Scanning electron microscopic studies on the methane hydrate decomposition using the freeze-fracture replica method

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Abstract

It is well known that methane hydrate exhibits abnormal stability, so-called “self-preservation effect” at temperatures of 240 K to 270 K and atmospheric pressure, though the equilibrium temperature of methane hydrate at atmospheric pressure is approximately 190 K. The ice shielding at the surface of methane hydrate would be one of the most important steps toward developing the self-preservation. That is, to observe the phase and morphology changes from methane hydrate to ice is significant. We have observed the microstructural change of the synthetic methane hydrate during its decomposition at the temperatures of 263 K and 293 K with a combination of scanning electron microscopy (SEM) and the freeze-fracture replica method. The SEM images reveal that the methane hydrate crystal has a structure arranging the clusters of 20 nm in diameter. When the methane hydrate is partially decomposed during taken from the high-pressure cell (rapid depressurization at 253 K), a part of the clusters changes to the cluster aggregates of 60–200 nm. The cluster aggregates gradually grow from their peripheries to the hexagonal ice crystals during gradual decomposition at 263 K. The microstructural change supports the decomposition mechanism of methane hydrate by ice-shielding under a temperature condition with self-preservation effect. At 293 K, the methane hydrate is immediately decomposed. The residual aqueous solution after complete decomposition contains the large number of ultrafine bubbles (nanobubbles) of 100 nm or less in diameter.

Key words: gas hydrate, ice, self-preservation, SEM, freeze-fracture replica method, ultrafine bubble

1. Introduction

Gas hydrate or clathrate hydrate, a kind of inclusion compounds, is stabilized by guest species in the cavity of hydrogen-bonded water cages (Sloan and Koh, 2008). In the methane hydrate, the methane molecules are enclathrated as the guest molecules in two kinds of cavities. Methane hydrate has become the object of much attention because enormous quantities of natural gas in the form of gas hydrate exist in the permafrost regions and the sediments under the deep-ocean floor. A significant characteristic of gas hydrates is relatively large gas storage capacity. Therefore, methane hydrate has been proposed as a storage and transportation medium of natural gas (Gudmundsson and Børrehaug, 1996; Shirota *et al.*, 2002; Takaoki *et al.*, 2002; Rehder *et al.*, 2012). To keep a gas hydrate form, generally speaking, gas hydrate must be stored or transported in a pressure-temperature condition where gas hydrate is thermodynamically stable. Yakushev and Istomin (1992) reported unexpected high stability of methane hydrate at

0.1 MPa and a temperature below 273 K which is under a non-equilibrium condition (Falabella and Vanpee, 1974; Makogon and Sloan, 1994). Yakushev and Istomin (1992) called the effect as “gas-hydrates self-preservation effect”. After that, Stern *et al.* (2001) reported anomalous preservation of methane hydrate at isothermal conditions between 242 and 271 K. Many researchers have investigated the self-preservation effect with kinetics and spectroscopic approaches (Falenty *et al.*, 2014; Kuhs *et al.*, 2004; Mel'nikov *et al.*, 2003; Melnikov *et al.*, 2009; Ohno *et al.*, 2011; Sato *et al.*, 2009, 2013; Takeya *et al.*, 2005; Takeya and Ripmeester, 2008; Takeya *et al.*, 2001, 2011; Uchida *et al.*, 2011b; Zhong *et al.*, 2016). Their vigorous investigations have revealed that the self-preservation depends on the temperature, guest molecules, and pressure. The temperature dependence is derived from the ice nucleation and shielding and the existence of (supercooled) aqueous solutions, according to the literature mentioned above. The ice nucleation from water released by gas hydrate decomposition exhibits very complicated behavior (Kuhs *et al.*, 2004).

Murakami *et al.* (1997) reported the preparation of

the replica film using mixed hydrocarbon plasma for field-emission scanning electron microscopy (SEM) observation. They adopted a CO_2 hydrate under decomposition as a sample to show the availability of the freeze-fracture replica method. They reported the existence of ultrafine bubbles released at the surface of CO_2 hydrate and the aggregates of 50–100 nm (they claimed gas aggregates, but we speculate the gas hydrate aggregates, not gas aggregates). Kuhs *et al.* (2000, 2004), Falenty *et al.* (2007, 2014), and Rehder *et al.* (2012) have observed the microstructural changes of gas hydrate formation from ice and back by means of cryo-SEM on a 100 nm-scale under 10 nm resolution limit. They have reported ice nucleation behavior at various temperatures and proposed the mechanism of the self-preservation effect. We believe the microstructural change occurs on a scale smaller than 100 nm, based on the literature on the nucleation behavior of many kinds of crystals (Hirokawa *et al.*, 1994; Ishizuka *et al.*, 2017; Machida *et al.*, 2017; Murakami *et al.*, 1997; Ohgaki *et al.*, 1991, 1992; Ueda *et al.*, 1995; Yamazaki *et al.*, 2017). In the present study, we observed the microstructural changes in the decomposition processes of a synthetic methane hydrate on a 10 nm-scale by means of SEM with freeze-fracture replica method.

2. Experimental

2.1 Freeze-fracture replica method

Freeze-fracture replica method (Ohgaki *et al.*, 1991; Hirokawa *et al.*, 1994; Murakami *et al.*, 1997; Fujimoto, 2017) was used as a method for observing the microstructures of the methane hydrate crystal and the aqueous solution after its complete decomposition. A sample (hydrates or aqueous solution) was dipped into liquid 2-methylbutane (isopentane, Wako) at its melting point (113 K). The quenched and vitrified sample was set in a vacuum chamber (JEOL, EM-19501 JFD-V) precooled at cryogenic temperatures of approximately 80 K. In general, soon after cutting the vitrified sample inside the chamber under vacuum of 10^{-5} Pa and 80 K, the carbon is vapor-deposited to the resulting cut surface to prepare a replica film. After removing the sample from the replica film (the thickness was estimated to be approximately 4 nm), it was picked up on a 200-mesh copper grid (VECO, square type). The surface morphology of a slightly inner parts from the perimeter of the replica film was observed by SEM (Carl Zeiss, ULTRAplus, acceleration voltage: 2 kV, detector: InLens). The original resolution of SEM is approximately 1 nm, but, considering the particle size of deposited carbon, the overall resolution limit of SEM images observed in the present study is a couple of nanometers.

2.2 Preparation of samples

In the present study, we observed the replica films derived from three samples: methane hydrate

(sample “A”), partially-decomposed methane hydrate at 263 K (“B”), and residual aqueous solution after complete decomposition of methane hydrate at 293 K (“C”). The pressure-temperature history that methane hydrate experienced and the relation of three samples with the phase diagram of methane hydrate are shown in Fig. 1.

Methane hydrate was prepared in a high-pressure cell with internal mixing bar (driven by a permanent magnet ring) vertically moving across the gas-liquid interface. The cell was essentially the same to that reported previously (Sugahara *et al.*, 2003). The high-pressure cell has a water jacket to maintain the cell temperature at 280 K by circulating thermostatic water. Distilled water (Wako) was introduced into the cell and then pressurized with methane at a pressure up to 6.0 MPa, which is slightly higher than the three-phase (gas, aqueous, and hydrate phases) equilibrium pressure of methane hydrate at 280 K. Mixing was started, and the methane hydrate was formed after an induction period. The pressure was regulated at 6.0 ± 0.2 MPa by intermittently supplying methane because methane was gradually consumed as methane hydrate was formed. When the consumption of methane had almost ceased, the residual aqueous solution was drained through the needle valve of the bottom of the cell. During this period, the cell pressure was also regulated at 6.0 ± 0.2 MPa. The remaining contents in the cell were kept at the same pressure for almost 5 days to convert the unreacted water to methane hydrate at the grain boundary region and then cooled with the high-pressure cell to 253 K for 1 day. The prepared methane hydrate was allowed to be depressurized to the atmospheric pressure at 253 K in a cold room. The obtained methane hydrate was quickly quenched and stored in a vessel at 77 K. Some of

Fig. 1. Schematic phase diagram of methane hydrate. The arrows represent the pressure-temperature history methane hydrate experienced. The points A, B, and C stand for the sample collecting points for freeze-fracture replica method.

translucent hydrate crystals were used for the replica film preparation as the methane hydrate samples without any change (Sample "A"). As a result of gas release measurement of the quenched hydrate samples, the hydrate ratio in the hydrate samples was approximately 70 ± 10 mol% and 20–30 mol% of water contained as unreacted water (or methane was partially released from the hydrate sample until quenching after depressurization at 253 K).

To observe the morphological change of methane hydrate during decomposition below 273 K, some of translucent methane hydrate crystals were put into the freezer and allowed to be partially decomposed at 263 K for 2 hours. After taken from the freezer, the samples were quickly quenched with liquid 2-methylbutane at 113 K and then used for the replica film preparation (Sample "B"). Sato *et al.* (2009) reported that, when the initial hydrate ratio was a standard (100 %), approximately 15 % of methane hydrate (prepared in almost the same manner as the present study) decomposed at 263 K for 10 hours. The hydrate ratio of the partially-decomposed hydrate at 263 K for 2 hours in the present study was estimated to be at least 60 ± 10 mol%, that is, approximately 10 mol% hydrate should be converted to ice at a maximum. To prepare the residual aqueous solution after complete methane hydrate decomposition, the crushed methane hydrate crystals were put on a hot stage at 293 K for 5 min. The hydrates were completely

decomposed in a few minutes. Droplets of the obtained aqueous solution were quickly quenched with liquid 2-methylbutane at 113 K and then used for the replica film preparation (Sample "C").

3. Results and Discussion

Figure 2 shows the SEM images of the replica films reflecting the internal microstructure of methane hydrate crystals without any change after quenched (sample "A"). The images have two types of aspect: one is the clusters of approximately 20 nm in diameter; the other is the cluster aggregates with a size of 60–200 nm in diameter. The 20 nm clusters are dominantly included in the sample "A" and methane hydrate crystal composes of densely-packed clusters as shown in the bottom of Fig. 2. The minimum cluster size of 20 nm in a methane hydrate crystal agrees well with that in a citric acid monohydrate crystal (Ohgaki *et al.*, 1991; Ohgaki *et al.*, 1992), a CO₂ hydrate (during decomposition) (Murakami *et al.*, 1997), and a sodium acetate trihydrate crystal (Machida *et al.*, 2017). Kuhs *et al.* (2000) reported that the bulk of methane hydrate was porous on a submicron scale of 100–400 nm on the basis of a cryo field-emission SEM observation. They could have observed only the aggregates, because they stated the 10 nm resolution limit of their setup. The cluster aggregates of 60–200 nm, consisting of the 20 nm clusters, resemble the "clustercysts" in the crystallization

Fig. 2. SEM images of the replica films reflecting the internal microstructure of synthetic methane hydrate just after taken out from the high-pressure cell (Sample "A"). The images are derived from different hydrate crystals at 50 thousands-fold (upper) and 150 thousands-fold (lower) magnifications.

mechanism of a citric acid monohydrate crystal reported by Ueda *et al.* (1995). Unlike a citric acid monohydrate crystal, however, the methane hydrate dominantly consists of the 20 nm clusters. The aggregates seem to be different from the clustercysts as discussed in the next paragraph.

As the methane hydrates were partially decomposed at 263 K for 2 hours (Sample "B"), the internal microstructure near the surface of the sample, where methane hydrate slowly decomposes, was drastically changed from that of the methane hydrate before decomposition (Sample "A"). As shown in Fig. 3, the cluster aggregates of 60–200 nm in diameter, which have a similar size to those included in the methane hydrate before decomposition (Fig. 2), were scattered. In addition to the spherical aggregates, the SEM images of the sample "B" contained the facets of hexagonal ice Ih that began growing from the periphery of the aggregates. Mimachi *et al.* (2015) have reported that the periphery of the thermal or mechanical cracks in a synthetic natural-gas hydrate tends to be a dissociation site. The ice formation behavior around the 60–200 nm aggregates implies that the cluster aggregates observed in Fig. 2 resulted from the partially decomposition of methane hydrate when the hydrate sample was taken from the high-pressure cell at 253 K.

The surrounding of the aggregates in Fig. 3 was relatively smooth, while that in Fig. 2 was filled with the

clusters of 20 nm. The smooth zone in Fig. 3 implies the surface resulting from ice shielding (Uchida *et al.*, 2011b) at the surface of clusters. Falenty *et al.* (2014) reported the SEM images (micrometer scale) of similar smooth surface observed at 260 K and 0.1 MPa. The smooth surface might imply the existence of mobile supercooled water suggested by Takeya *et al.* (2005), Mel'nikov *et al.* (2003), Melnikov *et al.* (2009), and Ohno *et al.* (2011). The ice-shielding would be supported by the existence of many holes (enlarged images around the holes are shown in Fig. 4) through which methane should be released from the inside of the sample. The fluid methane enveloped by ice shielding might be released in the fracture operation. The existence of many holes was observed by Falenty *et al.* (2014). Takeya *et al.* (2011) reported that the average thickness of ice layer at the surface of a synthetic methane hydrate pellets stored at 253 K for a day was approximately 100 μm . In the present study, ice layer formed at 263 K for 2 hours seems to be thinner than 100 nm because the asperities derived from residual clusters in the smoothed zone were still observable. Such thinner layer would be due to different experimental conditions of holding temperature and duration.

Figure 5 shows the SEM images of the replica films reflecting the internal microstructure of aqueous solutions after methane hydrate completely decomposed at 293 K. A number of ultrafine bubbles of 50–100 nm in diameter were observed. As long as the SEM images are seen, the

Fig. 3. SEM images of the replica films reflecting the internal microstructure of methane hydrate partially decomposed at 263 K for 2 hours (Sample "B").

Fig. 4. Enlarged images around the holes in Fig. 3.

size distribution seems to be narrow. It has been already reported that the ultrafine bubbles contain in the aqueous solution resulting from gas hydrate decomposition (Uchida *et al.*, 2016a). The bubble size is quite similar to that reported by Ohgaki *et al.* (2010) and smaller than that by Uchida *et al.* (2011a, 2016a, 2016b). The difference of the bubble size would be derived from how ultrafine bubbles were generated, especially in the case of “gas hydrate decomposition” method, how hydrate sample decomposed. The surface of bulk ultrafine bubbles is still subject to debate. The further investigation is needed to elucidate the bubble size and surface. The ultrasonic measurement recently reported by Leroy and Norisuye (2016) has been expected as a method to solve them simultaneously.

4. Summary

We observed the microstructural changes on a 10 nm-scale during the decomposition of a synthetic methane hydrate by means of SEM with freeze-fracture replica method. The mechanism of the self-preservation effect is very complicated and entangled with that of ice nucleation and growth. On the whole, our observation results support the hitherto proposed decomposition mechanism (unfortunately, the existence of supercooled aqueous phase was unable to be distinguished) of methane hydrates at a temperature of 240–270 K. Our results suggest the necessity of observing the microstructural changes on a nanometer scale.

Cryo-SEM has been used as a powerful tool to

Fig. 5. SEM images of replica films reflecting the internal microstructure of residual aqueous solution after methane hydrate completely decomposed at 293 K (Sample “C”). The images are derived from different droplets at 50 thousands-fold (upper and middle) and 100 thousands-fold (bottom) magnifications.

directly observe the decomposition behavior. From the restriction of the circumstance inside cryo-SEM chamber, it had been difficult to recognize the microstructural change on a 10 nm-scale or less. The freeze-fracture replica method, an indirect observation, breaks loose from the restriction inside SEM chamber and maximizes the performance of SEM observation.

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