1 INTRODUCTION

Gas hydrates (GH) form crystalline, non-stoichiometrid compounds belonging to the clathrate hydrate structural family in which gas molecules are trapped in hydrogen bonded water cages. While studies of the formation of GH from liquid water are numerous, the formation from ice is less well covered and will be one of the subjects of the present study; the latter has considerable importance for hydrate formation and decomposition in Solar system bodies, in particular for Mars, on which hydrates could play an important role in geomorphological processes. Two main formation stages can be distinguished: (1) an initial nucleation and growth limited stage and (2) a later diffusion-controlled stage. The latter can be easily investigated by gas consumption methods, X-ray or neutron diffraction, which give a good quantitative account of the reactions in a bulk sample. Unfortunately, for the initial phase, the application of these techniques is somewhat limited by the insufficient sensitivity of the methods (with neutron diffraction still performing best); moreover, they do not resolve information on the ongoing nucleation and growth processes like nucleation sites density, shape, size of the formed crystals and their mutual arrangement. The application of an imaging technique like field-emission scanning electron microscopy (FE-SEM) can provide the key to understand these processes, as has been demonstrated in our earlier work in which we developed a shrinking core model for gas hydrate growth. Equally interesting is the microstructural arrangement of ice crystals formed upon clathrate decomposition, in particular for a better understanding of the phenomenon of anomalous- (or self-) preservation. In this contribution we will discuss recent results concerning nucleation and initial growth processes on the ice / hydrate surface at various p-T conditions and various degrees of transformation. Cryo-SEM techniques will be mainly used for this purpose, performed on samples quenched to liq.N₂ temperatures and recovered at various stages of the transformation process (so-called “interrupted runs”). Neutron and X-ray diffraction will be used in addition to control the averaged transformation degree as a function of time.

2 EXPERIMENTAL SECTION

A custom-build low-pressure cryo system adapted to the high-intensity 2-axis neutron diffractometer D20 at the Institute Laue-Langevin, Grenoble, France, allowed us to study...
transformation processes *in-situ* with a time resolution of a few seconds. Unfortunately, the limited beam time allocations make this technique inadequate for longer experiments. Such runs, up to several months, require a supplementary system based on measurements of the gas consumption (formation) or release (decomposition) in a closed system.

To investigate transformation phenomena at the surface of the solid reactant we use an *ex-situ* FE-SEM imaging method, which provides a frozen-in visualization of the reaction fronts with a maximum resolution of a few tens of nm. The FE-SEMs used (LEO Gemini 1530, QUANTA 200F) are designed for work at low acceleration voltages of less than 2keV, which reduces to a minimum the destructive power of the electron beam and undesired charging effect. During the measurements, the uncoated samples are held in a cryo stage, cooled to about 90K with liq.N₂ at a pressure of about 0.1 Pa (1×10⁻⁶ bar). For all clathrates formation experiments discussed in this paper, we used ice spheres with a diameter of <350µm formed by quenching sprayed, demineralised water droplets in liq.N₂. The decomposition runs were carried out on powders ~250µm, prepared by crushing and sieving of CO₂ hydrate through a set of 200 and 300 µm meshes.

3 NUCLEATION AND GROWTH OF CO₂ HYDRATE

There is not much information in literature on the processes of nucleation and initial growth of gas hydrates coating ice particles. At temperatures of ~190K, it is assumed to be a relatively slow process, which needs several hours to transform the free ice surface exposed to the reacting gas. According to Schmitt below 200K a so-called incubation period often delays the onset of the nucleation. Whether this is truly an inhibition of nucleation or just a very slow start following a sigmoidal reaction pattern remains largely an open question. The neutron diffraction data shows no increase in the hydrate fraction during the first few hours. The shape of the reaction curve suggests rather sigmoidal

![Figure 1](attachment:image.png)

*Figure 1* The initial part of the CO₂ hydrates formation reaction at 193K and 80kPa in the gas consumption system (left). The complete coverage of the surface is expressed by a clearly visible bend of the reaction curve after 90min. Dashed line marks the position of each interrupted run on the reaction curve: 15, 30 and 90 min. The neutron diffraction experiment of the CO₂ hydrate formation at 185K and 36kPa (right) starts significantly only after 2 hours.
growth but do not rule out the possibility of an incubation period either (Figure 1). The recent formation experiments, performed on gas consumption system, at low temperatures and pressure (193K 80kPa) with CO$_2$ gas suggest that the time for the nucleation and total coverage could be much shorter. From our SEM work (discussed below) we can infer that this part of the reaction is most probably related to the formation of a hydrate layer on the surface of the ice spheres. With a transformation degree of about 2.5% (after 90 min), we have observed a significant slowing down of the formation process possibly caused by the depletion of ice surface exposed directly to the gas molecules and a corresponding switching to the diffusion controlled growth. It is worthwhile to notice that the reaction described above is still in the time frame of induction period, observed during the neutron diffraction experiments. To better understand the role of microstructure evolution, we have tracked down the surface changes in a series of interrupted runs with steps: 15 min, 30 min, and 90 min.

For the run interrupted after 15 min, the SEM images reveal an ice surface covered with clearly distinguishable nucleation sites and spreading fronts with a well visible sub-micron size porous structure (Figure 2D), which is characteristic for GH$^{10,12,18,19}$. The crystallites show a characteristic “jackfruit pattern” (Figure 2B). The average size of the observed seemingly radially grown features is estimated as 10-15 µm (Figure 2C, D, E, F). The roughly estimated density of nucleation centres is about 4.9-8.8·10$^7$ nuclei/m$^2$ (assigning one centre to one “jackfruit” area); the distribution of the nucleation centres is rather inhomogeneous. The shape of individual crystallites is “pancake like”, which is often related to heterogeneous nucleation$^{20}$ (Figure 2D, F). Most of the GH crystallites were developed along the cracks caused by shock freezing or other defective zones (e.g. grain boundaries, small frost particles electrostatically attached to the spheres), which apparently promote the formation of the new phase (Figure 2E, G). It is interesting to note that at some places nucleation did not occur while other areas were completely covered by GH. Yet, the free surfaces do not resemble typical properties for ice-like high resistance to etching by electron beam. EDX analyses show only the traces of carbon in measured areas, which additionally complicates identification. A striation pattern commonly seen on the ice starting material (Figure 2A) is also not present; instead, one could observe flat and smooth surfaces (Figure 2C, D, E). After 30 min. the reaction is approaching complete coverage. In those regions, where the surface transformation had been already completed, the grain boundaries between separate hydrate crystallites starts to disappear (Figure 2H). In spite of this, it is still relatively easy to see the original “jackfruit patterns” on the ice spheres as well as regions with sub-micron porous structures.

A quite different picture was observed after 90 min. The ice surface is completely replaced by growing clathrates (Figure 3A-D). All borders between crystallites are strongly blurred.

**Figure 2** SEM images of the initial ice spheres and after a reaction with CO$_2$ gas at 193K and 80kPa for 15 and 30 min. (A) surface of a polycrystalline ice sphere before the reaction with clearly visible grain boundaries and striation patterns (B) “jackfruit pattern”, (C) nucleation sites with clearly visible uneven surface, (D, F) one of the seemingly radially grown “pancake”, nucleation sites, (E) defect and cracks promote GH crystallization, (G) still well visible porous structure after 30min. reaction, (H) slow blurring of the borders between separate GH crystallites.
Figure 3  The SEM images after 90 min. of GH formation at 193K and 80kPa. (A-D) The borders between individual clathrate crystallites are barely visible or have completely vanished. Figure B visualizes the initial and figure D the advanced crack bridging and filling process as enlarged portions of figures A and C respectively.

and the sub-micron porous structures, previously easily visible, are not present. Instead, one could observe surfaces, which may be easily mistaken as water ice striation patterns (Figure 3B, D). Undulated pseudo-dendritic features building each crystallite, commonly observed after 15-30 minutes, become smoother; yet the differences between elevations and depressions are big enough to be mistaken with the ice striation patterns. A careful analysis of the SEM images reveal smoother and rounded edges (Figure 3B), which are untypical for ice surfaces. At this transformation stage, we have observed the growth of the hydrates in cracks of the initial ice spheres (Figure 3D). At higher temperatures\(^9\) this crack-filling process was assumed to be relatively fast and promote hydrate crystallization due to slightly smaller activation energy necessary to initiate the nucleation. The results at lower temperature presented here suggest the opposite situation: The bridging and crack filling appears to be a consequence of the surface transformation and thickness increase of the GH coating which covers whole surface. (Figure 3B, D). Apparently, the combination of volume expansion with the growth creates an effective mechanism for closing of the smaller cracks at this p-T condition.
4 DECOMPOSITION OF CO₂ HYDRATE

The decomposition of gas hydrates is a multi-stage\textsuperscript{15}, still not well-understood, process. In the initial stage different structures appear depending on the speed of growth related to the p-T conditions and the duration of the decomposition. Above 240K, the considerable mobility of water molecules increases the importance of stacking-fault annealing\textsuperscript{15} and Ostwald ripening process, which leads to additional surface changes. In this complex system, two different types of microstructures can be distinguished. Firstly, the series of the interrupted runs at low temperature (<200K at 0.6kPa) or close to the thermodynamic stability field (220K at 90kPa) reveal surfaces of the hydrate particles, which are covered with relatively well-developed subhedral ice crystals (Figure 4A-D). The slow nucleation and growth from decomposing hydrates leads in certain cases even to the development of clearly visible prismatic and basal planes (Figure 4B, E).
Figure 4  The SEM images exhibiting typical GH surface evolution during slow decomposition: (A) subhedral ice crystals after 5min at 220K and 90kPa, (B) euhedral and subhedral ice agglomerate on the GH surface after 12h at 180K and 0.6kPa, (C) Between densely packed ice crystals one can still see GH in the close-up (arrows), (D) Magnification of the previous image. The ice crystals look like some sort of melting into the hydrate surface due to the inward growth, (E) Euhedral ice crystals with very well visible prismatic and basal planes at 195K and 0.6kPa, (F) Ice crystals surrounded by a transition zone after 10 min. at 220K and 90kPa. Some of them have clearly visible kinks in the prismatic faces\(^{13}\) (arrow) indicative for stacking faults.

The average size of the ice crystals is 5-10µm and increases with the temperature (up to 20µm at 220K and 90kPa). The commonly observed small depressions surrounding ice crystals (Figure 4D-white arrow) suggest an inward growth. The distribution of the newly formed crystals is rather inhomogeneous and in the empty spaces between them one could still observe initial material (Figure 4A, C). It is worth noticing that at 220K 90kPa some of the ice crystals are surrounded by the undulated rim of a “transition zone” (Figure 4F). The thickness of this zone is not larger than few micrometers; typically it is about 1-2µm broad. The second type is related to a rapid growth of ice on the clathrate surface. The fast 5 to 10 minutes long decomposition at 220K and 60kPa (i.e. far from the field of thermodynamic stability of GH) leads to a nucleation of “pancake crystallites” (Figure 5A, B, D). Each of the disks is formed from ice growing in a dendritic manner starting from a central point (Figure 5C). The typical size of the observed features is 15-20µm.
Many crystals are surrounded by a transition zone (Figure 5A-white arrow). It is somewhat similar to the one observed for the case of slow growth. The distribution of nucleation sites appears to be rather inhomogeneous. In certain places one can still observe the primordial hydrate surface, where other areas exhibit an advanced transformation (Figure 5B). One possible explanation of this state might be the hindered gas outflow, which locally increases the fugacity of CO$_2$ gas and therefore slows down reaction.

5 CONCLUSIONS

Ice and gas hydrate surfaces in the initial stage of transformation to the other show rich variations in microstructures. Undoubtedly, the microstructures of the newly formed phases at the reacting surface influence the kinetics of these phase transformations. In most cases the observed growing GH exhibits a pancake-like shape; such structures are inhomogeneously distributed. The transformation at the investigated p-T conditions is characterised by a fast outward expansion. The total surface coverage, linked to the slowing down of the reaction curve, marks the transition to the development of a new surface structure, which persists also at later stages. Decomposition of GH shows clear differences in the microstructure depending on the speed of the process. The slow process is characterized by the development of rather well shaped ice crystals, sometimes with clearly visible basal and prismatic planes. In the fast decomposition process pancake-like ice crystallites are formed. The ice coating, developed with time, is almost free from voids. Consequently, the ice cover formed provides a good sealing and could well be related to the appearance of the phenomenon of self-preservation.

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