Time-resolved two-dimensional X-ray diffraction measurements of kinetic properties in polycrystalline high-pressure ices

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Abstract. Time-resolved two-dimensional X-ray diffraction method has been applied to observe kinetic properties of polycrystalline high-pressure ices in diamond anvil cell. The relationships between the number of diffraction spots and the number of grains per radiated volume were calibrated at several beamlines of SPring-8 and Photon Factory. Based on the relationships, we examined kinetics of grain growth in ice VI and VII, and kinetics of the ice VI-VII and VI-VIII transformations, from the evolution of the number of diffraction spots. Preliminary results on these kinetic experiments are presented in this paper.

1. Introduction

Various types of icy bodies are present in outer solar system. Differentiated icy bodies are generally composed of icy outer shell, icy mantle and rocky core. Some of them show recent tectonic activities on their surfaces, and some of them show the evidence of existence of liquid-water ocean beneath their icy outer shells [1]. Icy bodies greater than about 700 km in radius can have high-pressure polymorphs in their interiors. Central pressures of large icy satellites (~2500 km in radius) such as Ganymede, Callisto, and Titan are greater than 3 GPa. Thermal convection in icy outer shell and icy mantle has great influences on thermal evolution, internal dynamics and survival of internal ocean [2]. Rheological and kinetic properties in polycrystalline ice are key factors controlling the convecting current in the interiors of icy bodies.

Recent studies have revealed that the grain-size sensitive creep is possibly dominant in ice I_h and ice II at low stress conditions (~0.01-0.1 MPa) in interiors of icy bodies [3, 4]. As viscosity in the grain-size sensitive creep regime significantly changes with grain size, it is indispensable to examine kinetic processes controlling grain size in the convecting current such as grain growth, and nucleation and growth of high-pressure transformations and dynamic recrystallization [5].

We have conducted experiments on grain growth and transformation kinetics in high-pressure ices using diamond anvil cell (DAC) combined with time-resolved two-dimensional X-ray diffraction (2D-XRD) method. The number and intensities of diffraction spots recorded on 2D detector are used to observe kinetic behaviors of individual grains in polycrystalline ices. Preliminary results of these kinetic experiments are presented in this paper.
2. Experimental method

The number of diffraction spots on 2D detector that fulfill the Bragg condition is proportional to the grain density, and the intensity of each spot is proportional to the volume of the grain. We expect to observe grain growth, and nucleation and growth kinetics of individual grains in polycrystalline material from the evolution of numbers and intensities of diffraction spots as a function of time. This method has been extensively developed in kinetic studies of polycrystalline materials at ambient pressure conditions using high-energy synchrotron X-ray [6, 7]. We preliminarily adopted it for high-pressure experiments using DAC in the present study.

The experiments on grain growth in polycrystalline high-pressure ices were carried out using external-heated DAC at BL13A of Photon Factory, KEK, Japan. We used monochromatic X-ray (29 keV, collimated to 100 microns) and obtained 2D-XRD patterns every about 15 minutes using imaging plate (IP). On the other hand, high-pressure transformation experiments in water ice were carried out using the cryostat combined with a He-gas driven DAC at BL10XU of SPring-8 [8]. We used monochromatic X-ray (35 keV, collimated to 35-100 microns) and obtained time-resolved 2D-XRD patterns every about 15 seconds using X-ray CCD during the transformation. Pressure was measured from the shift of the ruby fluorescence in both experiments.

In addition to these high-pressure experiments, we also preliminarily examined relationships between the number of diffraction spots \(N\) and the number of grains per radiated volume \(n\) at several beamlines based on the following equation [9]: \(N = np\Delta \theta \cos \theta_b / 2\), where \(p\) is multiplicity factor, \(\Delta \theta\) is angle over which crystal reflects due to various factors such as lattice distortion and divergence of beam, and \(\theta_b\) is the Bragg angle. \(n\) can be described by \(S/t/v\), where \(S\) is incident beam area, \(t\) is sample thickness, and \(v\) is grain volume \((-d^3/2:\ d\ is\ grain\ size)\). We prepared standard materials those are equigranular sintered polycrystals of wadsleyite and alumina synthesized by using multi-anvil high-pressure apparatus at Kyushu University. These standard polycrystalline materials were used for the calibration of the \(\Delta \theta\) value in each beamline. In order to analyze the number of diffraction spots and their intensities quantitatively, the 2D-XRD pattern measured were unrolled along azimuth angle, and the azimuthal projection of the intensity along a Debye-Scherrer ring was made.

3. Results and discussion

3.1. 2D-XRD measurements of the standard polycrystalline materials

We measured 2D-XRD patterns of the standard polycrystalline materials at ambient conditions in BL04B1 of SPring-8, and BL13A and BL14C2 of Photon Factory. The light sources of these beamlines are bending magnet, multipole wiggler, and vertical wiggler, respectively. Results on the relationships between \(N\) and \(n\) are summarized in figure 1. Energy and beam size of the incident X-ray used in this measurements were 29-50 keV and 30-300 μm, respectively. The standard samples

![Figure 1. Relationships between the number of diffraction spots \(N\) and the number of grains per radiated volume \(n\) preliminarily calibrated at various beamlines. The numbers indicate the estimated \(\Delta \theta\) values (radian). In this logarithmic plot, the intercept of each line indicates the \(\Delta \theta\) value as \(\cos \theta_b\) is nearly equal to 1.](image)
measured include crystal systems of hexagonal and orthorhombic, average grain sizes of 9-16 μm, sample thickness of 169-255 μm, and multiplicity factors of 4-12. The average grain size of the standard samples was measured using the linear intercept method with a correction factor of 1.5 [10] based on optical microscopy.

Although this calibration is still preliminary and the data is rather scattered, the Δθ values are different among beamlines probably depending on the light source and focusing optics. Based on the estimated Δθ values, we can obtain the information on the number of grains per radiated area (i.e., average grain size) from the number of diffraction spots.

In order to estimate the grain volume from the spot intensity, it is necessary to take 2D-XRD patterns with the sample oscillation so that the corresponding Bragg reflection lies completely within the oscillation angle measured. Additionally, we have to make sure that the grain lies completely within the radiated volume by using different size of the incident beam. Because these have not been quantitatively checked yet, we focus on the evolution of the number of diffraction spots in the present study.

3.2. Time-resolved 2D-XRD observations of grain growth kinetics in ice VI and VII polycrystals

The grain growth occurs when annealing polycrystalline materials, in which the smaller grains are eliminated and the larger grains grow, constructing a lower energy configuration of grain boundaries. We synthesized fine-grained ice VI and VII polycrystals by isothermal compression of ice Ih at around 250 K, and annealed them at near the melting temperatures. Results on time-resolved 2D-XRD
observations during the annealing are shown in figure 2. The grain growth of polycrystalline ice VI was clearly observed at 2.1 GPa and 350 K by decreasing in the number of diffraction spots with time (figure 2a). We estimated the average grain size changed from 22 μm to 51 μm during the annealing for 53 minutes on the basis of the Δθ calibration shown in figure 1.

In contrast, the grain growth of ice VII was not observed when annealing at 2.5 GPa and 370 K for about 60 minutes (figure 2b). Although quantitative estimates of the grain size were difficult due to the overlapped diffraction spots, the grain size was kept less than about 10 μm during the annealing. The slower grain growth rate may be originated from the lower homologous temperature in the ice VII experiment (T/Tm = 0.96) than that in the ice VI experiment (T/Tm = 0.99).

The present study demonstrates that the time-resolved 2D-XRD measurements provide the unique information on the polycrystalline kinetics at high pressures. This method is useful especially for high-pressure ices because it is generally difficult to observe their polycrystalline textures by electron microscopy although some high-pressure ices can be recovered at room pressure [4, 11].

3.3. Time-resolved 2D-XRD observations of the ice VI-VIII and VI-VII transformation kinetics
The annealed polycrystalline ice VI was transformed to ice VIII at 230 K and 2.2 GPa, and 250 K and 2.2 GPa. Changes of 1D-XRD patterns during the transformation are shown in figure 3a. The X-ray CCD measurements every 15 sec could catch the initiation of the transformation. However it was difficult to quantitatively analyze the number of ice VIII diffraction spots, because many spots appeared simultaneously and overlapped (figure 3b) due to the large size of the incident beam (100
μm) compared to the number of the nucleated grains. The smaller incident beam size should have been used for this experiment so that the number of grains per radiated volume decreases and becomes countable.

We also observed the ice VI-VII transformation kinetics during isothermal compression at 290 K. In this case, only a few diffraction spots of ice VII newly appeared. This is because the incident beam size (35 μm) was too small compared to the number of new grains radiated. The balance between the incident beam size and the number of grains per radiated volume had not been optimized in both the ice VI-VIII and VI-VII experiments.

The number of grains and the grain size of the newly transformed phase largely depend on the relative ratio of nucleation and growth rates of the transformation, which changes with pressure and temperature conditions. The use of the appropriate beam size for each experimental condition is necessary in future experiments to observe kinetic behaviours of individual grains quantitatively.

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