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Small-Angle Neutron Scattering Study on Fe-Cu-Nb-Si-B Nanocrystalline Alloys

M. Ohnuma*†, J. Suzuki**, S. Funahashi**, T. Ishigaki*, H. Kuwano* and Y. Hamaguchi*††

*Muroran Institute of Technology, Muroran, Hokkaido 050, Japan
**Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan

Small-angle neutron scattering (SANS) from Fe-Cu-Nb-Si-B nanocrystalline alloys has been measured in a magnetic field. Significant differences between nuclear and magnetic scattering profiles have been observed. Most of the magnetic scattering profiles take an asymptotic form of $I(q) \sim q^{-3}$ in a high-q region, which indicates that the distribution of local magnetization is not uniform in a BCC-Fe grain. All the nuclear scattering profiles, on the other hand, take an asymptotic form of $I(q) \sim q^{-2}$, which implies that the concentration fluctuation of the Ornstein-Zernike type exists in nanocrystalline alloys. However, no such fluctuation is observed in Fe-Cu-Si-B and Fe-Nb-Si-B alloys which do not have any nanocrystalline structures. These results suggest that the concentration fluctuation of the Ornstein-Zernike type seems to be closely related to the nanocrystalline microstructures.

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I. Introduction

Fe-Cu-Nb-Si-B nanocrystalline alloys, known as FINEMET, are prepared by annealing amorphous Fe-Si-B alloys which contain a small amount of copper and niobium. These nanocrystalline alloys containing ultra fine BCC-Fe grains show much better magnetic permeability than the mother amorphous alloy[1]-[3]. Concentration distribution and local structures around dilute additives (copper and niobium) are very important to understand a mechanism for such a nanocrystalline structure and the excellent magnetic permeability. Atom probe field ion microscope (AP-FIM)[4] and EXAFS[5] have been carried out to examine the microstructure. The concentration distribution obtained by AP-FIM is restricted within a narrow region. Since small-angle neutron scattering (SANS) has the great advantage for observing nanoscale structures including magnetic structures, in this study the SANS has been measured in Fe-Cu-Nb-Si-B alloys in a magnetic field and separated into nuclear and magnetic components.

II. Experimental Procedures

1. Sample preparations

$Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ amorphous alloy ribbons with 20 mm wide and 0.02 mm thick were provided from Hitachi Metals Ltd. Heat treatments were performed in a nitrogen gas atmosphere at 723 K for 10 and 60 min, 773 K for 10 and 60 min, and 823 K for 60 min. The last heat treatment is the optimum condition for obtaining the excellent magnetic permeability. Transmission electron micrographs of these samples are shown in Fig. 1. A

Table. 1 Compositions and heat treatment conditions of Fe-Cu-Nb-Si-B amorphous alloys.

Compositions (at%)					Annealing temperature (K)	Annealing time (min)
Fe	Cu	Nb	Si	B		
75.8	1.0	2.5	13.5	7.2	723	10
					723	60
					773	10
					773	60
					823	60
74.5	0	3.0	13.5	9.0	773	60
					823	60
74.0	0.5	3.0	13.5	9.0	773	60
					823	60
73.5	1.0	3.0	13.5	9.0	773	60
					823	60
73.0	1.5	3.0	13.5	9.0	773	60
76.5	1.0	0	13.5	9.0	773	60
71.5	1.0	5.0	13.5	9.0	773	60
					823	60

† Graduate Student, Muroran Institute of Technology. Research Student of JAERI. Present address: National Research Institute for Metals, Tsukuba, Ibaraki 305, Japan.

†† Present address: Japan Atomic Energy Research Institute, Ibaraki 319-11, Japan.

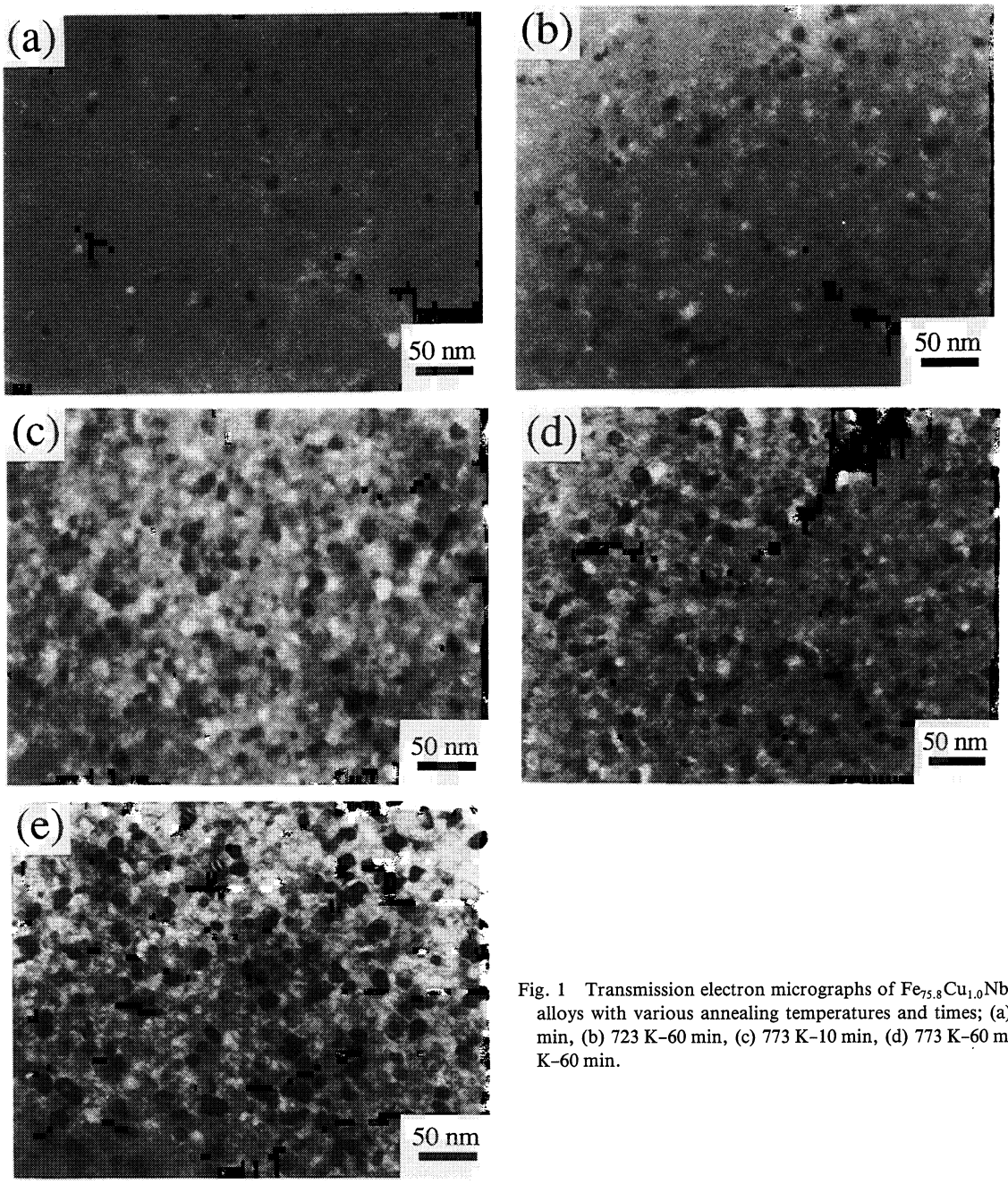


Fig. 1 Transmission electron micrographs of $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys with various annealing temperatures and times; (a) 723 K-10 min, (b) 723 K-60 min, (c) 773 K-10 min, (d) 773 K-60 min, (e) 823 K-60 min.

volume fraction of BCC-Fe grains in these samples increases in alphabetical order in Fig. 1.

$Fe_{77.5-x-y}Cu_xNb_ySi_{13.5}B_{9.0}$ amorphous alloys were also provided from Hitachi Metals Ltd. Compositions and heat treatment conditions of these alloys are shown in Table 1 together with the conditions of $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloy. These samples were prepared to investigate the effects of copper and niobium contents on SANS profiles. Transmission electron micrographs of these alloys are shown in Fig. 2. Ultra fine BCC-Fe grains can be seen only in the samples containing both copper and niobium.

2. SANS measurements

SANS experiments were performed by the small-angle neutron scattering instrument (SANS-J) installed at the cold neutron source of the research reactor (JRR-3M) in JAERI. Samples for SANS measurements were prepared by cutting the Fe-Cu-Nb-Si-B alloy ribbons into 20 mm × 20 mm and stacked up to 12 sheets. A magnetic field was applied on a sample surface perpendicular to the direction of neutron beams with the wavelength of $\lambda = 0.625$ nm. SANS intensity was collected with a 2-dimensional position sensitive detector. The experimental configuration is drawn in Fig. 3 schematically. For unpolarized neutrons SANS intensity $I(q=|q|)$ is expressed by

$$I(q) = I(q)_{nuclear} + \langle \sin^2 \alpha \rangle I(q)_{magnetic} \quad (1)$$

where α is an angle between scattering vector q and mag-

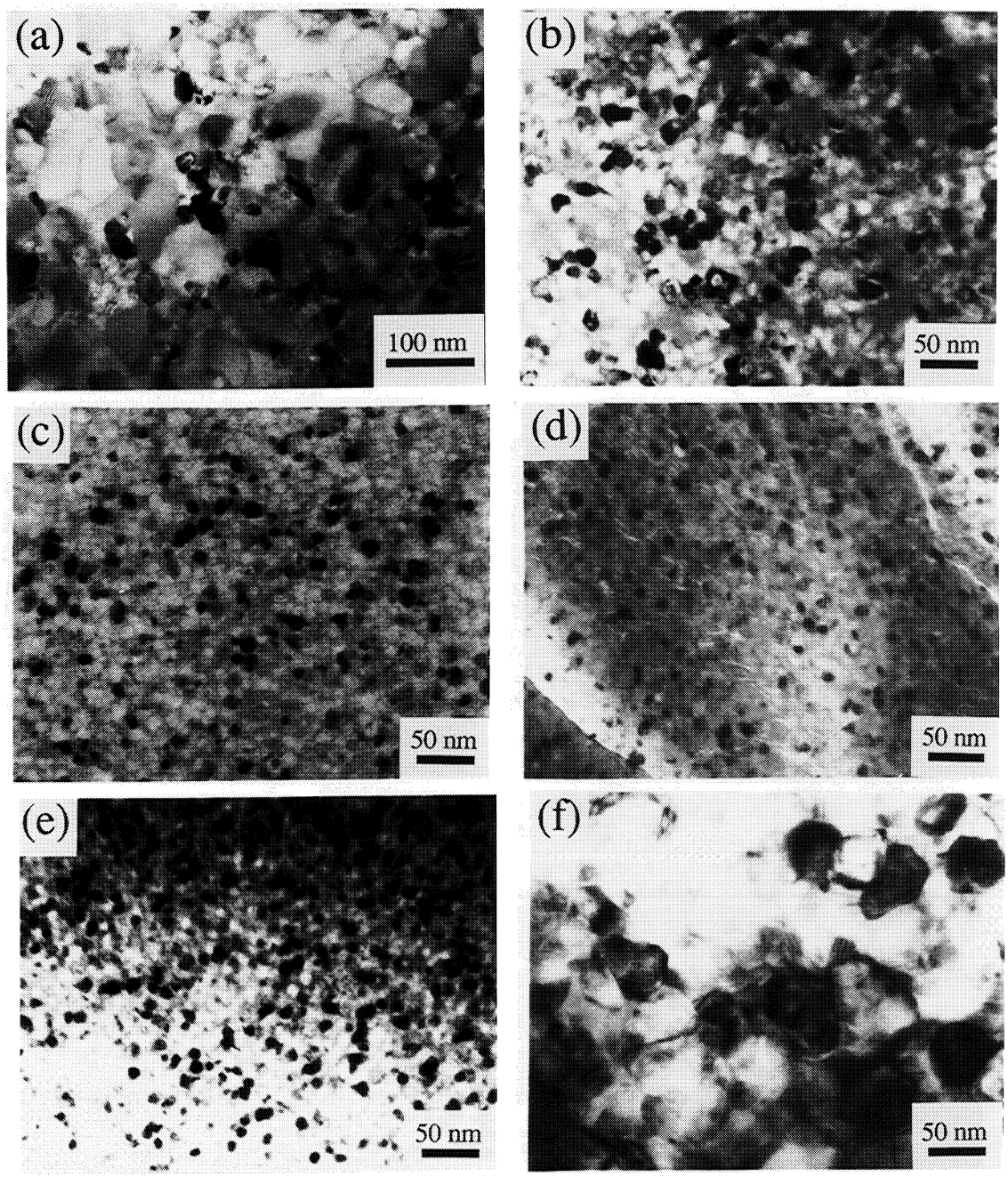


Fig. 2 Transmission electron micrographs of $Fe_{77.5-x-y}Cu_xNb_ySi_{13.5}B_{9.0}$ alloys with various annealing temperatures and times; (a) 0.0 at%Cu, 3.0 at%Nb, 823 K-60 min, (b) 0.5 at%Cu, 3.0 at%Nb, 823 K-60 min, (c) 1.0 at%Cu, 3.0 at%Nb, 823 K-60 min, (d) 1.5 at%Cu, 3.0 at%Nb, 823 K-60 min, (e) 1.0 at%Cu, 5.0 at%Nb, 823 K-60 min, (f) 1.0 at%Cu, 0.0 at%Nb, 773 K-60 min.

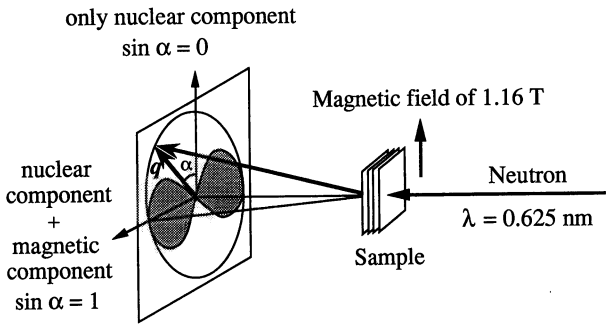


Fig. 3 Schematic drawing of small-angle neutron scattering measurement in a magnetic field.

netization vector of a magnetic domain in the sample and the bracket $\langle \cdots \rangle$ denotes the average over the domains. α corresponds to an angle between the scattering vector q and the direction of the magnetic field when the magnetic field is strong enough to saturate the sample. The magnetic field of $H=1.16$ T was applied for achieving this condition. A remarkable difference was observed between SANS patterns measured with and without the magnetic field as shown in Fig. 4. By analyzing the anisotropic SANS pattern in the saturation field, the magnetic scattering $I(q)_{magnetic}$ and the nuclear scattering $I(q)_{nuclear}$ can be separately determined.

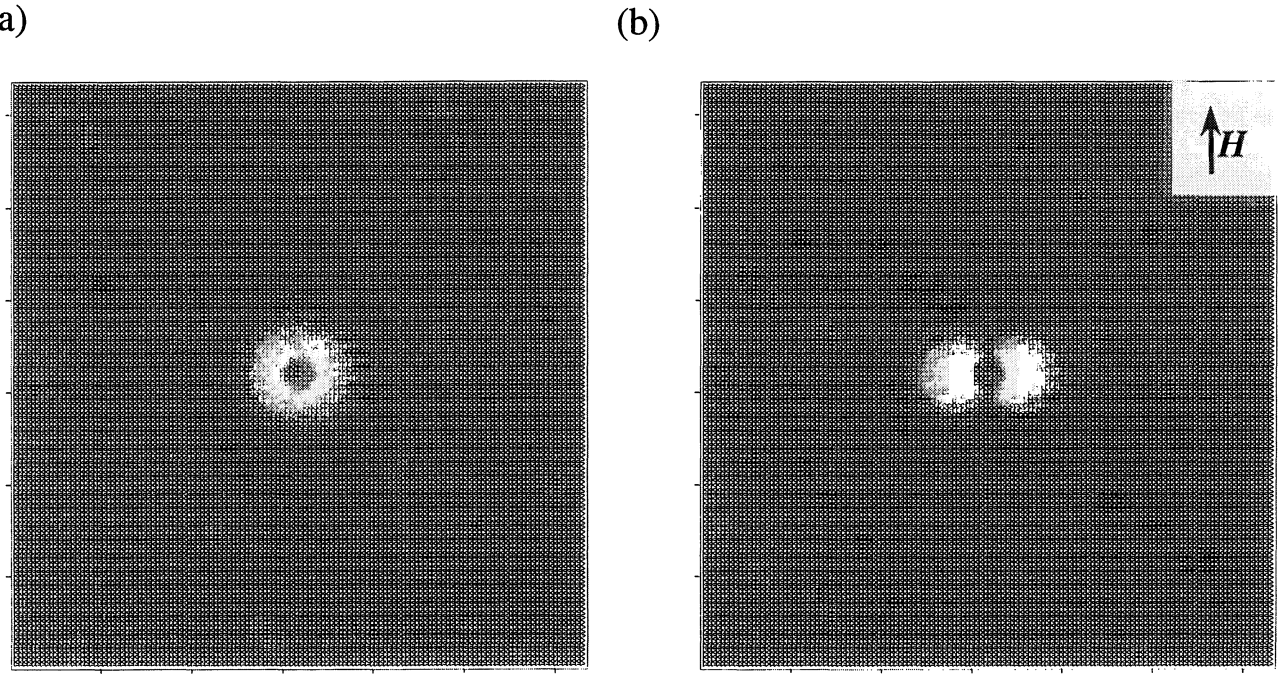


Fig. 4 2-dimensional scattering patterns of $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys annealed at 773 K for 60 min measured with magnetic fields of (a) 0 T and (b) 1.16 T. Brightness is propotional to scattering intensity.

III. Results and Discussion

1. Magnetic scattering from $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloy

Figure 5 shows magnetic scattering profiles of $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys with various annealing temperatures and times. Above $q=0.4\ nm^{-1}$, the scattering curves take an asymptotic form of $I(q)\sim q^{-3}$ except the curve of the sample annealed at 723 K for 10 min. This power (-3) of q indicates that the distribution of local magnetization is not uniform in a BCC-Fe grain, because the scattering from a grain with uniform local magnetization and rigid interface follows the well-known Porod law ($I(q)\sim q^{-4}$). Boucher *et al.*[6] showed that the asymptotic form of $I(q)\sim q^{-3}$ appears if a radial distribution of a scattering density $\rho(r)$ in a grain with a radius R is given by

$$\rho(r)=\rho(0)[1-(r/R)^2]^{-0.5} \quad (2)$$

where $\rho(r)$ corresponds to the deviation of local magnetization from the average magnetization. This function describes the density profile which is very large near the grain boundary. However, it is not adequate to express the actual profile because the local magnetization should not be large at the grain boundary but inside the BCC-Fe grain. Thus, the following density profile is proposed;

$$\rho(r)=\rho(0)\{2-[1-(r/R)^2]^{-0.5}\} \quad (3)$$

This formula shows that the local magnetization at the grain boundary is much lower than the average magnetization and leads to the scattering intensity

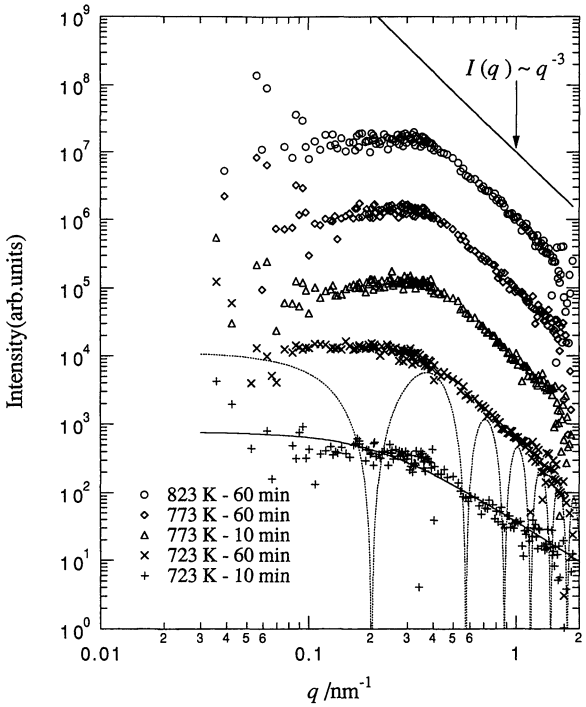


Fig. 5 Magnetic scattering profiles for $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys with various annealing temperatures and times, which were measured in the magnetic field of 1.16 T. The solid and dotted lines correspond to the ones calculated by eq. (6) for $\xi=4.4$ nm and by eq. (4) for $R=11$ nm, respectively. Each scattering profile is shifted by 10 along the y-axis, for convenience.

$$I(q)=\rho(0)^2R^3\{8\pi\,[\sin(qR)-qR\cos(qR)]/(qR)^3 - 2\pi^2J_1(qR)/(qR)\}^2 \quad (4)$$

where J_1 is a Bessel function of order 1. When $q\gg R^{-1}$,

the scattering intensity gives an asymptotic form of $I(q) \sim q^{-3}$. Consequently, the q^{-3} dependence in Fig. 5 is explained by the distribution of local magnetization in the Fe grains.

On the other hand, in scattering profiles in Fig. 5 except the profiles of the samples annealed at 723 K for 10 and 60 min, a peak around $q=0.3$ nm^{-1} owing to the inter-grain interference is observed. Thus, these samples may be thought to be composed of highly concentrated grains defined by eq. (3). From this peak position it is deduced that the space between grains is about 20 nm. This value almost coincides with the value ($\approx$20 nm) obtained by the TEM observation. For the sample annealed at 723 K for 60 min, such a peak is hardly observed. This indicates that the interference effect is not significant in this sample. Namely, the distance between grains is much larger than the radius of the grain. This radius includes the region near the grain boundary in which the local magnetization is lower than the average magnetization and is estimated from eq. (4). Though it is difficult to estimate the value of R exactly because of the grain size distribution, the value is about 11 nm. In the case of the alloy annealed at 723 K for 10 min, the scattering curve changes its slope around $q=0.4$ nm^{-1} and takes an asymptotic form of $I(q) \sim q^{-2}$ above this value. These features suggest that a magnetic fluctuation with a correlation length of 4.4 nm dominantly exist in an initial stage of crystallization. Such a fluctuation following the Ornstein-Zernike formula will be discussed in the next section.

2. Nuclear scattering from $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloy

Nuclear scattering profiles of the $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys shown in Fig. 6 are fairly different from the magnetic ones in Fig. 5. In a high-q region all the scattering profiles take a form of $I(q) \sim q^{-2}$, although in the samples annealed at 723 K for 10 and 60 min, the intensity profile deviates from the q^{-2} curve in the low-q region. No deviation in the low-q region for the scattering profiles of the samples annealed at 773 and 823 K implies the existence of structures with a long range correlation. Taking account of no significant change of a volume during crystallization, the fluctuation owing to a mass density difference between a BCC-Fe grain and an amorphous matrix is probably negligible. Then, we can conclude that the concentration fluctuation of the Ornstein-Zernike type exists in the $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys. The Ornstein-Zernike type's fluctuation takes the correlation of the scattering density $\rho(r)$ depending on the concentration distribution which is expressed as

$$\langle\{\rho(r)-\bar{\rho}\}\{\rho(r')-\bar{\rho}\}\rangle = |r-r'|^{-1} \exp(-|r-r'|/\xi) \quad (5)$$

where $\bar{\rho}$ is the average scattering density, the bracket $\langle\cdots\rangle$ is the thermal average and ξ denotes the correlation length. When the Ornstein-Zernike type's fluctuation exists, the scattering intensity $I(q)$ is given by

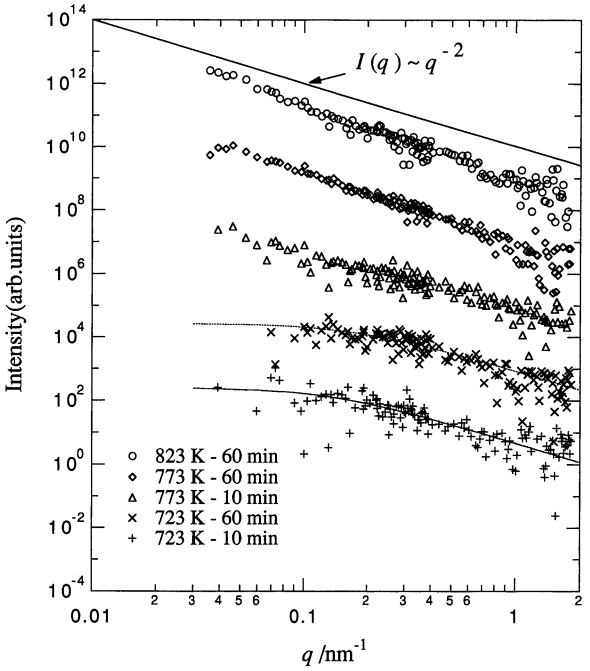


Fig. 6 Nuclear scattering profiles for $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys with various annealing temperatures and times, which were measured in the magnetic field of 1.16 T. The solid and dotted lines correspond to the ones calculated by eq. (6) for $\xi=7.2$ and $\xi=5.6$ nm, respectively. Each scattering profile is shifted by 100 along the y-axis, for convenience.

$$I(q)=I(0)/(1+\xi^2q^2) \quad (6)$$

Correlation lengths of 7.2 and 5.6 nm calculated in the samples annealed at 723 K for 10 and 60 min, respectively, are comparable to the BCC-Fe grain size ($\approx$10 nm) observed by the TEM. Although from the SANS measurement it is difficult to specify which element is fluctuating in concentration in a multicomponent system, these correlation lengths imply that there are some differences of concentration between even adjacent BCC-Fe grains. However for other samples the correlation lengths are longer than 50 nm estimated from a minimum of q measured in this study and can not be detected by TEM, suggesting that at least adjacent BCC-Fe grains have similar concentrations.

Namely the concentration distribution in these alloys taking the q^{-2} dependence seems to be a transition state where BCC-Fe crystals with various concentrations exist.

The great difference between the nuclear and the magnetic scattering profiles was observed, as described above. These results suggest that the concentration fluctuation does not have a clear boundary in the BCC-Fe grains, although the existence of the grain boundary which may be nonmagnetic is essential for describing the magnetic scattering profiles as discussed above.

3. SANS from $Fe_{77.5-x-y}Cu_xNb_ySi_{13.5}B_{9.0}$ alloys

We have also investigated the effects of copper and niobium contents on scattering profiles. Both nuclear and magnetic scattering from the alloys containing both

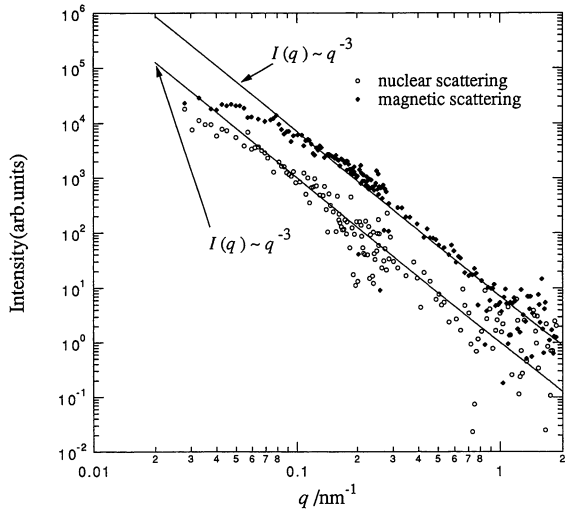


Fig. 7 SANS profiles for $Fe_{74.5}Nb_{3.0}Si_{13.5}B_{9.0}$ alloy annealed at 823 K for 60 min measured in the magnetic field of 1.16 T.

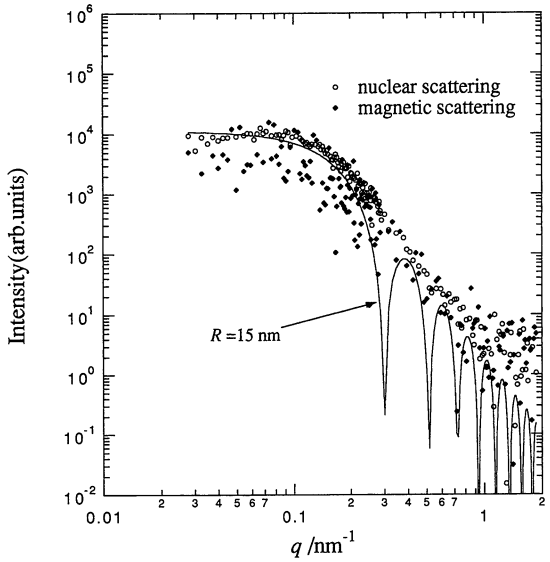


Fig. 8 SANS profiles for $Fe_{76.5}Cu_{1.0}Si_{13.5}B_{9.0}$ alloy annealed at 773 K for 60 min measured in the magnetic field of 1.16 T. The solid line corresponds to the one calculated by assuming a uniform grain model.

copper and niobium show the same features of $Fe_{75.8}Cu_{1.0}Nb_{2.5}Si_{13.5}B_{7.2}$ alloys described above. However, other alloys without copper or niobium contents show remarkably different profiles, especially in nuclear scattering. Both nuclear and magnetic scattering profiles of $Fe_{74.5}Nb_{3.0}Si_{13.5}B_{9.0}$ alloy show the asymptotic form of $I(q) \sim q^{-3}$ (eq. (4)) in a high-q region, and those of $Fe_{76.5}Cu_{1.0}Si_{13.5}B_{9.0}$ alloy show the asymptotic form of $I(q) \sim q^{-4}$ corresponding to the Porod law, which indicates the existence of grains with uniform scattering density and rigid interface. These results are shown in Figs. 7 and 8, respectively. From X-ray diffraction study, it has been identified that the matrix is iron boride crystals in these two samples (BCT-Fe_3B and $Fe_{23}B_6$ for the $Fe_{74.5}Nb_{3.0}Si_{13.5}B_{9.0}$ alloy and Fe_2B for the $Fe_{76.5}Cu_{1.0}Si_{13.5}B_{9.0}$ alloy). By assuming a uniform grain model without taking into account of size distribution, a grain radius is calculated to be 15 nm in Fig. 8. It is thought to originate from the BCC-Fe grains. The value is rather small in comparison with the TEM micrograph shown in Fig. 2(f). Thus, it is likely to be difficult to compare these scattering profiles directly with those of the alloys containing both copper and niobium which do not have any iron boride in their matrix. But it is confirmed that the asymptotic form of $I(q) \sim q^{-2}$ is observed only in the samples containing both copper and niobium. Because those samples consist of the ultra fine BCC-Fe grains and the amorphous matrix, the concentration fluctuation of the Ornstein-Zernike type seems to be closely related to these microstructures.

IV. Conclusions

Small-angle neutron scattering (SANS) of Fe-Cu-Nb-Si-B nanocrystalline alloys has been measured in the magnetic field. By separating SANS into the nuclear and the magnetic components, it is confirmed that;

(1) The magnetic scattering shows that the distribution of local magnetization is not uniform in a BCC-Fe grain,

(2) The nuclear scattering shows that the Ornstein-Zernike type's fluctuation of the concentration exists in nanocrystalline alloys,

(3) The concentration distribution in these alloys seems to be a transition state where BCC-Fe crystals with various concentrations exist.

(4) The asymptotic form of $I(q) \sim q^{-2}$ is observed only in the samples containing both copper and niobium.

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