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SEM observation on hydrate formation from TBAB aqueous solution and memory effect

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Clathrate hydrate of tetra-n-butylammonium bromide (TBAB) is expected as a cold storage material for air conditioning, but supercooling is a problem for practical use. The supercooling, widely known, is the state of maintaining the liquid phase even if it is cooled below freezing point, but the detailed mechanism is not clarified. For the purpose of visualization of the supercooling phenomenon, both the structures of TBAB clathrate hydrate and TBAB aqueous solution were observed. In general, although SEM is widely used in the observation of microstructure, it had not been possible to observe such as a solution or a gel directly since the inside of the SEM is under a high vacuum. Therefore, SEM observation was performed by a freeze-fracture replica method. Freeze-fracture replica method is utilized not only in medicine and biology fields but also in various fields since it is possible to obtain both of the information of a solution itself and the state of particles having a microstructure simultaneously. Specifically, cut-surface of the quenched sample was prepared and thin film is fabricated on the cut-surface. And by soaking it in an appropriate solvent, the thin film and the sample were separated to recover a replica film reflecting the morphology of quenched cut-surface. Finally, the replica film was observed by SEM.
From the observation results of TBAB clathrate hydrate, whose decomposition temperature is 285 K, the crystalline state has a closely packed structure with clusters of 10 ˜ 20 nm or more in diameter. As the decomposition proceeds, the cluster size shrinks overall, in part, on the contrary, expands larger than a diameter of 60 nm. Finally, there is no grain boundary and structural features disappear. As a result, remaining clusters are negligible. In the formation process, the presence of a cluster is sparse at 293 K which is 8 K higher than the equilibrium decomposition temperature. At 270 K, with the passage of time, loose network appears and in a part, the clusters also generate. When it comes to hydrate at 263 K, clusters with a diameter of about 20 nm are spread to the whole in the dense state.
In the decomposition and formation processes, since reversible behavior has been observed, the generation and disappearance of the clusters were found to be explained as a significant step for the phase change of TBAB clathrate hydrate. Specifically, in the decomposition process, while the cluster disappeared within 20 seconds when heated at a temperature 2 K higher than the decomposition temperature, in the formation process at 270 K which is 15 K lower than the decomposition temperature, even after 15 minutes or more, generation of clusters is limited to a small part. That is, supercooling degree and induction time are necessary for the generation of the cluster from a homogeneous solution structure without clusters. In other words, it was found that the supercooling phenomenon depends on how long it takes to generate the large number of clusters at temperatures below equilibrium decomposition temperature.

Significance statement

In the decomposition and formation processes of TBAB clathrate hydrate, since reversible behavior has been observed, the generation and disappearance of the clusters were found to be explained as a significant step for the phase change of TBAB clathrate hydrate.

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