diffusivity in the island-crack model is increased by the presence of the microcracks.

Secondly, experiments on wet polycrystalline halite deformed at temperatures between room temperature and 150°C in the nondilatant field indicate that halite recrystallizes readily both during and after deformation (Drury & Urai 1990; Peach et al. 2001; Spiers et al. 1990; Urai et al. 1986a,b; Watanabe & Peach 2002). The grain boundaries are interpreted to contain thin fluid films. A method to show the presence of such brine films in halite samples is the application of the ether test (Spiers et al. 1986): cooling during evaporation of the ether disrupts the fluid film into isolated droplets. Urai et al. (1986b) demonstrated the presence of fluid films from scanning electron microscope (SEM) observations on deformed, water-bearing halite samples: 1 month after cessation of deformation grain boundaries were smooth, whereas samples annealed for 1 year contained grain boundaries with isolated cavities marking former fluid inclusions. The authors interpreted these results as evidence of grain boundary brine films that shrink into isolated fluid inclusions after grain boundary migration stops. Similar observations were shown by in situ experiments conducted on wet bischofite, where water-filled grain boundaries neck down after cessation of grain boundary migration (Urai 1987).

The fluid-filled grain boundaries are interpreted to migrate by (i) dissolution of the deformed grains, (ii) diffusion through the brine film and (iii) precipitation on the low-index facets of the recrystallized grains forming smooth grain surfaces (e.g. Spiers et al. 1990; Urai et al. 1986a), comparable to the step model of Gleiter (1969). However, so far the nature of such fluid films in migrating boundaries has been inferred only indirectly.

A significant problem is that the observations were made after removal of the stress, and this could have led to a redistribution of the fluid by viscous flow of brine (Hickman & Evans 1991; Peach et al. 2001; Watanabe & Peach 2002). This problem was avoided in a recent study in which the microstructural evolution of wet, compacted, statically recrystallizing halite samples with different initial grain sizes was presented (Schenk & Urai 2004). The microstructural evolution in Schenk & Urai (2004) is briefly summarized in Fig. 1: in the coarse-grained samples, primary recrystallization resulted in the nucleation and growth of euhedral grains, which replaced the original, deformed grains (Fig. 1A). Inside the fine-grained samples, primary recrystallization was followed by normal grain growth, but stopped after a few hours because of contact healing (Fig. 1B). Exaggerated grain growth (secondary recrystallization) is initiated at this stage (Fig. 1C).

Schenk & Urai (2004) interpreted the growth of the euhedral primary and secondary recrystallized grains to be due to the presence of brine films on the grain boundaries, as dry grain boundaries only migrate at temperatures above approximately 400°C (Fransen 1993; Guillopé & Poirier 1979). However, the details of the fluid distribution and its influence on grain boundary migration were only partly resolved, because fluid was removed during sample preparation.

In this paper, we therefore set out to investigate directly, and in detail, the nature of the fluid in grain boundaries during different stages of recrystallization within compacted, polycrystalline halite samples. To do this we studied samples using the cryo-SEM. Small rock chips are shock-frozen to a very low temperature (approximately −190°C) and can be used for chemical characterizations (Samson & Walker, 2000; Timofeeff et al. 2001) and for visualization of the distribution of fluids in rocks, in particular to investigate qualitatively fluid–mineral interfaces (Durand & Rosenberg 1998; Mann et al. 1994; Monma et al. 1997). In order to characterize the crystallographic
orientations of grain boundaries we used electron backscatter diffraction (EBSD) analysis.

METHODS

Experimental methods

Preparation of compacted samples.

The sample preparation technique was that used by Schenk & Urai (2004). Here we summarize the procedure briefly. Wet sodium chloride powder of analytical grade (Roth, Art. 9265.3; NaCl content >99.9%) of two different grain size classes (<10 and 200–355 µm) was compacted (cold-pressed, T = approximately 25°C) uniaxially with a pressure of 150 MPa for 5 min. The resulting aggregates have connected brine-filled porosities of less than 2%, together with volumetrically very minor, localized occurrences of air-filled pores. The samples were annealed at room temperature (24 ± 1°C) over periods of up to 9 months in small, air-tight containers with small amounts of saturated salt solution. This solution was not in contact with the samples, ensuring that the vapour pressure of H2O around the samples was buffered at the equilibrium value. Only samples 139 and 141 were stored in a wet salt mush (see Table 1 for a detailed description of the compacted samples).

Analytical methods

Preparation for cryo-SEM observations.

For direct observation of the brine-filled grain boundary sections of synthetic halite samples, we used a field emission scanning electron microscope (FESEM JSM-6300F, JEOL) equipped with a dedicated cryo-preparation chamber (CT 1500 HF, Oxford Instruments) at the Department of Plant Cell Biology, Wageningen University, The Netherlands. Where necessary, the samples were ground to the required thickness of approximately 1.6 mm very carefully to minimize any damage, at a temperature of approximately 25°C. The sample was then placed into the slot of the cryo-SEM holder and fixed with carbon conductive cement (Leit-C, Neubauer chemicals). It was secured additionally by tightening carefully the screw of the holder. Subsequently, the whole assembly (sample with holder) was immersed in liquid nitrogen (−196°C). Once frozen, the whole unit was transferred into the cryo-preparation chamber at a temperature of −90°C and a pressure of 1.3 × 10⁻² Pa (high vacuum conditions), in which the sample was fractured using a cold knife (−196°C) at adequate distance from the tightened holder (see sketch in Fig. 2A). After approximately 5 min (sublimation stage), the sample was sputter coated with 8 nm platinum and subsequently transferred into the SEM on the sample surface.

Table 1. Overview of samples described in this paper.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of salt</th>
<th>Starting grain size (µm)</th>
<th>Annealing time (days)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-XXs</td>
<td>Brine: Roth</td>
<td>&lt;10</td>
<td>0.50</td>
<td>Segregation pattern</td>
</tr>
<tr>
<td>085a</td>
<td>Roth</td>
<td>200–355</td>
<td>252.23</td>
<td>Primary recrystallization</td>
</tr>
<tr>
<td>111a</td>
<td>Roth</td>
<td>&lt;10</td>
<td>180.97</td>
<td>Normal grain growth</td>
</tr>
<tr>
<td>138a</td>
<td>Roth</td>
<td>&lt;10</td>
<td>29.93</td>
<td>Exaggerated grain growth</td>
</tr>
<tr>
<td>139*</td>
<td>Roth</td>
<td>&lt;10</td>
<td>6.70</td>
<td>Normal grain growth</td>
</tr>
<tr>
<td>141*</td>
<td>Roth</td>
<td>&lt;10</td>
<td>1.10</td>
<td>Normal grain growth</td>
</tr>
<tr>
<td>146</td>
<td>Roth</td>
<td>200–355</td>
<td>139.98</td>
<td>Primary recrystallization</td>
</tr>
<tr>
<td>152</td>
<td>Roth</td>
<td>200–355</td>
<td>0.50</td>
<td>Primary recrystallization</td>
</tr>
</tbody>
</table>

*Stored in salt mush.
holder, at a temperature between $-170$ and $-190^\circ$C. Images were recorded digitally.

**Bicrystal ‘calibration’ tests.**

To interpret the frozen structure of brine inside the compacted samples, we compared them with the structure of a thin film of frozen, saturated sodium chloride solution between halite plates. For this an industrially grown halite single crystal was cleaved along [100] cleavage facets into two thin wafers, which were bonded with a droplet of saturated sodium chloride solution (Roth, Art. 9265.3; NaCl content >99.9%) for 12 h, relying on capillary action to avoid applying any external stress. Subsequently, this assembly was inserted into a cryo-SEM holder and frozen at a temperature of $-90^\circ$C for 5 min, before it was fractured inside the cryo-preparation chamber.

**EBSD.**

Detailed EBSD analysis was conducted on selected samples to investigate the nature of grain boundaries of primary and secondary recrystallized grains in the annealed samples. To obtain a high-resolution EBSD pattern, the samples (thick, compacted, unfrozen sections) were mechanically polished using 1200-, 2400- and 4000-grade carborundum paper, removing dust at regular intervals with a blast of dry compressed air. To remove surface damage, the samples were chemically polished in pure analytical grade methanol for 10 sec, and then immediately and vigorously rinsed in a jet of diethyl ether. Finally, samples were carbon coated to reduce charging during EBSD analysis.

Samples were analysed in a field-emission gun (FEG) CamScan X500 SEM at the University of Liverpool. Full crystallographic orientation data were obtained from EBSD patterns using a 20 kV acceleration voltage and a beam current of 7 nA. EBSD patterns were auto-indexed using the CHANNEL 5.03 software of HKL Technology. The centre of five to six Kikuchi bands was detected automatically, whereby the solid angles calculated from the patterns were compared with the calculated halite patterns originating from 47 reflectors. Data were obtained by moving the beam at a fixed step size of 2 nm. The average percentage of EBSD patterns that could not be indexed ranged between 30% and 35%; most of the unindexed analyses were at high-angle grain boundaries. The maps were processed to remove erroneous data in order to provide a more complete reconstruction of the microstructure (Prior et al. 2002). The accuracy of individual EBSD orientation measurements is better than $1^\circ$. The misorientation angle between grains was calculated by selecting the minimum misorientation angle and its corresponding axis from all possible symmetric variants (cf. Wheeler et al. 2001). We present data obtained in a combination of displays: (i) maps showing the spatial distribution of grains and their crystallography in different grey scales and (ii) three-dimensional representation of the crystallographic orientation of individual grains of special interest.

**Observations**

The microstructural evolution of the samples is identical to that observed by Schenk & Urai (2004). Both the

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**Fig. 2.** Cryo-SEM micrographs of the single crystal – brine setup: (A) two thin wafers of halite single crystals (XX-1 and XX-2) were attached to each other parallel to the (100) facets with a droplet of saturated brine and broken with a cold knife inside the cryo-chamber; (B and C) details of the segregation pattern of the frozen brine film with the two phases, hydrohalite and ice, the latter as negative imprint because of evaporation during sublimation.
fine- and coarse-grained samples are characterized by a porosity connected through triple junction tubes (to prevent confusion we use the terms triple junction and triple junction tubes solely in a geometric sense, without relating them to textural equilibrium as those conditions were not attained in our experiments). In the present study, grain boundary morphology during recrystallization was studied on broken surfaces of samples annealed for different periods using the cryo-FESEM. An overview of the samples described in this paper and the main observations are given in Table 1.

**Segregation patterns of frozen brine**

**Setup with halite single crystals and brine.**

In order to correctly identify the earlier presence of brine at grain boundaries, we ‘calibrated’ our observations against the segregation pattern on faces of a sample in which brine was enclosed between the cleavage faces of two single crystal wafers of halite (Fig. 2A). Because of the rapid cooling, the saturated brine shock-freezes and is transformed into the two phases, i.e. ice and hydrohalite \((\text{NaCl} \times 2\text{H}_2\text{O})\) (Bodnar 1993; Roedder 1984). During the sublimation period at the sample stage (5 min at \(-90^\circ\text{C}\)), the ice crystals evaporate leaving behind voids in a hydrohalite foam (Fig. 2B,C) (we call the resultant texture a ‘segregation pattern’). Accordingly, if such pores and ‘foam’ are observed in our samples, we suggest that they are indicative of the earlier presence of brine.

**General comparison of segregation patterns observed in experimental samples.**

Brine inclusions are common in halite, as illustrated in a coarse-grained sample inside an original, deformed grain (Fig. 3). This frozen fluid inclusion shows the characteristic segregation pattern described above, indicating that it represents frozen salt solution, i.e. with the two phases hydrohalite and (evaporated) ice. Inside both the coarse- and fine-grained samples, similar patterns were observed in pores, triple junction tubes and on grain boundaries, demonstrating that they are also brine in a frozen state. Thus, these patterns provide direct evidence for the distribution of brine inside the compacted samples.

The volume increase of approximately 15% that is associated with the transformation of saturated brine into the two phases hydrohalite and ice might result in misinterpretations of the microstructure as the previously brine-filled grain boundaries or triple junctions expand. However, Fig. 3B shows that the shock-freezing did not result in fracturing of the surrounding grain. Furthermore, this photomicrograph illustrates that the size of the pores left by the evaporated ice is five times smaller than that in the single crystal brine setup (Fig. 2). As the cooling rate was the same for all samples, it is suggested that the dimensions of the segregated components are related to the volume of the fluid.

**Observations on coarse-grained samples during primary recrystallization**

Inside the coarse-grained aggregates (initial grain size: 200–355 \(\mu\text{m}\)), primary recrystallization dominated textural evolution. Nucleation of primary recrystallized grains occurred in high-strain zones close to the contact regions of original, deformed grains. These new grains are characterized by a cubic shape, and replace the surrounding deformed material. This microstructural evolution is documented by the three samples that were annealed for 0.5 days, 4.5 months and 8.5 months (samples 152, 146 and 085a, respectively; see Table 1). Segregation patterns of the frozen fluids indicate that brine was present in all samples. If three or more recrystallized grains (i.e. strain-free grains smaller than approximately 20 \(\mu\text{m}\)) are in contact, the frozen brine is only present in triple junctions (however not in the sense of textural equilibrium) (Fig. 4).
Grain boundary migration occurs if a strain-free grain is in contact with a deformed grain. Inside sample 146 (annealed for 4.5 months), some of these grains are larger than 100 μm (Fig. 5). This contact zone between the new grain (recrystallized) and the old grain (deformed) is characterized by a very thin segregation pattern indicating a fluid film with a thickness of less than 30 nm (Fig. 5C). Additionally, tiny pores visible on the lower crystal face of the deformed crystals suggest that they are related to frozen fluids (see arrow in Fig. 5C). This is supported by the fact that no air-filled pores were observed inside new grains. Backscatter analysis indicates that there are no measurable differences in chemistry between the original deformed grain, the recrystallized grain and the solid phase of the segregation pattern (cf. Heard & Ryerson 1986), suggesting that second phases other than brine did not influence this contact region. Inside the same sample, a different but rare situation is displayed (Fig. 6). Here, the porosity is predominantly air-filled, as shown by the lack of segregation pattern. However, remnants of a frozen fluid phase are observed at the contact zone between a recrystallized grain and a deformed grain. The thickness of this fluid film is approximately 200 nm (Fig. 6B,C) with a segregation pattern similar to that shown in the grain boundary region of Fig. 5C.

Observations on fine-grained samples during primary recrystallization, normal grain growth and exaggerated grain growth

Microstructural evolution of the fine-grained samples (initial grain size <10 μm) starts with primary recrystallization, followed by a reduction of irregularities in grain boundary morphology and rearrangement of porosity. These processes occur only in the first hours (see Schenk & Urai 2004). There is no sign of significant normal grain growth; however, at this stage exaggerated grain growth begins in some samples.

Fluids are present in all the fine-grained samples, whether they were stored in brine saturated environment or salt mush, regardless of the annealing time ranging from 1 day to 6 months (samples 141, 139, 138a and 111a) (see Table 1 for the detailed sample description). During
the first few days, fluids – indicated by the characteristic segregation pattern – reside on all irregular and on some curved grain boundaries, forming films with a thickness of less than 150 nm, but predominantly they are present in triple junctions or in pores that developed by impingement of the growing grains (Fig. 7) (see also Elliot et al. 1997).

After 1 week of annealing at room temperature the microstructure is characterized by solid–solid contacts (Fig. 8; see solid arrow). The pores remain irregular

Fig. 6. Cryo-SEM micrographs of sample 146 showing a primary recrystallizing grain growing into an old, deformed grain. The arrow in (C) points to the remnants of a frozen fluid film at the contact region. Note that this is a rare region in which porosity is predominantly air-filled.

Fig. 7. Cryo-SEM micrographs of sample 141 showing that fluids are present in triple junctions and in grain boundaries in the early stages of annealing. Close to large pores the grains grow normal to the (100) facets; however, at grain–grain contacts the grain boundaries are irregular and curved. The details in (B) are interpreted to represent the first step of contact healing (arrow).

Fig. 8. Cryo-SEM micrograph of sample 139 with the typical segregation pattern of brine-filled porosity. The fine-sized grains grow with low-index facets into the fluid-filled pore (dashed arrow). Note the high diversity of apparent dihedral angles. The solid arrow points to an immobile solid–solid contact region of two recrystallized grains.
because of the lattice-dependent (euhedral) growth of the crystals into the porosity (Fig. 8; see dashed arrow) with apparent dihedral angles varying over a broad range because of impingement of the growing grains. An isolated brine-filled inclusion (250 x 50 nm) (Fig. 9) is interpreted to represent an inclusion left behind from a migrating fluid-filled grain boundary. However, this might also be explained by the presence of a fluid-filled pore resting on the grain boundary. The microstructure of sample 111a (annealed for 6 months) is characterized by predominantly straight or smoothly curved grain boundaries without interactions of fluids and an interconnected porosity with fluids present only along triple junctions (Fig. 10).

Exaggerated grain growth is common inside these fine-grained samples as shown by reflected light microscopy and SEM (see EBSD pattern of sample 138a; annealed for 1 month; Fig. 11). However, cryo-SEM did not allow detailed observations on the contact of exaggerated grains with the fine-grained matrix, probably because of the plucking-out of the large grains during the low-temperature preparation.

Crystallographic nature of grain boundaries of primary and secondary recrystallized grains

After an annealing period of 8 months in a brine-saturated, humid environment, the coarse-grained sample 085a (initial grain size 200–355 μm) contained several large, euhedral grains. They show little to no lattice distortion within any individual grain, and a dominance of boundaries...
parallel to [100] facets (Fig. 12). The misorientation angle between the faceted boundaries of the primary recrystallized grains and surrounding grains is always >15°.

Similar features are observed in the samples exhibiting exaggerated grain growth. We investigated the crystallographic nature of the boundaries of such grains in sample 138a (see Table 1 for experimental details). In this sample, most of the grains are very fine grained (<10 μm), with only few significantly larger grains of up to 300 μm. The straight boundaries of these grains already described in the SEM backscatter analysis are characterized by crystal orientations that are compatible with [100] facets (Fig. 11).

**DISCUSSION**

Our cryo-SEM observations of segregation patterns along grain boundaries and triple junctions show that small amounts of fluids are present in the majority of mobile grain boundaries and in larger pores. In the cryo-SEM, these boundaries have a resolvable structure, which indicates fluid films being thinner than 30 nm. The small-scale structure seen in Fig. 5C, however, can be interpreted in two ways: it can be an island-channel structure or a segregation pattern in a continuous fluid film. Thus, although there is clear evidence of fluids in these mobile boundaries, we cannot obtain conclusive information on the nanoscale structure from our observations (Fig. 13) because of the unknown morphology of the segregation pattern in very thin, frozen brine films and because of the limited resolution of the SEM for structures smaller than a few nanometres. The euhedral shape of the recrystallized grains is

**Fluid-filled grain boundaries in the cryo-SEM**

![Fluid-filled grain boundaries in the cryo-SEM](image)

**Fig. 13.** Schematic illustration of mobile, fluid-filled grain boundaries as shown by segregation pattern from cryo-SEM observations (A). The arrows indicate the euhedral growth of the primary recrystallizing grain (white) into the deformed grain. The true nature of these boundaries in terms of a semi-continuous fluid film (B) or an island-channel structure (C) cannot be resolved with the cryo-SEM.
related to such fluid-filled grain boundaries (Fig. 5C). The surface of the recrystallized grain is inferred to be an F-facet. However, the nature of the fluid-filled grain boundary, i.e. whether it is a semi-continuous fluid film (Fig. 13B) or has an island-channel structure (Fig. 13C), remains unclear.

The presence of fluids in grain boundaries agrees with previous observations on mobile grain boundaries in wet halite (Drury & Urai 1990; Peach et al. 2001; Schenk & Urai 2004; Urai et al. 1986a,b; Watanabe & Peach 2002), whereas experiments on dry sodium chloride show that the grain boundaries are immobile below temperatures of 400°C (Franssen 1993; Guillopé & Poirier 1979). The fact that recrystallized grains are characterized by an euhedral shape with a clear crystallographic relationship in terms of facets (Figs 5, 11 and 12) is in agreement with observations of similar microstructures in other fluid-bearing, recrystallizing materials (e.g. Kingery 1974; Skrotzki & Welch 1983).

Such a preferred growth of primary or secondary recrystallized grains is interpreted to be either (i) a result of the high surface energy anisotropy of the wetted NaCl grain boundaries, (ii) a growth mechanism similar to that seen in crystal-melt systems where a ledge mechanism leads to the euhedral shape according to the step model of Gleiter (1969) or (iii) a combination of (i) and (ii). High surface energy anisotropies are expected to play a major role in fully wetted grain boundaries. Observations in olivine-ultramafic melt systems showed that completely wetted grain boundaries are often found parallel to low-index facets [(010), (110) and (021)] (Jung & Waff 1998). These are similar to our observations of growing primary recrystallizing and exaggerated grains normal to the [100] faces.

Walte et al. (2003) have questioned the importance of surface energy anisotropy. They showed that completely wetted grain boundaries can simply form by consumption of small grains during fluid-enhanced static recrystallization, and concluded that there is no need to relate the structures to surface energy anisotropy, even though this might enhance the effect.

Another possible explanation for the euhedral shape of the primary and secondary recrystallized grains is the ledge jump grain boundary migration mechanism described by Gleiter (1969). The assumption of a fluid-filled grain boundary with two solid–fluid interfaces and a fluid layer in between is similar in terms of the sharp transition of crystal lattice and adjacent grain boundary and the influence of the orientation of the crystal on the migration rate. According to the step model, the motion of the grain boundary in the presence of a driving force proceeds by: (i) dissolution of ions from favoured sites (steps) of the shrinking old grain and from deformation-related dislocations that reach the surface, (ii) diffusion through the fluid layer and (iii) re-attachment at preferential steps of the growing strain-free grain. The euhedral shape suggests that diffusion is not restricted to the shortest distance. However, the fluid layer regulates (balances) the transport of ions, such that they are precipitated at favoured steps to preserve the character of the [100] facet.

Inside the coarse-grained samples, grain boundary migration stops if two or more recrystallized grains come into contact because of the reduction in driving force as the grains have the same (low) dislocation density. Only the grain boundary energy can drive further grain boundary migration. In this situation, the grain boundary fluid is accumulated along triple junctions leaving behind healed, brine-free grain boundaries. These immobile solid–solid contacts could have developed by boundary annealing, i.e. the surface energy driven attraction of grain boundary fluids into the triple junction network, a process that is controlled by the contact angle.

The cessation of normal grain growth inside the fine-grained samples is also interpreted to be caused by such boundary healing: below a critical grain size the fluid-filled grain boundary contracts and accumulates in the triple junction network because of the effect of surface energy forces (Visser 1999).

CONCLUSIONS

Cryo-SEM observations offer direct evidence of fluid-filled grain boundaries in statically recrystallizing wet, polycrystalline sodium chloride samples. The frozen fluid phase is represented by the segregation pattern composed of the two phases, hydrohalite and evaporated ice.

The thickness of such migrating brine-filled grain boundaries is usually less than 30 nm. Finer scale structure is obscured by resolution of SEM and segregation of brine during freezing.

Primary recrystallized growing and exaggerated-grown grains exhibit euhedral shapes with [100] facets. We interpret this type of growth as a consequence of either significant anisotropic grain boundary energy and/or a solid-melt/brine type growth mechanism with a ledge jump mechanism.

The results are in agreement with a model of brine-filled grain boundaries during primary recrystallization and exaggerated grain growth, and healed grain boundaries in normal grain growth.

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