

Crystal Growth Control of (100)-AgCl-Tabular-grains

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Abstract

In an theoretical approach the controlling growth mechanisms of AgCl were described as functions of supersaturation and crystal size. The resulting precipitation map af AgCl has been calculated upon physical data available in literature. Controlling the supersaturation in such a way that the controlling growth mechanism is always growth due to screw dislocation mechanism leads to a new precipitation scheme of (100)-AgCl Tabular grains. Additionally no physical ripening is allowed in this precipitation scheme. The resulting (100)-AgCl Tabular grain emulsion has a portion of >90 % tabular grains with an aspect ratio of 10 to 15.

Theory

Crystallization of AgHal-Tabular grains is a result of nucleation, selection and crystal growth. A common selection method is physical ripening. During this process the bigger crystals can be selected out of a population with a size distribution due to the Gibbs Thompson effect. On the other hand it is possible to select (111)-Tabular grains out of a population of crystals with different shapes. Anisotropic growth of (111)-twins is caused by rapid growth of the side surfaces with reentrant corners. The desired twins are in equilibrium with a remarkable lower supersaturation, than the compact crystals, so that the later ones can be easily removed again by physical ripening.

In case of (100)-Tabular grains the situation is more complicated. In the nucleation step anisotropic growth of these crystals is introduced by the existence of heterohalogen ions. (100)-Tabular grains often contain two dislocation lines that extend from one of their corners in the <310> direction. The growth mechanism is described in [1,2] as growth of faces with screw dislocations. That means that the surface integration process is dominated on two crystal faces by the screw dislocation process while the other faces grow by the mononuclear or polynuclear mechanism. The problem has to be solved to select between different faces of one crystal, which are only slightly differentiated by the dominance of another surface integration mechanism.

In this case physical ripening is not useful because the nucleus formed at the nucleation stage may be reorganized and dislocations may move and fade away. This results not in lateral but in thickness growth of the crystals. A selection of the desired growth mechanism can be done, with the knowledge of the kinetics of the separate processes. It is unusual for the rate of crystal growth to be controlled by a single mechanism. If several mechanisms can take place in parallel, the mechanism with the higher growth rate controls the overall rate. The overall growth rate is in general a function of supersaturation, crystal size and physical parameters of the system.

Precipitation maps are a representation of the relative importance of the different growth controlling processes. They can be calculated, if all physical parameters of a given system are known. The lower limit of the precipitation map represents the dependence of the critical nucleus size on supersaturation. The boundaries between regions in which growth is controlled by different mechanisms are represented by lines of equal growth rates of neighboring mechanisms. In case of the anisotropic growth of (100)-AgCl Tabular grains especially the low supersaturation low crystal size region, where the screw dislocation mechanism is located, is of interest. This region of the precipitation map has been calculated for AgCl.

The critical nucleus size has been calculated for AgCl-cubes as function of supersaturation for homogeneous nucleation. The phase boundaries between screw dislocation mechanism and mononuclear growth and between screw dislocation mechanism and polynuclear growth have been obtained, respectively. It was deduced from the precipitation map that screw dislocation mechanism is dominating in a region for supersaturation < 1,3. In this region will be mainly lateral growth of (100)-AgCl Tabular grains. On the other hand, if supersaturation is higher the mononuclear and very soon the polynuclear growth mechanism will dominate, which leads to thickness growth of the crystals.

Experimental and results

The supersaturation can be correlated to basic precipitation parameters as follows:

$$\mathbf{S = (C_{ad} \cdot q_{ad} \cdot t) / (V_R(t) \cdot C_{eq})} \qquad (1)$$

with S = supersaturation, C_{ad} = concentration and q_{ad} quantity of added substances in the time = t, V_R = reaction volume.

Different (100)-AgCl Tabular grain emulsions have been prepared by adding the solutions of silver nitrate and potassium chloride in such a way, that the resulting supersaturation during growth was controlled to a value S > 1,3 or S < 1,3, respectively. The crystal population in the first case shows a portion of about 70% tabular grains by number with an aspect ratio of 8. In the case, where the supersaturation has been controlled to S < 1,3 during the whole time of crystal growth a portion of 95% tabular grains was obtained with an spect ratio of 12.

Conclusion

The theoretical approach to control the growth mechanism of AgCl results in a new precipitation scheme for (100)-AgCl Tabular grains without physical ripening.

A clear effect of supersaturation control on the (100)-AgCl Tabular grain population could be observed. If the controlling growth mechanism is surface integration due to screw dislocation mechanism, which dominates in a supersaturation regio < 1,3, an extremely high portion of (100)-AgCl Tabular grains can be obtained with an aspect ratio > 10.

References

[1] W. van Renterghem et al., J. Crystal Growth **187**, 410 (1998).
[2] T. Oyamada et al., J. Imaging Sci. Technol. **42**, 483 (1998).