In-situ observation of salt crystallization using environmental scanning electron microscopy

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Keywords: crystallization, in-situ study, environmental SEM, salt

The variable pressure scanning electron microscopy allows observation and investigation of specimens that are difficult or impossible to image in a conventional high vacuum scanning electron microscope (SEM). The basic difference between the environmental SEM and SEM is that the specimen chamber of Environmental SEM can contain a certain amount of gas, mostly water vapour [1].

The pressure of water vapour in the specimen chamber of the Environmental SEM together with specimen temperature play a crucial role in obtaining and maintaining the state of thermodynamic equilibrium between the environment of the specimen chamber and the sample itself, as demonstrated by Cameron and Donald [2]. In thermodynamic equilibrium of 100% relative humidity we must follow the dependence of saturated water vapour pressure on the specimen temperature. A small change of temperature from the stable pressure of the water vapour can be used for the study of transition between the hydration and dehydration phenomena but also to a more limited extent for the study of reactions [3]. These dynamical "in-situ" experiments are the aim of this work.

Crystallization process was observed using the salt K_3 $[Fe(CN)_6]$ (potassium ferricyanide) water solution, which was prepared before the experiment and a in their liquid state placed on the cooled specimen holder placed inside the specimen chamber of microscope. All experiments were carried out under constant operating conditions of experimental environmental SEM AQUASEM-II which was designed in the Institute of Scientific Instruments (ISI) of the Academy of Sciences of the Czech Republic as a non-commercial apparatus for research on environmental SEM detection systems and special experiments in high pressure conditions [4] (beam accelerating voltage 25 kV, probe current 100 pA, working distance 2.5 mm, positive bias of the electrode system 350V) and in the water vapour environment with high relative humidity. Microscope AQUASEM-II is equipped with special hydration system, which enable fine control of water vapour flow into the specimen chamber and Peltier cooled specimen holder enable to cool the specimen in the range from -20°C to room temperature.

The Peltier stage was cooled to -5°C and a specimen chamber was pumped to the pressure 520 Pa. After pressure stabilization the temperature of a specimen stage was increased to -0,2°C. Approximately 20 minutes after reaching above mentioned conditions the rapid crystallization process starts, see Figure 1A. Crystal growth process is presented in figures 1B, C, D, E and F recorded in 10 seconds intervals. The crystallization process takes place under surface of solution covering the crystal.

This paper is focused to study of crystallization of a salt K_3 $[Fe(CN)_6]$ from water solution and shows a typical dynamical "in situ" experiment, presents basic dependence of a relative humidity inside the specimen chamber of environmental SEM on a value of pressure and a temperature of the sample.

G. Kothleitner, M. Leisch (Eds.): MC2009, Vol. 1: Instrumentation and Methodology,
DOI: 10.3217/978-3-85125-062-6-111, © Verlag der TU Graz 2009

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5 This work was supported by the grants No. AV0Z20650511 and MSM 0021630516.

Figure 1. Growth of the crystal of K_3 [$Fe(CN)_6$] from water solution recorded at the stage temperature -0,2°C and pressure 520 Pa in water vapour environment. Conditions: working distance 2,5mm, probe current 100pA, and ionisation detector with bias of the electrode system 350V. Figures A-F were recorded in 10 seconds intervals by ionisation detector of environmental SEM AQUASEM II.