Time-resolved and In-situ Observation of Solidification in TiAl Alloys

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(Received on December 17, 2020; accepted on February 9, 2021; J-STAGE Advance published date: March 12, 2021)

Time-resolved and in-situ observation of solidification by X-ray imaging is a powerful method to empirically understand the solidification process of metallic materials. Observations began with low-melting-point alloys such as Al, and were later applied to the observation of Fe-based alloys in the temperature range above 1750 K. In Ti–Al binary system, there is a γ phase (TiAl intermetallic compound) in addition to an α phase and a β phase, which results in a relatively complex phase diagram with multiple peritectic solidification. Therefore, although there are various possibilities for phase selection and microstructure formation during the solidification process, the solidification process has not been empirically clarified. Therefore, we used single crystal MgO as the sample holding container to suppress the reaction with the reactive molten Ti as much as possible, and for the first time, we successfully observed the solidification process of TiAl alloys. Time-resolved and in-situ observations showed that a solid state phase transformation with repeated nucleation and growth was selected instead of the peritectic solidification from α to γ phases shown in the Ti–Al binary phase diagram. The α′γ transformation should also be taken into account in TiAl alloys since the α′γ transformation formed a fine γ phase and affected the microstructure formation. This understanding of the α′γ transformation was expected to provide new guidelines for controlling the solidification structure of TiAl alloys.

KEY WORDS: TiAl alloy; Time-resolved and in-situ observation; X-ray imaging; peritectic solidification.

1. Introduction

Ti-based alloys are materials with the properties1) of light weight, heat resistance, low temperature toughness, high strength and corrosion resistance. Because of these properties, it has been used in a wide range of applications,1) such as aircraft engine parts, heat exchangers, automotive parts, and golf clubs, and its application is expected to expand in the future. In addition, a number of alloy systems1) have been developed for each application, such as Ti-6Al-4V, Ti-6Al-2Sn-4Zr-6Mo and Ti-10V-2Fe-3Al as an α-β type alloy and Ti-5Al-2.5Sn as an α type alloy and Ti-13V-11Cr-3Al as a β type alloy.

On the other hand, the production costs of Ti-based alloys are relatively high due to the high cost of raw materials and poor machinability. In addition, because it is a reactive metal, casting methods such as vacuum arc remelting (VAR)2) and electron beam melting (EBM)2) are limited due to reactivity problems with molds, which is one of the reasons for increased production costs. Among the production processes such as heat treatment and forging, especially casting is used in all Ti-based alloys. Therefore, the development of technology to reduce production costs in casting is very common and is expected to lead to further expansion of the use of Ti-based alloys.

In the casting process of metallic alloys not limited to Ti-based alloys, casting defects inevitably form in the solidification structure. Casting defects can be classified as cracks, inclusions, and macrosegregation,3) and various reduction techniques have been developed for continuous casting and ingot casting. While some casting defects can be eliminated by heat treatment or forging, others may be difficult to be completely eliminated and may cause the product to be out of specification. Therefore, it is expected that reducing casting defects will not only reduce the costs of casting production, but may also lead to improvements in the subsequent heat treatment and forging processes. Since casting defects form during the solidification process, an empirical understanding of the solidification process is needed to develop technologies to reduce them.

Pure Ti is the α phase (HCP) at room temperature, but at high temperatures, the β phase (BCC) becomes the stable

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phase. For example, the Ti-Al binary system undergoes a complex solidification process, including the formation of the \( \gamma \) phase (TiAl intermetallic compound) and the selection of the peritectic solidification as the Al composition increases. On the other hand, there are few studies on the solidification process of Ti-based alloys and therefore little knowledge about it. This is partly because it is a reactive metal and partly due to the limited methods of laboratory-level casting experiments.

In recent years, the development of observational techniques that allow direct understanding of the solidification process have become popular. One of them is time-resolved and in-situ observation of solidification by X-ray imaging using synchrotron radiation. This observation method was established at SPring-8 (Hyogo, Japan), a third-generation synchrotron radiation facility, as a result of the availability of an experimental environment that allows the use of monochromatic light in the high-brightness, high-parallelism and hard X-ray region. It started with the observation of low-melting-point alloys such as Al, Sn, and Zn alloys, and now it is possible to observe a wide range of alloys with high melting points such as Fe-based alloys. For example, it is found that the peritectic solidification, which has been considered to be the conventional is not selected in Fe–C alloys, which increases the significance of in-situ observation of solidification from both academic and industrial perspectives.

Time-resolved and in-situ observation by X-ray imaging requires the sample to be held in a liquid film, such as in steel sample, where single crystal Al\(_2\)O\(_3\) is used as a holding container. However, because Ti-based alloys are reactive metals, single crystal Al\(_2\)O\(_3\) cannot be used and because of this technical challenge, there are still no examples of observations in Ti-based alloys. Therefore, time-resolved and in-situ observation of solidification in Ti-based alloys is expected to lead to an empirical understanding of the solidification process and a new guideline for solidification structure control.

In this study, we report an attempt to establish a technique for time-resolved and in-situ observation of solidification in Ti-based alloys by X-ray imaging.

### 2. Experiments

#### 2.1. Sample

Ti-33.3mass%Al-4.8mass%Nb-2.55mass%Cr (Ti-48at%Al-2at%Nb-2at%Cr) alloy was used for the observations. According to the Ti–Al binary phase diagram generated by Thermo-Calc (Fig. 1), the sample used in this study starts solidification at the primary \( \beta \) phase (BCC) in equilibrium solidification, and then the peritectic reaction takes place to form the \( \alpha \) phase (HCP). The solidification is then completed in the \( \alpha \) phase, and after the solidification is complete, the \( \gamma \) phase (TiAl intermetallic compound) is formed by solid state phase transformation. In the vicinity of 33mass%Al, the \( \beta \), \( \alpha \), and \( \gamma \) phases are present, and the stability of each phase is in close proximity near the liquidus temperature. The solidification process is relatively complex, including solid state phase transformation from \( \beta \) phase to \( \alpha \) phase and the presence of multiple peritectic solidification. Therefore, the solidification process is not empirically clear.

![Composition of Ti–Al–Nb–Cr alloys used for time-resolved and in-situ observations on the Ti–Al binary phase diagram generated by Thermo-Calc.](image1)

![Setup of time-resolved and in-situ observations using synchrotron radiation X-rays.](image2)
as it involves various possibilities for phase selection and microstructure formation during the solidification process.

2.2. Setup of Experimental

Time-resolved and in-situ observations were performed at an imaging beamline BL20XU in SPring-8. A schematic diagram of the experimental apparatus \(^\text{14}\) is shown in Fig. 2. Monochromatized X-rays were injected from upstream (left side in the figure), which were monochromatized by a monochromator. From upstream, a slit was installed to shape the beam shape, an absorber to adjust the intensity of incident X-rays to the sample, an ion chamber to measure the X-ray intensity or photon flux, a graphite heater in the vacuum chamber, a sample in the furnace, and a beam monitor to observe the transmission image. A flat panel was also installed at a position where diffracted X-rays could be observed with respect to the incident X-rays. The X-ray energy was set to 16 keV. The pixel size of beam monitor for transmission images was 6.5 \(\mu\text{m} \times 6.5 \mu\text{m} \) for the wide view observation and 0.5 \(\mu\text{m} \times 0.5 \mu\text{m} \) for the high spatial resolution observation, respectively. Typical frame rates were 1 fps. The pixel size of flat panel for X-ray diffraction was 100 \(\mu\text{m} \times 100 \mu\text{m} \). It should be noted that the X-ray of 48 keV was contained in the incident X-ray beam and could cause X-ray diffraction spots on the flat panel for X-ray diffraction. In the X-ray diffraction setup used in the present study, X-ray diffraction spots caused by 48 keV could be observed. In addition, diffraction angle resolution was relatively large because the beam size was approximately 10 mm \(\times\) 10 mm for the transmission imaging. Thus, X-ray diffraction images were used to detect phase transformation.

For time-resolved and in-situ observations, the samples were heated and cooled using a graphite heater under vacuum (< 10 Pa) that was shaped to produce little or no thermal gradient (below 2 K/m) in the samples. Therefore, it could be assumed that the temperature was uniform across the observed area of the transmission image. The holder for holding the sample was of the same shape as in previous observations. \(^\text{14}\)

2.3. Sample Holding Container

Single crystal MgO was used as the holding container for the samples. A sample with approximately 10 mm in width and in height and 0.2 mm in thickness and a single crystal MgO plate of 0.15 mm in thickness were inserted between single crystal MgO plates of 150 \(\mu\text{m} \) in thickness. The MgO plate was used as a spacer plate to keep the sample thickness.

There are other oxides with lower standard formation Gibbs energy than TiO\(_2\) such as CaO. We used single crystal MgO for this observation because of its use in previous time-resolved and in-situ observations. \(^\text{10}\) Although it is difficult to completely suppress the reaction with the sample, we achieved both reaction suppression and shape retention by using single crystal MgO.

3. Results and Discussion

3.1. Radiography

Figure 3 shows transmission images (left) and diffraction images (right) of the solidification process when the sample was cooled at 0.83 K/s, taken at one image per second. The setup for the wide view observation was used. The observation area of the transmission image was about 2 mm \(\times\) 4 mm. The starting time for taking transmission and diffraction images was set to 0 s. At the beginning of the imaging (0 s), the entire sample was superheated to 10 K above the liquidus temperature, and the entire observation area was in the liquid phase. No diffraction points from the liquid phase were observed in the diffraction images. Cooling was started from 10 s after the start of shooting. Subsequently, at 24 s, when the temperature dropped by about 11 K, solidification in the equiaxed crystal began from the lower right of the observation area. The probability that a grain satisfies the Bragg condition is low because of the low divergence of

\[\text{Fig. 3. Transmission images (left) and diffraction images (right) during cooling at 0.83 K/s from the melt in Ti-33.3Al-4.8Nb-2.55Cr. Light region corresponded to solidification shrinkage. The observation area of the transmission images was about 2 mm \(\times\) 4 mm. The pixel size of the transmission images was 6.45 \(\mu\text{m} \times 6.45 \mu\text{m} \). The time resolution of taking transmission and diffraction images was 1 fps. X-ray energy was 16 keV.}\]
less than $10^{-4}$ rad and the X-ray energy resolution ($\Delta E/E$) of $10^{-4}$ at the beamline. Thus, there was no change in the diffraction image. The solidification progressed from the bottom to the top of the observation area, as shown in 27 s and 33 s. After 40 s, the entire observation area was covered with equiaxed crystals. At 40 s, a single diffraction point was observed in the lower left corner of the diffraction image. The solidification rate calculated from the migration of the equiaxed crystal region was about 0.2 mm/s.

Then, solidification was almost complete at 250 s with a drop of about 175 K. The light region in the transmission image was the area where the sample became thinner due to solidification shrinkage and the intensity of X-ray transmission increases. In the present observation, solidification was completed without any peritectic reaction observed during the solidification process. There was no change in the diffraction point between 40 s and 250 s, which indicated that no peritectic reaction took place in the diffraction images.

The transmission and diffraction images changed between 250 s and 317 s when solidification was completed. For example, the black region indicated by the arrows in the 250 s transmission image (the region where the transmitted X-ray intensity was reduced due to diffraction of a part of the incident X-rays satisfying Bragg’s condition) was not observed in the 317 s transmission image. Changes in the black area indicated that the crystal structure has changed due to phase transformation or that there has been strain in the sample. In addition, both the number and position of diffraction points in the diffraction images changed, indicating a change in the crystal structure. Not a few diffraction spots in Fig. 3 indicates that fine grains were formed. Therefore, it meant that solid state phase transformation took place in 67 s. The migration velocity of the solid/solid interface was about 0.1 mm/s, measured from the change in the black area in the transmission image.

In this study, we succeeded in time-resolved and in-situ observation of the solidification process and the solid state phase transformation in Ti-33.3mass%Al-4.8mass%Nb-2.5mass%Cr alloy by X-ray imaging. As a result, unlike the Ti-Al binary phase diagram, no peritectic solidification was observed and solidification paths other than peritectic solidification were selected. In the present study, no peritectic solidification was observed in all four experiments performed at varying superheat levels between 5 K and 20 K, and the solid state phase transformation was always selected.

### 3.2. Selection of $\alpha$ Phase in Primary Phase

Transmission image during cooling at 0.83 K/s from the melt is shown in Fig. 4. Superheat was set at 15 K. The setup for the high spatial resolution observation was used and the observation area was 1 mm $\times$ 1 mm. Cooling began 10 s after the start of imaging and showed the solidification process at 30 s as an example. Focusing on the equiaxed crystals shown by arrows, a dendrite with six secondary arms (six times symmetry) was observed.

As shown in the Ti-Al binary phase diagram in Fig. 1, the three phases, $\beta$, $\alpha$, and $\gamma$, are in close proximity to each other near the liquidus temperature, and the stable phase is similar. Here, there are two possible reasons for the observation of six times symmetry dendrites: the $\alpha$ phase, which is an HCP structure, was selected, and the $<100>$ directional primary arm of the $\beta$ phase, which is a BCC structure, was observed from the $<111>$ direction.

In this observation, it was likely that a reaction between the sample and MgO took place during the heating and cooling process, and that O was solubilized in the sample. O is an $\alpha$ stabilizing element and has a significant effect on the phase equilibrium of TiAl alloys. Therefore, electron probe microanalysis (EPMA) of O on the post-experimental samples showed that the O composition was about 3 mass% on average.

The Ti–Al–O pseudo-binary phase diagram with O composition fixed at 3 mass% generated by Thermo-Calc is shown in Fig. 5. At a composition of 33.3 mass% Al, the primary phase in equilibrium solidification becomes the $\alpha$ phase, and the $\gamma$ phase is formed by the peritectic reaction during the $\alpha$ solidification process. In the present observation, the six times symmetry of dendrites could be explained by the selection of the $\alpha$ phase at the primary phase due to the solid solution of O in the molten Ti. And the solid state phase transformation observed after solidification was the transformation from $\alpha$ phase to $\gamma$ phase. It has also been reported that in TiAl alloys with a composition where the primary phase is the $\alpha$ phase, the solidification takes place in the equiaxed crystal, which is consistent with the present equiaxed solidification.

### 3.3. Mechanism of $\alpha$-$\gamma$ Transformation

The temperature at which the $\alpha$-$\gamma$ transformation took place (nucleation temperature of the $\gamma$ phase) is plotted on the Ti–Al–O pseudo-binary phase diagram, as shown in Fig. 6. This temperature indicated the temperature at which the $\alpha$-$\gamma$ transformation started. In each of the four experiments, the $\alpha$-$\gamma$ transformation took place in the range of about

![Fig. 4. Transmission image during cooling at 0.83 K/s from the melt in Ti-33.3Al-4.8Nb-2.55Cr. The observation area of the transmission images was about 1 mm $\times$ 1 mm. The pixel size of the transmission images was 0.5 $\mu$m $\times$ 0.5 $\mu$m. The time resolution of taking transmission and diffraction images was 1 fps. X-ray energy was 16 keV.](image)
place even below peritectic temperature, and solidification proceeded in the \( \alpha \) phase along the line extending the temperatures of the liquidus and solidus temperatures shown by the dashed line in Fig. 6. Subsequently, with undercooling from the peritectic temperature, the driving force for nucleation of the \( \gamma \) phase in the \( \alpha \) phase and the liquid phase increased, and the \( \alpha-\gamma \) transformation took place at about 1 520 K. Because of the nucleation of the \( \gamma \) phase between the extended liquidus and solidus temperatures, the liquid phase should exist at the \( \alpha-\gamma \) transformation from the viewpoint of the phase diagram, but no liquid phase was observed in the transmission image. Even if a liquid film existed between the sample and MgO, the solid fraction should be nearly unity. There may have been problems with the accuracy of the phase diagram, but the reason for this was not clear at this time.

The result that peritectic solidification was not selected in the solidification process indicated that the interface between the liquid and the \( \alpha \) phase did not function as a nucleation site for the \( \gamma \) phase. Thus, the difficulty of nucleation of the \( \gamma \) phase has led to the selection of solid state phase transformation instead of the peritectic solidification.

### 3.4. Characteristics of \( \alpha-\gamma \) Transformation

As shown in Fig. 6, the \( \alpha \) phase was undercooled from the \( T_0 \) temperature to about 150 K, and nucleation of the \( \gamma \) phase took place in the two-phase region of the \( \alpha \) and \( \gamma \) phases, so thermodynamically, part of the \( \gamma \) phase was allowed to grow at the interface between the \( \alpha \) and \( \gamma \) phases with no solute partition of the \( \gamma \) phase. As described in 3.1, the growth rate of the \( \gamma \) phase was about 0.1 mm/s. If solute partition took place at the \( \alpha/\gamma \) interface, a thickness of diffusion layer that could be estimated in 2D/V formed ahead of the \( \alpha/\gamma \) interface. \( D \) is the diffusion coefficient in the \( \alpha \) phase and \( V \) is the growth rate of \( \gamma \) phase. If the diffusion coefficient of Al in the \( \alpha \) phase at 1 500 K was \( 5 \times 10^{-16} \) m\(^2\)/s\(^2\)\(^{-1}\) and the growth rate of \( \gamma \) phase was \( 10^{-4} \) m/s, the diffusion layer thickness could be estimated to be as short as \( 10^{-11} \) m. This was well below the lattice constant of the \( \alpha \) phase,\(^{24}\) which meant that the diffusion layer was not formed. This suggested that Al was not partitioned at the \( \alpha/\gamma \) interface. Therefore, kinetically, there was no solute partition in this \( \alpha-\gamma \) transformation. A similar argument can be made for Nb and Cr. The small thickness suggested that the \( \alpha-\gamma \) transformation followed negligible – partition local equilibrium (NP-LE) mode.\(^{25-27}\)

As shown in Fig. 3, few diffraction spots were observed during solidification in the \( \alpha \) phase, while many diffraction spots were observed during the \( \alpha-\gamma \) transformation. Since we used a monochromatized X-rays with high coherency in this observation, the probability of diffraction of incident X-rays satisfying Bragg’s condition was low. Therefore, the diffraction spots indicated the formation of multiple fine \( \gamma \) grains within a single \( \alpha \) grain. In other words, the \( \alpha-\gamma \) transformation was characterized by repeated nucleation and growth of the \( \gamma \) phase near the \( \alpha/\gamma \) interface (crystallographic discontinuity of the \( \gamma \) phase growth).

A solid state phase transformation, which proceeds with repeated nucleation and growth, is consistent with a massive-like transformation from undercooled \( \delta \) phase (BCC) to \( \gamma \) phase (FCC), which has been reported for peritectic
Fe-C\textsuperscript{16,17} and Fe-Cr-Ni\textsuperscript{19} alloys. The massive-like transformation has the following characteristics.

1. Difficulty in nucleation of the $\gamma$ phase causes the massive-like transformation.

2. It is the transformation of the solid state from the $\delta$ phase to the $\gamma$ phase.

3. Nucleation and growth of the $\gamma$ phase is repeated near the $\delta\gamma$ interface.

4. Fine $\gamma$ grains form in a single $\delta$ grain.

5. The closed-packed plane (111) of the $\gamma$ phase is likely to adjoin the close-packed plane (110) of the $\delta$ phase.

6. After the $\delta\gamma$ transformation, the $\gamma$ phase coarsens rapidly.

7. Partitioning of substitutional elements at the $\delta\gamma$ interface is difficult, while kinetics allows for the partition of interstitial elements.

Whether the $\alpha$$\gamma$ transformation has the characteristics of (5) and (6) cannot be concluded from the present observations. Further study on the crystallographic orientation is required to understand whether the $\alpha$$\gamma$ transformation has the characteristics of (5) and (6).

It has been reported that the massive-like transformation is a common transformation in a wide range of Fe-based alloys\textsuperscript{19} and dendrite fragmentation is induced by the massive-like transformation.\textsuperscript{20} In addition, the massive-like transformation can be selected from the surface to the center in the continuous casting of Fe-based alloys.\textsuperscript{21} Therefore, mechanism of the massive-like transformation is an interesting phenomenon. The isotropic transformation from $\alpha$ phase to $\gamma$ phase in Ti-based alloys and the isotropic transformation from $\delta$ phase to $\gamma$ phase in Fe-based alloys are essentially the same cannot be concluded from the present observations. However, this observation suggested that the mechanism for selecting the solid state phase transformation, in which nucleation and growth were repeated, rather than the peritectic solidification, was a common solidification/transformation path for both steel and nonferrous materials. Therefore, this observation will be useful to understand the solidification process and the peritectic solidification in peritectic alloy systems.

### 3.5. Constitutional Undercooling Ahead of the Solidification Interface

In this observation, the $\alpha$ phase solidified in the equiaxed crystal. The presence of $\alpha$ nucleation sites in the sample and the driving force for $\alpha$ nucleation was relatively low. While it was difficult to identify nucleation from the spatial resolution of the transmission images, the driving force for $\alpha$ nucleation could be examined from the constitutional undercooling ahead of the solidification (liquid/$\alpha$) interface.

According to the Ti–Al–O ternary isothermal cross section at 1 700 K, generated by Thermo-Calc, the partition coefficient of Al at the solidification interface for 33.3 mass% Al was about 0.76. In this observation, we could assume that a local equilibrium was established at the solidification interface, and therefore Al was preferentially partitioned from the $\alpha$ phase to the liquid phase at the solidification interface.

In such binary alloy systems, a solute profile is formed ahead of the solidification interface under the steady state solidification. To be precise, we should consider solidifica-

![Fig. 7. Solute profiles of Al near the planar solidification interface.](image)

<table>
<thead>
<tr>
<th>$C_0$ (mass%)</th>
<th>$k$</th>
<th>$V$ (m/s)</th>
<th>$D$ (m$^2$/s)</th>
</tr>
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<td>33.3</td>
<td>0.76</td>
<td>$2 \times 10^{-4}$</td>
<td>$10^{-9}$</td>
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</tbody>
</table>

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4. Summary

Time-resolved and in-situ observations were performed to observe solidification process of the reactive metal TiAl alloys.

(1) Time-resolved and in-situ observations of the solidification process in TiAl alloy were successfully achieved by selecting single crystal MgO as the sample holding container, and the target of time-resolved X-ray imaging was extended to the reactive metal.

(2) The αphase was selected as the primary phase in the solidification due to the α-stabilizing element, O. The α phase was solidified in the equiaxed crystal (the equiaxed grain structure).

(3) The interface between the liquid and the α phase was not an effective nucleation site for the γ phase, and the peritectic solidification was not selected.

(4) The α phase was undercooled at about 100 K below the peritectic temperature, and the γ phase was formed by the solid state phase transformation.

(5) At the αγinterface, solute elements were not partitioned thermodynamically and kinetically, and the αγ transformation proceeded with repeated nucleation and growth of the γ phase, which is similar with the massive-like transformation selected for Fe–C and Fe–Cr–Ni alloys. The solid state phase transformation with repeated nucleation and growth will be a common solidification/transition process in peritectic alloy systems.

(6) The formation of the equiaxed α grains showed that the supersaturation required for nucleation and growth of the α phase was relatively small.

Acknowledgements

Time-resolved and in-situ observations using synchrotron radiation X-rays is the result of a general proposal (2019A1654 and 2019B1687) from Japan Synchrotron Radiation Research Institute (JASRI/SPRING-8). The time-resolved and in-situ observations were performed using an apparatus developed by a Grant-in-Aid for Scientific Research (S) (No. 17H06155).

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