EFFECTS OF MICRO-BUBBLES ON NUCLEATION AND MORPHOLOGY OF XENON GAS HYDRATE CRYSTALS

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ABSTRACT

Gas hydrate is usually regarded as a huge potential energy resource as well as its promising industrial application for gas separation, storage and transportation. Previous researches have shown that gas hydrate phase transition is mainly controlled by heat and mass transfer, while limited work concerns the mass transfer effects of gas micro-bubbles on the hydrate crystallization. In this study, variations in microscopic morphology of hydrate crystals growth in a liquid-gas phase have been observed using a microscope imaging system. The results indicate that the nucleation of hydrate firstly tends to occur at a bubble interface. And the cooling rates increase exponentially with the crystal growth rates and play an important role in the morphology of hydrate crystal growth. In addition, the hydrate crystals tend to grow in the direction of the bubbles affected by the Ostwald ripening effects, which suggests that the bubbling is an efficient measure to promote the application of hydrate-based technologies.

Keywords: green energy resources, natural gas hydrate, crystal growth morphology, micro-bubbles, hydrate nucleation

1. INTRODUCTION

Gas hydrates have attracted an increasing attention recently since they offer a largely unexploited means of energy recovery and transportation as well as the industrial applications in gas separation and storage, moreover, they could play a significant role in past and future climate change [1]. Generally, the gas hydrate nucleation is a complex multiphase crystallization process. Previous works report that gas hydrate further



crystallization at the interface of gas and water are mainly controlled by the heat and mass transfers [2, 3]. The degree of driving force is the key factors that controlled the hydrate crystal types, and the larger driving force results in poly-crystal formation while smaller generate a single crystal [4]. The reported works also show that subcooling [5, 6] could control the morphology of hydrates by influencing the growth rates and configuration of crystals. Generally speaking, the morphology of gas hydrate crystals could be classified into columnar, skeletal and dendritic depending on the driving force [7]. Morphological observations have also contributed toward the mechanistic understanding of hydrate crystal growth. However, limited research concerns the effects of gas micro-bubbles on the hydrate nucleation and its crystal growth. Thus, we need a systematic understanding of the morphology of hydrate

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crystals formed at the interface of liquid water and guest gas as well as at the bubbles surface.

systems consisting of a high-resolution polarized light microscope (Axio Scope A1 pol, 0.3 um in resolution, Carl Zeiss Co. Ltd., Germany). The most widely used heating

2. MATERIAL AND METHODS



Fig. 2 Morphology of gas hydrate crystal growth at different cooling rates. (a) Different cooling-rate curves for case 1-6. (b)Morphology of Xeon hydrate crystal growth at different cooling rates for case 1-6. (c) The crystal growth rate for case 1-6.

As shown in Figure 1, the visual observation experiments are performed at the microscope imaging

and freezing microscope stages (THMS600, Linkam Scientific Co. Ltd., UK) was used to supply a controlled



Fig. 3 Bubble effects on the morphology of gas hydrate crystal growth at different conditions. The yellow rectangle areas represent the dendritic crystal growth habits.

reactor, which has a temperature range of -196°C to 600°C, high heating/freezing rates of up to 150°C/min and 0.01°C accuracy. In this study, the pure water was manufactured by the ultra-pure water machine (Aquaplore 2S, Aquapro International Co. LLC., US) with a resistivity of 18.2 M Ω .cm, and the Xenon (Xe) gas was purchased from commercial approach (purity: 99.99%, Dalian Special Co., Ltd., China).. Please use this template to prepare your paper.

3. RESULTS AND DISCUSSION

3.1 Effects of cooling rates on morphology of Hydrate crystal growth

Previous research has reported that degree of the subcooling or driving force depending on pressure might control the morphology and growth rate of the hydrate crystals. However, limited research investigate the effects of the cooling rate on the morphology of hydrate crystal growth. In this work, Xenon gas hydrate crystallization process is performed at pressure of 0.3 MPa and temperature of 1°C from the hydrate dissociation solutions. The different cooling rates in case 1-1 to 1-6 are set for initial nucleation as shown in Figure 2a. The morphology of hydrate crystals growth is clearly shown in these six cases in Figure 2b. The results of case 1-1 indicates that higher cooling rates tend to engender a thin polycrystalline layer, and the hydrate film propagates along the interface. While the results in case

1-2 to 1-6 show that slow cooling rates could lead to single crystals nucleation and growth. In addition, it could be also found that different single crystal morphology like hexagon, pentagram and rhombus appears affected by the cooling rates. As shown in Figure 2c, the total reaction time of the hydrate crystal growth and the crystal growth rates are calculated. The results manifest that the cooling rates are approximately proportional to the total reaction time of crystal growth and increases exponentially with the crystal growth rate. Thus, the results suggest that increasing the cooling rates might be an effective approach to promote the hydrate formation without any additional energy consumption

3.2 Effects of mirco-bubbles on morphology of Hydrate crystal growth

Figure 3 has shown the morphology of hydrate crystal growth close to the bubbles. From the two cases of case 2-1 and case 2-2, it could be clearly found that the hydrate preferentially nucleates at the bubble interface and then propagates along the interface, which indicates that bubbles can supply the nucleation sites of gas and liquid interface. The results also imply that bubbles in hydrate dissociation water perhaps contribute to the explanations of memory effects. As shown in case 3-1 and case 3-2, the results indicate that dendritic crystal tend to grow to the direction of bubbles, resulting in the polycrystalline hydrate nucleation at the bubbles interface. The results of case 4 also prove the conclusion that hydrate crystals have a tendency to grow in the direction of the bubbles since these bubbles provides a source of guest molecules. The hydrate crystal growth in turn accelerates the Ostwald ripening mechanisms [8, 9] between the large and small bubbles. Herein, the Ostwald ripening represents the coarsening process of bubbles which big bubbles consume smaller bubbles due to differences in pressure and inter-bubble gas diffusion. The diffusion of gas molecules between bubbles will affect the nucleation and crystal growth of hydrate, which also means that bubbling is an efficient measure promote the application of hydrate-based to technologies.

4. CONCLUSIONS

The experiments report here have demonstrated that the cooling rates play a significant role in the morphology of gas hydrate crystal growth. And the hydrate preferentially nucleates at the bubble interface and then propagates along the gas and liquid interface. The hydrate crystal growth could accelerate the Ostwald ripening mechanisms between the large and small bubbles. And the crystal morphology could also be influenced by these bubbles.

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REFERENCE

[1] Sloan ED. Fundamental principles and applications of natural gas hydrates. Nature. 2003; 426:353-9.

[2] Uchida T, Ebinuma T, Kawabata J, Narita H. Microscopic observations of formation processes of clathrate-hydrate "Ims at an interface between water and carbon dioxide. Journal of Crystal Growth 1999; 204:348-56.

[3] Ohmura R, Matsuda S, Uchida T, Ebinuma T, Narita H. Clathrate Hydrate Crystal Growth in Liquid Water Saturated with a Guest Substance: Observations in a Methane + Water System. Crystal Growth & Design. 2005; 5:953-7.

[4] Kashchieva D, Firoozabadib A. Driving force for crystallization of gas hydrates. Journal of Crystal Growth 2002; 241:220–30.

[5] Lee JD, Song M, Susilo R, Englezos P. Dynamics of Methane-Propane Clathrate Hydrate Crystal Growth from Liquid Water with or without the Presence of n-Heptane. Crystal Growth & Design. 2006; 6:1428-39.

[6] Ohmura R, Shimada W, Uchida T, Mori YH, Takeya S, Nagao J, et al. Clathrate hydrate crystal growth in liquid water saturated with a hydrate-forming substance: variations in crystal morphology. Philosophical Magazine. 2004; 84:1-16.

[7] Sun CY, Peng BZ, Dandekar A, Ma QL, Chen GJ. Studies on hydrate film growth. Annual Reports Section "C" (Physical Chemistry). 2010; 106:77.

[8] Baldan A. Progress in Ostwald ripening theories and their applications to nickel-base superalloys Part I: Ostwald ripening theories. Journal of Materials Science 2002; 37:2171–202.

[9] Stevenson P. Inter-bubble gas diffusion in liquid foam. Current Opinion in Colloid & Interface Science. 2010;15:374-81.