

Our purpose is to study the crystal growth kinetics of sodium and potassium nitrates and the morphology change due to the presence of foreign atoms into the crystallizing solution. Moreover, we also investigate the different growth rate as a function of those 'impurity' atoms. We also study the theoretical equilibrium morphology and the possible epitaxy between nitrates that can conduct to a change in morphology.

As a first step of the work we designed and built a special device to study growth kinetics either in pure systems or with impurities addition mainly of other nitrates.

The unit consists in four main bodies: an observing cell, a peristaltic pump, 2 thermostat baths with heat exchangers and a reservoir. The solution (of known concentration) leaves the reservoir at a temperature somewhat higher than the target temperature with the aim of the pump. It goes through a heat exchanger directly to the observing cell, where a crystal is glued and can be observed in a microscope. Immediately after leaving the cell its temperature is raised again with another heat exchanger that conducts to the reservoir. A 1 liter reservoir of solution is enough to have a constant concentration throughout all experiment. True growth temperature can be recorded continuously; there are two sensors into the solution at less than 5mm from the crystal.

With this unit we are able to control the main parameters that have an influence in the crystal growth which are: flow rate and growth temperature i.e. the supersaturation ratio.

It was found that  $\text{NaNO}_3$  is very temperature sensitive. The metastable region is quite narrow, for a given concentration the gap between crystallization and dissolution can be less than  $1^\circ\text{C}$  [1]. Therefore we have to work in a very accurate way in order to control its behavior. Thus, all precaution cited above are self-explained to monitor experiments.

As in the literature found there is not an agreement in the  $\text{NaNO}_3$  solubility curve we first re-determined it by the method proposed by Beckmann, W., Boistelle, R., and Sato, K. [2]. It consists in observing a crystal looking for a temperature in which it neither dissolves nor grows. This allows us to work at known supersaturation in the following experiments.

[1] R. Benages, E. Vilau, M. Costa, M.A. Bruno, T. Cuevas-Diarte, C. Pallas, *Crystal Research & Tecnology*. In Press. [2] W. Beckmann, R. Boistelle, K. Sato, *Journal of Chemical & Engineering Data* **1984**, 29, 211-214.

**Keywords: growth, nitrate, solution.**

## MS35.P16

*Acta Cryst.* (2011) **A67**, C461

### The effect of foreign particles on the interface shape during solidification of crystals

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The shape of a solidifying interface is generally affected when it encounters foreign inert particles. The degree of deformation depends on the morphology and physical properties of the particles [1-4]. The overall effect also affects the pushing and captures process, when pushing is present.

In the present report the interaction between particle and interface is analyzed by means of a mathematical model employing the finite element method. The effect on the interface of different particle shapes and relative thermal conductivities between particle and melt was studied.

The results shown that for an isolating particle with respect to the melt the interface is convex in a degree that changes depending on the

particle shape and separation distance from the interface. The particle geometries considered for simplicity were spherical, cylindrical, conical and semi-spherical. For a conducting particle the interface changes to concave.

From the observation of the present results the trapping of the particles by the solid starts in different places; for a conducting particle the first points touching the solids are the corners while for an isolating particle this occurs at the particles center.

The analyses of these observations indicate that the probability of pore formation could be higher when isolating particle are present in the melt.

[1] A.A. Chernov, D.E. Temkin, *Crystal Growth and Materials*, North Holland, Amsterdam **1977**, 3-77. [2] J.K. Kim, P.K. Rohatgi, *Acta mater.* **1998**, 46(4), 1115-1123. [3] A.V. Catalina, S. Mukherjee, D. Stefanescu, *Metallurgical and Materials Transactions* **2000**, A31, 2559-2568. [4] J.W. Garvin, Y. Yang, H.S. Udaykumar, *International Journal of Heat and Mass Transfer*, **2007**, 50, 2969-2980.

**Keywords: Solidification, Crystal growth, FEM**

## MS35.P17

*Acta Cryst.* (2011) **A67**, C461-C462

### Nucleation of gypsum at low supersaturations

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Crystallization from solution in natural environments mostly occurs at low to very low supersaturation. An example of this are the giant gypsum crystals of Naica (Mexico), where nucleation occurred at supersaturations very close to solution equilibrium [1]. Although nucleation is a well studied process in the laboratory, the majority of investigations focus on a high to medium supersaturation range. To attain a meaningful extrapolation from kinetic data obtained in the laboratory to natural conditions information on nucleation kinetics from low to very low supersaturated solutions are necessary. Therefore in this work, a method for studying the nucleation process at low supersaturations is proposed and this approach is applied to the case of crystallization of giant gypsum crystals at Naica.

Nucleation of gypsum was studied within low supersaturation ranges at 20 and 55 °C. Experiments were carried out in 0,2 ml batch reactors with no stirring, using a temperature controlled chamber at 20 °C, and a peltier based thermostatic multi-well set up, coupled to an inverted microscope (Nikon Eclipse TE2000-S) for the experiments at 55 °C [2]. All experiments were covered by a layer of mineral oil and sealed hermetically in order to avoid evaporation. The induction period (the time necessary for nucleation to take place) was measured by single microscope observation in all experiments.

As predicted by classical nucleation theory, an inverse relation in the induction period with temperature and supersaturation was found. Estimating the value of interfacial tension from the experimental data, we have compared the calculated values with values reported in literature obtained for homogeneous nucleation experiments [3,4,5]. Applying the kinetic model proposed by Liu [6,7] we found that gypsum has a very large susceptibility for heterogeneous nucleation (which also corresponds with our observations), and values of interfacial tension found in literature should be higher than reported. From these data we were able to extrapolate induction times for very low supersaturations (similar to those found in the waters of Naica, Mexico [1]). Thus, studying nucleation kinetics at low supersaturations allows us to access information on geological time scale crystallization processes occurring in Nature through laboratory experiments.