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DIAMOND AND cBN CRYSTALLIZATION: THERMODYNAMICS AND KINETICS

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Spontaneous crystallization of diamond and cubic boron nitride (cBN) takes place at high pressures and temperatures from melt solutions of systems, which contain carbon or boron nitride, in the thermodynamic stability regions of dense cubic phases. The solubility of the low-density phase (graphite, hBN) in the melt exceeds that of the high-density phase (diamond, cBN), therefore, in dissolution of the low-density phase, the solution reaches its supersaturation first of all in respect to the high-density phase. The thermodynamic incentive of the crystallization is the difference in chemical potential between the cubic and graphite-like phases μ_c-μ_h. In the equilibrium line between the graphite-like and cubic phases, the crystallization rate is zero. The stable liquidus of the dense phase in the phase diagrams of multicomponent systems is the necessary thermodynamic condition for spontaneous crystallization of the phase.

The crystal formation consists of nucleation and growth. In most cases, the cubic phase nucleation is heterogeneous. The probability of the formation of a critical-sized nucleus, and hence the nucleation rate, increases abruptly with decreasing surface energy at the melt-crystal nucleus interface. With a decrease in the surface energy, the crystal growth rate also increases. The nucleation rate depends exponentially on pressure. The pressure increase abruptly increases the formation rate of the phase of a lower volume. Thus, the negative difference of chemical potentials μ_c-μ_h is a necessary but insufficient condition for diamond or cBN spontaneous crystallization. Even the stable liquidus of the cubic phase in the phase diagram at high pressures does not ensure the spontaneous crystallization of the cubic phase in the presence of kinetic difficulties. The latter may involve (a) a low nucleation rate due to a high surface energy at the crystal–growth medium interface, or to low pressure, (b) a low growth rate of the cubic phase, due to a low difference in solubility between the cubic and graphite-like phases in the melt and low values of diffusion coefficients of clusters of carbon or boron nitride in the melt.

Various models are used to describe the crystallization kinetics. Based on the experimental data, the models allow one to estimate the activation energy of the crystallization process, to ascertain, what stage controls the process (diffusion delivery of the building material, or its integration into a growing crystal), to judge if the nucleation is a continuous process or it exhausts with time, and make a conclusion about the crystallization mechanism. The Avrami-Kolmogorov model has proved to be best suited to describe the process of the spontaneous crystallization of diamond and cubic boron nitride.