Isothermal Transformation in Fe–N Hypereutectoid Alloy

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In order to understand the mechanism of isothermal transformation of Fe–N alloy, the isothermal transformation microstructure that forms in a wide temperature range below $Ae_1$ was investigated in Fe–2.6 mass%N hypereutectoid alloy by means of the electron back scatter diffraction method in addition to the conventional microstructural observation methods. High-nitrogen austenite fully decomposed to ferrite and Fe$_4$N over the entire temperature range, and the time-temperature-transformation ($TTT$) diagram had a C shape with a nose temperature around 700 K. The hardness linearly increased with decreasing transformation temperature because the microstructure became finer, but the morphology of the (ferrite + Fe$_4$N) structure changed discontinuously at around 800 K. From the microstructural and crystallographic analyses, it was concluded that the microstructure formed at higher temperature is a lamellar eutectoid structure, braunite, while the other is an upper bainitic structure containing bainitic ferrite formed through a displacive mechanism and Fe$_4$N formed by concentration and ordering of the nitrogen. Since Fe$_4$N is a counterpart of the cementite in Fe–C alloy, the respective structures are similar to pearlite and upper bainite in carbon steel.

KEY WORDS: Fe–N alloy; high-nitrogen; austenite decomposition; isothermal transformation.

1. Introduction

When steel is subjected to nitriding at around 900 K (above $Ae_1$) in a NH$_3$-containing gas, the ferrite phase transforms into an austenite phase by absorbing a significant amount of nitrogen atoms into the solid solution (high-nitrogen $\gamma$). Since the high-nitrogen $\gamma$ has quench hardenability, such a high-temperature gas nitriding process has recently been used as an effective surface hardening technique that is applicable to not only alloy steels containing nitride-forming elements but also plain carbon steels (e.g., N-QUENCH). The effect of nitrogen on the martensitic transformation and the steel’s mechanical properties has been investigated in various nitrogen-bearing martensitic steels. The martensite of nitrogen steels was found to have much in common with that of carbon steels in terms of lattice distortion, $M_s$ temperature, and dislocation density under the same carbon/nitrogen content, although there is a slight difference in the hardness of the as-quenched martensite.1–3) However, the diffusional transformation of high-nitrogen $\gamma$ is less well studied than the martensitic transformation. In 1950, Bose et al. investigated the decomposition behavior of austenite in an Fe–2.35%N binary eutectoid alloy and reported a time-temperature-transformation ($TTT$) curve with a C shape similar to that of a Fe–C binary alloy.4) However, the microstructural features were not sufficiently understood then. After that, several studies focusing on the low-temperature transformation in high-nitrogen $\gamma$ were conducted.5–10) This is because the hardness obtained after the low-temperature transformation was remarkably high, and this transformation could be expected to lead to a new surface-hardening technique.10) J. Focq et al. reported that the austenitic Fe–N alloy decomposes into a fine dual-phase structure composed of ferrite ($\alpha$) and Fe$_4$N ($\gamma'$) at 483 K. They explained the phase transformation sequence as a two-step process involving destabilization of the high-nitrogen $\gamma$ by a diffusional process leading to $\gamma'$ precipitation and depleted $\gamma$, followed by a shear transformation from the depleted $\gamma$ to supersaturated $\alpha$ or martensite accompanied by further $\gamma'$ precipitation.11) On the contrary, Aaronson et al. proposed that the formation of $\alpha$ occurs through a purely diffusional process.7) At present, no consensus seems to have been built regarding the phase transformation mechanism of high-nitrogen $\gamma$ at either low or high temperature because of the lack of a systematic investigation. In this study, the phase transformation behavior of high-nitrogen $\gamma$ during isothermal heat treatment was reinvestigated by means of the electron back scatter diffraction (EBSD) method, in addition to the conventional microstructural observation methods. The transformation mechanism is discussed from the viewpoint of the crystallographic characteristics of the transformation microstructure.
2. Experimental Procedure

The specimens of Fe–N binary alloy were produced by gas nitriding a commercial iron foil with a thickness of 100 μm. The gas nitriding was carried out at 923 K for 58 ks in a gas mixture of N₂–11%NH₃, after which the specimens were water-cooled. The nitrogen content measured after the nitriding was 2.6 mass% (9.62 at%), as determined by the thermal conductivity technique. No segregation or precipitation was found in the specimen. Since the high nitrogen content decreases the \( M_s \) temperature to less than ambient temperature, the nitride specimens exhibit a stable austenitic single-phase structure. The specimens with austenitic structure were subjected to isothermal heat treatment at 843 to 473 K for different periods in a salt-bath furnace, followed by water cooling. The phase transformation caused by the heat treatment was examined at ambient temperature by X-ray diffraction (XRD). The hardness was evaluated by micro hardness testing machine (0.49 N for 10 s). The microstructure was observed with scanning and transmission electron microscopes (SEM and TEM). The crystallographic orientation of each phase was identified by means of the EBSD method using the SEM. The data obtained from EBSD were analyzed with the OIM™ system, and then the analyzed data with confidential index (CI) values over 0.1 were used. The nitrogen distribution in the microstructure was evaluated using an electron probe micro analyzer (EPMA).

3. Results and Discussion

3.1. \( TTT \) Diagram and Transformation Temperature Dependence of Microstructure and Hardness

Figure 1 shows an XRD profile illustrating the phase transformation during isothermal holding. The changes in the diffraction peaks reveal that the original \( \gamma \) structure gradually decomposes to \( (\alpha + \gamma') \), while the diffraction angle of the \( \gamma \) is unchanged in all temperature ranges. This result demonstrates that the phase transformation \( \gamma \rightarrow (\alpha + \gamma') \) occurs over the whole temperature range below the \( A_{e1} \) temperature (863 K) in the Fe–N system and that the lattice parameter of the untransformed \( \gamma \) is macroscopically constant during the transformation. After further XRD analysis, the \( TTT \) diagram of Fe–2.6%N alloy was created, as drawn in Fig. 2. Especially, we distinguished the start and finish of the austenite decomposition by SEM observation. It is understood that the Fe–N binary alloy has a C-shaped \( TTT \) curve with a short incubation period similar to that of the Fe–C eutectoid steel. However, the nose temperature, around 700 K, is much lower than that in the eutectoid carbon steel (around 823 K) because of the lower \( A_{e1} \) temperature in the Fe–N system. Such features agree well with the result obtained by Bose et al.4

Figure 3 shows the relation between the transformation temperature and hardness of the produced \( (\alpha + \gamma') \) structure in the Fe–2.6%N alloy. The hardness linearly increases with decreasing transformation temperature within a wide range from 2.2 to 8.5 GPa. Figure 4 presents SEM images showing the \( (\alpha + \gamma') \) structures fully transformed at various transformation temperatures. The two phases, \( \alpha \) and \( \gamma' \), are clearly distinguished with different shades. The size of the microstructures becomes significantly finer with decreasing temperature, which corresponds to the increase in hardness shown in Fig. 3. It should be noted that the morphology of the dual-phase structure changes discontinuously at around 800 K, corresponding to the self-diffusion limit of iron atoms (between (b) and (c)). The microstructure formed at

![Fig. 1. XRD profile showing austenite decomposition at varied temperatures.](image)

![Fig. 2. \( TTT \) diagram of Fe–2.6%N alloy.](image)

![Fig. 3. Relation between the transformation temperature and hardness of the produced \( (\alpha + \gamma') \) structure in the Fe–2.6%N alloy.](image)
higher temperature is characterized by lamellar alignment, like the pearlite in carbon steel (a, b). Such a microstructure in Fe–N alloy is called “braunite,” after the name of its discoverer.\textsuperscript{12–14} The other microstructure, formed at lower temperature, exhibits an acicular structure with straight $\alpha$-$\gamma'$ interfaces (c, d, e). The details of the distinction between these microstructures will be discussed in the following paragraphs considering the transformation mechanism.

3.2. Microstructural Features of Lamellar ($\alpha + \gamma'$)

Figure 5 shows magnified SEM (a, b) and TEM (c, d) images illustrating the braunite structure formed at a transformation temperature of 843 K. Proeutectoid $\gamma'$ preferentially forms along the $\gamma$ grain boundary, as indicated by the arrows (a), while the lamellar braunite forms at the proeutectoid $\gamma'$ and grows into the interior of the $\gamma$ grain (b). Although the $\gamma$ is decomposed into $\alpha$ and $\gamma'$ in the braunite, the untransformed region still retains $\gamma$ structure. TEM observation of the braunite reveals that the dislocation density in the $\alpha$ phase is quite low and that the morphology of $\gamma'$ (shown in the dark-field image) is not a straight plate but a wavy one with an interlamellar spacing of approximately 100 nm (c, d). In addition, the $\alpha$ and $\gamma'$ phases seem to have almost the same volume fraction in the braunite, which is reasonable in accordance with the equilibrium phase diagram. The selected area electron diffraction (SAED) pattern (d) indicates that the Kurdjumov-Sachs (K-S) relationship \textit{((111)\gamma'//(011)\alpha, \quad [-101]\gamma'//[-1-11]\alpha)} holds between both
Fig. 6. Orientation imaging map of Fe–2.6%N alloy transformed at 843 K for 3.6 ks (CI > 0.1). (a) Image quality map, (b) Inverse pole figure map of fcc + bcc, (c) Inverse pole figure map of fcc, (d) Inverse pole figure map of bcc.

Fig. 7. (a) Composition image and (b) EPMA map for nitrogen of specimen partially-transformed at 843 K for 3.6 ks.

Fig. 9. Orientation imaging map of Fe–2.6%N alloy transformed at 723 K for 70 s (CI > 0.1). (a) Image quality map, (b) Inverse pole figure map of fcc + bcc, (c) Inverse pole figure map of fcc, (d) Inverse pole figure map of bcc.
phases. An EBSD orientation imaging map of the specimen partially transformed at 843 K is shown in Fig. 6. Both the $\gamma'$ phase and untransformed $\gamma$ phase are identified in the same fcc phase in the inverse pole figure maps (b, c), but it is easy to distinguish between them in the image quality map (a). Point A indicates that the proeutectoid $\gamma'$ grains formed along the $\gamma$ grain boundary have the same orientation as the adjacent $\gamma$ grain. In addition, point B reveals that the orientation of the proeutectoid $\gamma'$ grain extends out into the directly connected lamellar $\gamma'$ in braunite. These results demonstrate that each nucleus of proeutectoid $\gamma'$ should have a similar orientation relationship, with the adjacent high nitrogen content. Eventually, the lamellar $\gamma'$ grows even further, accompanied by $\alpha$ precipitation and migration of incoherent braunite-$\gamma'$ boundary in a preferred direction. Figure 7 shows an EPMA map illustrating the nitrogen distribution in the partially transformed specimen. The probe diameter is not narrow enough to distinguish between the fine lamellar $\alpha$ and $\gamma'$ in the braunite, but the proeutectoid $\gamma'$ with high nitrogen content is clearly apparent along the $\gamma$ grain boundaries. In order to understand the mechanism of braunite transformation, it is important to know the long-range nitrogen concentration profile from untransformed $\gamma$ to the growing braunite structure. Figure 7 clarifies that the nitrogen concentration of untransformed $\gamma$ is nearly the same as the average nitrogen concentration of braunite, and, besides, no depleted zone is observed in the vicinity of the braunite-$\gamma$ interface. This suggests that the braunite-$\gamma$ interface should migrate without long-range diffusion of nitrogen, resulting in the constant lattice parameter of the untransformed $\gamma$ (see Fig. 1). From these results, it is concluded that braunite has a lamellar eutectoid structure that is similar in many respects to that of the pearlite in Fe-C alloys. It was also confirmed previously that braunite has hierarchical substructures, such as block and colony structures, similar to those typically found in pearlite.\(^{16,17}\)

3.3. Microstructural Features of Acicular ($\alpha + \gamma'$)

Figure 8 presents SEM (a, b) and TEM (c, d) images illustrating the acicular ($\alpha + \gamma'$) structure formed at a transformation temperature of 673 K. The SEM images show that the $\gamma'$ had completely transformed to a fine acicular structure. In this structure, the prior $\gamma$ grain boundaries clearly remain, as indicated by the arrow, and seem to affect the arrangement of the acicular structure. The acicular structures located close to the prior $\gamma$ grain boundary tend to be arranged in the same direction (a), while the ones formed in the interior of the prior $\gamma$ grain grow in various directions. These microstructural features are in good agreement with the ($\alpha + \gamma'$) structure formed at 498 K.\(^{19}\) TEM images and the SAED pattern (c, d) reveal that the former acicular structures are composed of fine parallel $\alpha$ laths with $\gamma'$ entrapped between them and that each phase has an identical crystal orientation following the K-S relationship. In addition, the $\alpha$ laths contain high-density dislocations (d), which strongly suggests that they were formed through a displacive mechanism. It is therefore evident that the acicular ($\alpha + \gamma'$) structure is morphologically identical to the classic bainite formed in conventional Fe-C systems, where the $\gamma'$ is the counterpart of the cementite in the classic upper bainite or of the retained $\gamma$ in carbide-free bainite.\(^{18}\) Figure 9 presents an EBSD orientation imaging map showing the specimen partially transformed at 723 K. In this map, the prior $\gamma$ grain boundary is drawn as white line. A bainitic ($\alpha + \gamma'$) structure forms preferentially at the prior $\gamma$ grain boundary and grows into the interior of the $\gamma$ grain. Although $\alpha$ laths have some variants against untransformed $\gamma$ matrix, i.e., 24 K-S variants, the ones formed at the prior $\gamma$ grain boundary tend to have an identical variant, as indicated by the arrows in (d). This implies that the orientation of an $\alpha$ lath is strongly affected by the nucleation site, which results in an arrangement of acicular structures (see Fig. 8) similar to that in upper bainite.\(^{19}\) On the other hand, the map for the fcc phase (c) reveals that the orientations of the $\gamma'$ in the bainitic ($\alpha + \gamma'$) structures (A) are identical and the same as that of untrans-

![Fig. 8. SEM and TEM images showing acicular ($\alpha + \gamma'$) transformed at 623 K for 600 s.](image-url)
formed $\gamma'$ (B) in a whole $\gamma$ grain. This suggests that the $\gamma'$ entrapped between $\alpha$ laths is formed from $\gamma$ without changes in not only crystal structure but also crystal orientation. From these experimental results, the mechanism of the bainitic ($\alpha + \gamma'$) structure formation should be concluded to be as follows. The bainitic ($\alpha + \gamma'$) structure evolves in distinct stages, beginning with the nucleation of an $\alpha$ lath via a displacive mechanism. Since the $\alpha$ lath is at first substantially supersaturated with nitrogen, the excess nitrogen should be soon afterward ejected into the adjacent $\gamma$ entrapped between the $\alpha$ laths. Eventually, the $\gamma$ should transform into $\gamma'$ through the concentration and ordering of the nitrogen. Thus, the formation of an acicular ($\alpha + \gamma'$) structure is similar to the upper bainite transformation in Fe–C alloys.

However, the driving force for the nucleation of the bainitic $\alpha$ lath remains unclear. An Fe–N binary phase diagram calculated by Thermo-Calc (SBIN2 database) is shown in Fig. 10. In addition, the $T_0$ curve and extrapolated $\alpha$-$\gamma'$ and $\gamma$-$\gamma'$ solvs are drawn in this diagram. Since Bhadeshia calculated the driving force necessary for bainite formation to be 400 J/mol,20) the nitrogen content of $\gamma$ must lie to the left of the $T_0$ curve, where the Gibbs energy of $\alpha$ is lower than that of $\gamma$ by 400 J/mol, in order to form the bainitic $\alpha$ lath. TEM observations made by J. Foct et al. and D. Jiao et al. have proven that $\gamma'$ precipitates first within the $\gamma$ matrix, after which the bainitic ($\alpha + \gamma'$) structure forms during low-temperature aging at around 500 K.20) although this structure could not be detected by XRD.10) Supposing that $\gamma'$ precipitates within the $\gamma$ matrix as a first reaction, in principle the bainitic $\alpha$ lath would be able to nucleate at a low temperature below approximately 600 K, because the extrapolated $\gamma$-$\gamma'$ solvs is located to the left side of the $T_0$ curve (case A). However, the extrapolated $\gamma$-$\gamma'$ solvs is on the right of both the $T_0$ and $T_0'$ curves above 650 K, which means that the bainitic transformation does not occur even if the $\gamma'$ precipitation is taken into account in this temperature range. The precipitation of other nitrides, such as $\varepsilon$-Fe$_4$N, and the inhomogeneous distribution of nitrogen may be speculated to cause the transformation of nitrogen-depleted $\gamma$, as is the case in the formation of bainite in steel.21,22) However, the leading phase and/or phenomenon leading to the formation of the bainitic ($\alpha + \gamma'$) structure is still controversial in high-nitrogen $\gamma$.

4. Conclusions

The isothermal microstructure transformation in the temperature range from 843 to 473 K was investigated in an Fe–2.6 mass%N hypereutectoid alloy by means of the EBSD method in addition to the conventional microstructural observation methods. The results obtained are summarized as follows:

(1) High-nitrogen austenite fully decomposes into ferrite and Fe$_4$N over the entire temperature range, and the $T_0T$ diagram has a C shape with a nose temperature of around 700 K. The hardness linearly increases with decreasing transformation temperature because the (ferrite + Fe$_4$N) structure becomes finer, but the morphology of the dual-phase structure changes discontinuously at around 800 K, corresponding to the self-diffusion limit of iron atoms.

(2) The microstructure formed at higher temperature is a lamellar eutectoid structure consisting of ferrite and Fe$_4$N with a low dislocation density, namely, braunite. The braunite forms at a proeutectoid Fe$_4$N grain and grows into the interior of the austenite grain, with migration of the incoherent braunite/$\gamma'$ boundary in a preferred direction. The braunite/$\gamma'$ interface migrates without long-range diffusion of nitrogen, resulting in the constant nitrogen content of untransformed $\gamma$.

(3) The microstructure formed at lower temperature is an upper bainitic structure that is composed of fine parallel ferrite laths with high dislocation density and Fe$_4$N entrapped between them. Since the crystal orientation of Fe$_4$N in the upper bainitic structure is the same as that of untransformed austenite, the Fe$_4$N may transform from $\gamma$ entrapped between the ferrite laths through the concentration and ordering of nitrogen.

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