Kinetics of the $\delta/\gamma$ interface in the massive-like transformation in Fe-0.3C-0.6Mn-0.3Si alloys

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Abstract. In Fe-C alloys, it has been considered that the peritectic reaction occurs during solidification. Recently, the massive-like transformation, in which $\delta$ phase undercooled below the peritectic temperature transforms into $\gamma$ phase, has been observed by X-ray imaging. It is of interest to know how the $\delta$ phase transforms into the $\gamma$ phase, because the transformation is related to deformation of solidifying shell. Time-resolved and in-situ X-ray imaging with frame rate up to 500 fps was performed to know the $\delta/\gamma$ interface motion in the massive-like transformation in Fe-0.3C-0.6Mn-0.3Si alloys (mass%). The moving velocity of the $\delta/\gamma$ interface locally fluctuated. The average velocity ranged from several mm/s to 200 mm/s. However, no relationship between the moving velocity and the undercooling from the peritectic temperature was observed. The interface was not planar and the morphology continuously changed. The results showed that the stress / strain induced though the transformation from the $\delta$ phase to the $\gamma$ phase in the steel solidification was not simply explained by the conventional peritectic reaction.

1. Introduction

The bcc ($\delta$) phase can transform into the fcc ($\gamma$) phase below the peritectic temperature (1766 K) in Fe-C alloys with 0.1-0.5 mass%C. Due to the volume change in the transformation has been known to cause deformation of solidifying shell [1]. To avoid defect formation due to the transformation, many efforts have been done to understand the peritectic reaction / solidification [2]. In Fe-C alloys with 0.1-0.5 mass%C, it has been considered that the peritectic solidification, in which the $\gamma$ phase was produced at the interface between the $\delta$ phase and the liquid phase, took place. Thus, the solidification of the Fe-C alloys has been considered on the basis of the peritectic reaction [2].

Radiography using synchrotron radiation X-rays has been developed [3]. For example, dendritic solidification of Sn and Al alloys has been reported [4-5]. Recently, the technique has been extended to observe solidification of Fe-C alloys [6-8] and deformation of semisolid [9]. Since the in situ observation allows us to know how the solidification and the phase transformation proceed, the technique provides direct and valuable information for modelling microstructural evolution and defect formation. In addition, the technique can be used to obtain experimental data for validating model and numerical simulation.

In our previous study [7-8], the massive-like transformation from the undercooled $\delta$ phase to the $\gamma$ phase dominantly occurred, comparing to the peritectic solidification. The $\gamma$ phase hardly nucleated in the $\delta$+L state and consequently the $\delta$ phase continued to grow even below the peritectic temperature. Once the $\gamma$ phase nucleated in the undercooled $\delta$ phase, the massive transformation completed within
1s in the observation area (5 mm x 5 mm). Since the massive-like transformation can induce higher strain rates for the viscoelastic solidifying shell, the influence of the massive transformation on deformation and crack can differ from that of the peritectic solidification [8]. Thus, it is valuable to know the transformation behaviour (i.e. moving velocity and morphology of the $\delta/\gamma$ interface) for building a model of the massive-like transformation.

The in-situ observation with a frame of 1 fps in the previous study [7] was too slow to observe the $\delta/\gamma$ interface during the massive transformation. done with a frame rate of 1 fps. This study presents the moving velocity and the interface morphology for a conventional carbon steel (Fe-0.3C-0.6Mn-0.3Si in mass%) by using in-situ observation with a relatively high rate up to 500 fps. The kinetics of the $\delta/\gamma$ interface in the massive-like transformation is also discussed.

![Figure 1. Setup for observing the massive-like transformation of Fe-0.3C-0.6Mn-0.3Si.](image)

| Table 1. Experimental conditions for observing. |
|-----------------------------------------------|
| **Composition** | Fe-0.3C-0.6Mn-0.3Si (mass%) |
| **Dimension**   | 10 mm x 10 mm x 0.1 mm     |
| **X-ray energy**| 21 KeV                      |
| **Detector**    | C-MOS type camera           |
| **Pixel size**  | 5 $\mu$m x 5 $\mu$m         |
| **Observation area** | 5 mm x 5 mm          |
| **Frame rate**  | 125 fps, 250 fps, 500 fps  |
| **Cooling rate**| 0.17 K/s, 0.33 K/s, 0.87 K/s|
2. Experiments

2.1. Setup for observing

The in situ observation was performed at a beamline of BL20XU in SPring-8, Hyogo, Japan. Figure 1 shows a setup for observing the massive-like transformation. Details of the setup were described in the previous work [6]. 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 beam monitor are placed along X-ray beam stream. The monitor consisting of a fluorescent screen, an optical lens and a high speed CMOS-type camera was used. The images with a format of 1024 x 1024 pixels and 12-bit depth were stored. The pixel size was 5 µm x 5 µm and the frame rate was 125 – 500 fps.

2.2. Observation condition

The observation conditions for Fe-0.3C-0.6Mn-0.3Si alloys are listed in Table 1. Mother alloy with a composition of 0.3mass%C, 0.6mass%Mn and 0.3mass%Si was made by arc melting of electrolytic Fe, C, Mn and Si. A specimen cell made of Al₂O₃ window plates (0.15mm) and BN retainer plates was used [6]. The specimen with a dimension of 10 mm x 10 mm x 0.1 mm was heated by graphite heaters. X-ray energy used for absorption images was 21 keV.

Procedures for observing the δ/γ interface motion were as follows; (1) the primary δ phase was remained in the bottom part to avoid nucleation undercooling of the δ phase, (2) observation position was set at the center of the specimen, (3) the specimen was cooled at a constant cooling rate ranging from 0.17 K/s to 1.67 K/s, (4) Temperature when the dendrite tips reached at the center of the observation area was assumed to be the liquidus temperature, (5) Recording the images was quited when the δ/γ transformation was observed.

3. Results

3.1. Average moving velocity of the δ/γ interface

Figure 2 shows typical dendritic growth of the primary δ phase. According to the phase diagram of Fe-C system, the peritectic reaction in which the γ phase is produced from the δ and the liquid phases could start at the peritectic temperature. However, the γ nucleation did not occur and consequently the solidification was nearly competed without the γ phase.

The difficult of the γ nucleation resulted in the massive-like transformation. Figure 3 shows an example of the δ/γ interface motion during the massive-like transformation in the Fe-0.3C-0.6Mn-0.3Si alloy. Cooling rate was 0.83 K/s and frame rate of radiography was 250 fps. Fig.3(a) shows a snap shot of the δ phase before the massive-like transformation. The γ nucleation followed by the massive-like transformation occurred at a undercooling of 60 K from the peritectic temperature. Fig.3(b) shows a snap shot of the δ/γ interface moving from the right to the left. The δ/γ interface positions were indicated by black lines. The interface position was detected by many dark regions, where the Bragg condition was satisfied to the incident X-ray. Namely, the strain / stress were introduced in the γ phase and even the multiple grains of the γ phase were produced from the γ single grain in Fig.3(c). Shape of the δ/γ interface was not planar and fluctuated. For example, the concave shape changed to the convex shape even within the frames (1/250 s). The duration of the δ/γ interface motion in the observation areas was 0.044 s and the moving length was 5 mm. The duration and the length give the average moving velocity of the δ/γ interface in the observation area. The moving velocity in Fig. 3 was 100 mm/s. It should be noted that the local moving velocity of the δ/γ interface remarkably fluctuated and the motion was far from the steady state.

Figure 4 shows relationship between the average moving velocity and the undercooling from the peritectic temperature. The average moving velocity ranged from several mm/s to 200 mm/s in the undercooling ranging from several K to 100 K. There was no clear relationship between the average moving velocity and the undercooling.
3.2. Local moving velocity of the $\delta/\gamma$ interface

Since the $\delta/\gamma$ interface in the massive-like transformation was not planar and remarkably fluctuated, the average moving velocity does not represent the motion of the $\delta/\gamma$ interface sufficiently. In this study, the local moving velocity was also defined to know the $\delta/\gamma$ interface motion. Fig.5 shows an example to explain the estimation of the local velocity. The line indicated by “line” was the shortest
line from A to the interface at the previous frame. It means that the local velocity was estimated to be as low as possible. The local moving velocity was simply calculated by the length of the shortest line and the interval between the frames. Figure 5 shows the local motion (black arrows) of the δ/γ interface (black line). The length of the arrow (black) corresponds to moving distance of the δ/γ interface at the position. The local velocity at the position is calculated from the distance and the interval between the frames. Figure 6 shows histogram of the local velocity. The local moving velocity ranged from several mm/s to 200 mm/s. The results show that the moving velocity of the δ/γ interface locally fluctuated significantly.

4. Discussion

4.1. Contribution of undercooling to the δ/γ interface motion

Since the γ nucleation occurred at an undercooling as high as 60 K. The transformation from the δ phase to the γ phase does not require the solute partition at the δ/γ interface. If the solute partition does not occur and the elastic energy is ignored, the driving force, which is defined by the difference in the Gibbs energies between the δ phase and the γ phase, is a function of the undercooling. Thus, the moving velocity should depend on the undercooling. However, the relationship between the average moving velocity and the undercooling was not observed, as shown in Fig.4. Even the local velocity fluctuated frame by frame. The discrepancy suggested that the solute partition and/or the elastic energy induced by the transformation may modify the driving force and consequently fluctuated the local moving velocity.

4.2. Influence of solute partition at the δ/γ interface

Since diffusivity in the δ phase is much larger than that in the γ phase [10], the solute profile at the δ/γ interface is essentially the same as that at the steady state solidification with planar interface [11]. Thickness of diffusion layer is given by 2D/V (D: diffusivity, V: velocity). The thicknesses for carbon, manganese and silicon are 10⁻⁸ m, 10⁻¹⁰ m and 10⁻¹⁰ m, respectively. Here, the diffusivities of carbon, manganese and silicon were 10⁻⁹, 10⁻¹² and 10⁻¹¹ m²/s [10]. Since the thicknesses for manganese and silicon is in the order of atomic distance, the two substitutional atoms are hardly partitioned at the δ/γ interface. On the other hand, the thickness for C (interstitial atom) is in the order of 10⁻⁸ m. It suggested that carbon atoms could be partitioned at the δ/γ interface in the massive-like transformation. The partition of carbon atoms may change the driving force and induce the instability of the planar interface.

4.3. Morphology of the δ/γ interface and solute partition

It is of interest to consider the curved interface from a viewpoint of the solute partition of carbon atoms to know an origin of the fluctuation. As mentioned in the previous section, the diffusivity in the γ phase is much smaller than that in the δ phase. Thus, the instability of the solidifying front due to the solute partition can be used to consider the interface in the massive-like transformation. According to the marginal stability theory [12], a specific wavelength $\lambda$ given by eq. (1) is introduced when temperature gradient is negligibly small.

$$\lambda = 2\pi \left( \frac{\Gamma}{mnG_c} \right)^{\frac{1}{2}}$$

Here, $\Gamma$ is Gibbs-Thomson coefficient, m is a gradient of liquidus line and $G_c$ is a gradient of solute concentration at the interface. The wavelength roughly gives a wavelength of interface fluctuation.

If the wave length is calculated in Fe-C, Fe-Mn and Fe-Si binary system. The lengths for carbon, manganese and silicon are estimated to be 0.1µm, 2µm and 2µm, using the typical physical properties. The interval of fluctuation observed in the massive-like transformation was in the order of 10µm or 100µm. Thus, the observed interval is not explained by the solute partition at the δ/γ interface. In addition, the transformation from the convex shape to the concave shape is not explained by the instability induced by the solute partition and vice versa.
5. Conclusion
The in situ observation with relatively high time resolution was performed to observe the δ/γ interface motion in the massive-like transformation in Fe-0.3C-0.6Mn-0.3Si.
(1)The average moving velocity ranged from several mm/s to 200 mm/s. Since there were no relationship between the velocity and the undercooling, it was not determined just by the undercooling.
Other factors such as elastic energy or solute partition can also play a role for determining the $\delta/\gamma$ interface motion.

(2) Mn and Si were hardly partitioned at the $\delta/\gamma$ interface while C can be somewhat partitioned. The partition of C may influence the $\delta/\gamma$ interface motion.

(3) The morphology of the $\delta/\gamma$ interface was not planar and fluctuated during motion. The period of the $\delta/\gamma$ interface could not be explained just by the solute partition. Other factors such as elastic energy can also play a role for determining the $\delta/\gamma$ interface morphology.

(4) The local moving velocity ranged from several mm/s to 200 mm/s and fluctuated. The $\delta/\gamma$ interface could not grow in the steady state.

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