MONITORING OF SALT-INDUCED DEFORMATIONS IN POROUS SYSTEMS BY MICROSCOPIC SPECKLE PATTERN INTERFEROMETRY

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Abstract

Electronic speckle pattern interferometry (ESPI) has been used to monitor micro-deformations produced by phase transitions of magnesium sulfate in a porous material. Samples of fritted glass were chosen as a standard porous substrate because of its mean grain size, its porosity distribution, and its negligible humidity expansion. The glass samples, soaked with salt solution, were exposed to changes in the relative humidity of the surrounding air. Due to the small grains of the samples in the range of 10 to 100 µm an ESPI-system with high lateral resolution was realized by imaging through a microscope and using a HeCd-laser of short wavelength. For the first time deformations produced in a porous substrate during a hydration-dehydration cycle were successfully registered with high spatial resolution. The results are discussed on the basis of theoretical predictions.

Keywords: electronic speckle pattern interferometry, deformation measurement, salt crystallization, phase transition, porous material, dilation measurements, scanning electron microscopy.

1. Introduction

The crystallization of soluble salts in porous materials has been recognized to have a pronounced deteriorating potential. In historic as well as in modern buildings and monuments, salt weathering has been found to be responsible for significant damages which are apparently caused by the generation of high crystallization and hydration pressures. Although known for a long time, the basic mechanisms of salt deterioration are not completely understood and the situation is suffering from a lack of fundamental insight in the underlying processes.

One approach to study the onset and the dynamics of salt-induced pressure is to measure micro-deformations in the neighborhood of single pores within a porous substrate during the crystallization or hydration of salt. For this purpose electronic speckle pattern interferometry (ESPI) was used. ESPI is a non-contact and full field method, which is able to detect deformations in the sub-micron range and in video real-time. Full field means that the displacements within the field of view can be detected spatially resolved. This has the big advantage that deforming parts of the object's surface can be immediately identified and further examined in detail, e.g. with scanning electron microscopy (SEM). Since the main goal of the ESPI measurements was the investigation of deformations in the neighborhood of single pores an ESPI system with a small and well-adapted field of view was realized by using a microscopic objective. To increase the sensitivity of the system, a HeCd-laser emitting deep-blue light at a wavelength of 442 nm was used. In this paper first results obtained with this microscopic ESPI are presented and discussed on the basis

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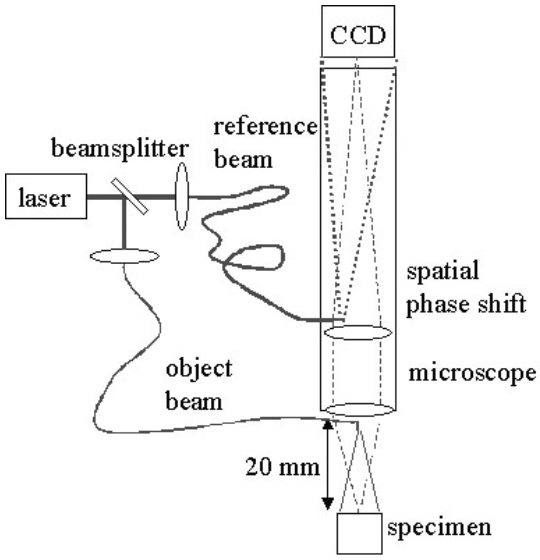

Figure 1: Scheme of the setup used for microscopic ESPI measurements.

of the present theories.

2. Microscopic ESPI

In the field of optical metrology, ESPI has been found to be a very useful technique for measuring the deformation or displacement of an object surface. The underlying principles of ESPI are widely known and comprehensively described in literature, e.g. in Sirohi 1993. The method is based on holography with the main difference that a CCD camera is used to capture the interference patterns, which are then digitally stored in a computer. Therefore, in many reports the technique is called TV-holography or digital holography, too. Our group has been using this technique for a long time for the investigation of deterioration processes in works of art and for the development of procedures for their preservation (Hinsch 2001). Usually the method is used to monitor micro-deformations of objects with sizes ranging from a few centimeters to some meters. There are only few articles in literature dealing with ESPI in a microscopic mode. A very fundamental discussion of microscopic ESPI can be found in Løkberg 1997.

In Figure 1 a scheme of the setup used is shown. The test specimen is illuminated by the coherent light of a laser. Since sensitivity and spatial resolution of the method increase with decreasing wavelength of the light a HeCd-laser with a short wavelength of 442 nm and an output power of 45 mW was used. The object beam, guided by an optical fiber, illuminates the specimen at a small angle to the viewing direction. To perform humidity variations during the measurements, the objects under investigation were placed in a small computer controlled climatic chamber where they could be exposed to well defined ambient temperature and relative humidity. For high resolution in object space a microscope objective with a numerical aperture of 0.42 was used for imaging. The Mitutoyo infinity corrected objective M Plan APO 20 has been chosen because of its long working distance of 20 mm. The geometry of the climatic chamber as well as the kind of air conditioning require quite long a distance between the object's surface and the front lens of the imaging system. To create the image on the CCD-target different simple tube lenses were used with focal lengths varying between 250 mm and 400 mm. The CCD-camera used is an Adimec MX 12P with 8 bit dynamic resolution and 1024 x 1024 pixels. The effective pixel size is

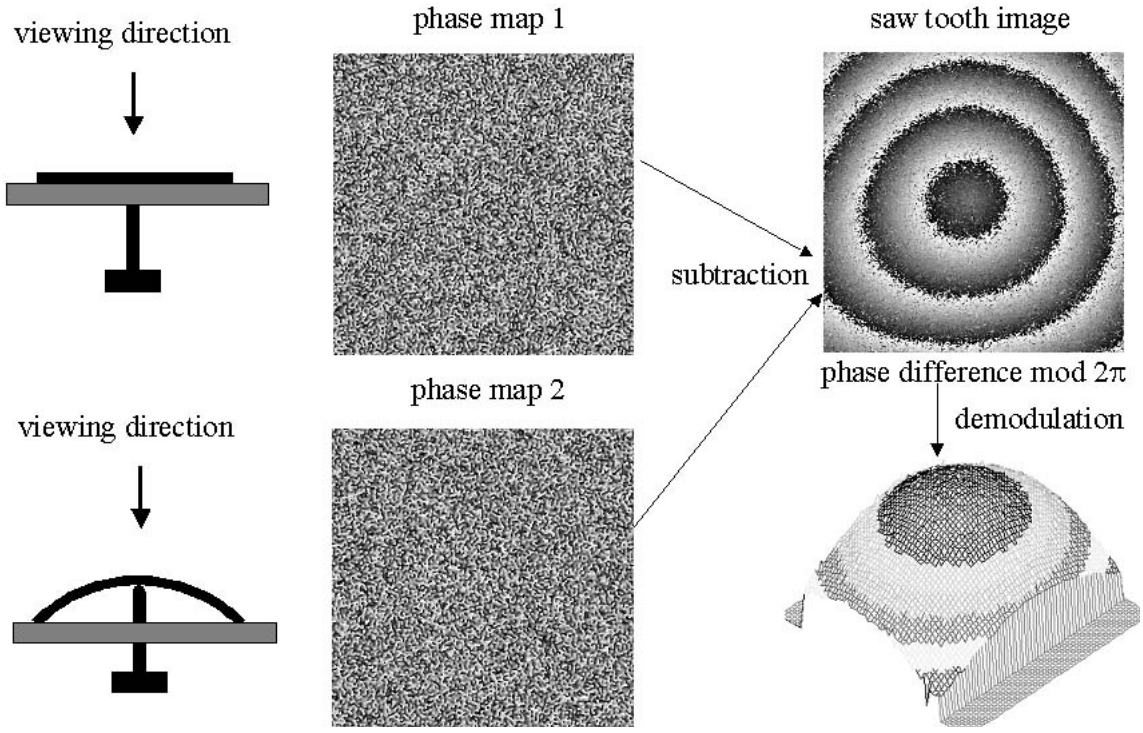

Figure 2: Example of a dented metal plate measured by ESPI. Left: sketch of loading the object. Middle: phase maps before and after denting. Upper Right: phase difference. Lower right: 3-D representation of deformation. Maximum deformation about 1 µm.

about 10 µm. The given fields of view vary between $(250\ \mu m)^2$ and $(400\ \mu m)^2$. Further details can be found in El Jarad et al. 2003.

As in conventional holography not only the intensity of the light scattered by the object under investigation but also its phase has to be registered. Therefore, a part of the laser light is separated by a beam splitter and acts as a reference beam. It is superimposed onto the object image thus forming an image plane hologram directly on the CCD target. The source point of this reference beam, which actually is the fiber exit, is located in the plane of the aperture with a small but well defined horizontal shift out of the center of the aperture. This so-called spatial phase shift method permits the calculation of the phase map of the object wave modulo 2π (Williams 1991). When the object deforms due to an external load, the phase map of the object wave will change according to the path differences thus introduced. Therefore, after loading the object the phase map is calculated again and is subtracted from the original phase map. In the result the changes in phase modulo 2π are obtained representing the deformation or displacement. During our measurements, series of phase maps are recorded enabling us to compare arbitrary states of the object.

For means of illustration, a typical result of ESPI is shown in Figure 2. In this example a standard system instead of a microscopic ESPI was used to measure the tiny denting of a metal plate from the rear by a screw, which is outlined in the left part of Figure 2. The phase maps of the two states of the object before and after denting are calculated. In the middle of Figure 2, these phase maps encoded in gray values are shown. The subtraction of the two phase maps then leads to the difference phase modulo 2π, also known as saw tooth image, which in the case of the denting is a concentric fringe system. The fringes can be interpreted as contour lines of deformation. Knowing the deformation difference corresponding to adjacent fringes, the fringe system can be demodulated and the amount of deformation can be determined. This is shown in a 3-D representation in the lower right of

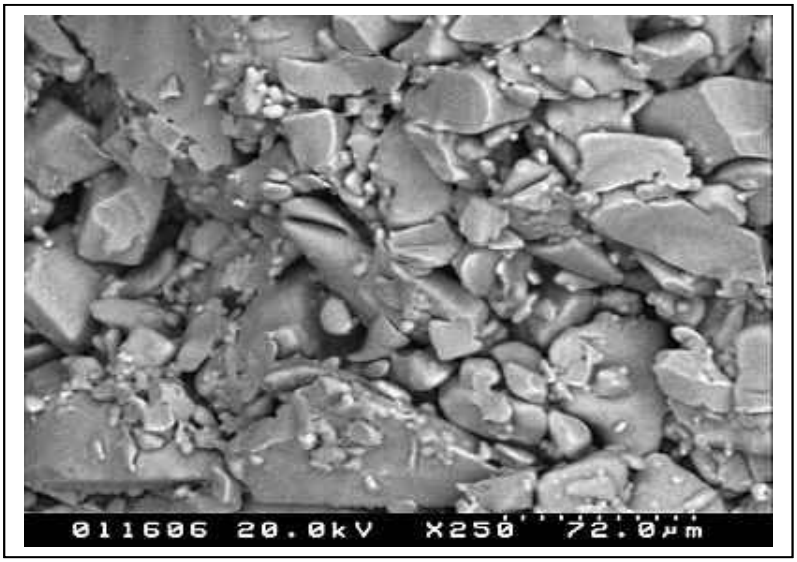

Figure 3: SEM-micrograph of fritted glass specimen.

Figure 2. In this example the fringe spacing is about 350 nm, thus yielding a maximum deformation at the top of the bump of about 1 micron.

3. Experimental results

To investigate the dilation caused by phase transitions of salts, in most of the experiments fritted glass with a well-defined and very narrow pore size distribution was used as a porous substrate. This material, pore class 4, produced by Schott, Germany, has a mean pore radius of 6 µm. It has the big advantage that its chemical composition is simple and that its humidity expansion coefficient is known to be extremely small. This guarantees, that in our experiments any material expansion detected is exclusively caused by crystallization or hydration pressure and is not a response of the material itself.

In Figure 3 a SEM-micrograph of such a fritted glass specimen is shown. Obviously, the grain size of the substrate is non-uniform: bigger grains with dimensions in the order of 100 µm are covered by smaller ones down to less than 10 µm. It must be assumed, that most of the bigger grains near the surface deform individually to each other due to the

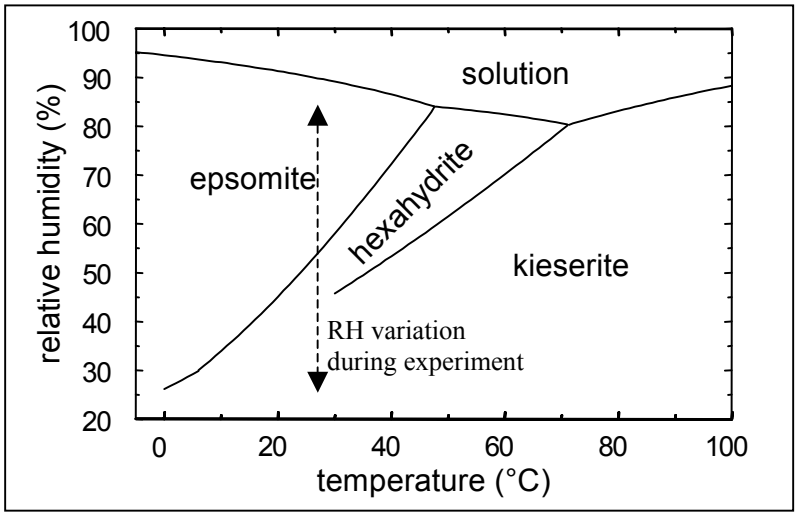

Figure 4: Temperature–humidity diagram of the $MgSO_4$–H_2O system. Variation in RH during experiment marked.

formation of pressure. Thus, at least these bigger grains must be spatially resolved by the ESPI-system, which is guaranteed in the present setup by the microscopic imaging and by using the HeCd-laser.

In most of our experiments small cubes of fritted glass with dimensions of about (1 cm)^3 were soaked until saturation with 10% (w/w) magnesium sulfate ($MgSO_4$) solution. This salt is known to be deleterious in salt crystallization tests and is subject to a number of different phase changes depending on temperature and relative humidity (RH), which can clearly be deduced from its phase diagram shown in Figure 4. In this temperature–humidity diagram only the stable phases in the temperature range from about 0-100 °C are considered. Since the samples were inserted in a climatic chamber during the measurements it was thus possible to produce climatic conditions for expected phase transitions of the salt.

In first measurements the specimen were dried at room temperature after soaking. Unfortunately, severe problems occurred in this case due to efflorescence of salt crystals on the surface of the samples. Increasing the humidity of the air in the climatic chamber caused dissolution of salt crystals and accordingly a change in the micro-topography of the surface. Thus, the light field scattered by the object was significantly altered, leading to a de-correlation of the underlying phase maps impairing the method. Several approaches were made to avoid efflorescence, e.g. a water repellent treatment of the samples or the covering of the surface with a thin layer of gold. Unfortunately, all of these attempts failed so far. Instead, different drying procedures were tested, which finally proved to be successful. The use of high temperatures and/or a hot and dry air flow turned out to shift the evaporation horizon into the substrate, that means, salt crystallization mainly happened below the surface.

In the following experiments, the former drying procedure was used. In first ESPI-measurements the transition from low-hydrated $MgSO_4$, probably mainly kieserite, to a highly hydrated form, probably epsomite, was investigated. After soaking the sample until

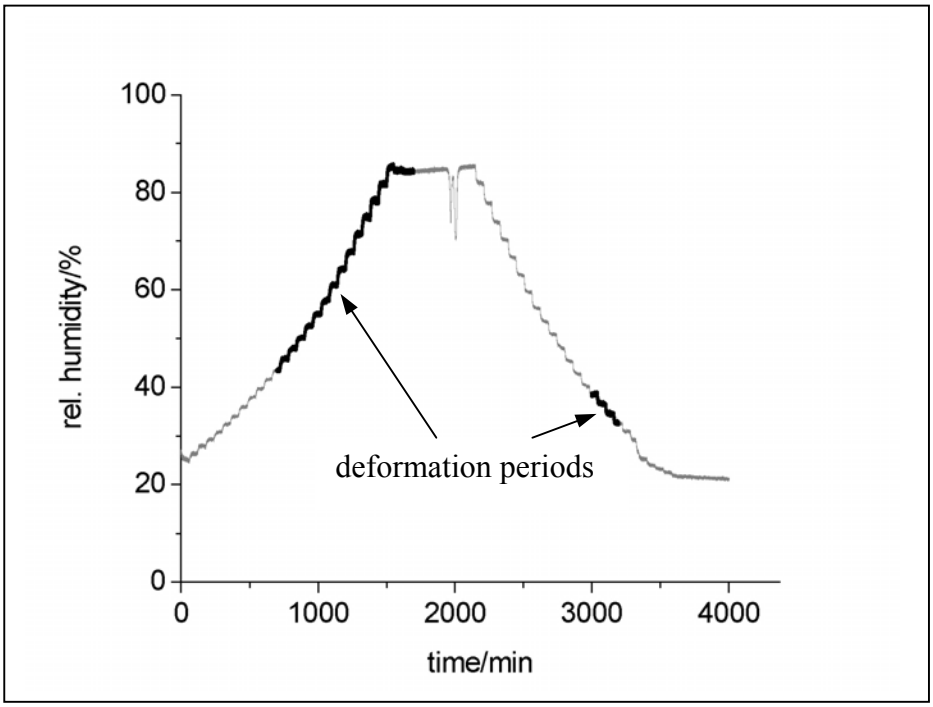

Figure 5: Relative humidity within the climatic chamber vs. time during deformation measurement. Periods of pronounced deformation are marked by black arrows.

Figure 6: Phase difference modulo 2π representing deformations during time period of 4 minutes at 85% RH. Several sub-areas deform independently.

saturation it was dried outside the ESPI-setup for several hours at 200°C in an oven. Subsequently, the specimen was inserted in the climatic chamber. The air temperature within the chamber was kept constant at about 27°C and the humidity was set to a low starting value of about 25% RH. The specimen was then exposed to a humidity cycle. The course of humidity vs. time during the measurement is shown in Figure 5. A phase transition within the substrate was induced by a stepwise increase of humidity from 25% RH to 85% RH within a period of about 25 hours. Thereafter, the humidity was kept constant at 85% RH for about 10 hours. Some deviations from the constant value as shown in Figure 5 are due to a failure in the control loop of the climatic chamber, however there was no detectable influence on the measurement. Finally, the RH was decreased again within about 20 hours to the starting value. The estimated changes of the salt phase can be recognized from the phase diagram in Figure 4, where the variation of RH during the measurement is marked by an arrow.

To specify the principal behavior of the specimen during the hydration-dehydration of $MgSO_4$, a basic evaluation of this first deformation measurement was performed. Those periods in time were determined where parts of the surface significantly deformed. These periods are marked in Figure 5. The main results can thus be summarized as follows: in the beginning of the experiment almost no deformation within the investigated area could be observed. The situation changed significantly when the relative humidity was increased to about 43%. Now, first sub-areas underwent displacements, indicating the onset of pressure induced deformation. It can be seen from Figure 4 that this is in agreement with the theoretically expected humidity value, where a phase transition to higher hydrates should occur. In Figure 6 a typical ESPI result from this state of the experiment is shown in a modulo 2π phase representation. In this saw tooth image, the deformation of an area of $(300\ \mu m)^2$ is shown which occurred during a time period of about 4 minutes at 85% RH. In contrast to the very regular fringe system in the example of Figure 2, the phase map in

Figure 6 is much more complex and irregular. Several sub-regions are apparent with different density and orientation of the fringes. This is for the simple reason that the surface of the substrate consists of single grains which each may deform independently. Since the fringe spacing in this case corresponds to about 230 nm the maximum deformation is about 500 nm.

Obviously, such results can be used to localize areas and to determine the moment in time where deformation starts. Thus, ESPI can guide the sampling of such regions for further cryo-SEM examinations, which is intended in upcoming measurements. It should thus be possible to visualize the deformation-producing salt crystals directly and to study their morphologies and temporal behavior.

Although the final value of 85% RH was reached about 25 hours after starting the experiment the deformation continued to increase for about another 3 hours, then slowed down and stopped after about 29 hours. In the further course of the experiment the humidity was decreased again stepwise. No deformation was detected until the humidity dropped to less than 40% RH. Thus, the hydration-dehydration cycle seems to have a small amount of hysteresis, which, of course, has to be verified in further measurements. Between about 38 % and 32 % RH, deformation patterns were observed, but only for this short period. The resulting fringe systems clearly showed, that the deformation process due to the hydration-dehydration cycle was not reversible at all. Thus, it can be concluded from this measurement, that most of the single grains did not return to its starting positions at the beginning of the experiment. A simple visual observation of the specimen at the end of the experiment furnished evidence for this result. The probe appeared in a poor condition: at least the outer zones of the fritted glass sample showed a pronounced amount of disintegration from the bulk material – and this after only a single transition cycle of $MgSO_4$, which demonstrates the enormous deterioration potential of the salt.

4. Conclusions

It could be shown that ESPI is a well suited method to detect micro-deformations in a porous substrate caused by the transition of salt phases. The first results, which underline the deterioration potential of phase changes in porous material, can contribute to develop a better understanding of dilation processes caused by crystallization and hydration. Further measurements, including phase transitions under varying experimental conditions and especially in combination with results from integral dilation measurements and with the cryo-SEM visualization, will provide a set of data, which can help to verify or to discard present theories of the phase behavior of salts. More details of this combined approach can be found in a separate paper within this proceedings volume.

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