A Study of Spinodal Decomposition in Fe–Ni–Al Alloys by Mössbauer Effect*

By Makoto Saito**, Hiromitsu Ino*** and Yoshio Sumitomo****

Using the Mössbauer effect of $^{57}$Fe, the process of phase separation in Fe–Ni–Al alloys was studied with an attempt to clarify whether the separation is made by the spinodal decomposition or the nucleation and growth type decomposition. Two compositions, Fe$_{1/2}$(NiAl)$_{1/2}$ and Fe$_{1/3}$(NiAl)$_{2/3}$, were chosen. The specimens were aged for various periods of time at constant temperatures after quenching from the one-phase region, and the Mössbauer spectra were taken. The hyperfine field of $^{57}$Fe in the Fe-rich phase gradually increased with the aging time until the final value was attained, while the isomer shift of $^{57}$Fe in the paramagnetic NiAl-rich phase shifted gradually to that of $^{57}$Fe surrounded by eight Al atoms. Spreading of the width of each ferromagnetic absorption peak indicated that the Fe-rich phase had no definite composition but a wide composition distribution. These results directly showed that the Fe–Ni–Al alloy system was decomposed by the spinodal decomposition mechanism.

(Received July 1, 1974)

I. Introduction

In general, when a supersaturated solid solution is decomposed into two phases on isothermal aging, two types of phase separation mechanism are possible. One, called the nucleation and growth mechanism, requires the formation of nuclei having critical sizes or critical compositions to grow as one phase. In the other, called the spinodal decomposition mechanism, small composition fluctuations spread over a large volume in the parent solid solution and grow continuously into two phases with equilibrium concentrations. In the latter case, the unstable phase changes its composition continuously from that of the initial solid solution to the equilibrium composition on the isothermal aging. Hillert(1) and Cahn(2) derived in the case of spinodal decomposition the spatial composition distribution with a periodic modulated structure with a critical wave length, from considerations of the composition gradient term in the free energy. Cahn’s model has been applied to the cases of various alloy systems(2)–(6). Subsequently, it was concluded that the periodic modulated structures which were observed by electron microscopy and X-ray diffraction arose from the mechanism of spinodal decomposition. However, for example, in an electron microscope study of NiAl alloys, Ardell and Nicholson(7) found that the precipitated particles which were initially distributed at random ultimately took on a ⟨100⟩ periodic structure and that the rate of growth of the particles was proportional to $t^{1/3}$ as expected for the Ostwald growth. Their result suggests that the periodic modulated structure of precipitated particles can occur by a nucleation and growth mechanism as well. Therefore, one must be cautious in deciding whether the phase separation mechanism is made by the spinodal decomposition or not when a periodic structure is only a result of the observation.

In this study, we have tried experimentally to follow the change in composition of each separated phase during aging, and to determine whether or not their compositions change continuously in going from the initial to the final state, which is considered to be the fundamental difference between the two phase separation mechanisms—nucleation and growth and spinodal decomposition. Up to the present time, we had no effective method for observing the change in composition of precipitated particles, although it has been roughly estimated from measurements of the Curie temperature. The Mössbauer effect method which has often been quite useful in the study of atomic arrangements in solids is believed to be very effective to the present problem. Some studies using this method have been recently reported. In the case of Cu–Ni–Fe alloys, the change in composition expected for the spinodal decomposition was not observed(9), although the periodic modulated structure had previously been observed in this alloy. For Fe–Cr alloys, the change in the Mössbauer absorption spectra expected for the spinodal decomposition has been observed but precise aspects of the composition change have not been revealed(9). In the present study, a slight change in composition during the phase separation process in Fe–Ni–Al alloys, and especially a composition change in the initial stages, was observed using the Mössbauer effect.

* This paper was originally published in Japanese in J. Japan Inst. Metals, 37 (1973), 540; Awarded Jeffries Prize at Annual Spring Meeting of the Japan Institute of Metals, Tokyo, in April 2, 1974.

** Graduate School, Osaka University, Toyonaka. Present address: Central Research Laboratory, Kobe Steel Ltd., Kobe 651, Japan.

*** The Institute of Industrial Science, University of Tokyo, Tokyo 106, Japan.

**** Graduate School, Osaka University, Toyonaka. Present address: Ames Laboratory, Iowa State University, Ames, Iowa, U.S.A.

Trans. JIM
II. Experimental

1. The Mössbauer effect

The Mössbauer effect is a resonance absorption phenomenon of the recoil free γ-ray arising from the transition between nuclear energy levels. The interactions between the nucleus and its surrounding and penetrating electrons give rise to isomer shifts, quadrupoles, and the magnetic hyperfine splitting effect in the Mössbauer spectrum. Since these interactions are sensitive to the electronic state and, therefore, atomic configuration around the nucleus of the Mössbauer probe, the Mössbauer effect can be a useful method for observing composition changes in appropriate alloys.

In this study, Mössbauer effect measurements were carried out at room temperature by a multiscaler, constant acceleration method. The 14.4 keV radiation of $^{57}$Fe from the 30 mCi $^{57}$Co source dissolved in metallic copper was detected by a proportional counter. The results of all Mössbauer effect measurements described in the present report were corrected after running a blank.

2. Specimens

(1) Selection of the alloy

It is necessary to select alloys of a type whose composition change accompanying the phase separation process can be measured effectively by the Mössbauer effect. In practice, it is desirable that a slight change in composition will have a large influence upon the internal magnetic field or isomer shift of the Mössbauer nuclei. Alloys in the Fe–Ni–Al ternary system meet the requirement. In fact, Fe–Ni and Fe–Al alloys have already been studied by Mössbauer effect methods, the results of which are available for the present study. According to these studies, the hyperfine field of iron atoms in Fe–Al alloys decreases as the number of aluminum atoms around the iron atom increases, and vanishes when the concentration of aluminum exceeds about 33 at%. The isomer shift of iron atom shifts toward the positive doppler velocity direction as the number of aluminum atoms around the iron increases, because the electron density at the nucleus of $^{57}$Fe decreases for aluminum atoms around the iron atom.

In the case of Fe–Ni alloys, the influence which nickel atoms have upon the hyperfine field of the iron atom turns out to be very small in comparison with that of aluminum atoms. Nickel atoms that are neighbors of iron atoms have little influence upon the isomer shift of the iron, because the electronic condition of the nickel atom is quite similar to that of the iron atom. These aspects of Fe–Al and Fe–Ni alloys are shown in Fig. 1.

(2) Selection of the composition

Figure 2 shows the phase diagram of the Fe–Ni–Al ternary system at 750°C, and it is well known that in the shadowed portion this system decomposes into the two phases, $\alpha'$—an iron-rich phase and $\alpha$—a NiAl-rich phase. Recent electron microscopic observations revealed that the alloys in the middle part of this range takes a modulated structure. In this range, the two kinds of specimens were chosen for the present study. Their compositions were Fe$_{1/2}$(NiAl)$_{1/2}$ (denoted as specimen A hereafter) and Fe$_{1/3}$(NiAl)$_{2/3}$ (specimen B). The chemical analysis of the alloys is shown in Table 1. In the homogeneous solid solution of the pseudo Fe–NiAl binary alloy, it was clarified by our investigation that the transition from a ferromagnetic state to a paramagnetic one occurs in the composition range of 30–35 at%Al ($\text{Fe}_{0.4}$(NiAl)$_{0.6}$–$\text{Fe}_{0.3}$(NiAl)$_{0.7}$) with increasing NiAl content at room temperature.

The specimen A was selected in the region where the alloy is ferromagnetic and the iron nuclei have large

![Figure 1: Variation of the hyperfine field at $^{57}$Fe nucleus in Fe–Ni and Fe–Al alloys](image)

![Figure 2: Section of Fe–Ni–Al phase diagram at 750°C](image)

Table 1. Compositions of the specimen (at%).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>48.9</td>
<td>23.9</td>
<td>27.2</td>
</tr>
<tr>
<td>B</td>
<td>33.2</td>
<td>32.3</td>
<td>34.5</td>
</tr>
</tbody>
</table>
internal magnetic fields in the state of a homogeneous solid solution. In contrast, specimen B was selected in the region where the alloy is almost paramagnetic and the iron nuclei have no or weak internal fields at room temperature. Both the specimens decompose into two phases, Fe rich $\alpha'$ phase and NiAl $\alpha$ phase, with isothermal aging.

Therefore, when a precipitated phase changes its composition and crosses over the boundary composition range during aging, it is expected that the magnetic behavior of the iron atoms in the precipitated phase should remarkably change. On aging the specimen A, NiAl rich $\alpha$ phase will precipitate. If the composition of the $\alpha$ crosses the ferromagnetic paramagnetic boundary, the iron atoms in the precipitate lose their magnetic moments. Then, a paramagnetic absorption line will appear in the Mössbauer spectrum. In the same way, on aging specimen B, the Fe rich $\alpha'$ phase will precipitate, and the iron atoms in the precipitate acquire the magnetic moments when the composition of the precipitate crosses over the boundary. The six ferromagnetic absorption lines will appear in this case.

(3) Specimen preparation

Fe–Ni–Al alloys used in this study were prepared from electric iron of 99.9 wt% purity, electric nickel of 99.9 wt% purity and aluminum of 99.99 wt% purity. They were melted in an induction furnace under argon atmosphere, quenched into a water-cooled copper mold and then homogenized at 1200°C for 24 hr. A quantity of powder was obtained from Fe$_{1/2}$(NiAl)$_{1/2}$ by grinding, the individual particles being less than 30µ in size. This powder was sealed in an evacuated quartz tube and then annealed at 1200°C for 2 hr. A homogeneous, supersaturated, solid solution was obtained by quenching into iced water and simultaneously breaking the quartz tube. (Special care was needed, because the quenching speed of the powder sample depended on the breaking of the quartz tube.) Specimens of Fe$_{1/3}$(NiAl)$_{2/3}$ in the state of a supersaturated solid solution were prepared by a hammer-quenching method which achieved a constant and sufficient quenching speed.

For Fe$_{1/3}$(NiAl)$_{1/2}$, it was ascertained by the following facts that the phase separation did not occur during the quench; no trace of the paramagnetic absorption was found in the Mössbauer spectrum of an as-quenched specimen and the B2 type ordered superlattice lines, as discussed later, were very faint in X-ray diffraction patterns. (For the slowly quenched specimens, because of failure in breaking the quartz tube, the paramagnetic absorption line was found in the Mössbauer spectrum and strong B2 type ordered lines were observed by X-ray diffraction.) As the Mössbauer spectra of all Fe$_{1/3}$(NiAl)$_{2/3}$ specimens quenched by the hammer quenching method show essentially the same patterns, it is believed that the quenching speed of the hammer quenching was efficiently high, and the composition of the Fe$_{1/3}$(NiAl)$_{2/3}$ was homogeneous. In the Mössbauer spectrum of as-quenched Fe$_{1/3}$(NiAl)$_{2/3}$, broad absorption bands are seen along the paramagnetic single absorption line. It is supposed that the iron atoms in the Fe$_{1/3}$ (NiAl)$_{2/3}$ surrounded by fewer nearest neighbor aluminum atoms have small ferromagnetic moments since the composition of the specimen Fe$_{1/3}$(NiAl)$_{2/3}$ is very close to the composition boundary between paramagnetism and ferromagnetism. Therefore, the broad absorption band may not be due to the occurrence of the phase separation.

III. Results

1. Fe$_{1/2}$(NiAl)$_{1/2}$(Specimen A)

The results of Mössbauer effect measurements for the as-quenched and aged states of specimen A(Fe$_{1/2}$ NiAl)$_{1/2}$ are shown in Fig. 3(a) and (b). After aging at 750°C, the paramagnetic absorption line appeared near the zero doppler velocity of the spectrum, as shown in Fig. 3(b). It is concluded that the paramagnetic absorption line arises from iron atoms in the NiAl rich $\alpha$ phase, as mentioned in Chapter II. To see the variation of the paramagnetic absorption in detail, the central parts of the Mössbauer spectra after aging at 750°C for 3 min, 30 min, 4 hr and 40 hr are shown in Fig. 4. The positions of absorption peaks from the two kinds of iron atoms which are surrounded by four (4 n.n. Al) and eight (8 n.n. Al) aluminum atoms in the first neighbor sites, respectively, those from $\alpha$-Fe (0 n.n. Al) and those from $\gamma$–Fe are shown in the same figure. The central paramagnetic absorption is thought to be composed of various absorption lines having different isomer shifts. The spectrum of a sample aged for 3 min at 750°C shows that its paramagnetic absorption has an unlocalized, widely distributed pattern. The mean position of the paramagnetic absorption peak shifts toward the plus velocity side on further aging, as shown in Fig. 4, and finally after aging for 40 hr the peak for the 8 n.n. Al dominates the paramagnetic absorption. The intensity and the average isomer shift of the paramagnetic absorption line are plotted against aging time in Fig. 5. As seen from this figure, the components of the paramagnetic iron do not increase equally with aging time.
and, in fact, the components decrease after the aging for 30 min. On aging this alloy, superlattice lines of the B2 type are also observed by X-ray diffraction. The variation of the intensity of the (100) superlattice line (2θ = 36° ± 10°) is shown in Fig. 6; they are the diffraction profiles of the sample in the as-quenched state and after aging for 3 min, 30 min, 4 hr, and 40 hr, normalized by the intensity of (110) fundamental line (2θ = 52° ± 20°). The intensity of the (100) superlattice line become stronger with increasing aging time.

2. Fe$_{1/3}$(NiAl)$_{2/3}$ (Specimen B)

The Mössbauer absorption spectrum of as-quenched specimen B (Fe$_{1/3}$(NiAl)$_{2/3}$) is shown in Fig. 7(a) along with the spectrum after aging for 30 min at 650°C in Fig. 7(b). Six ferromagnetic absorption lines appeared in the latter spectrum. It is believed that the ferromagnetic absorption spectrum is caused by the iron atoms in the Fe-rich α' phase which is thought to be one of the separated phases. To depict the change of these ferromagnetic absorption spectra on aging, the left sides of the Mössbauer spectra are compared in Fig. 8. The figure clearly shows that the average internal magnetic field increases with aging and, in contrast with the early stage of aging, the spectra evolved into well separated sharp components. This tendency is found more clearly in the series of Mössbauer spectra obtained from a sample aged at a lower temperature (for example, at 550°C). To follow precisely the concentration variation during the initial stage of the aging process, lower temperature (550°C) aging treatments were made. Figure 9 shows the Mössbauer absorption spectra after 5, 25, 125 and 900 min aging. A dotted line in each figure indicates the spectrum prior to each aging. After aging for 1 or 5 min, ferromagnetic absorption lines which have small internal magnetic fields and large half-width values...
A Study of Spinodal Decomposition in Fe-Ni-Al Alloys by Mössbauer Effect

IV. Discussion

1. Fe$_{1/2}$(NiAl)$_{1/2}$ (Specimen A)

From the Mössbauer measurements of specimen A, it can be concluded that the composition of the NiAl-rich $\alpha$ phase gradually approaches its equilibrium composition. The first reason is as follows; the change of the isomer shift of the paramagnetic absorption shows that the circumstance of the iron atoms in the $\alpha$ phase gradually changes with aging and that finally most iron atoms in the $\alpha$ phase translate into the 8 n.n. Al type iron. It was known that in the Fe-Al alloy containing less than 33 at% aluminum both B2 and DO$_3$ ordered phases are ferromagnetic and no paramagnetic absorption line was observed in the Mössbauer spectra. Therefore, it may be concluded that no paramagnetic line appears as a result of ordering in a homogeneous solid solution of sample A (Fe$_{1/2}$(NiAl)$_{1/2}$). Therefore, the observed paramagnetic line is due to the NiAl rich $\alpha$ phase produced by the phase separation. As it is thought that the iron atoms in the $\alpha$ phase change places with nickel atoms, the above result in the isomer shift change can be interpreted to indicate that the concentration of aluminum in the $\alpha$ phase increased gradually and approaches 50 at% $\alpha$. The second reason is as follows; from the change in paramagnetic component of the Mössbauer spectra (in Fig. 5) it can be interpreted that the iron atoms in the $\alpha$ phase have been removed from the phase during aging. If the iron concentration is unchanged, we are forced to conclude that the change in the intensity of the paramagnetic component was caused by a volume change of the $\alpha$ phase, but, of course, such a volume change is believed to be impossible on isothermal aging. Since the absorption is caused by $^{57}$Fe nuclei, the intensity of the paramagnetic component is proportional to the product of the volume and the concentration of iron atoms in the $\alpha$ phase. The change in the paramagnetic component in Fig. 5 can be explained as follows. In the initial stage of aging, the total number of iron atoms in the $\alpha$ phase may increase because it is thought that the increase of the volume of the $\alpha$ phase is more dominant than the decrease of the iron concentration from the $\alpha$ phase. On further aging, the increase of the volume of the $\alpha$ phase may become slowed down, and
the decrease of the iron concentration in the $\alpha$ phase should have the effect of increasing the total number of iron atoms. As the iron concentration decreases continuously with further aging, the total number of iron atoms in the $\alpha$ phase turns out to decrease finally.

The results mentioned above is summarized below:

(i) From the appearance of the paramagnetic absorption line, NiAl-rich $\alpha$ phase is known to appear,
(ii) from the change in the isomer shift of paramagnetic absorption line, aluminum concentration in the $\alpha$ phase is known to increase gradually with aging, and
(iii) from the change in the intensity of paramagnetic absorption, the iron concentration in the $\alpha$ phase is known to decrease continuously with aging.

The observed paramagnetic absorption is regarded as the superposition of paramagnetic absorption lines with the various isomer shifts. Assuming approximately that the isomer shift is proportional to the number of aluminum atoms in the nearest neighbor sites of an iron atom, and the $\alpha$ phase is homogeneous, the distribution pattern of the paramagnetic absorption line observed in the spectrum of the specimen aged for 3 min at 750$^\circ$C, Fig. 4 is expected when the aluminum concentration in the $\alpha$ phase is about 35 at.%, by the result of a simple calculation based on the B2 type ordered structure of the $\alpha$ phase. Various distribution patterns depending on the aluminum concentration of the $\alpha$ phase are shown in Fig. 10. Accordingly, it is concluded that the $\alpha$ phase separated from the initial homogeneous solid solution changes its composition from 25 at.% Al to about 35 at.% Al by aging for 3 min at 750$^\circ$C. As the equilibrium composition of the $\alpha$ phase is known from the phase diagram (Fig. 2) to be about 45 at.% Al, a nearly middle point between the initial composition and the equilibrium composition was observed in the spectrum by aging for 3 min at 750$^\circ$C. The (100) superlattice line of the as-quenched specimen in X-ray diffraction is faint but by aging it becomes pronounced (Fig. 6), because the separated $\alpha$ phase takes the B2 type ordered structure. It is well known that the NiAl alloy takes the B2 type ordered structure at 750$^\circ$C. Accordingly, in this alloy the phase separation progresses accompanied by ordering.

2. Fe$_{1/3}$(NiAl)$_{2/3}$ (Specimen B)

The appearance of the ferromagnetic absorption lines for the Mössbauer spectra of specimen B in Fig. 7–9 shows the existence of the iron-rich $\alpha'$ phase caused by the phase separation, as described in Chapter III. Each peak of the ferromagnetic absorption spectra has a very large half-width value. From this, it is thought in the $\alpha'$ phase various iron atoms having different internal fields are distributed. This is a consequence of the fact that the iron atoms are in various environments due to the inhomogeneity of composition in the $\alpha'$ phase induced by the phase separation process. Thus the spectrum contains the components different from those expected from the average concentration. The average internal magnetic field determined from the Mössbauer spectrum is thought to correspond to the average iron concentration of the $\alpha'$ phase. Accordingly, the increase of the average internal field clearly shows that the iron concentration in the $\alpha'$ phase increases with aging. Furthermore, it should be emphasized that the change in the iron concentration of the $\alpha'$ phase has proceeded gradually and continuously with aging, as seen in a series of aging at 550$^\circ$C.

Next, we estimate the composition of the iron-rich $\alpha'$ phase during the phase separation process. Since the peak position of the ferromagnetic absorption line of specimen B aged for 30 min at 650$^\circ$C agrees well with that of as-quenched specimen A as shown in Fig. 11, the average composition of the iron-rich $\alpha'$ phase of specimen B aged for 30 min at 650$^\circ$C is thought to be almost equal to that of as-quenched homogeneous specimen A, Fe$_{1/2}$(NiAl)$_{1/2}$. (Since each of iron and nickel atoms makes a very similar contribution to the internal magnetic fields of neighbouring iron atoms, the composition in this case should

---

1 In the Fe–Be alloy, the phase separation accompanied by B2 type ordering was also observed using electron microscopy and the Mössbauer effect. An explanation of the phenomena was given by one of the present authors in terms of the pair interactions between 1st nearest neighbor atoms ($V = V_{AA} - (V_{AA} + V_{BB})/2 < 0$) and 2nd ones ($U = U_{AB} - (U_{AA} + U_{BB})/2 < 0$).
be said to be \((\text{Fe, Ni})_{0.75}\text{Al}_{0.25}\). Besides, we supposed that the direction of the phase separation as viewed in Fig. 2 must have only a slight component perpendicular to the Fe-NiAl line, since no \(\gamma\)-phase has been observed by Mössbauer and X-ray measurements.

As shown in Fig. 8, since the internal magnetic field of specimen B aged for 30 min is greater than that of the same specimen aged for 3 min, it can be concluded that the \(\alpha\)' phase of specimen B aged for 3 min contains Al more than 25 at\/% (less than 50 at\/% Fe). As the equilibrium composition of the \(\alpha\)' phase corresponds to about \(\text{Fe}_{0.9}(\text{NiAl})_{0.1}\) at 750\(^\circ\)C in the phase diagram (Fig. 2), it is evident that the iron-rich \(\alpha\)' phase appeared by phase separation wherein its composition changed gradually and on a large scale by isothermal aging.

From a more careful observation of Fig. 11, some other interesting results were found. The half-width value of the absorption line of aged specimen B was slightly larger than that of as-quenched specimen A. Moreover in the spectrum of specimen B aged for 30 min, the tails of absorption lines with smaller internal magnetic fields are seen inside the absorption lines of as-quenched specimen A. These results suggest that the composition of the \(\alpha\)' phase is not homogeneous but has the spatial distribution expected from the spinodal decomposition mechanism.

The changes in the composition of the iron rich ferromagnetic \(\alpha\)' phase during aging for specimen B have been discussed in the above paragraph. Next, the changes in the composition of the NiAl rich paramagnetic \(\alpha\) phase will be discussed. It is clear from Fig. 9 that the components of paramagnetic absorption due to the NiAl rich \(\alpha\) phase decrease with aging. In the series of specimens aged at 550\(^\circ\)C, the ratio \(R\), of the paramagnetic absorption component of these spectra is plotted in Fig. 12 as a function of aging time. As shown in the figure, \(R\) changes little for aging times longer than 25 min. While, it is found from the change of internal magnetic fields in the ferromagnetic absorption spectra shown in Fig. 9, that the iron concentration of the iron rich \(\alpha\)' phase increases continuously even after 25-min aging. In these experimental results, the change in the iron concentration of the NiAl-rich \(\alpha\) phase can be derived from the following equation.

Let \(C_0\) be the initial iron concentration of the as-quenched specimen B, \(C_f\) and \(V_f\) be the average iron concentration and the volume of iron-rich ferromagnetic \(\alpha\)' phase, and \(C_p\) and \(V_p\) be the average iron concentration and the volume of the NiAl-rich paramagnetic \(\alpha\) phase. The total number of iron atoms contained in each phase is \(V_f C_f\) and \(V_p C_p\) respectively. Since the intensity of the absorption line is proportional to the total number of iron atoms in each phase, we may write

\[
R = \frac{I_{\text{paramag}}}{I_{\text{ferromag}} + I_{\text{paramag}}} = C_p V_p (C_f/V_f + C_f/V_p),
\]

Using the lever law:

\[
V_p (C_0 - C_p) = V_f (C_f - C_0),
\]

and substituting eq. (2) into eq. (1), we obtain

\[
R = C_p (C_f - C_0)/(C_f (C_0 - C_p) + C_p (C_f - C_0)).
\]

From eq. (3), \(C_p\) is expressed as follows:

\[
C_p = R C_0 / (1 - (1 - R) C_0 / C_f).
\]

If we assume that \(R\) is constant after aging for 25 min and equal to 0.1, the relationship between \(C_f\) and \(C_p\) is indicated as shown in Fig. 13. Even if the value of \(R\) is changed slightly, for example, to \(R=0.12\), it displaces the \(C_p\) vs \(C_f\) curve very little. This result indicates that when \(C_f\) increases, \(C_p\) must decrease. That is, it was proved by the present experiment on specimen B that both the iron-rich \(\alpha\)' phase and the NiAl-rich \(\alpha\) phase change their compositions gradually and continuously with aging.

3. Distinction between the spinodal decomposition and the nucleation and growth decomposition mechanism

Not only the continuous change in the composition with aging, but also the spatial distribution of the composition were observed in this study. As noted already, the results appear to agree well with the characteristics expected from the spinodal decomposition mechanism. Next, we discuss whether or not the nucleation and growth decomposition mechanism can also explain our experimental results. In the classical nucleation theory of Becker(22), the composition of the nucleus arising from the homogeneous solid solution is sup-

![Fig. 12 Variation of paramagnetic component in Mössbauer absorption spectra of Fe\(_{1/3}\) (NiAl)\(_{2/3}\) by aging.](image-url)
posed to be very close to that of the equilibrium phase, and it can be concluded that the change in composition of the precipitated particles during aging should be very small. In the fluctuation theory of Bolerius(23), the composition of the nucleus is not prescribed and may vary with time. However, the essential point of this theory may be that the critical composition $C^*$ has been taken into consideration. In this theory also, embryos with solute concentrations less than $C^*$ must be redissolved into the matrix. This is the consequence of the fact that the initial composition $C_0$ is located outside the spinodal line and satisfies the condition $(\partial^2 f/\partial C^2)_{C=C_0}>0$. For the reason mentioned above, the nucleation and growth mechanism must be clearly distinguished from the spinodal decomposition mechanism, since in the latter a fluctuation having a small concentration difference and extending over a wide region can develop continuously from the initial composition, $C_0$, to the equilibrium composition without the formation of a nucleus.

In order to distinguish experimentally the two decomposition mechanisms, the difference $C^*-C_0$ should be large and measurable. Hobstetter(24)(25) calculated a free energy as a function of the composition and the radius of a nucleus and derived the critical concentration $C^*$. He found that in the range $T=0.8-0.7T_c$, where $T_c$ is the critical temperature for decomposition, $C^*$ is sufficiently different from $C_0$ and that $C^*$ is close to the equilibrium composition. According to the nucleation theory by Cahn and Hilliard(26), which includes the composition gradient term for the free energy of a nonuniform system, the composition of a nucleus $C^*$ rapidly approaches $C_0$, when $C_0$ approaches the spinodal composition from outside the spinodal line. Nevertheless, if $C_0$ differs by 2 at% for instance, from the spinodal composition in their theory, the composition difference, $C^*-C_0$, between the center of the nucleus and the initial phase is indicated to be about 20 at%. Therefore, it appears that if $C_0$ is not close to the spinodal composition, the critical nucleus of the nucleation and growth mechanism has a composition which can be distinguishable from the initial composition $C_0$.

The composition changes which were observed in the phase separation process of the Fe–Ni–Al alloys in this study are summarized in Fig. 14. In the case of specimen A which has the initial composition of 27 at% Al from chemical analysis, the NiAl-rich $\alpha$ phase containing about 35 at% Al was observed after aging for 3 min at 750°C. Thereafter the composition of the $\alpha$ phase changed gradually and continuously towards the equilibrium composition (45 at% Al). For specimen B having the initial composition of 34 at% Al, it was confirmed that the composition of the iron-rich $\alpha'$ phase had about 27 at% Al after aging for 30 min at 650°C. (The precise composition of these presumed points will be determined experimentally by measuring the Mössbauer spectra of several as-quenched specimens whose composition may be selected in the neighborhood of each presumed point.) The occurrence of the gradual change in composition of the $\alpha$ phase of specimen B was also confirmed as shown in Fig. 13.

From the large and continuous change in the composition of both phases during aging, it can be concluded that the phase separation observed in these Fe–Ni–Al alloy has occurred and progressed by the spinodal decomposition mechanism, or, in little possibility, by the nucleation and growth mechanism when the composition of specimen A or specimen B happens to be extremely close to the spinodal composition. In general, the spinodal composition may change with the temperature of aging. To determine whether the initial composition $C_0$ was close to the spinodal composition in the nucleation and growth region, or inside the spinodal line, aging was performed at a higher temperature than that used in this study. From the measurement of the Mössbauer spectrum of specimen B aged at 800°C for 30 sec, the average internal magnetic field of the ferromagnetic absorption was found to be less than that of the as-quenched specimen A. This shows that the Fe-rich $\alpha'$ phase which contains more aluminum than 27 at% (less iron than 49 at%) appeared with aging. As the equilibrium composition of $\alpha'$ phase at 800°C is thought to be about Fe$_{0.8}$(NiAl)$_{0.2}$ the composition of specimen B (Fe$_{1/3}$(NiAl)$_{2/3}$) is believed to be inside the spinodal composition or very close to the spinodal
A Study of Spinodal Decomposition in Fe-Ni-Al Alloys by Mössbauer Effect

composition in the nucleation and growth region at 800°C. From the results, it is concluded that the compositions of specimen B is well inside the spinodal composition at 650 or 550°C. (If the composition of specimen B is outside and close to the spinodal composition at 800°C, it must be very different from the spinodal composition at 800°C. So, if the case is realized for specimen B, the absorption caused by the nuclei having the composition near the equilibrium one must be observed after aging at 800°C.)

Furthermore, we performed the study for the specimen with the composition of Fe_{0.3}(NiAl)_{0.7}. After aging the specimen for 5 min at 550°C, the Mössbauer spectrum with very small internal magnetic field was observed. This result shows that the specimen (Fe_{0.3}(NiAl)_{0.7}) is inside or very close to the spinodal line at 550°C, which, in turn, shows that the specimen B with the composition of Fe_{1/3}(NiAl)_{2/3} is sufficiently inside the spinodal compositions.

It can be concluded that the phase separation process observed in this study progresses by the spinodal decomposition mechanism and such a large composition change as anticipated from spinodal theory has turned out to be an experimental evidence and one of the most important characteristics of the spinodal decomposition.

From this study, it was known that the Mössbauer effect is one of the most useful and interesting methods to study the decomposition process of alloys. Various interesting knowledges will be obtained in near future. The spatial distribution of the composition and its changes during aging are now investigated by the present authors. We expect that the detail of the phase separation processes associated with the spinodal decomposition and nucleation and growth will be clarified.

Acknowledgment

The authors wish to express their hearty thanks to Professor F. Eiichi Fujita for valuable advices and discussions. Further, our thanks are due to Professor Akira Adachi and his staff for allowing the use of the instrument of hammer quenching.

REFERENCES