Micro Structural Development of *in Situ* Heated and Deformed Pure and Silica Gel-Doped Polycrystalline Halite Using High Energy Synchrotron Radiation

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Abstract: This paper presents an experimental investigation of the microstructural development upon *in situ* compression and heating of pure and SiO₂ gel-doped (5 wt%) polycrystalline halite, with grain sizes ranging from 45 µm to >70 µm (cold pressed at 200 MPa and heated at 150 °C for one week), using high energy synchrotron x-ray radiation. Texture development of the samples was studied at room temperature, 100, 200 and 300 °C. At each temperature, the samples were axially compressed keeping the load constant at every ~500 N step up to the maximum 2,400 N (~ 48 MPa). At the different loads and temperatures, 2D images and load/elongation curves were recorded *in situ* to get information about the texture development and the rheological behaviour of the polycrystalline halite samples. At high stresses, the doped halite samples show an increase in the elastic moduli and in the microstrain. The results were confirmed by the single grain orientation analyses using the FABLE program, where a sharpening of the texture was observed.

Key words: Polycrystalline halite, *in situ* experiments, microstructural development, silica gel.

1. Introduction

Numerous experiments have been conducted on synthetic and natural single and polycrystalline halite confirming its complex deformation behaviour as a function of different physical and chemical parameters. Halite has a high energy storing capacity due to its viscoplastic behaviour. During the viscoplastic deformation of the grains the cracks and pores in the aggregate are closing, hindering the permeability of gases and liquids. This is of big advantage in the final disposal of radioactive waste, gas and oil storage, the energy storing processes [1-3], and the storage of hydrocarbon [4, 5].

The rheological behaviour is of great importance in order to make prediction about the storing capacity of salt. In fact, the rheological properties of NaCl have

been studied over the past thirty years under extension, compression or indentation, whether on single crystals or polycrystalline aggregates, natural or synthetic halite and are still of great interest for both materials scientists and mineralogists. Experiments have been carried out in a temperature range from room temperature to 780 °C, and under a confining pressure ranging from one atmospheric pressure to 250 MPa [6-16]. In geology, for example, the main interest is connected to deep Earth rheology since halite has the same structure and similar slip systems to ferropericlase (Mg, Fe)O [17, 18]. In materials science, MgO, the pure end member of ferropericlase, is used as a ceramic but also as an additive to cement due to its energy storing capacity.

Studies of Pennock and Trimby show that water/fluids play an important role in the micro structural and rheological behaviour of salt. The wet samples are weaker than dry NaCl at low strains

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probably due to pressure solution creep, while at higher strains (> 0.1) the weakening is associated to recrystallization [19]. A few years before [20] was shown that misorientation angle distributions at high strains were different for wet and dry samples due to the fact that dynamic recrystallization removes subgrain boundaries in wet NaCl.

In a recent paper of the author [21] the pressure solution phenomena enabled by second phase in the grain boundary and the resulting grain boundary sliding through diffusion of matter along the grain boundaries was confirmed. Additionally the author could demonstrate that the deformation mechanisms operating simultaneously to grain boundary sliding is not only diffusional creep but also dislocation creep.

Recent work [22] in Material Science and Engineering showed that the addition of 5% wt silica sol in ultra-low and refractory castables improves both fluidity and strength of the material due to gelation mechanisms and the development of siloxane (Si-O-Si) bond. In the polycrystalline halite the amorphous SiO_2 gel additives have the same strengthening effect at this modal proportion, but the processes taking place are not understood in detail.

Furthermore, the study of the bi-phase system in relation to salt caverns gives additional hints for the design/optimization construction of caverns for underground storage of radioactive material, which requires intimate knowledge of stability and convergence behaviour of an underground system. A typical repository will be at a depth in the range of 350-1,000 meters with waste in canisters and the remaining voids backfilled with crushed salt. An admixture with silica sol could ensure an immobilization of liquid radioactive waste in the case of long-term corrosive problems. In fact, it was developed a low-temperature (5-60 °C) procedure to immobilize low-level liquid radioactive waste using aqueous silica sols [23]. An additional temperature increase can result from the radioactive decay of high level waste, which may cause geomechanical and

geochemical reactions within the host rock. Therefore the design and operation of the facility and the assurance of long-term isolation rely on knowledge of the geomechanical response.

Further on amorphous silica forms natural cementing structural bonds in clays, developing very strong, water-resistant and slightly strained rocks [24]. On early stages of rock formation these developed bonds prevent the rocks from further consolidation during sedimentation and provide the chance to keep a lot of weakly coherent or free interstitial water, forming potentially plastic and fluid rocks. In the simplified experimental systems [25] halite-halite and halite-silica were studied. From the observed deformation mechanisms information about seismic events and fault rheology can be deduced as will be explained in detail later.

The uniqueness of the study presented in this paper is the elaborated/subtle combination of obviously dependent main factors (listed below) worth to be taken into account in the approach of complex problems faced during seismic events/fault rheology and in the final disposal of radioactive material in salt caverns.

The motivation for uniaxial compression experiments at room temperature and *in situ* heating and deformation experiments until 300 °C were to investigate the mechanical behaviour of deep rock salt to temperature and pressure. The temperature and pressure sensitive mechanical properties of rock salt is necessary to demonstrate the operational conditions of storage. Here for the first time *in situ* deformation and heating experiments both on wet pure and silica gel-doped polycrystalline halite (~ 700 ppm for the silica gel-doped polycrystalline halite and ~900 ppm for the pure salt) were performed. The studied samples were uniaxially compressed to understand their textural development and rheological behaviour. *In situ* experiments can directly shed light on the fundamental mechanisms of the processes taking place during texture development. The bulk texture is

composed of different texture components (specific orientation of grains). In the experiments presented in this paper the specific orientation of grains are expressed by “hkl” planes and “uvw” directions in correlation to the compression direction.

Also in geology there are still many relevant problems to be understood in fault zone rheology and the dynamics of the Earth’s crust. Ductile evaporates (salt) control the dynamical evolution of many sedimentary basins. The deformation mechanisms take place at temperatures relevant for engineering and natural halokinetic conditions (20-240 °C).

The main motivation for the study of the influence of silica gel on the texture development of polycrystalline halite lies in improving our understanding of the most complex polymineralic systems present in the natural salt caverns used for CAES (Compressed Air Energy Storage) and final disposal of radioactive material, where, in addition to the main phase, various rock forming silicate phases, which stabilize the system are also present. Both man-made and natural silicate and silica phases as additives and main actors show their relevance in many important fields. Furthermore they open the view for new questions and new occurring problems worthwhile to be studied.

The results in this paper show the influence of amorphous silica gel in the texture development and the physical properties (i.e. stress/ductility behaviour) of polycrystalline halite, focusing not only, on bulk texture but also on the changes in single grain orientations, which give additional information on possible deviation from the original grain orientation and therefore on the strain accumulation during the deformation and heating experiments.

2. Experimental

2.1. Sample Preparation

The polycrystalline NaCl used in this study was obtained from Sigma Aldrich. The purity of the polycrystalline salt is 99.9%, with trace amounts of

bromide, iodide, potassium hexacyanoferrate, nitrite, phosphate, sulphate and heavy metals (e.g. Pb). The salt was supplied as an analytical fine-grained powder with a grain size of around 50-150 µm. Small portions of the powder were ground in an agate mortar with different grinding times to get an homogeneous grain size powder. The polycrystalline material was separated by a set of sieves ranging from < 45 µm to >70 µm, from which four powder sets were prepared to press the cylindrical samples as described below. The powder sets had a grain size of < 45 µm, 45-50 µm, 50-70 µm and > 70 µm, from which 8 samples per powder set were prepared. Half of the samples were doped with around 5 wt% homogeneously distributed SiO₂ gel (amorphous and water free), and the other half without admixture. We performed *in situ* heating and deformation experiments from room temperature to 300 °C at 100 °C steps, using a new sample for each temperature.

For the deformation experiments presented in the literature, grain sizes from 300-400 µm [19, 20, 26] and grain sizes < 10 µm [26] have been used. For the first time grain sizes ranging from 45 µm to 70 µm were chosen for the study presented in this paper to show possible variations in microstructural and rheological behaviour of the polycrystalline material in small grain size intervals.

Starting material was produced by cold pressing pure polycrystalline halite (and with SiO₂ gel additives) of different grain sizes using a uniaxial pressure (100 tons). Approximately 60-70 g of powder was poured into a steel container enclosed by upper and lower pistons for pressing and produce a pellet of 5 cm diameter and 2-3 cm height. The powder was cold pressed at 200 MPa for 20 seconds, and finally heated at 150 °C for 7 days. After this period, a diamond tipped core drill (dry drilled) was used to extract a cylindrical sample of 8 mm diameter and 2-3 cm height.

The thin sections of the *in situ* heated and deformed samples (Fig. 1) were prepared as follows: The halite

Fig. 1 Thin section images in transmitted light of the a+b pure and c+d SiO₂ gel-doped polycrystalline halite samples (> 70 μm grain sizes) shown at a+c lower and b+d higher magnification.

samples were ground down to 100 μm thickness and after that polished with the finest sand paper (2,400 grade). Finally the surface was etched with an iron chloride (FeCl₃·6H₂O) solution (0.5 wt.-%) prepared by adding 100 ml deionized water to the 500 ml halite saturated solution and adding iron chloride (FeCl₃·6H₂O). For better handling the 2.5 gram iron chloride was dissolved in the 100 ml deionized water before adding to the halite saturated solution. The thin section was then suspended in the etching solution for about 60 seconds and then rinsed with n-hexane. Immediately after rinsing the thin sections were dried with compressed air.

2.2. Methods and Testing Procedure

The uniaxial compression experiments at room temperature were performed at the institute of applied geosciences in the department of engineering geology at Ernst-Reuter Platz (Berlin). The length (2-3 cm), surface area (0.5 cm²) of the cylindrical sample, and the displacement rate (0.14 mm/sec) were input as starting parameters. Using the acquired stress/strain curves, these initial parameters allow me to get

information about the strength and ductility of the studied samples. This information could be used for the setting parameters of the *in situ* experiments to choose a suitable stress range where the samples do not break.

The *in situ* heating and deformation experiments on polycrystalline halite were performed at the BW5 beamline at the German synchrotron in Hamburg (DESY—Deutscher Synchrotron). For the experiments a monochromatic X-ray beam ($\lambda = 0.124$ Å in the first beamtime run and 0.127 Å in the second beamtime run) was focused through 500×500 μm slits on the cylindrical sample.

The measurements were performed at beamline BW5 in 1° steps in the omega angle range of $\pm 20^\circ$ (rotation axis perpendicular to the compression direction). In a second beamtime run the measurements were performed in 0.2° steps in the omega angle range of $\pm 40^\circ$. The cylindrical samples with 8 mm diameter were heated and deformed under axial compression with the tensile- compression device of Kammrath and Weiss [27] from DESY and from TU Clausthal. The machines were laid out for 5

kN where of max. 2,400 N were applied on the sample. Heating was applied by supplying direct current to self-made ceramic rings wound with isotan wire. The rings were mounted at opposite ends of the sample core. The temperature range varied from room temperature to 300 °C in 100 °C steps (with 10 °C/second gradients), which are relevant temperatures for engineering and natural halokinetic conditions (20-200 °C), as the operational conditions for example in the case of radioactive waste and gas storage. A thermocouple was mounted on the sample and near the ceramic rings to detect the temperature and to prove that there is no temperature gradient due to the very high heat conductivity of salt. At each fixed temperature, the samples were axially compressed at a rate of 4 N/sec until, for example, a pressure of 500 N is reached. During this constant load period (15-20 min.), the texture measurements were performed. Afterward, the samples were compressed with increasing loads until a maximum load of 700 N, 1,000 N, 2,000 N, 2,400 N (Fig. 2).

The 2D images of the synthesized polycrystalline salt samples were recorded with a Perkin Elmer X-ray detector PE 1621. For the single grain orientation analysis, the program FABLE (Fully Automatic BeamLine Experiments) was used, which is a suite of programs developed by the authors listed in [28]. FABLE is an open-source software package complete with a graphical user interface, options for use of parallel computing and GPUs (graphic processing units), documentation, and a developers corner (<http://fable.wiki.sourceforge.net/> and publications therein). For the analyses of the bulk texture the softwares StressTex [29] and MTEX (a Matlab toolbox for quantitative texture analysis) running under MATLAB (matrix laboratory) were used [30, 31].

2.3. Analyses

The FABLE (Fully Automatic BeamLines and Experiments) program enables extraction of single

Fig. 2 Diagram of the *in situ* heating and deformation experiments. Stress/strain curves versus time.

grain orientations, while StressTex integrates over a specific azimuthal angle. In the analyses of the diffraction data with FABLE, the positions of the diffraction peaks were first located. This step was performed using the 2-D (two-dimensional) peak search module from the FABLE suite of programs (<http://sourceforge.net/apps/trac/fable/wiki> and publications therein). The program Grain Spotter was then used to index the grains, i.e. assign the diffraction spots to grain orientations. The refinement of the centre of mass positions, orientations etc. of the indexed grain was performed as a simultaneous 12 parameter per grain fit to the assigned reflections using the FitAllB module of FABLE.

In the second run too much grain overlap was present, and therefore the program StressTex was used. The StressTex spectra were obtained by integrating the images over 3° and 5° azimuthal angular slices, resulting in 120 or 72 spectra per image. To have a comparison between the data from the first and second beamtime runs, and to ensure reliability of the obtained results, all analyses from the first beamtime run were again analysed with the StressTex program.

3. Results

The analysis of the pure and silica gel-doped polycrystalline halite samples reveal contrasting

(a)

(b)

Fig. 3 Stress-strain curves recorded during *in situ* deformation of a the pure and SiO₂ gel-doped polycrystalline halite (> 70 μm grain size); b Stress-strain curves recorded during *in situ* uniaxial compression of the SiO₂ gel-doped polycrystalline halite in dependence of the grain size (50-70 μm and > 70 μm grain sizes). The stair steps in the diagrams are representative for the constant load period of 15-20 min.

rheological behavior. The results of these analyses are reported in Figs. 3-10.

3.1. Stress/Strain

Strain curves of the pure and silica gel-doped polycrystalline halite were acquired during the performed *in situ* deformation and heating experiments (Figs. 3-5). At constant grain size, the strain/stress

Fig. 4 Stress-strain curves recorded during *in situ* heating and uniaxial compression of the pure polycrystalline halite with grain sizes around 45-50 μm and 50-70 μm in dependence of the temperature.

Fig. 5 Stress-strain curves recorded during *in situ* deformation at 200 °C of pure and SiO₂ gel-doped polycrystalline halite (50-70 μm grain size).

curves of pure polycrystalline halite reveal a decrease in the Young's modulus, in the yield strength and an extended plastic regime. However, the curves of the silica gel-doped sample show contrasting behaviour (Fig. 3a). Moreover, the pure polycrystalline halite sample shows a pronounced creep behaviour relative to that of the silica gel-doped sample (Fig. 3a).

The same trend is also confirmed and observed with increasing grain size (Fig. 3b). The sample with the larger grain size (> 70 μm) shows a higher strain for both the pure and gel-doped samples.

Additionally, the stress/strain curves of the pure polycrystalline halite samples reveals a decrease in the yield strength with increasing temperature (Fig. 4). The inclusion of the polycrystalline sample with a larger grain size of 50-70 μm in this comparison should clarify that the increasing grain size in addition to the increasing temperature results in an even lower yield strength. Since the increase of both parameters (grain size and temperature) generate a decrease in the yield strength the comparison with the only sample with bigger grain size and treated at higher temperature should confirm, as expected, an even bigger decrease in yield strength in correlation to the samples with lower grain sizes (Fig. 4). Furthermore the heated sample at 300 $^{\circ}\text{C}$ could not be deformed to the same high stress conditions due to onset of rupture at around 12 MPa. A decrease in the yield strength is also observed in the pure samples in comparison to the doped sample heated at 200 $^{\circ}\text{C}$ (Fig. 5). Additionally an increase in strain at constant load and fluctuations in stress are observed (Figs. 4-5).

The stress/strain curves acquired at room temperature until rupture occurred, described below, confirm the trends observed in the strain curves acquired during heating and deformation experiments. Here a steeper (nearly linear) increase in stress is observed demonstrating an increase in strength of the material with SiO_2 gel additives. Furthermore the rupture strain tends to decrease in the doped samples and at the same time the strength and stiffness increase. In the pure samples the curves are linear at low strain followed by plastic deformation in the region of around 3% strain until a maximum of 25%, while in the doped samples only a low strain of maximum 5% is observed (Fig. 6). Further evidence for the contrast between strength and elastic behaviour of the pure and doped polycrystalline material is observed in the shift and broadening of the reflections at high two theta angles in the integrated diffractograms (Fig. 7). In the diffractograms of the pure samples a shift of the 400 peak is observed (Fig. 7a and b) while the doped halite samples show a

Fig. 6 Stress-strain curves recorded at room temperature of pure and SiO_2 gel-doped polycrystalline halite.

broadening of the 400 peak with increasing temperature and stress (Fig. 7c).

3.2. Texture Development

The results of the texture analyses, obtained from the single grain orientation and bulk texture, clearly show that the texture development of the samples starting from predeformed (not completely healed) depends on temperature, stress and silica gel additives. These results provide us with, despite the lower texture, an insight into the changing grain orientations during the uniaxial compression and heating experiments of the predeformed polycrystalline halite. The texture components observed during the *in situ* experiments using the single grain orientation analyses were mainly: (011) [100], (001) [100], (001) [1-10] accompanied by the texture components (011) [3-11], (011) [0-11] (Fig. 9).

The results obtained from the two analysis methods (bulk texture and single grain orientations) show similar trends. In the pure polycrystalline halite, a change in the bulk texture in response to stress and temperature is observed, accompanied by a broadening of the single texture components (deviation from the original grain orientation) (Fig. 8). This observation is consistent with the increasing plastic behavior observed in the stress-strain curves and with the shifting of

Fig. 7 (a) Each curve represents the Bragg reflection 400 of the diffractogram, obtained from the summation over all in 5° steps integrated 2D images at each omega angle (+/-20°) for every applied stress (0 N until 2,400 N). The peak shifting of the Bragg reflection (400 peak) provides a measure of macrostrain in the pure polycrystalline sample (> 70 μm grain size) with increasing stress; (b) Each curve represents the Bragg reflection 400 of the diffractogram, obtained from the summation over all in 5° steps integrated 2D images at each omega angle (+/-20°) for every applied stress. The plastically deformed sample at 700 N (near rupture) at 300 °C shows a stronger shift of the Bragg reflection (400 peak); (c) Each curve represents the Bragg reflection 400 of the diffractogram, obtained from the summation over all in 5° steps integrated 2D images at each omega angle (+/-20°) for every applied stress (0 N until 2,400 N). The peak broadening of the Bragg reflection (400 peak) provides a measure of microstrain in the SiO₂ gel-doped polycrystalline sample (> 70 μm grain size) with increasing stress.

the Bragg reflections. In fact, the most deformed sample (50-70 μm grain size) at 300 °C in the performed experiments shows a very broadened (011) [0-11] texture component (Fig. 9).

In the silica gel-doped polycrystalline halite, the initial texture is stabilized and reinforced (Fig. 10). The texture development was first shown with help of the crystallite ODF (orientation distribution function)

Fig. 8 (a) Orientation distribution function (left), inverse pole figure (middle) and pole figures (right) showing the poles to {100}, {110} and {111} planes of the pure polycrystalline halite (50-70 μm grain size) heated at 200 °C (with compression in x direction). (b) Orientation distribution function, inverse pole figure (middle) and pole figures (right) showing the poles to {100}, {110} and {111} planes of the pure polycrystalline halite (50-70 μm grain size) heated at 200 °C and deformed with an applied stress of 2,000 N. The texture differs significantly from the starting texture (of the pre-deformed and heated sample).

Fig. 9 ODF (Orientation distribution functions) (left), inverse pole figure (right) and pole figures (below) showing the poles to {100}, {110} and {111} planes of the pure polycrystalline halite (50-70 μm) *in situ* deformed and heated at 300 °C (near rupture) (perpendicular to the compression direction x).

(Fig. 8a, 8b left + Fig. 10a, 10b left), which describes the frequency of occurrence of particular orientations in the three-dimensional orientation space. This space is defined by three Euler angles, which constitute a set of three consecutive rotations that must be given for each crystallite in order to bring its crystallographic axes into coincidence with the specimen axes. For the cubic/orthorhombic crystal/specimen symmetry, a three-dimensional orientation volume may be defined by using three orthogonal axes for ϕ_1 , ϕ , ϕ_2 with each of the Euler angles ranging from 0° to 90°.

The inverse pole figures are used to further show the texture development in the samples. These inverse pole figures technique is, particularly, useful for axial deformation, where the crystal directions are perpendicular to the compression direction in the sample. The texture is described in units of multiples of a random distribution (m.r.d.).

In the inverse pole figures, most of samples

developed a maximum around 100 with a shift towards 111 and 110. Especially in the case of the deformed sample at 300 °C (Fig. 9) a maximum at 100 is observed with an additional weak intensity near 111 in the starting material, which transforms to a weak maximum in 110.

The pole figures of the starting material, heated at 200 °C and 300 °C and the deformed material after heating of the pure (Fig. 8 right and 9 below) and SiO₂ gel doped (Fig. 10 right) polycrystalline halite show the poles to the 100, 110 and 111 planes and the compression direction x.

3.3 Thin Sections

The examination of the thin sections of the relaxed/unstressed pure (Fig. 1a+b) and SiO₂ gel-doped (Fig. 1c+d) polycrystalline halite samples reveal relative differences in the quantity of the fluid inclusions and the grain deformation. The pure

Fig. 10 (a) Orientation distribution function (left), inverse pole figure (middle) and pole figures (right) showing the poles to {100}, {110} and {111} planes of the SiO_2 gel-doped polycrystalline halite (50-70 μm grain size) heated at 200 $^\circ\text{C}$ (perpendicular to the compression direction x). (b) Orientation distribution function (left), inverse pole figure (middle) and pole figures (right) showing the poles to {100}, {110} and {111} planes of the SiO_2 gel-doped polycrystalline halite (50-70 μm grain size) heated at 200 $^\circ\text{C}$ and deformed with an applied stress of 2000 N (perpendicular to the compression direction x). The texture is similar to the starting texture.

polycrystalline halite matrix (Fig. 1a) is more damaged and has more fluid inclusions than the matrix of the doped polycrystalline halite (Fig. 1c). Furthermore, the fragmentation of the grains results in a lower grain size in the pure material (Fig. 1b). However, in the doped material, a few grains show subgrain structure (Fig. 1d).

4. Discussion

4.1. Stress/Strain

In situ heating and deformation experiments on salt, presented for the first time in this paper, show unique results on the rheological and microstructural behavior of polycrystalline salt. The chosen parameters as temperature, grain size, load and SiO₂ gel additives for the performed *in situ* experiments play an important role in the understanding of complex processes taking place during final disposal of radioactive material in salt. Therefore the knowledge about the rheological and microstructural behavior assure to take right steps in the design and operation of the facility for long-term isolation.

Furtheron the observed deformation mechanisms from the complex *in situ* experiments for which the main acting parameters temperature and pressure in nature were set simultaneously free in dependence of grain size and SiO₂ gel additives, complement the results obtained from earlier studies on simplified systems [25].

The increased strength observed in the SiO₂ gel doped salt samples in contrary to the pure samples indicate that even little quantities of SiO₂ gel additives influence the deformation mechanisms/processes in polycrystalline salt drastically.

Earlier studies [32] showed that clay particles trapped along salt grain contacts enhance mechanically pressure solution by sustaining open grain contacts. The presence of clay particles has therefore important consequences on the ductile behavior of the crust in diagenetic conditions as well as in the gouges of active faults. In the case of

intergranular pressure solution the two models of water film diffusion and undercutting are possible. In both cases the removal of material at grain-to-grain contacts causes the grains to move together (i.e. converge) without requiring internal deformation of the grains. This process leads to macroscopic densification and/or shear creep of a rock, fault gouge or sediment.

Deformation studies [25] at the contact between single-crystal halite and fused silica lenses immersed in brine, showed that intergranular pressure solution occurs. The contact area between two pressed halite lenses (one convexed and one flat) increases/grows as halite dissolved from the free surface of the lenses, diffuses through the pore fluid and precipitates at the perimeter of the contact spot. This process is called neck growth, analogous to crack healing, and is driven by gradients in surface curvature [33].

From the observed dissolution/diffusion processes taking place at grain contacts they could hypothesize/deduce a macroscopic densification and/or creep of a rock, fault gouge or sediment.

With the *in situ* heating and deformation process presented in this paper also a strengthening of the SiO₂ gel doped material was observed, demonstrated with the increasing yield strength in the stress/strain curves. In addition at constant load a higher increase in strain in contrary to the doped samples was observed. This increase in strain could be strengthened with the qualitative single diffraction peak analyses in the diffractograms. In the diffractograms of the pure samples a shift of the 400 peak is observed (Fig. 7a and b), which indicates that macrostrain is mainly developing during the deformation processes. During plastic deformation one of the main accommodation mechanisms is the slip of dislocations, whose geometry is crystallographically controlled. The slip directions vary from crystal to crystal, and movement will be constrained by less favorably oriented neighbours. Dislocations interact among themselves. As a result the ability to deform plastically depends on

the ability of dislocations to move [34]. The doped halite samples show a broadening of the 400 peak with increasing temperature and stress, which is mostly correlated to an increase in the microstrain (Fig. 7c). Microstrain is the result of small changes in local lattice parameters resulting from defects, imperfections and variations in the crystal structure. Strengthening is based on the fact that it is difficult for a dislocation to pass into another grain, especially if it is very misaligned. Atomic disorder at the grain boundary causes discontinuities in slip planes. For high-angle grain boundaries, stress at the end of a slip plane may trigger new dislocations in adjacent grains. Small angle grain boundaries are not effective in blocking dislocations [35].

The resulting stress/stress relaxation, obviously due to strain accumulation, are visible through fluctuations in stress at constant load (Figs. 4 and 5). The stress/stress relaxation processes could arise from competition between work hardening mechanisms, intracrystalline processes, recovery and fluid assisted grain boundary migration. This competition even increase with temperature and grain size. In fact the grain size also plays an important role. The smaller the grains, the larger the area of grain boundaries for impeding dislocation motion. Smaller grain sizes usually improve strength as observed in the experiments due to the greater ratios of surface area to volume, which means a greater ratio of grain boundary to dislocations. The more grain boundaries that exist, the higher the strength becomes because of the higher square unit of grain boundary for each dislocation and therefore there is a much greater chance for a dislocation to be stopped at a grain boundary in the smaller grain.

Despite the influence of the decreasing grain size to the strength of the sample, the SiO₂ gel additives are by far more effective (Fig. 6).

4.2. Texture Development

Although halite has a simple ionic structure and

well-defined slip systems, the mechanical behavior of the polycrystal is rather complicated, resulting in a quite heterogeneous deformation. Therefore the resulting microstructures indicate that differently oriented grains deform by different amounts. The texture components observed during the *in situ* experiments using the single grain orientation analyses were mainly: (011) [100], (001) [100], (001) [1-10] accompanied by the texture components (011) [3-11], (011) [0-11] (Fig. 9).

Uniaxial compression of single crystals of halite parallel to [001] ([36], [37]) show that the primary slip system was {110}<1-10>. The secondary slip systems, {100}<110> and {111}<1-10>, were later identified for crystals deformed in other orientations [38, 39]. In a recent study [40] the crystal preferred orientation (CPO) developed during shear deformation is characterized by two texture components, a pronounced {111}<110> and a weaker {001}<110> component. With increasing shear strain dynamic recrystallization becomes dominant. Dynamic recrystallization occurred by two processes: subgrain rotation recrystallization and grain boundary migration. Recrystallization is characterized by a single and strong {001}<110> texture component, while in the grain growth regime a slightly rotated {110}<110> texture component is present.

In addition from the microstructural analyses of the *in situ* heating and deformation experiments a broadening of the single texture components (deviation from the original grain orientation) in the pure sample is observed. This observation is consistent with the increasing plastic behavior shown in the strain/stress curves (Fig. 2-6) and in the shifting of the Bragg reflections (Fig. 7a + b).

Usually when the texture component is very sharp, then the mean misorientation is small and there are many low angle boundaries within a particular texture variant, whereas if the texture components are more diffuse (broadened) then the boundaries have a high mean misorientation. Evidently, recrystallization

occurs as the material deforms, involving both nucleation of new grains and replacement of a texture component by another. The driving force for recrystallization is the strain energy stored in individual grains. Highly deformed grains (or highly deformed regions within a grain) have a tendency to nucleate new grains, given the availability of significant misorientations [41].

In a recent study [42] *in situ* annealing experiments on single crystals using EBSD, boundaries were associated with different slip systems, in which (011)[0-11] plays an important role in the different deformed parts of the sample. Secondary boundaries for example with (101) [-101] and (-101) [101] were found in the most deformed part of the crystal. The experiments were performed in the temperature range from 280 °C until 470 °C. The observed texture components are mainly attributed to recrystallization and are secondary to the deformation and also growth.

Especially in the case of the deformed sample at 300 °C (Fig. 9) a maximum at $\langle 100 \rangle$ is observed belonging to recrystallization. In addition a weak intensity near $\langle 111 \rangle$ in the starting material is observed, which transforms to a weak maximum in $\langle 110 \rangle$, demonstrating the disappearance of deformation texture and the appearance of growth texture components in the halite sample. As known also from earlier studies [43-46] recrystallization mechanisms are dependent on a number of variables as pressure, temperature, strain rate, total strain, grain size and fluid content and are still a point of debate.

A first approach to understand the complex behaviour of the samples are the unique results obtained from the simultaneous heating and deformation of the samples presented in this paper. Furthermore, the thin-section analyses of the relaxed pure and doped halite samples first show a difference in stability, correlated with the relative fluid inclusion content, the fragmentation of the grains and the subgrain development. In fact, the high fragmentation of the grains in the pure sample, probably due to lower

strength, is comparable with the lower elastic moduli observed in the acquired stress/strain curves during the *in situ* heating and deformation experiments. By contrast, the grains in the SiO₂ gel-doped halite samples show no lowering of their grain sizes. Instead, subgrains are observed in most of the grains, which is an indication of plastic deformation. Nonetheless, the pure samples show a higher degree of deformation than the doped ones do, as expected from the stress/strain curves.

The polycrystalline halite samples doped with silica gel show an increase in strength (stiffness), and elastic behavior persisting until high stresses and a lowering of strain. This is confirmed with the stress-strain curves (Fig. 3-6), the peak broadening (demonstrating the presence of microstrain) at high two theta angles in the diffractogram (Fig. 7), and finally with the single grain orientation analyses (Fig. 8-10), using the FABLE software, from which the spread of the single grain orientations is also calculated. The deviation of the texture components from the original grain orientation can be seen as distortion of the lattice parameter of the single grain, resulting in microstrain on grain level and hence macrostrain in the aggregate. All these aspects give an indication for a higher grain shape preservation possibility in the doped samples. For this hypotheses several general aspects of earlier studies can be taken into account. For example polyminerale rocks show larger field of pressure solution dominance than the monomineralic rocks accompanied by grain boundary sliding [47]. The preservation of the grain shape can be caused by extensive grain boundary sliding [48], occurring as a secondary but necessary mechanism for accommodation of local strain incompatibilities between neighboring grains. In contrary diffusion or dislocation multiplication and climb can account for changes in grain shape [49].

5. Conclusion

In general a decrease in yield strength in the pure

samples is observed, compared to those doped with silica gel. Further decrease is seen with increasing temperature and grain size. Under the same stress conditions the pure samples show a decrease in the Young's modulus and the yield strength and an extended plastic regime compared to those doped. All samples, irrespective of grain size, show a higher yield strength with silica gel additives. These observations show that some grains deform much more than others, resulting in a large variation in dislocation microstructure such as dislocation density and subgrain geometry. Silica gel additives in the bulk halite cause a lower strain accumulation, expressed through a larger Young's modulus, a strengthening of the samples, which correlates with a decrease in plasticity. In the texture development a sustainability of the starting texture is observed, which correlates well with the mechanical behavior. The amorphous phase likely protects the single grains in the crystalline phase from deformation, alleviating strain accumulation by introduction of defects and therefore the preservation of the grain shape. The degree of stress and strain partitioning in the deforming salt depends strongly on the proportion of silica gel additive, as well as on the temperature and grain size dependencies, which bears important implications for long-term lithospheric rheology and radioactive waste disposal.

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