Two-dimensional time-resolved X-ray diffraction study of liquid/solid fraction and solid particle size in Fe-C binary system with an electrostatic levitator furnace

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Abstract. Liquid state provides functions such as matter transport or a reaction field and plays an important role in manufacturing processes such as refining, forging or welding. However, experimental procedures are significantly difficult for an observation of solidification process of iron and iron-based alloys in order to identify rapid transformations subjected to fast temperature evolution. Therefore, in order to study the solidification in iron and iron-based alloys, we considered a combination of high energy X-ray diffraction measurements and an electrostatic levitation method (ESL). In order to analyze the liquid/solid fraction, the solidification of melted spherical specimens was measured at a time resolution of 0.1 seconds during rapid cooling using the two-dimensional time-resolved X-ray diffraction. Furthermore, the observation of particle sizes and phase identification was performed on a trial basis using X-ray small angle scattering with X-ray diffraction.

1. Introduction
It is important for the industrial or materials science fields to crystallographically-comprehend the nature of solidification phenomena. On the other hand, the simulation techniques for the microstructure formation such as the phase-field method have been developed in the field of model simulations and property predictions [1]. In order to correlate the mathematical theory to the practice, the experimental kinetics that synchronize computing time with real time are important for the microstructure formation. However, experimental setups are significantly difficult for an observation of the solidification process of iron or iron-based alloys because of their high melting points, high evaporation pressures and very fast time-dependent phenomena. We focus on the observation of the homogeneous nucleation with isothermal kinetics. Then, it is essential for the study of isothermal transition or nucleation kinetics to facilitate the X-ray transmission method without the nucleation by the specimen container in order to obtain better integral intensities during solidification. Then, the electrostatic levitator (ESL) [2] provides the capability of undercooling and solidifying metals and alloys in a contactless high vacuum and quiescent environment. In the present study, we analyzed the isothermal kinetics of solid phase fraction in melts using the two-dimensional time-resolved X-ray diffraction (2D-TRXRD) system with the ESL. Furthermore, the observation of solid
particle size and phase identification was conducted on a trial basis using X-ray small angle scattering with X-ray diffraction.

2. Experimental procedure
The chamber housed a specimen charged by electronic emission and levitated between electrodes via a feedback loop. The specimen was heated and melted using the focused radiation of three 100 W semiconductor laser beams emitting at a wavelength of 808 nm. Then, the temperature of the specimen was measured with a radiation thermometer to obtain cooling curves. The features of our experimental system are (i) containerless, (ii) convenient for high energy X-ray transmission and absorption correction due to a spherical specimen of a 1 ~ 2mm size, (iii) available in a compact instrument size and (iv) not blind for incident and diffracted X-rays. The ingot for the specimen was produced by arc melting 99.999 mass% electrolytic irons and 99.7 mass% carbon powders in argon. The specimen with a spherical shape of a diameter of approximately 2 mm was prepared by arc melting tips cut from the ingot on a copper cooling plate. The specimen component was conclusively Fe-1.7mass%C.

In this study, the solidification of iron-based alloys was dynamically observed by collaboration with an intense X-ray of an undulator beamline, the ESL technique and an X-ray photon counting pixel detector of PILATUS-100K [3]. Figure 1 shows the experimental set-up that was used at the BL22XU beamline of SPring-8 in Japan. In the BL22XU, the high intensity, high-energy X-rays can be obtained by using an undulator and double crystal monochromator with {111}Si cooled with liquid nitrogen. The X-ray energy was accurately confirmed as 69.5 KeV using a standard silicon powder. The focused monochromatic beam was passed through a 0.1 x 0.1 mm slit and irradiated to the spherical specimen that was levitated and melted by the ESL furnace. The PILATUS was mounted on an arm of the four-axis diffractometer at a distance of 212.6 mm behind the specimen. Then, the solidification was dynamically observed at a time resolution of 0.1 seconds as functions of time and temperature at various cooling rates. This time resolution is small enough to obtain critical information on the solidification mechanism [4].

3. Results and discussion
3.1. Cooling curves and 2D-TRXRD patterns during cooling
Figure 2 shows the cooling curves and the 2D-TRXRD patterns. The inflection points such as recalescence points or some shoulders were related to the crystallization of γ-Fe phase, the precipitation of Fe₃C carbides and the solid phase transformation from γ-Fe phase to α-Fe phase were exhibited at 1200°C, 1050°C, and 750°C. Furthermore, the shoulder in the vicinity of 1150°C corresponds to the temperature of the eutectic point. The cooling rates, which are 53°C/s, 40°C/s, 26°C/s and 13°C/s at 1300°C, were controlled with the laser output. Figure 2(a)-(e) shows an example of the 2D-TRXRD patterns that were observed with a cooling rate of 53°C/s at 1300°C and at a time resolution of 0.1 seconds. In Fe-1.7mass%C, the diffraction pattern of liquid halo is first observed at approximately 1300°C as shown in Figure 2(a). Next, the spotty γ-Fe phase appears in the halo pattern at 1220°C as shown in Figure 2(b). The diffraction of the γ-Fe phase broadens along Laue rings with the residual halo pattern at 1100°C with a temperature drop as shown in Figure 2(c). At 1000°C, the diffraction pattern of Fe₃C carbides appears as shown in Figure 2(d). At 725°C, the diffraction patterns

![Figure 1 Experimental setup](image-url)
of $\alpha$-Fe phases appear while the diffraction intensity of the $\gamma$-Fe phase decreases as shown in Figure 2(e).

The sharp $\{111\}_\gamma$ diffraction peaks at each temperature were separated from the liquid phase by the Lorentz function. Then, it was assumed that the atomic scattering factor of solid is approximately equivalent to that of liquid since the $\gamma$-Fe phase is crystallized from the liquid-Fe phase. Next, the integral intensity ratio of $\{111\}_\gamma(I_r)$ was expressed by dividing the integral intensity of $\{111\}_\gamma$ by the total integral intensity of the observed profile. Then, the volume fraction of solid phases was normalized by dividing $I_r$ at each temperature by the saturated $I_r$ at the temperature of the eutectic point. The curves of volume fractions during solidification were compared at any temperature.

3.2. Isothermal kinetics of solid phase fraction

Variations of solid phase fraction along the cooling curve include information about both time and temperature. In order to obtain the isothermal kinetics of solid phase fractions, the contour curves were approximated by typical measured points as shown in Figure 3(a). Therefore, the contour curves mean the distribution of volume fraction of solid-$\gamma$ as functions of temperature and time. Then, it is possible to obtain the isothermal kinetics of volume fraction at any temperature. Figure 3(b) shows the isothermal kinetics of volume fraction at 1474 K. The curve of volume fraction with cooling time was approximated by the JMAK equation [5] in the case of surface growth controlling [6]. Consequently, the volume fraction was saturated at 4.9 seconds. The crystal growth rate decreased with a decrease of temperature and the saturated time was marginally delayed. It is expected that the diffusion of carbon atoms is enhanced with a temperature drop and follows the formation of Fe$_3$C carbides as the activation energy decreases with a temperature drop.

Figure 3 Contour mapping (a) and isothermal kinetics of volume fraction at 1474K (b)
3.3. Small angle X-ray scattering on a trial basis

The particle distribution was analyzed by small angle X-ray scattering (SAXS) on a trial basis. Figure 4 (a) shows the example of analysis at 1325°C for 60 seconds. The SAXS profiles were analyzed by two-phase (solid-γ and liquid-γ) spherical model as the solid-γ is crystallized from the liquid phase. The tendency is acquired although there is a lot of noise at a high angle. Figure 4 (b) shows the particle distribution of solid-γ in the liquid at various cooling temperatures. With a temperature drop, localized distribution extends and average particle size is coarsened. Particles were identified as γ particles by simultaneous measurement with X-ray diffraction (c).

Figure 4 Small angle X-ray scattering at 1325°C (a) and change of particle distribution of solid-γ (b) with X-ray diffraction(c).

4. Summary

The system of in-situ high-energy X-rays of a synchrotron source with an X-ray photon counting pixel detector combining with the electrostatic levitation technique has been developed for a homogeneous nucleation and was applied to quantify the solid phase fraction during rapid solidification. (1) The homogeneous nucleation and the crystal growth in the levitated 1.7%C-Fe were observed at various cooling rates by 2D-TRXRD. (2) The isothermal kinetics of volume fraction, which is saturated at several seconds, was obtained at different temperature levels. (3) The particle distribution was observed on a trial basis by simultaneous measurement of small angle scattering with X-ray diffraction. We indicated the possibility of observing the particle distribution during cooling.

Acknowledgments

This work was performed under the Shared Use Program of JAEA Facilities. The synchrotron radiation experiments were performed at JAEA beamline in SPring-8. (Proposal No. 2011B 3786, BL No.BL22XU)

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