Control of a Nanocomposite Structure in Fe\textsubscript{86}Nd\textsubscript{9}B\textsubscript{5} Alloy by Electron Irradiation

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Change in nanocomposite structure in rapidly solidified Fe\textsubscript{86}Nd\textsubscript{9}B\textsubscript{5} alloy during electron irradiation was investigated. Nanocrystalline structure composed of \(\alpha\)-Fe, Fe\textsubscript{5}B, Nd\textsubscript{2}Fe\textsubscript{23}B\textsubscript{3} and Nd\textsubscript{3}Fe\textsubscript{2}B\textsubscript{3} crystalline phases was formed by rapid solidification. Electron irradiation can introduce amorphization of intermetallic compounds and crystallization of an amorphous phase, resulting in the formation of a novel nanocomposite structure in which \(\alpha\)-Fe and Nd\textsubscript{2}Fe\textsubscript{2}B nanocrystals are embedded in the amorphous matrix. The mechanism of nanocomposite structure formation was discussed based on the phase stability of amorphous and crystalline phases under electron irradiation.

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1. Introduction

Nanocrystalline and nanocomposite materials are known to exhibit superior mechanical and functional properties which are rarely realized in conventional crystalline materials and amorphous materials.\textsuperscript{1–3} Fe–Nd–B alloys with a nanocomposite structure are of significant interest as a superior hard magnetic material. Nanocrystalline materials can be obtained by several thermal processes such as rapid solidification of thermal melt and thermal crystallization of an amorphous phase.\textsuperscript{4–7} A large number of studies have been carried out focusing on the effects of alloy composition, additional elements, cooling rate of the melt and annealing conditions of an amorphous phase on the formation of nanocomposite structures in Fe–Nd–B alloys.\textsuperscript{8–11} Since magnetically harmful Nd\textsubscript{2}Fe\textsubscript{23}B\textsubscript{3} phase is often formed during rapid solidification, several annealing processes were examined to annihilate the Nd\textsubscript{2}Fe\textsubscript{23}B\textsubscript{3} phase.\textsuperscript{10,11}

Recently, not only amorphization of crystalline phases but also crystallization of an amorphous phase was found in several metallic glasses by a non-thermal process of electron irradiation.\textsuperscript{12} Electron irradiation stimulates mechanical atomic displacement in crystalline phases and an amorphous phase by the electron knock-on effect. When the amorphous phase is unstable under electron irradiation, electron irradiation induced crystallization occurs. Since the phase stability is different under electron irradiation and thermal annealing, a new phase can be produced by electron irradiation.

The melt-spun Fe\textsubscript{86}Nd\textsubscript{9}B\textsubscript{5} is known to form nanocrystalline structure containing magnetically harmful Nd\textsubscript{2}Fe\textsubscript{23}B\textsubscript{3} phase. The aim of this work was to examine the electron irradiation induced amorphization and crystallization behavior in the melt-spun Fe\textsubscript{86}Nd\textsubscript{9}B\textsubscript{5} nanocrystalline alloy focusing on control of nanocomposite structure and annihilation of the magnetically harmful Nb\textsubscript{2}Fe\textsubscript{23}B\textsubscript{3} phase by electron irradiation.

2. Experimental Procedure

A master ingot of Fe\textsubscript{86}Nd\textsubscript{9}B\textsubscript{5} (at%) alloy was prepared by arc melting under highly purified Ar atmosphere using raw materials of Fe, Nd and Fe–18.94 mass%B mother alloy. Rapidly quenched ribbon was produced from the ingot by a single roller melt-spinning method at roll surface velocity of 10, 21, 31 or 42 ms\textsuperscript{-1} in an Ar atmosphere. The structure of the ribbon was examined by X-ray diffractometry using Cu-K\(\alpha\) radiation, transmission electron microscopy (TEM) using a JEM-3010 microscope operated at 300 kV and high resolution transmission electron microscopy (HREM) using a JEM-2010 microscope operated at 200 kV. Thin foils for TEM and HREM observation were prepared by an ion milling method. Electron irradiation on the melt-spun ribbon was performed by an ultra-high voltage electron microscope (UHVEM) of H-3000 operated at 2.0 MV in the temperature range between 121 and 298 K. The applied dose rate was chosen to be between 6.3 \(\times 10^{24}\) and 8.3 \(\times 10^{24}\) m\textsuperscript{-2} s\textsuperscript{-1}. Change in the microstructure during electron irradiation was observed by bright field images (BFIs) and selected area diffraction patterns (SADPs) in the UHVEM.

3. Results

3.1 Formation of nanocrystalline structure by rapid solidification

Figure 1 shows TEM microstructures and the corresponding SADPs of melt-spun specimens prepared at the roll surface velocity of 10, 21, 31 or 42 ms\textsuperscript{-1}. Polycrystalline phases with dark and bright contrast were observed in BFIs. SADPs show discontinuous Debye rings and/or sharp diffraction spots corresponding to crystalline phases. In order to investigate the formation of an amorphous phase during rapid solidification, thermal analysis of melt-spun specimens was performed. DSC curves for melt-spun specimens are shown in Fig. 2. Exothermic peaks corresponding to crystallization of an amorphous phase cannot be seen. No significant evidence of amorphous phase was obtained by DSC, XRD, TEM and HREM observations.

Table 1 shows constituent phases determined by XRD analysis and TEM observations for melt-spun specimens, together with the data of mean grain size. The mean grain size was determined by TEM observation. \(\alpha\)-Fe, Fe\textsubscript{5}B, Nd\textsubscript{2}Fe\textsubscript{2}B and Nd\textsubscript{3}Fe\textsubscript{2}B\textsubscript{3} phases were formed during rapid solidification and the constituent phases were not sensitive to
cooling rate in \( \text{Fe}_{86}\text{Nd}_{9}\text{B}_{5} \) alloy. The magnetically harmful \( \text{Nd}_{2}\text{Fe}_{23}\text{B}_{3} \) phase was also formed during rapid solidification. The mean grain size significantly decreased with increasing roll surface velocity in the range between 10 and 21 ms\(^{-1}\), while the effect of grain refinement was moderated at a roll surface velocity higher than 21 ms\(^{-1}\).

Figure 3 shows a HREM image of a melt-spun specimen prepared at the roll surface velocity of 42 ms\(^{-1}\). The nanocrystalline \( \text{Nd}_{2}\text{Fe}_{23}\text{B}_{3} \) phase is observed together with \( \text{Fe}_{11} \). Since the crystallization of magnetically harmful \( \text{Nd}_{2}\text{Fe}_{23}\text{B}_{3} \) phase often occurs during rapid solidification, thermal annealing processes to annihilate the \( \text{Nd}_{2}\text{Fe}_{23}\text{B}_{3} \) phase were achieved and a good nanocomposite structure with good hard magnetic property was obtained.\(^{10,11} \)

### Table 1

<table>
<thead>
<tr>
<th>Roll Surface Velocity (ms(^{-1}))</th>
<th>Soft Phase</th>
<th>Hard Phase</th>
<th>Harmful Phase</th>
<th>Mean Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>( \alpha\text{-Fe} )</td>
<td>( \text{Nd}<em>{2}\text{Fe}</em>{14}\text{B} )</td>
<td>( \text{Nd}<em>{2}\text{Fe}</em>{23}\text{B}_{3} )</td>
<td>134</td>
</tr>
<tr>
<td>21</td>
<td>( \text{Fe}_{3}\text{B} )</td>
<td>( \text{Nd}<em>{2}\text{Fe}</em>{14}\text{B} )</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>31</td>
<td>( \text{Fe}_{3}\text{B} )</td>
<td>( \text{Nd}<em>{2}\text{Fe}</em>{23}\text{B}_{3} )</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>42</td>
<td>( \text{Fe}_{3}\text{B} )</td>
<td>( \text{Nd}<em>{2}\text{Fe}</em>{23}\text{B}_{3} )</td>
<td></td>
<td>16</td>
</tr>
</tbody>
</table>

### 3.2 Control of nanocrystalline structure by electron irradiation

The melt-spun \( \text{Fe}_{86}\text{Nd}_{9}\text{B}_{5} \) ribbon at the velocity of 42 ms\(^{-1}\) was composed of \( \alpha\text{-Fe} \), \( \text{Fe}_{3}\text{B} \), \( \text{Nd}_{2}\text{Fe}_{14}\text{B} \) and \( \text{Nd}_{2}\text{Fe}_{23}\text{B}_{3} \) crystalline phases with a mean grain size of about 16 nm. Change in the microstructures of the \( \text{Fe}_{86}\text{Nd}_{9}\text{B}_{5} \) nanocrystalline alloy during electron irradiation was investigated by in situ TEM observation. Figure 4 shows BFIs and corresponding SADPs of the specimen as melt-spun and electron irradiated at 121 K with a dose rate of \( 8.3 \times 10^{24} \text{ m}^{-2}\text{s}^{-1} \). The melt-spun specimen shows nanoscale dark and bright granular contrast in BFI (a). Sharp Debye rings corresponding to \( \alpha\text{-Fe} \) and discontinuous Debye rings corresponding to intermetallic compounds can be seen in
SADP (d). At the total dose of \(3.8 \times 10^{26} \text{ m}^{-2}\), no significant change in BFI (b) can be observed, while SADP shows the disappearance of some discontinuous Debye rings corresponding to Fe\(_3\)B, Nd\(_2\)Fe\(_{14}\)B and Nd\(_2\)Fe\(_{23}\)B\(_3\) crystalline phases in Fig. 4(d). Broad halo rings appear accompanied by Debye rings corresponding to \(\alpha\)-Fe. Almost all intermetallic compounds were unstable under electron irradiation and electron irradiation induced amorphization occurred. After irradiation for \(7.6 \times 10^{27} \text{ m}^{-2}\), new Debye rings indicated by A appear in SADP (f). The electron irradiation induced amorphous phase cannot retain its original glassy structure under the ongoing electron irradiation resulting in its crystallization. Both electron irradiation induced amorphization and crystallization are known to be very sensitive to irradiation temperature.\(^{13,14}\) Figure 5 shows changes in TEM microstructures and corresponding SADPs during electron irradiation at 298 K. At the total dose of \(5.1 \times 10^{26} \text{ m}^{-2}\), discontinuous Debye rings corresponding to intermetallic compounds of Nd\(_2\)Fe\(_{14}\)B, Nd\(_2\)Fe\(_{23}\)B\(_3\) and Fe\(_3\)B disappeared in SADP (c). The detail is given in Fig. 6. After irradiation at the total dose of \(1.0 \times 10^{28} \text{ m}^{-2}\), new Debye rings indicated by B appear in SADP (d). The change in SADPs during electron irradiation at 298 K is the same as that at 121 K. The grain refinement through electron irradiation induced amorphization and crystallization occurred at 121 and 298 K.

To examine the detailed phase change under electron irradiation, the electron diffraction intensity profiles were analyzed using a PICTRO STAT DIGITAL 400 image analyzer. Figure 6 shows change in intensity profiles of the
Specimen electron irradiated at 298 K. The melt-spun nano-crystalline specimen shows many diffraction peaks corresponding to α-Fe, Fe₂B, Nd₃Fe₁₄B and Nd₃Fe₂₃B₃ crystalline phases, which are analogous to those of XRD analysis. After irradiation at the total dose of 5.1 × 10²⁸ m⁻² (b), some diffraction peaks corresponding to Fe₁₃B, Nd₂Fe₁₄B and Nd₂Fe₂₃B₃ intermetallic compounds disappear. A new broad peak corresponding to an amorphous phase appears at around 1/d = 3.4 nm⁻¹ accompanied by sharp diffraction peaks of α-Fe. The crystal structures of the compounds were destroyed resulting in formation of an amorphous state by electron irradiation so that a nanocrystalline structure composed of nanoscale α-Fe particles embedded in an amorphous phase was formed. With further electron irradiation, new diffraction peaks except for those of α-Fe phase appeared in the specimen irradiated at 1.1 × 10³⁸ m⁻². Diffraction peaks corresponding to Nd₂Fe₁₄B again appeared, although their identification is difficult because of many candidates. The crystal structure was confirmed by HREM observation.

Figure 7 shows HREM images of nanocrystalline structure obtained by electron irradiation at 298 K with the total dose of 1.8 × 10²⁸ m⁻². A nanocrystalline structure with an average grain size under 10 nm can be seen in Fig. 7(a). Each crystalline lattice image with nanoscale grain size is randomly oriented. The HREM image also shows a maze-like contrast corresponding to residual amorphous phase between nanocrystalline precipitates as shown in schematic illustration Fig. 7(b). From the spacing and geometry of the cross-fringe image, the nanocrystalline phase was identified as Nd₁₄Fe₁₄B; the periodic fringe contrast with spacing of 0.28 and 0.25 nm corresponds to (222) and (132) of the Nd₁₄Fe₁₄B, and other fringe with spacing of 0.25 and 0.24 nm corresponds to (132) and (124) of the Nd₁₄Fe₁₄B, respectively.

Thus, a nanocomposite structure composed of α-Fe soft magnetic phase and Nd₂Fe₁₄B hard magnetic phase with nanoscale grain size embedded in a small amount of residual amorphous phase can be formed by electron irradiation induced amorphization and crystallization. Compared with thermal annealing process, electron irradiation is a very effective method to control the crystalline structure at the localized region and to obtain a well-controlled α-Fe/Nd₂Fe₁₄B nanocomposite structure in Fe₈₆Nd₆B₅ alloy.

4. Discussion

4.1 Formation of nanocomposite structure under electron irradiation

Figure 8 shows a schematic illustration of electron irradiation induced phase transformation behavior observed in the present study. This unique phase transformation behavior under electron irradiation can be summarized as follows:

\[ \alpha\text{-Fe} + \text{Fe}_2\text{B} + \text{Nd}_3\text{Fe}_{14}\text{B} + \text{Nd}_3\text{Fe}_{23}\text{B}_3 \rightarrow \alpha\text{-Fe} + \text{Amorphous} \]

\[ \rightarrow \alpha\text{-Fe} + \text{Nd}_2\text{Fe}_{14}\text{B} + \text{Amorphous}. \]

The melt-spun specimen consists of α-Fe solid solution, Fe₂B, Nd₃Fe₁₄B and Nd₃Fe₂₃B₃ intermetallic compounds. Under 2.0 MV electron irradiation at 121 and 298 K, intermetallic compounds cannot retain their original crystalline structure and electron irradiation induced amorphization of these phases occurs. The magnetically harmful Nd₃Fe₂₃B₃ phase was completely annihilated during irradiation, while α-Fe solid solution shows high phase stability against electron irradiation and transformation to the other phases does not occur. The nanocrystalline structure composed of α-Fe solid solution embedded in an amorphous phase shown in Fig. 8(b) is formed through electron irradiation induced amorphization. With further electron irradiation, only hard magnetic Nd₂Fe₁₄B phase precipitates again appeared from an amor-
4.2 Stability of amorphous and crystalline phases under electron irradiation

The electron irradiation induced amorphization and crystallization behavior in Fe$_{86}$Nd$_9$B$_5$ alloy is explained by discussing the phase stability of amorphous and crystalline phases under this irradiation.

Solid state amorphization by electron or neutron irradiation and mechanical milling are often explained by change in Gibbs free energy due to the induced defects. Electron irradiation raises the energy of a crystalline phase due to lattice defects created by the electron knock-on effect. The crystalline phase cannot maintain its original structure under electron irradiation if atomic displacement by the electron knock-on effect occurs more frequently than recovery of the original positions of atomic sublattice by thermal diffusion. When a critical energy is provided to the crystalline phase by electron irradiation, transformation to the amorphous phase with a higher energy state is believed to occur. However, such a phase, namely, transformation mechanism to the higher energy state under a supply of external energy, is not applicable for the thermal crystallization or electron irradiation induced crystallization from an amorphous phase.

Under 2.0 MV electron irradiation, the atomic movement of almost all constituent elements occurs resulting in the mixing of constituent atoms in an irradiated area. This mixing effect is favorable for the formation and maintenance of a glassy structure; in contrast, the effect is unfavorable for maintaining the crystalline structure since it destroys the original order structure. Lattice defects increase under electron irradiation resulting in a rise of the Gibbs free energy. The phase stability of amorphous and crystalline phases under electron irradiation is considered based on change in Gibbs free energy. Figure 9 shows change in Gibbs free energy of α-Fe crystalline phase, Fe$_3$B, Nd$_2$Fe$_{14}$B and Nd$_2$Fe$_{23}$B$_3$ intermetallic compounds, and an amorphous phase in Fe$_{86}$Nd$_9$B$_5$ alloy with and without electron irradiation. In Fig. 9(a), the vertical and horizontal axes represent Gibbs free energy corresponding to phase stability and dose rate corresponding to the maximum quantity of atomic displacement. Under no electron irradiation, the free energy of thermal equilibrium α-Fe and Nd$_2$Fe$_{14}$B crystalline phases is lower than that of metastable Fe$_3$B and Nd$_2$Fe$_{23}$B$_3$ crystalline phases. The Gibbs free energy of an amorphous phase is highest and the phase stability is the lowest in the alloy. Under electron irradiation, the Gibbs free energy of the crystalline phases increases with increasing quantity of electron irradiation induced lattice defects and the phase stability decreases as total dose increases.

Change in phase stability of crystalline phases under electron irradiation is thought to be sensitive to their crystal structure. As the degree of complexity of a crystalline structure becomes greater, phase stability of a crystalline phase weakens against the mixing effect. The greater the complexity of the crystal structure becomes, the more difficult is the recovery by thermal diffusion. High complexity of the crystalline structure increases the accumulated lattice defects by electron irradiation resulting in increase in the Gibbs free energy. The degree of complexity of the crystal structure is thought to be proportional to the size of

![Fig. 7 HREM images and a schematic illustration of nanocrystalline structure of the specimen electron irradiated at 298 K with total dose of 1.8 x 10^28 m^-2.](image1)

![Fig. 8 A Schematic illustration of nanocomposite structure modification process during electron irradiation.](image2)
the unit cell of the crystalline phase. As the unit cell enlarges, the number of constituent atoms in the cell increases and the configuration of the atoms becomes topologically and chemically more complicated. The volume of unit cell in crystalline phases decreases in the order $\text{Nd}_2\text{Fe}_{14}\text{B} > \text{Nd}_5\text{Fe}_{12}\text{B}_2 > \text{Fe}_3\text{B} > \alpha$-Fe. When melt-spun Fe$_{86}$Nd$_{14}$B$_5$ alloy is electron irradiated, the Gibbs free energy of crystalline phases increases due to the irradiation induced lattice defects. In contrast, recovery by thermal diffusion in these phases contributes to the decrease of the energy under electron irradiation. Since no significant change in free energy of the amorphous phase occurs under electron irradiation, the free energy of Nd$_2$Fe$_{23}$B$_3$, Nd$_2$Fe$_{14}$B and Fe$_3$B in the specimen irradiated at the total dose of $5.1 \times 10^{20}$ m$^{-2}$ becomes higher than that of the amorphous phase as shown in Fig. 9. In contrast, the free energy of $\alpha$-Fe still remains lower than the amorphous phase because of its simple crystal structure. Therefore, Nd$_2$Fe$_{23}$B$_3$, Nd$_5$Fe$_{14}$B and Fe$_3$B intermetallic phases transform to the amorphous phase under electron irradiation at the total dose of $5.1 \times 10^{20}$ m$^{-2}$. Since chemical composition of the amorphous phase is changed through the mixing effect by annihilation of the intermetallic phases, the free energy of this phase may increase during electron irradiation, which is shown in Fig. 9(b). At the total dose of $1.0 \times 10^{20}$ m$^{-1}$, the energy of Nd$_2$Fe$_{14}$B becomes lower than that of the amorphous phase resulting in precipitation of Nd$_2$Fe$_{14}$B. In this stage, electron irradiation induced crystallization of Nd$_2$Fe$_{14}$B phase occurs, while Fe$_3$B and Nd$_5$Fe$_{23}$B$_3$ phases do not precipitate. Formation of a nanocomposite structure under electron irradiation in rapidly solidified Fe$_{86}$Nd$_{14}$B$_5$ alloy can be explained by change in the Gibbs free energy and the phase stability of amorphous and crystalline phases under electron irradiation.

5. Conclusions

Change in microstructure of rapidly solidified Fe$_{86}$Nd$_{14}$B$_5$ alloy under electron irradiation was investigated in the present study. Electron irradiation is very effective in controlling the nanocomposite structure through electron irradiation induced amorphization and crystallization in a Fe–Nd–B alloy system. The results obtained were summarized and the following conclusions reached.

1) Nanocrystalline structure composed of $\alpha$-Fe, Fe$_3$B, Nd$_5$Fe$_{14}$B and the magnetically harmful Nd$_5$Fe$_{23}$B$_3$ phase was formed by rapid solidification in Fe$_{86}$Nd$_{14}$B$_5$ alloy.

2) Solid-state amorphization of Fe$_3$B, Nd$_2$Fe$_{14}$B and Nd$_5$Fe$_{23}$B$_3$ intermetallic compounds occurred under 2.0 MV electron irradiation at 121 and 298 K, while $\alpha$-Fe was stable. Nanocrystalline structure composed of $\alpha$-Fe phase embedded in an amorphous phase was formed through electron irradiation induced amorphization.

3) Nd$_2$Fe$_{14}$B crystalline phase precipitates under electron irradiation from the amorphous phase formed through electron irradiation induced amorphization.

4) Nanocomposite structure composed of soft magnetic $\alpha$-Fe and hard magnetic Nd$_5$Fe$_{14}$B crystalline phases embedded in a small amount of residual amorphous phase was obtained through electron irradiation induced amorphization and crystallization in Fe$_{86}$Nd$_{14}$B$_5$ alloy.

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