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Investigations of spherulitic growth in industrial crystallization

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ABSTRACT

The discrimination between crystal growth and aggregation is of crucial importance for the control of morphology and particle size in crystallization processes, as they are influenced in very different ways by the industrial processing environment. A collection of resembling solution-grown polycrystalline particles that differ widely in chemical nature, like elemental nickel, calcium and sodium carbonate, L-glutamic acid and an aromatic amine have been identified to grow by a spherulitic growth mechanism usually only associated with the crystallization of polymers or melts. The particles are not growing by agglomeration of small individual crystals, as often claimed in the literature. The effect of initial supersaturation, temperature and solvent composition on the spherulitic growth of calcium carbonate (vaterite) has been used to demonstrate how spherulites can grow from solution both by central multidirectional growth (in water) and by unidirectional growth followed by low angle branching (in 90 wt% ethylene glycol). The progression of non-crystallographic branching could be monitored as a function of time at intermediate initial supersaturation values, supplying direct visual evidence for spherulitic growth in this system. A reduction in initial supersaturation and temperature resulted in insufficient branching and dumbbell particles, whereas increased levels of supersaturation rapidly produced fully grown spherulites.

Keywords: Polycrystalline; Spherulites; Spherulitic growth; Vaterite; Calcium carbonate ($CaCO_3$); Supersaturation

1. Introduction

The discrimination between crystal growth and aggregation is of crucial importance for the control of morphology and particle size in crystallization processes, as they are influenced in very different ways by the industrial processing environment. The nature of the mechanism of the formation of polycrystalline particles produced in some crystallization processes is currently not firmly established in the literature. Their formation is usually explained by agglomeration, although there is evidence that the morphology might be the result of complex growth processes such as spherulitic growth (Andreassen, 2005). This is the case for spherical colloidal crystals, where the alleged aggregating precursor crystals are in the nanometer range, as well as for larger particles where the primary units are in the micrometer range (Goia and Matijević, 1998). A mechanism based on the aggregation of precursor particles suffers from several short-comings. It offers no explanation for the different and often symmetric shapes encountered in polycrystalline particles, although there are attempts to describe this by directional aggregation (Ocaña et al., 1995). It also requires very high nucleation rates, within the regime of homogeneous nucleation, in order to account for the numbers of crystals inside the aggregates, although the particles are often observed at supersaturation values well below this regime. In our view, the proposed aggregation mechanism needs be based on number accounting, proper supersaturation measures and direct observation of the alleged primary particles.

We have collated morphology observations of similarly spherical shaped polycrystalline particles precipitated from solution (Fig. 1) that differ widely in chemical nature and preparation techniques. Molecular L-glutamic acid crystals of the β-polymorph were precipitated by the equimolar addi-

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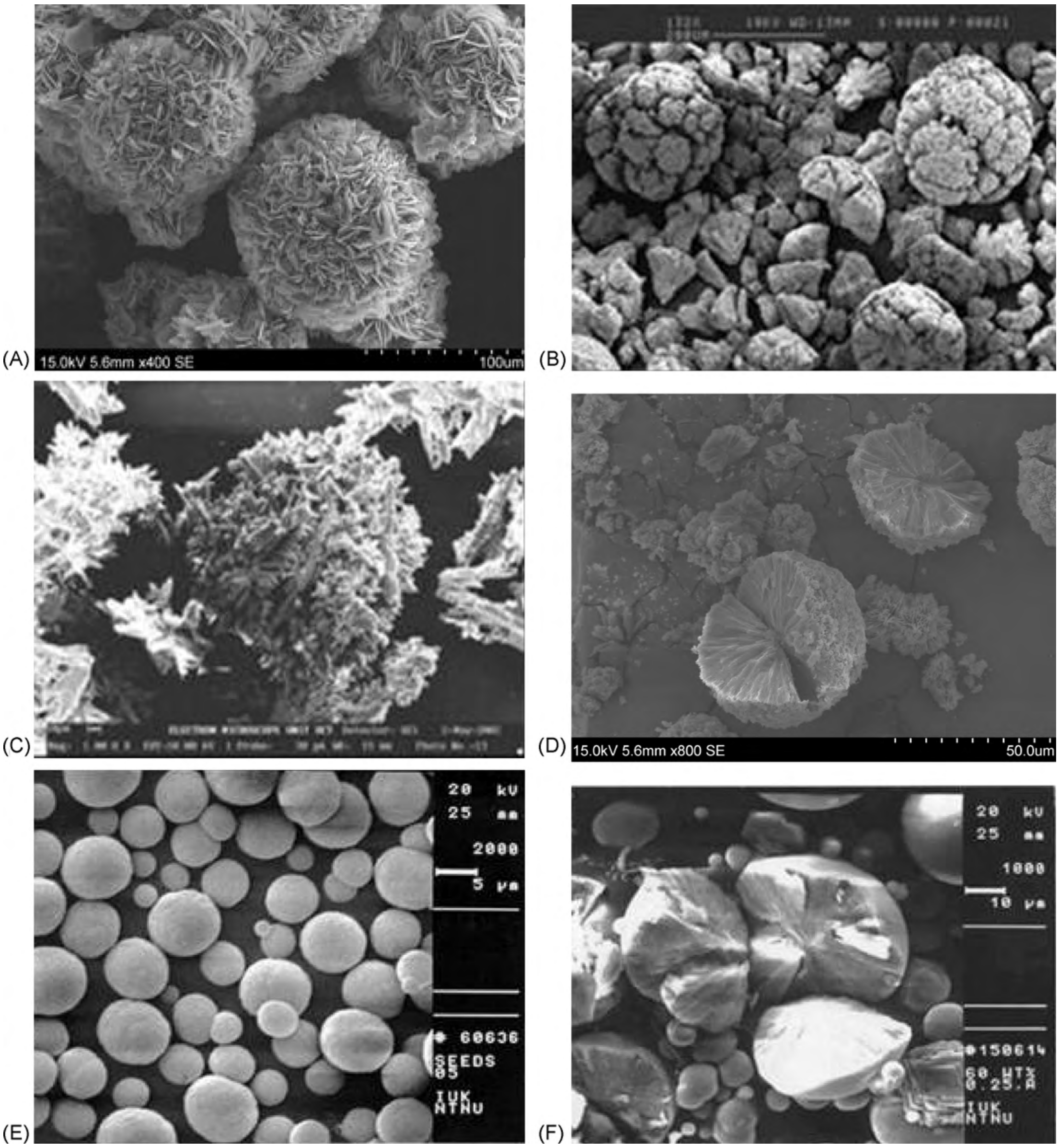

Fig. 1 – Polycrystalline particle systems. (A) L-Glutamic acid precipitated by equimolar addition of hydrochloric acid to sodium glutamate. (B) Elemental nickel precipitated from solution by hydrogen reduction. (C) Sodium bicarbonate precipitated from sodium carbonate brine by CO_2-bubbling. (D) An aromatic amine precipitated at 5 °C by an initial supersaturation of 8. (E) Vaterite polymorph of calcium carbonate precipitated by mixing 0.2 M solutions of sodium carbonate and calcium nitrate. (F) Fractured particles of vaterite.

tion of hydrochloric acid to sodium glutamate at an initial supersaturation of 15 with respect to the β-polymorph at 25 °C (Beck et al., 2009). Elemental nickel crystals were produced by the reduction with hydrogen at 28 bar pressure at 180 °C from a 45 g/L nickel diamine sulphate solution (Ntuli and Lewis, 2006). Ionic crystals of sodium bicarbonate were precipitated by CO_2-bubbling through a brine consisting of sodium carbonate and sodium chloride with small quantities of potassium and sulphate at ambient conditions. Molecular crystals of an aromatic amine were produced by neutralization with hydrochloric acid at 5 °C and an initial supersaturation of 8 (Beck et al., 2009). Spherical calcium carbonate crystals of the vaterite polymorph were produced by mixing 0.2 M solutions of sodium carbonate and calcium nitrate (Andreassen, 2005). One of the characteristic features of these particles is the way they break up in fragments evident of a structure of crystal segments radiating from the centre of the particle (Fig. 1B, D and F).

Spherulitic crystal growth has been extensively studied in systems of polymeric blends of large molecules and in cooling of high temperature melts. High viscosity or presence of impurities is often regarded as an essential prerequisite for this growth phenomenon. Gránásy et al. (2005) claim that spherulitic particles form by growth front nucleation (GFN) when new crystal grains nucleate at the surface with a different lattice orientation than the parent crystal, by a randomized orientation, which accounts for the isotropy of spherulitic growth at large length scales and long times. Three different mechanisms can give rise to polycrystalline growth. The growth can be a result of dynamic heterogeneities when the reorientation of molecules is slow compared to the propagation of the growing surface (viscous systems) or it can be caused by the action of foreign particles in the system (static heterogeneities). When spherulites have been observed in pure systems at lower undercoolings a mechanism of “noncrystallographic branching” is considered as a third alter-