Local Atomic Structures of Amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$ Alloys Formed under Different Cooling Rates and Their Relations to the Structures in the Early Stage of Crystallization

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A difference of amorphous structures of magnetic $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$ alloys formed under two different cooling rates was investigated by means of electron microscopy, electron diffraction and X-ray diffraction techniques. In spite of no appreciable difference in the high resolution electron microscope images, an atomic structural difference especially in the B-centered polyhedral structures was found in these specimens in their as-formed states. The effect of the initial local structure difference on the process of primary crystallization in these alloys on annealing was discussed.

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1. Introduction

Nanocomposite magnets with high remanence and high maximum energy product (BH_{max}) value due to the exchange coupling between hard and soft magnetic nano-sized particles have been attracting much interest for high performance permanent magnets.¹⁾ According to the exchange spring model,²⁾ the critical length of exchange coupled soft and hard-phases is as small as 8 nm for $\text{Nd}_2\text{Fe}_{14}\text{B}/(\text{Fe}_3\text{B}$ or $\alpha\text{-Fe}$) nanocomposite magnet. The control of the grain sizes of these hard and soft-phases has been a subjects of these alloys in these years. In order to control the grain sizes to form an ideal nanocomposite structure, a nanostructure fabrication technique taking advantage of the annealing process of Nd-Fe-B amorphous alloys has been utilized in recent years.³⁻¹⁶⁾ In the alloys the nanocomposite phases are composed of hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ and soft magnetic Fe_3B or $\alpha\text{-Fe}$ phases. The soft phase varies from Fe_3B to $\alpha\text{-Fe}$ depending on the B composition. These nanocomposite phases are formed on annealing at about 850-950 K through a transformation process such as, $\text{Fe}_{3.5}\text{B} + \text{Nd}_2\text{Fe}_{23}\text{B}_2 \rightarrow \text{Nd}_2\text{Fe}_{14}\text{B} + \text{Fe}_3\text{B}$, where Fe_3B and $\text{Nd}_2\text{Fe}_{23}\text{B}_2$ are the metastable phases appearing in the primary crystallization stage. It is known that the magnetic properties of nanocomposite alloys can be improved by reducing their grain sizes under high cooling rates in the formation of amorphous structures.^{15,17)} The change of magnetic properties must be originated from a difference in nucleation frequencies of the primary phases in crystallization of the alloy formed under different cooling rates. It is, therefore, worth to investigate atomic structures of a amorphous Nd-Fe-B alloys prepared under different cooling rates.

In this study, we prepared two amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$

alloy ribbons using roll-quenching technique with different cooling rates in order to investigate the cooling rate dependence of amorphous atomic structures and its relation to the primary crystallization processes on annealing. Structural studies were performed by mean of transmission electron microscopy (TEM), electron diffraction and X-ray diffraction.

2. Experimentals

2.1 Specimens

Two ribbon specimens with a nominal composition $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$ were prepared by single roll melt-spin technique at wheel surface velocities of 10 and 20 m/s. The sample formed under the surface velocities of 10 and 20 m/s are called, hereafter, Sample-10 and Sample-20, respectively. The width of ribbon specimens were 0.8 mm in both samples, and the thickness were 75 μm for Sample-10 and 45 μm for Sample-20, respectively. The crystallization temperatures of the specimens were 856 K for Sample-10 and 860 K for Sample-20 which were measured by differential scanning calorimetry (DSC) at a heating rate of 0.0167 K/s. For annealing the specimens were sealed in vacuum and heat treated at 853 K – 953 K for 600 s. The temperature 953 K is known as the optimum annealing temperature for good magnetic property.¹²⁾ Specimens for TEM observation were prepared by low angle Ar ion milling (Gatan, PIPS and LINDA, IV3/L¹⁸⁾).

2.2 TEM, X-ray and electron diffraction

Structural observations by HREM were made using TEM (JEM 2010 and JEM 3000F) operated at 200 kV. The identification of crystalline phases appeared on annealing were made by X-ray diffraction with $\text{CuK}\alpha$ radiation. X-ray diffraction profiles were collected within a scattering angle range from 20 to 100 degrees in steps of 0.01 deg. using a conventional diffractometer.

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Fig. 1 HREM images and selected area electron diffraction patterns of Sample-10(a) and Sample-20(b) of amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$.

Selected area electron diffraction (SAED) intensity profiles were collected for amorphous structure analysis using TEM (LEO 922) equipped with an in-column-type energy filter. Inelastic part of intensities in electron diffraction was removed using an energy window with a width of 20 eV. In electron diffraction, the multiple scattering effect must be taken into account in the intensity analysis.¹⁹⁾ Energy-filtered electron diffraction patterns which enable us to analyze intensities on the basis of the kinematical scattering theory were taken from thin specimen areas. The diffraction intensities were recorded on imaging plates (IP). The measurable limit of Q -range was as large as 200 nm^{-1} . The Q vector is defined here as $Q = 4\pi \sin \theta / \lambda$ where θ is the half scattering angle and λ is the electron wave length. The scattering angles of the halo pattern were corrected using a reference Debye-ring diffraction pattern from fine gold particles. In the electron diffraction pair distribution function (PDF) analysis, the recorded intensities were divided into 16384 gray levels and digitized using a computer.

In analyzing atomic structure after obtaining PDF profiles, we used the reverse Monte-Carlo (RMC) structure simulation.^{20–22)} In the simulation, an atomic initial structure composed of randomly distributed 2500 atoms was first prepared, followed by the structure relaxation using Lennard-Jones-type atomic potentials between the constituent atoms. The L-J potential parameters were determined using melting point of Fe, B, FeB, NdB_4 and $\text{Nd}_2\text{Fe}_{17}$. In each of the RMC simulations for Sample-10 and -20, the experimental “total PDF” was used as a reference PDF for the structure refinement. In order to know local atomic coordinations, the Voronoi polyhedral analysis²³⁾ was used for each of the final RMC simulated structure. Details of the electron diffraction PDF analysis, the RMC simulation and the Voronoi analysis for amorphous alloys are written elsewhere.²²⁾

3. Results

3.1 Cooling rate dependence of structural morphology in as-formed state and early stage of crystallization

Figures 1(a) and (b) show HREM images of the as formed Sample-10 and -20 with SAED patterns in the insets. In both of the SAED patterns, halo patterns typical of amorphous structure are seen. On the other hand, local lattice fringe regions extending beyond 2 nm were frequently observed by HREM in both of the specimens. These lattice fringe regions can be taken as nanocrystalline regions which were developed in the ribbon specimens during the slow cooling (roll speeds: 10 and 20 m/s) processes. Local atomic order in amorphous structures is generally called atomic medium range order (MRO), and such nanocrystalline regions coherently formed in the amorphous matrix as observed here can be called “extended MROs”. Although it is known that MRO size and observed frequency of MROs in amorphous alloys are largely depended on their amorphous-forming conditions,^{24,25)} it was difficult to find a difference in observation frequencies and sizes of the nanocrystalline regions in the present two as-formed specimens. The observed extended MROs in the present specimens are thought to be belonging to metastable phases of these alloys which were formed during cooling from the liquid states. Due to the variety of lattice fringe spacing of the extended MRO regions ranging from 0.21 to 0.29 nm, it was difficult to identify crystal structures of these MROs using HREM.

Figure 2 compares the X-ray diffraction profiles of Sample-10 and -20 in the first stage of crystallization at 853 K. In Fig. 2, diffraction peaks from Sample-10 appear at $2\theta = 43.3, 44.9, 48.4, 50.6$ and 54.5° , clearly, which correspond to those of $\text{Fe}_{3.5}\text{B}$ (usually identified as Fe_3B)²⁶⁾ and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$.²⁷⁾ For the identification of these phases, X-ray diffraction profiles of Fe_3B , $\text{Fe}_{3.5}\text{B}$, $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$, Fe_{23}B_6 and $\alpha\text{-Fe}$ were simulated. In the case of Sample-20 a broad and high background intensity due to the amorphous structure is observed even after the annealing at

Fig. 2 X-ray diffraction profiles of Sample-10 and Sample-20, annealed at 853 K.

853 K. No diffraction peaks corresponding to the stable $\text{Nd}_2\text{Fe}_{14}\text{B}$, Fe_{23}B_6 and $\alpha\text{-Fe}$ phases appeared at this annealing stage. Characteristic diffraction peaks from $\text{Fe}_{3.5}\text{B}$ and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ which do not overlap each other appear at $2\theta = 37.7, 44.9, 48.4$ and 54.5° for $\text{Fe}_{3.5}\text{B}$ and at $2\theta = 34.6, 39.1, 41.3$ and 50.6° for $\text{Nd}_2\text{Fe}_{23}\text{B}_3$. In the intensity profile from Sample-10, diffraction intensities from both of the $\text{Fe}_{3.5}\text{B}$ and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ phases are strong and the peak-widths of $\text{Fe}_{3.5}\text{B}$ are wider than those of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$. On the other hand, in the profiles from Sample-20, the intensities from $\text{Fe}_{3.5}\text{B}$ are much stronger than those from $\text{Nd}_2\text{Fe}_{23}\text{B}_3$. It was suggested that the primary phase in crystallization are soft magnetic $\text{Fe}_{3.5}\text{B}$ and $\text{Nd}_2\text{Fe}_{23}\text{B}_3$, and the grain size of $\text{Fe}_{3.5}\text{B}$ precipitates becomes smaller than those of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ in the first stage of crystallizations. At the beginning of crystallization, however, the $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ phase with a complex crystal structure is thought to grow later than the growth of $\text{Fe}_{3.5}\text{B}$. Figure 3 compares the TEM bright field images of Sample-10 and -20 annealed at 853 K. In Sample-10 (Fig. 3(a)) the grains of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Fe}_{3.5}\text{B}$ are mostly larger

than 10 nm, while in Sample-20 (Fig.3(b)) smaller precipitates of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Fe}_{3.5}\text{B}$ are observed in the amorphous matrix. These structural morphologies are in agreement with those expected from X-ray diffraction.

From TEM and X-ray diffraction studies for the as-formed and early stage of crystallization (Figs. 1 to 3), a large difference has been found between the structural morphologies of the two samples especially in the primary stage of crystallization. It is considered that the difference is closely related to their structural difference in the as-formed amorphous structures. In order to obtain a detailed structural relation between the amorphous and annealed structure in these alloys, it is worth to perform atomic pair distribution function (PDF) analysis of the as-formed specimens of these alloys in detail.

3.2 Electron diffraction PDF analysis for as-formed amorphous alloys

Although we could not find an appreciable structural difference in the as-formed amorphous structures of the two specimens by HREM, there must be a difference in atomic arrangements in these structures. Because of the advantage of electron diffraction with strong electron scattering up to a high special frequency range, we used electron diffraction PDF analysis technique to obtain structural information from the as-formed amorphous alloys with different cooling rates. Averaged intensities $\langle I(Q) \rangle$ were obtained along the radial direction in reciprocal space. In recording the halo diffraction intensity profiles, the energy-filtered diffraction intensity profiles were used up to the Q values of 120 nm^{-1} . And the SAED intensity profiles from $Q = 120$ to 200 nm^{-1} taken without energy filter were used for higher frequency part of $\langle I(Q) \rangle$. This is because the second-order aberration of the energy filter causes a diffraction intensity dumping in higher scattering angle in the energy filtering. After subtraction the background intensity which smoothly links the middle points between the intensity maxima and minima of the halo-intensity profile, the reduced interference function $i(Q)$ can be obtained. The PDF $g(r)$ can be calculated from $Qi(Q)$ by

Fig. 3 Bright field images of Sample-10 (a) and Sample-20 (b) annealed at 853 K.

Fig. 4 PDF profiles of amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$ for Sample-10 (a) and Sample-20 (b).

way of the Fourier transform of the function. Figures 4(a) and (b) show the experimental PDF profiles obtained from Sample-10 and -20, respectively. In these, two subsidiary risings appear at the radial distances $r = 0.20$ and 0.30 nm beside the first main peak at $r = 0.25$ nm. Allowing for the atomic radii of Nd, Fe, and B, the distances of 0.20 , 0.25 and 0.30 nm were judged to be B-Fe, Fe-Fe, Nd-Fe correlation peaks, respectively. It should be noted that the correlation peak for Fe-B was clearly obtained in the present electron diffraction PDF analysis due to the large electron scattering from B atoms. Because of the difficulty in separating the Fe-B and Fe-Nd subsidiary correlation profiles from mean Fe-Fe profile, the detailed structural difference between the two specimens was not able to be understood until the Reverse Monte-Carlo (RMC) structure simulations were performed.

The RMC simulated PDFs for both of the Sample-10 and -20 are shown in Figs. 5(a) and (b), and are in good agreement with their corresponding experiment PDFs. The simulated partial PDFs for Fe-Fe, Fe-Nd, and Fe-B are also shown in Figs. 5(a) and (b). Table 1 summarizes the atomic coordination numbers obtained from the partial pair distribution functions. The coordination polyhedra with central Nd atoms in the crystalline phase of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ ²⁷⁾ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ ²⁸⁾ have the 20 coordination atoms. Both of the total coordination number for the nearest neighbor Nd-Fe, Nd-Nd and Nd-B (shown as CN_{total}) around Nd in the as-formed specimens are less than that of the crystalline phases. On the other hand, the CN_{total} around Fe in as-formed specimens are comparable to those of the crystalline phase; bcc-Fe($CN:12$), $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ ($CN:12-14$) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($CN:12-14$).²⁸⁾ The obtained CN_{total} with central Fe atoms are as comparable as the averaged CN values for Fe in these phases. The coordination polyhedra with central B in the crystalline phase of $\text{Fe}_{3.5}\text{B}$, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ have distorted trigonal prism structures and these have 8 or 9 coordination atoms. These coordination numbers are comparable to those of B-centered polyhedra in the as-formed specimens. It is concluded from Table 1 that (1) the atomic coordination number around Fe and B atoms in the as-formed structures are more or less similar to those found in crystalline $\text{Fe}_{3.5}\text{B}$, $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ while (2) the atomic arrangements surrounding Nd atoms have less coordination atom than those

Fig. 5 Experimental and RMC-calculated $g(r)$ profiles for Sample-10 (a) and Sample-20 (b). Partial $g_{\text{Nd-Fe}}(r)$, $g_{\text{Nd-Fe}}(r)$ and $g_{\text{Fe-B}}(r)$ are shown together with the calculated total $g(r)$.

Table 1 Atomic coordination numbers from the partial pair distribution functions on the basis of RMC-simulated structure models for sample-10 and 20.

Pairs	Sample-10		Sample-20	
	CN	CN_{total}	CN	CN_{total}
Nd-Nd	0.68		0.71	
Nd-Fe	12.60	16.25	12.81	16.51
Nd-B	2.97		2.99	
Fe-Nd	0.76		0.76	
Fe-Fe	11.54	14.03	11.56	14.04
Fe-B	1.73		1.72	
B-Nb	0.72	7.91	0.73	7.87
B-Fe	7.19		7.14	

in crystalline $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phases, and (3) in spite of different cooling rates there are no appreciable differences in averaged CN values with constituent atoms in these alloys.

In order to investigate a difference of local atomic configurations in the RMC simulated structure models for the two as-formed specimens, the Voronoi polyhedral

Fig. 6 Fraction of Voronoi-polyhedra around B atoms obtained from the RMC data for amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$.

analysis was performed which enables us to understand degree of distortion of polyhedra around the constituent atoms. Figures 6(a) and (b) are the environmental polyhedral structures for the central B atoms for Sample-10 and -20, respectively. In Fig.6, the index '044000' is for the Archimedean anti-prism structure, and the index '036000' is for the 9-coordinated trigonal prism structure with three capping atoms. The indexes '028000' and '036100' are deformed prism type structure. These prism structures can be seen in the crystalline phase of Fe_3B , $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$. In Fe-B amorphous structures, B centered prism structures have been reported in many studies.^{29,30)} It has been revealed that the B-centered prism structures with indices of '044000' and '036000' forming structural units of crystalline borides are found more frequently in Sample-10 than in Sample-20. Figures 7(a) and (b) are the environmental polyhedral structures for the central Fe atoms for Sample-10 and 20, respectively. In Fig. 7, the index '0364000' is for the deformed bcc structure. These coordination polyhedra are frequently observed in $\text{Fe}_{90}\text{Zr}_7\text{B}_3$.²¹⁾ Other indexes '038200' and '028400' are also the deformed bcc type structure, and '00 12 000' and '01 10 200' correspond to the icosahedron and the deformed icosahedron type structure, respectively. These are all closely linked with respect to the pentagonal dominance.³¹⁾ In both of the figures with central Fe-atoms, we find variety of Voronoi polyhedra with coordination numbers of 12-14, and no appreciable characteristic structural difference was found between these structures. Consequently, the environmental polyhedra structures with central Fe and B atoms similar to those in the Fe_3B , $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystalline phase can be found, and B central prism structure can be found more in the as-formed structure in Sample-10 than in Sample-20. With respect to the Nd-centered polyhedra, their coordination numbers are distributing between 12 to 20 in both of the specimens with

Fig. 7 Fraction of Voronoi-polyhedra around Fe atoms obtained from the RMC data for amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$.

the average coordination of about 16 (much smaller than those in the crystalline phases), and we could not find a characteristic difference in Nd-centered polyhedral structures in these specimens. It has been demonstrated that the Voronoi-polyhedral analysis is thus effective in finding differences of polyhedral structures with respect to the distortions of polyhedra.

4. Conclusion

In the HREM images, local lattice fringe regions caused by atomic MRO structure were observed in both of the amorphous $\text{Nd}_{4.5}\text{Fe}_{77}\text{B}_{18.5}$ specimens formed under different cooling rates. Electron diffraction structural analysis of the two amorphous phase revealed that atomic local order structures with B-centered deformed prism-clusters and Fe-centered deformed bcc or icosahedral clusters typical of the basic structural units of the related crystalline phases are found in both of the as-formed specimens. The frequent observation of the B-centered prism structures with the Voronoi indices '044000' and '036000' in Sample-10 with a lower cooling rate strongly supports the experimental easier formation of the Fe_3B nanocrystals in Sample-10 on the primary crystallization stage than in Sample-20. The average coordination number of Nd-centered polyhedra is much smaller than that of crystalline phases, meaning that the structural environment for the central Nd differs largely from that in the related crystalline phases. Atomic arrangements around Nd different from those in crystalline phases must be closely related to the slow nucleation of the Nd-compound phase on annealing. This scheme is able to explain the experimental result that the appearance of the Nd-compound phase ($\text{Nd}_2\text{Fe}_{23}\text{B}_3$) is retarded on annealing compared with the appearance of the Fe_3B phase (see Fig.2). Not only the growth of Fe_3B but also the growth of $\text{Nd}_2\text{Fe}_{23}\text{B}_3$ are slower

in Sample-20 than in Sample-10, in spite of the no clear difference in the Nd-circumstances in the Voronoi polyhedral analysis. A more detailed structure analysis, especially for the Nd-circumstances, is necessary to explain the result.

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