Development of X-ray Imaging for Observing Solidification of Carbon Steels

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Time-resolved X-ray imaging of dendritic solidification for pure Fe and carbon steels with sufficient spatial and time resolutions has been developed for the first time by overcoming essential problems in low contrast between solid and liquid phases and in high melting temperatures. Static observation showed that the solid/liquid interface in pure Fe specimen was determined by the absorption contrast at photon energy ranging from 16 to 30 keV. In addition, the phase contrast was also observed in the vicinity of the interface. Dynamic observation showed that cellular growth in pure Fe specimen was observed at a growth velocity up to 400 \( \mu \text{m/s} \). Feasibility observation was also performed for two different carbon steels (0.0025 mass\% C and 0.45 mass\% C). Growing dendrites were observed in-situ at a growth velocity up to 500 \( \mu \text{m/s} \). This study proves that the developed imaging enabled to observe solidification phenomena in-situ for various kinds of steels.

KEY WORDS: in-situ observation; radiography; synchrotron radiation; dendrite.

1. Introduction

In the last decade, time-resolved X-ray imaging has been extensively used to investigate solidification phenomena of metallic alloys.\(^{1-20}\) In the third generation synchrotron radiation facilities such as SPring-8,\(^{21}\) hard X-rays with photon energy ranging from 10 to 100 keV can be used for the X-ray imaging. The hard X-ray penetrates through bulk specimen of metallic materials. The advantages of using the synchrotron radiation X-ray are 1) a monochromatic light, 2) high coherency and 3) high brightness. The monochromatic light with appropriate photon energy produces high contrast in transmission images. The high coherency achieves high spatial resolution. The brightness improves time resolution.

Alloy systems for which the X-ray imaging was allowed were mostly Sn, Zn and Al alloys.\(^{1-14,16-18,20}\) They have relatively low melting temperatures. The observations have provided unique and useful information on microstructure evolution during dendritic solidification, dendrite arm fragmentation followed by the columnar/equiaxed transition, and development of segregation. In addition, imaging using a conventional X-ray source was also developed for estimating melt flow velocities in Ga–In alloy.\(^{21}\) The analysis for estimating convection can be obviously used in transmission images obtained by the synchrotron X-ray. Therefore, the in-situ observation has been recognized as a useful tool for investigating solidification phenomena in metallic alloys, though it has been limited to alloys and metals with low melting points.

Because of the potential of the in-situ observation, to develop an imaging technique for solidification of steels will be in the ordinary course. There were, however, only few studies on Fe-based alloys until now. The first report\(^{23}\) dealt with solidification of Fe–Si alloys by using the X-ray topography technique. Solidification with the planar interface and the cellular interface were observed in Fe–3mass\%Si alloys. Recently, imaging of dendritic growth in Fe–Si–Al alloys was successfully performed by the absorption imaging technique.\(^{19}\) To the best of author’s knowledge, no notable development for an imaging technique for carbon steels has been done.

Confocal scanning laser microscope\(^{24}\) is an alternative observation technique for observing solidification of carbon steels. Although the microscope observes just surface of molten alloys, solidification events can be detected due to modification of surface profile. Enulfment and pushing of inclusions in the vicinity of solidifying front were investigated for the carbon steel.\(^{24}\) The observation provided valuable information on solidification and inclusion behavior in melt. However, the microscope cannot allow to observe the microstructure evolution in the inside of specimen, in a timely manner. Thus, it has been desired to develop X-ray imaging technique that is suitable for carbon steels.

Recently, preliminary results have been reported for observing solidification of carbon steels.\(^{25,26}\) This paper demonstrates further development of X-ray imaging technique for observing solidification for pure Fe and carbon steels. First of all, requirements for observing solidification...
2. Preparation of X-ray Imaging

2.1. Requirement for Transmission X-ray Imaging

Important parameters for developing X-ray imaging using the absorption contrast are intensity of transmission X-ray through a specimen and contrast between different phases. One estimates the intensities through Fe–C alloys and pure Fe for building X-ray optics and for choosing dimension of specimen. In general, intensity of transmission X-ray, \( I \), is expressed by

\[
I = I_0 \exp(-\mu_{\text{avg}} t) \quad \text{(1)}
\]

Here, \( I_0 \) is the intensity of incident beam and \( t = \frac{\text{thickness}}{\text{density}} \) is thickness. The linear X-ray absorption coefficient of the specimen, \( \mu_{\text{avg}} \), is given by

\[
\mu_{\text{avg}} = \sum_i \left( \frac{\mu}{\rho} \right)_i \rho_i = \bar{\rho} \sum_i \left( \frac{\mu}{\rho} \right)_i w_i \quad \text{(2)}
\]

\((\mu/\rho)\) and \( \rho \) are the mass X-ray absorption coefficient and the mass density, respectively. The suffix, \( i \), indicates constituent element species. \( \bar{\rho} \) is average density and \( w_i \) is mass fraction of the constituent element, \( i \). The mass X-ray absorption coefficient, \((\mu/\rho)\), is a function of photon energy, uniquely defined by the element.

The linear X-ray absorption coefficient of Fe–C alloys is given by

\[
\mu_{\text{Fe-C}} = \bar{\rho} \left( \frac{\mu}{\rho} \right)_\text{Fe} w_{\text{Fe}} + \left( \frac{\mu}{\rho} \right)_\text{C} w_{\text{C}} \quad \text{(3)}
\]

The mass X-ray absorption coefficient of C is 0.044 m²/kg at 20 keV while that of Fe is 2.57 m²/kg at 20 keV. Since the mass fraction of C is mostly less than 0.01 in conventional carbon steels, the mass X-ray absorption coefficient and the density of Fe dominantly determine the linear X-ray absorption coefficient of the Fe–C specimen.

Conventional carbon steels contain Mn as well. The mass X-ray absorption coefficient of Mn is 2.25 m²/kg at 20 keV. Since the partition coefficient of Mn in Fe matrix is approximately 0.75, difference in Mn concentration between solid and liquid phases is estimated to be 0.1–0.3 mass% for a specimen with average Mn concentration of 0.3–0.9 mass%. Change in the linear X-ray absorption coefficient is evaluated by the same procedure as for Fe–C system. The solute redistribution gives only 0.01–0.03% change in the linear X-ray absorption coefficient. The change is too small to be detected dynamically.

Thus, Mn as a solute element does not produce sufficient contrast at the solid/liquid interface in transmission X-ray imaging.

As mentioned above, the essential requirement for observing the solid/liquid interface for carbon steels is to develop observation system that can detect contrast due to density difference between solid and liquid phases in pure Fe. In the case of pure Fe, the difference in density between solid and liquid phases is 4.2%.

2.2. Dimension of Specimen

Thickness of a specimen has to be carefully chosen so that objective phenomena can be observed. Since the present study focused on dendritic growth in carbon steels, thickness was chosen in accordance with characteristic length of dendrites. Tip radius of dendrite ranges from several micrometer to several 10 µm in conventional solidification conditions. Primary dendrite arm spacing also ranges from several 10 to 1000 µm. Crossover of dendrites in the X-ray beam direction has to be eliminated because X-ray optic systems used in the present study does not have any focus function. Therefore, thickness was set to be 100–200 µm in this study. In specimens with the thickness range, dendrite tips are expected to evolve three-dimensionally while coarsening of dendrite arms in the final stage of solidification takes place nearly two-dimensionally.

2.3. Choice of Photon Energy

In the case of pure Fe, the linear X-ray absorption coefficients of solid and liquid phases are expressed by

\[
\mu_{\text{solid}} = \left( \frac{\mu}{\rho} \right)_\text{Fe} \rho_{\text{Fe, solid}} \quad \text{(4)}
\]

\[
\mu_{\text{liquid}} = \left( \frac{\mu}{\rho} \right)_\text{Fe} \rho_{\text{Fe, liquid}} \quad \text{(5)}
\]

respectively. Critical parameters for time-resolved observation of the solid/liquid interface are to obtain sufficient photon flux to a detector and to obtain appropriate contrast in transmission images. Here, the normalized intensity, \( \tau \), is defined by the following equation.

\[
\tau = \frac{I_{\text{liquid}}}{I_0} = \exp(-\mu_{\text{Fe, liquid}} t_{\text{Fe}}) \quad \text{(6)}
\]

The contrast of solid phase to liquid phase in the transmission image, \( \chi \), is also given by

\[
\chi = \frac{I_{\text{liquid}} - I_{\text{solid}}}{I_{\text{liquid}}} = 1 - \exp(-\mu_{\text{Fe, liquid}} t_{\text{Fe}})
\]

\[
= 1 - \exp \left[ -\left( \frac{\mu}{\rho} \right)_\text{Fe} (\rho_{\text{Fe, solid}} - \rho_{\text{Fe, liquid}}) t_{\text{Fe}} \right] \quad \text{(7)}
\]

Figure 1 shows the normalized intensity, \( \tau \), as a function of specimen thickness and photon energy. Here, one considers the normalized intensity for a specimen with a thickness of 100 µm. The normalized intensity becomes less than 0.1% when photon energy is lower than 10 keV. In the present setup in a beamline BL20B2 of SPring-8\(^{22}\) (See Sec. 3.1), the value of 0.1% is too small to perform time-resolved imaging. As photon energy increases, the normalized intensity monotonically increases. The normalized intensity becomes more than several percent when photon energy exceeds 15 keV. Several percent of the incident X-ray
beam can be detected by detectors. Thus, the X-ray beam with photon energy more than 15 keV is required for the X-ray imaging.

Figure 2 shows the contrast, $\chi$, defined by Eq. (7). As photon energy increases, the contrast decreases while the intensity increases. In the present setup, if the contrast is less than 1%, it was difficult to detect the interface between solid and liquid phases (See Sec. 3.1).

As shown in Figs. 1 and 2, the intensity and the contrast in transmission images have a trade-off relationship. In the case of a specimen with a thickness ranging from 100 to 200 mm, X-ray beam with photon energy ranging from 15 to 30 keV satisfies the required conditions.

It should be noted that photon energy influences conversion efficiency and sensitivity of X-ray detector. When the efficiency of X-ray detector is improved in future, X-ray beams with lower photon energy can be used for the observation. Lower photon energy results in the higher contrast. The alloy systems that are suitable for the observation will be extended. Even if the performance is improved, the appropriate condition for the observation can be obtained by the presented manner.

3. Setup of Observation

3.1. Setup of Observation Apparatus

The observation experiments were performed at the beamline of BL20B2 in SPring-8, Hyogo, Japan. A bending magnet was employed as an X-ray source, and the radiation was monochromatized with Si double crystal monochromator (36.8 m from the X-ray source point). The beam divergences of 1.5 mrad in the horizontal direction and 0.06 m rad in vertical direction provide a high coherent X-ray beam at the sample position. Both an absorption contrast due to the difference in absorption and a phase contrast due to the difference in density, which enhances phase boundaries in a specimen, are obtained in the X-ray transmitted images.

Figure 3(a) shows a setup for observing solidification of pure Fe. An ion chamber for measuring intensity of incident X-ray beam, vacuum chamber in which a specimen with a heating system is set, and an X-ray detector are placed along X-ray beam stream. The image detector consisting of an X-ray direct-sensing pickup tube SATICON was used to observe transmitted X-ray images. The image signals were converted into a digital format and stored in frame memory with a format of 1024×1024 pixels and 10-bit resolution. The pixel size was 5 mm. The detector acquired 32 frames per second. The transmitted images stored in frame memory were obtained by integrating a given number of frames to improve S/N ratio. In the present setup, the spatial resolution was 10–20 mm.

The furnace in the vacuum chamber is shown in Fig. 3(b). Graphite heater was used for heating. The heater was covered with BN plates for shielding radiation from the heater. The furnace consisting of the graphite heater and the BN plates had a hole (roughly 10 mm×10 mm) at the center for X-ray beam, as shown in Fig. 3(c). Since the X-ray beam pass through the hole, the furnace did not degrade the transmission image.

3.2. Specimens for Observation

The experimental conditions for pure Fe are listed in Table 1. Mother alloy of pure Fe was produced by arc melting of electrolytic Fe. A specimen cell was made of Al$_2$O$_3$ window plates and BN retainer plates. Pure Fe specimen with a dimension of 7 mm×7 mm×0.1 mm was placed between the two Al$_2$O$_3$ window plates with a thickness of 0.15 mm. The specimen and the window plates were retained by the BN plates. The configuration of the specimen cell in the furnace is illustrated in Fig. 3(c). The specimen in the cell was placed between the graphite heaters. Temperature distribution in the furnace was essentially determined by shape of graphite heaters. In addition, tempera-
ture gradient in the specimen depended on vertical position of the specimen. It should be noted that, since the thermal transfer was dominantly controlled by radiation in the observation, the holes in the graphite heaters and the BN plates somewhat complicated the temperature distribution.

For the static observation, a specimen was partially melted and temperature was kept at a given temperature such that the solid/liquid interface placed nearly at the center of observation area. For the dynamic observation, a specimen was melted once and was cooled under a vacuum at a given cooling rate. Namely solidification occurred at a constant cooling rate. One requires care about the cooling rate. In the dynamic observation, most of latent heat due to solidification can be immediately released by radiation from thin specimen surface. On the other hand, latent heat is released only by conduction through the solidifying shell in conventional casting. Thus, the local solidification time in the dynamic observation is shorter than that in the conventional casting when the cooling rates before solidification are the same each other. The cooling rate in the dynamic observation should be treated as a rough guide for solidification rate. The local solidification time and the growth velocity should be used for characterizing solidified structure.

During the cooling procedure, the position of specimen was fixed. Since the specimen was placed at the centre of graphite furnace, the temperature gradient at the observation area was less than 1 K/mm for pure Fe.

The dynamic observations of two different carbon steels were also performed. One is a ultra low carbon steel (ULC steel) with a composition of Fe–0.0025mass%C–0.6mass%Mn–0.3mass%Si and the other is a high carbon steel (HC steel) with a composition of Fe–0.44mass%C–0.6mass%Mn.

### 3.3. Image Processing

Intensity of transmission X-ray through specimen and cell, \( I_{\text{sample}} \), is expressed by

\[
I_{\text{sample}}(x, y) = I_0(x, y) \exp(-\mu_{\text{cell}}(x, y)) \exp[-\mu_{\text{sample}}(x, y)I_{\text{sample}}(x, y)]
\]

The suffixes “sample” and “cell” indicate specimen and cell, respectively. Since the specimen cell was made of two polished Al\(_2\)O\(_3\) plates with a thickness of 150 \( \mu \)m, the linear absorption coefficient and thickness are constant.

Intensity of transmission X-ray through absorber SiO\(_2\) glass with a constant thickness, \( I_{\text{absorber}} \), was also measured.

\[
I_{\text{absorber}}(x, y) = I_0(x, y) \exp(-\mu_{\text{absorber}}I_{\text{absorber}})
\]

The normalized X-ray intensity, \( I_{\text{norm}}(x, y) \), is calculated by the above intensities.

\[
I_{\text{norm}}(x, y) = \frac{I_{\text{sample}}(x, y)}{I_{\text{absorber}}(x, y)} = \exp(-\mu_{\text{cell}}(x, y)) \exp(\mu_{\text{sample}}I_{\text{sample}}(x, y)) \times \exp[-\mu_{\text{sample}}(x, y)I_{\text{sample}}(x, y)]
\]

As expressed in Eq. (10), the contrast in \( I_{\text{norm}}(x, y) \) reflects the product of linear X-ray absorption coefficient and thickness in a specimen. Thus, the normalized images are suit-
able for observing solidification morphology. This procedure was used for the static and the dynamic imaging of pure Fe.

Another normalized procedure was also done. Intensity of transmission image just before solidification is expressed by

\[ I_{\text{sample, liquid}}(x, y) = I_{0}(x, y) \exp(-\mu_{\text{cell,\text{cell}}}(x, y)) \times \exp[-\mu_{\text{sample, liquid}}(x, y)I_{\text{sample}}(x, y)] \] .......(11)

Here, one assumed that thickness of specimen did not change during cooling procedure. The normalized intensity was obtained by the following equation.

\[ I_{\text{norm, liquid}}(x, y) = \frac{I_{\text{sample}}(x, y)}{I_{\text{sample, liquid}}(x, y)} = \exp[-\{\mu_{\text{sample}}(x, y) - \mu_{\text{sample, liquid}}(x, y)\}I_{\text{sample}}(x, y)] \] ...........................................(12)

Since \( I_{\text{norm}}(x, y) \) reflects the change of linear X-ray absorption coefficient, the solidified region can be easily detected. In this study, this normalization procedure was used for the observation of carbon steels.

4. Observations

4.1. Static Observation

Figure 4 shows the results of the static observations. The exposure time for obtaining transmission images was 4 s. The brightness of photographs corresponds to the intensity expressed by Eq. (10). The upper part is the liquid phase and the lower part is the solid phase. The horizontal stripes with a period of several 10 µm in the transmission images, which were superimposed on the interface, were caused by the fluctuation of incident X-ray beam. The solid/liquid interface of pure Fe was clearly observed using the absorption contrast at photon energy ranging from 16 to 28 keV.

Figure 4(f) shows a close-up view of the interface. The phase contrast, which originated in the interference of X-ray beam with high coherency, caused a couple of white and black fringes in the vicinity of the interface. Since the solid/liquid interface was sharp and was not completely parallel to X-ray beam, reflection of X-ray beam on the solid/liquid interface can occur. The reflections also caused fuzzy contrast around the interface. In the transmission images at any photon energy, the absorption contrast between solid and liquid phases was also detected while the phase contrast and the reflection were superimposed around the interface.

As shown in Fig. 4(a), the transmission image at 16 keV has low signal to noise ratio (S/N ratio), but high contrast between solid and liquid phases. As photon energy increases, the S/N ratio was improved while the intensity while the intensity decreases. The contrast became rather weaker at photon energy exceeding 24 keV, as shown in Figs. 4(d) and 4(e). It should be note that since S/N ratio depends on exposure time, appropriate photon energy should be carefully chosen with possible exposure time.

Figure 5 shows the profiles of the normalized intensity, \( I_{\text{norm}}(x, y) \) defined by Eq. (10), along the line A–A’ in the transmission images in Fig. 4. The solid/liquid interface was set to be 0. Sharp jumps in the intensity at the interface correspond to the phase contrast. The dash lines drawn in Fig. 5 are guides for the absorption contrast. The contrast due to the absorption was as large as 10% at photon energy of 16 keV, while it was only several percent at 28 keV. The observed tendency essentially agreed with the calculation in the previous section. There was, however, slight discrepancy in the values. The discrepancy may result from the performance of X-ray detector.

If rather long exposure time, i.e. several seconds, is acceptable in observations, the photon energy of 16 keV is suitable for obtaining the transmission images. As the required time resolution becomes higher, the photon energy should be increased.

4.2. Dynamic Observation

Figure 6 shows the solid/liquid interfaces during solidification of pure Fe. Table 2 lists the observation conditions and the analyzed growth velocity. For the dynamic observa-

![Figure 4](image1)

**Fig. 4.** Transmission images of solid/liquid interface of pure Fe. Photon energy: (a) 16 keV, (b) 18 keV, (c) 20 keV, (d) 24 keV, (e) 28 keV, (f) Close-up view of the interface.

![Figure 5](image2)

**Fig. 5.** Intensities of transmission X-ray around solid/liquid interface of pure Fe.
tion, the exposure time has to satisfy the required conditions. The exposure time was set as long as possible for improving the $S/N$ ratio. The growth velocity was measured from the sequential images. Some bubbles remained in the melting procedure as shown in Fig. 6. Since the chamber was evacuated, some of them were eliminated during observation.

Cooling procedure began when the solid/liquid interface exhibited planar. As the solid phase grew, the interface morphology changed from the planar interface to the cellular interface. Impurities such as C and O, which were rejected at the solidifying front, destabilized the planar interface.

As shown in Fig. 6, the solid/liquid interface was observed for all the cooling conditions. As listed in Table 2, the growth velocity of cells ranged from 60 to 360 $\mu$m/s. In the case of 1.33 K/s, the growth length during the exposure time of 62.5 ms is approximately 20 $\mu$m. Namely, the interface moved as long as 4 pixels in each image. The solid/liquid interface somewhat bled on the transmission images. However, the bleeding was nonfatal for determining the interface position and for observing growing morphology.

During the solidification, the interface had curvature in the growth direction. The fringes of the phase contrast become unclear due to the curvature. Motion of interface during exposure time also makes the fringes unclear. As a result, the phase contrast was not observed in the dynamic imaging.

<table>
<thead>
<tr>
<th>Cooling rate (K/s)</th>
<th>Growth velocity (µm/s)</th>
<th>Exposure time (s)</th>
<th>Frame rate (fps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>60</td>
<td>0.5000</td>
<td>2</td>
</tr>
<tr>
<td>0.33</td>
<td>110</td>
<td>0.2500</td>
<td>4</td>
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<tr>
<td>0.67</td>
<td>150</td>
<td>0.1250</td>
<td>8</td>
</tr>
<tr>
<td>1.33</td>
<td>360</td>
<td>0.0625</td>
<td>16</td>
</tr>
</tbody>
</table>

4.3. Feasibility Observation of Carbon Steels

The dynamic observation for pure Fe essentially showed that the solid/liquid interface position in carbon steels was determined by the absorption contrast. In the pure Fe specimen, the interface morphology was planar or cellular. Some observations were additionally performed for the two different carbon steels for observing the dendritic growth and for characterizing the dendrite shape.

Figure 7 shows the snapshots of dendrites observed in the ULC steel and the HC steel. Photon energy used in this observation was 21 keV. As expected from the dynamic observation for pure Fe, growing dendrites were clearly observed for the ULC steel and the HC steel. In the case of the ULC steel (0.17 K/s), the growth velocity of dendrites was roughly 100 $\mu$m/s and the local solidification was 30–50 s. The primary dendrite arms were rather thick, comparing to the secondary arms. Since the solute concentration was low, coarsening of dendrite arms rapidly occurred and the solid fraction behind the dendrite tip increased. In contrast, the dendrite became thin for the HC steel (1.67 K/s). The liquid phase clearly remained behind the dendrite tips. The growth velocity and the local solidification time were 540 $\mu$m/s and 30–40 s, respectively. The dendrites and the related phenomena could be characterized by the in-situ observation.

The growth velocity of dendrites in the HC steel exceeded 500 $\mu$m/s at the highest cooling rate. The velocity observed in the HC steel was roughly in the same order of the growth velocity in the surface region of solidified shell in conventional continuous casting processes. Therefore, the present setup enables to simulate solidification phenomena, which may occur in the continuous casting.

Since time-evolution of solidifying structure cannot be obtained by the observation of the solidified structure with the convention microscope, the developed imaging technique provides exclusive information on dynamics of solidification phenomena for steels.

5. Summary

Fundamentals for observing solidification of carbon steels were determined in terms of the time-resolved X-ray imaging using the absorption contrast. The estimation of intensity and contrast in transmission images indicated that
the solid/liquid interface in a specimen with a thickness ranging from 100 to 200 μm could be detected at photon energy from 15 to 30 keV.

The static observation was performed for pure Fe. The growth of cells was observed at growth velocity as high as 360 m/s. The phase contrast was clearly detected by the absorption and the reflection of incident X-ray beam at the solidifying front. The intensity of transmission X-ray images was also observed around the interface on the transmission images. The S/N ratio decreased. The growth velocity was observed at photon energy ranging from 16 to 30 keV.

The dynamic observation was also performed for pure Fe. The growth of cells was observed at growth velocity as high as 360 μm/s. The bleeding due to the relatively long exposure time with respect to the growth velocity was not fatal for determining interface position and for observing growing morphology.

The feasibility observations were performed for the ULC and the HC steel. The dendrites were observed at growth velocity as high as 500 μm/s. The observed dendrites could be characterized. The X-ray imaging technique developed in this study realizes the in-situ observation for solidification of various steels.

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