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Microstructure of nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy

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Nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens with a wide range of different nanostructures can be produced by annealing the amorphous alloy in the temperature range from 700 K to 1060 K. The nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens prepared between 700 K and 760 K have a microstructure of the 4–9 nm fcc (Fe, Ni) solid solution crystallites embedded in the amorphous matrix. The nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens obtained between 780 K and 910 K show a polycrystalline microstructure of the major cubic $(Fe, Ni, Mo)_{23}B_6$ phase with grain sizes from 20 nm to 40 nm and the minor fcc (Fe, Ni) solid solution crystallites of about 10 nm. The nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens produced between 930 K and 1060 K represent a polycrystalline microstructure of the 12–25 nm fcc (Fe, Ni) solid solution crystallites and the 45–240 nm cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites. © *1999 Kluwer Academic Publishers*

1. Introduction

Crystallization of amorphous alloys has been much studied, and recently crystallization has been exploited as a means to produce nanostructured alloys. Since the first report of the nanostructured Fe-Si-B-Nb-Cu alloy prepared by crystallization of the amorphous alloy and its excellent soft magnetic properties [1], several nanostructured systems such as Fe-M-B (M=Zr, Hf, and Nb) [2] and Fe-P-C-Ge-Cu [3] which have excellent soft magnetic properties have been produced by the crystallization technique. Similar to the preparation of the amorphous alloys, nanostructured alloys can be also obtained by directly quenching liquid alloys in a suitable cooling rate [4]. In our previous works, the Ni-based and (Cu, Ni)-based nanostructured alloys were prepared by the crystallization technique, and their microstructure, mechanical, and thermal properties have been studied [5–7].

Amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy is one of the good soft magnetic materials, owing to its moderate saturation magnetization, high permeability, low coercivity, low saturation magnetostriction, and low core loss [8]. Judging by experience with the soft magnetic nanostructured alloys, the crystallization of the good soft magnetic amorphous alloys into nanostructure, sometimes called nanocrystallization, may lead to the improvement of the soft magnetic properties.

With the purpose to seek new soft magnetic nanostructured alloys, the amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy has been heat-treated to obtain the nanostructure in the present work. So far all the soft magnetic nanostructured alloys prepared by the crystallization technique have had a homogeneous nanostructure of the body-centered cubic (bcc) iron solid solution crystallites with grain sizes of typically 10–15 nm and random orientation. However, it is of interest to examine whether the nanostructured alloys based on the face-centered cubic (fcc) iron solid solution can possess good soft magnetic properties. The primary crystallization phase from the amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy during crystallization is an fcc iron solid solution. In our work the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ with a wide range of nanostructure, from fcc (Fe, Ni) solid solution crystallites of a few nanometers in amorphous matrix, through the mixture of a major fraction of cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites of 20–40 nm and a minor fraction of fcc (Fe, Ni) solid solution crystallites of about 10 nm, to the mixture of coarse cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites of 45–240 nm and fcc (Fe, Ni) solid solution crystallites of 12–25 nm, have been obtained by crystallizing the amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy.

While the studies of the magnetic properties and other properties of the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ with different microstructures are still in progress, we report in the present paper the preparation processes, the X-ray diffraction and transmission electron microscope analysis results, and the relationship between the microstructure and the preparation processes of the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ alloys.

2. Experimental procedure

The amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy (Metglas 2826MB) in the form of ribbons about 20 μm thick and 4 cm wide was purchased from the Nippon Amorphous Metals Corporation. The amorphous ribbons were annealed in a vacuum furnace at various temperatures and then analyzed by X-ray diffraction and transmission electron microscopy to get information about the crystallization kinetics of the amorphous alloy. On the basis of the crystallization kinetics of the amorphous alloy the amorphous ribbons were annealed in vacuum of about 6×10^{-4} Pa at various temperatures in order to obtain the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens with different nanostructures.

All the specimens annealed at various temperatures were analyzed by X-ray diffraction (XRD). The XRD analysis was performed on a Rigaku D/Max-2400 diffractometer using $\mathrm{Cu}K\alpha$ radiation (40 kV, 40 mA), scan steps of 0.02°, a receiving slit of 0.15 mm, and a graphite monochromator for the diffracted beam. Some diffraction peaks were fitted with Gaussian curves by a least-squares refinement to determine the original full widths at half maxima (FWHM). The real FWHM were obtained by subtracting the instrument FWHM measured with a coarse-grained specimen from the original FWHM. The mean grain sizes of the observed phases were estimated from the real FWHM according to the Scherrer formula. The mean grain sizes of the as-annealed specimens were finally determined by the transmission electron microscope (TEM) observations. The annealed specimens were thinned by a double-jet thinner for TEM analysis. The TEM observations and the selected-area electron diffraction (SAD) were undertaken on a Hitachi H600 electron microscope working with a voltage of 100 kV.

3. Results and discussion

The amorphous state of the as-received amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy ribbons was proved by an amorphous diffuse peak in XRD. The crystallization temperature T_x of the as-received amorphous ribbons was determined to be 700 K by differential thermal analysis measurements at a heating rate of 10 K/min on the Du Pont 1090B thermal analyzer. To analyze the crystallization kinetics of the amorphous alloy, the specimens obtained by different annealing treatments were examined by XRD. The diffraction pattern of the primary crystallization phase of the amorphous alloy can be indexed with the face-centered cubic (Fe, Ni) solid solution [9, 10]. The diffraction pattern of the secondary crystallization phase can be easily indexed with the diffraction data of the cubic $(Fe,Ni,Mo)_{23}B_6$ compound [11]. Our results of the crystallization kinetics analysis in the temperature range of interest on the amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy are in good agreement with the radial distribution function analysis results of the annealed $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens [11]. An early crystallization study on the amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ alloy found the primary crystallization phase of the amorphous alloy to be the cubic $Fe_{23-x}Ni_xB_6$ phase [9]. In the crystallization study the crystallization behaviors of the amorphous alloy were not carefully examined in the temperature range from its crystallization temperature to 770 K in which the primary crystallization phase crystallizes from the amorphous matrix. The crystallization sequence determined from the samples containing two crystallized phases obtained by annealing the amorphous alloy above 770 K would be unreliable. In our present work more than five specimens were annealed in this temperature range. The systematic phase analysis of these specimens may give a reliable result of the crystallization sequence of the amorphous alloy. In our work the fcc (Fe, Ni) solid solution was found to be the primary phase to crystallize from the amorphous matrix. The cubic $(Fe,Ni,Mo)_{23}B_6$ compound is the secondary phase to crystallize from the amorphous matrix.

It was found in our experiments that the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens with a wide range of different nanostructures can be produced by annealing the amorphous ribbons in the temperature range from its crystallization temperature $T_x = 700$ K to 1060 K. For simplicity, the microstructure of the nanostructured specimens are discussed in three groups according to the annealing temperature ranges with the annealing time fixed for an hour: (1) the low temperature range from 700 K to 760 K; (2) the moderate temperature range from 770 K to 910 K; (3) the high temperature range from 910 K to 1060 K.

Annealing the amorphous ribbon in the low annealing temperature range from 700 K to 760 K produces a nanostructure of the fcc (Fe, Ni) solid solution crystallites with an average grain size from 4 nm to 8 nm embedded in the residual nanometer-thick amorphous matrix with a mass fraction from 50% to 30%. The specimen obtained by annealing the amorphous ribbon at 740 K is a typical example for this annealing temperature range. The XRD pattern of this specimen shows several broad diffraction peaks overlapped on a diffuse peak. The broad diffraction peaks result from the nanometer-sized crystallites crystallized from the amorphous matrix, whereas the diffuse peak comes from the residual amorphous matrix. The broad diffraction peaks could be easily indexed with the diffraction data of the fcc (Fe, Ni) solid solution obtained in the same system [9]. The diffraction pattern was fitted with broad diffraction peaks and a diffuse peak as a base line by a least-squares refinement. The lattice constant of the fcc (Fe, Ni) solid solution was calculated to be $a = 0.3574$ nm from the observed diffraction peaks by Cohen's least-squares method. According to the composition dependence of the lattice constant of the fcc (Fe, Ni) solid solution [10], the fcc (Fe, Ni) solid solution crystallites in this specimen have the composition of approximately 47% Fe and 53% Ni (atomic percentage). The mass fraction of the residual amorphous phase was estimated to be about 40%. The average grain size of the fcc (Fe, Ni) solid solution crystallites was estimated to be about 6 nm from the real FWHM with the Scherrer formula. The SAD pattern of this specimen supports the identification of the fcc (Fe, Ni) solid solution in this specimen. The even intensity distribution on the SAD rings is indicative of the random orientation of the nanometer-sized fcc (Fe, Ni) solid solution crystallites. The B atoms may be mainly enriched in the grain boundaries as well as in the residual amorphous phase. The Mo atoms may be dissolved in the fcc (Fe, Ni) solid solution as well as in the amorphous matrix and the grain boundaries. The TEM observations revealed that this specimen represents a microstructure of the copious nanometer-sized fcc (Fe, Ni) solid solution crystallites. The nanometer-sized (Fe, Ni) crystallites are relatively uniform in size and equiaxed in shape. The mean grain size of the crystallites was determined to be 6 nm by the TEM dark and bright field observations. The residual amorphous matrix isolating the nanometer-sized fcc (Fe, Ni) solid solution crystallites is about 3 nm thick.

As the annealing temperature increases from the low temperature range, the cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites are formed at the cost of the fcc (Fe, Ni) phase and the amorphous matrix and become the major phase. The nanocrystallized fcc (Fe, Ni) solid solution crystallites decrease in fraction. The residual amorphous matrix decreases, and disappears at 780 K. Since the average grain size of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase is about twice greater than that of the fcc (Fe, Ni) phase, the mean grain size of the specimen increases drastically with increasing fraction of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase. Hence, the microstructure becomes nonuniform in grain size. Annealing the amorphous ribbon in the moderate temperature range from 770 K to 910 K produces a nanostructure of the fine nanometer-sized fcc (Fe, Ni) solid solution crystallites of about 10 nm in a minor fraction and the relatively coarse nanometer-sized cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites with an average grain size from 20 to 40 nm as a major phase. The mean grain size of the specimen increases from 9 nm to 38 nm, as the annealing temperature increases from 770 K to 910 K. For example, the specimen obtained by annealing the amorphous ribbons at 790 K shows an XRD pattern which can be indexed with the cubic $(Fe, Ni, Mo)_{23}B_6$ compound [12] and the fcc (Fe, Ni) solid solution. No diffuse peak was needed as a base line in fitting the XRD pattern for the FWHM determination, indicating no residual amorphous phase present in this specimen. The average grain size of that of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase and the fcc (Fe, Ni) phase in this specimen were estimated from their real FWHM by the Scherrer process to be 26 nm and 10 nm, respectively. The mass fraction of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase and that of the fcc (Fe, Ni) phase in this specimen were estimated to be about 98% and 2%, respectively. The lattice constant of the fcc (Fe, Ni) solid solution were calculated to be $a = 0.3573$ nm from the fitted peak positions by the Cohen's least-squares refinement, and that of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase was calculated to be $a = 1.0636$ nm. The rest of the B atoms may be dissolved in the grain boundaries. The TEM dark and bright field observations revealed that this specimen has a nonuniform microstructure. The fine crystallites distribute in the relative coarse crystallites. According to the XRD analysis results, the fine crystallites are mainly the fcc (Fe, Ni) phase, and the relatively coarse ones are mainly the cubic $(Fe, Ni, Mo)_{23}B_6$ phase. The mean grain size of this specimen was determined to 25 nm by the TEM dark and bright field observations. The even intensity distribution on the SAD diffraction rings is indicative of the random texture of the crystallites in the specimen.

As the annealing temperature increases further from the moderate temperature range, the fraction of the fcc (Fe, Ni) solid solution crystallites increase again and their average grain size increases gradually, and the cubic $(Fe, Ni, Mo)_{23}B_6$ phase decreases in fraction and increases drastically in grain size. As the annealing temperature increases in the high temperature range from 930 K to 1060 K, the fraction of the fcc (Fe, Ni) solid solution crystallites increase from 30% to 60% and their average grain size increases from 12 nm to 25 nm. Meanwhile, the fraction of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase decreases from 70% to 30% and its average grain size increases drastically from 45 nm to 240 nm. The mean grain size of the specimen increases from 42 nm to 100 nm. The microstructure becomes more nonuniform in the high temperature range. For example, the specimen obtained by annealing the amorphous ribbons at 960 K shows an XRD pattern of superimposed diffraction peaks of the fcc (Fe, Ni) solid solution and the cubic $(Fe, Ni, Mo)_{23}B_6$ phase. Both the fcc (Fe, Ni) solid solution and the cubic $(Fe, Ni, Mo)_{23}B_6$ phase in this specimen have almost an equal mass fraction, i.e., 50%. The diffraction peaks of the fcc (Fe, Ni) solid solution are broader than those of the cubic $(Fe, Ni, Mo)_{23}B_6$ phase, indicating that the fcc (Fe, Ni) solid solution crystallites are finer than the cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites. The average grain size of the fcc (Fe, Ni) solid solution crystallites and that of the cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites were estimated from their real FWHM by the Scherrer process to be 15 nm and 150 nm, respectively. The TEM dark and bright field observations revealed that this specimen has a polycrystalline microstructure with the grain size distribution from 10 nm to 200 nm. The crystallites are very nonuniform in size. The mean grain size of the specimen was determined to be 50 nm by the TEM observations. The SAD of this specimen indicates the presence of the fcc (Fe, Ni) solid solution and the cubic $(Fe, Ni, Mo)_{23}B_6$ phase, as identified by XRD. The random texture of the nanometer-sized fcc (Fe, Ni) solid solution and cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites was proved by the even distribution of the diffraction spots on the SAD rings.

The dependence of the microstructure (mass fractions and average grain sizes of phases, mean grain size d of specimen) of the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ on the annealing temperature T with the annealing time fixed for 1 h is summarized in Table I. Since the fcc (Fe, Ni) solid solution crystallites are surrounded by the boron-rich amorphous matrix in the nanostructured specimens prepared in the low temperature range, the

TABLE I Microstructure of nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ prepared at various temperatures

T	Crystallization	Crystalline phases (mass fraction, average gain size)	d
700 K	50%	fcc (Fe, Ni) (50%, 4 nm)	4 nm
730 K	57%	fcc (Fe, Ni) (57%, 5 nm)	5 nm
740 K	60%	fcc (Fe, Ni) (60%, 6 nm)	6 nm
750 K	65%	fcc (Fe, Ni) (65%, 7 nm)	7 nm
760 K	70%	fcc (Fe, Ni) (70%, 8 nm)	8 nm
770 K	80%	fcc (Fe, Ni) (78%, 9 nm) + $(Fe, Ni, Mo)_{23}B_6$ (2%, 20 nm)	9 nm
780 K	100%	fcc (Fe, Ni) (2%, 10 nm) + $(Fe, Ni, Mo)_{23}B_6$ (98%, 22 nm)	20 nm
790 K	100%	fcc (Fe, Ni) (2%, 10 nm) + $(Fe, Ni, Mo)_{23}B_6$ (98%, 26 nm)	25 nm
810 K	100%	fcc (Fe, Ni) (3%, 10 nm) + $(Fe, Ni, Mo)_{23}B_6$ (97%, 33 nm)	30 nm
830 K	100%	fcc (Fe, Ni) (4%, 10 nm) + $(Fe, Ni, Mo)_{23}B_6$ (96%, 35 nm)	33 nm
860 K	100%	fcc (Fe, Ni) (5%, 10 nm) + $(Fe, Ni, Mo)_{23}B_6$ (95%, 37 nm)	35 nm
910 K	100%	fcc (Fe, Ni) (8%, 10 nm) + $(Fe, Ni, Mo)_{23}B_6$ (92%, 40 nm)	38 nm
930 K	100%	fcc (Fe, Ni) (30%, 12 nm) + $(Fe, Ni, Mo)_{23}B_6$ (70%, 45 nm)	42 nm
960 K	100%	fcc (Fe, Ni) (50%, 15 nm) + $(Fe, Ni, Mo)_{23}B_6$ (50%, 150 nm)	50 nm
1010 K	100%	fcc (Fe, Ni) (55%,18 nm) + $(Fe, Ni, Mo)_{23}B_6$ (45%, 200 nm)	80 nm
1060 K	100%	fcc (Fe, Ni) (60%, 25 nm) + $(Fe, Ni, Mo)_{23}B_6$ (40%, 240 nm)	100 nm

growth of the fcc (Fe, Ni) solid solution crystallites is impeded. Therefore, the fcc (Fe, Ni) solid solution crystallites grow very slowly, as the annealing temperature increases from 700 K to 760 K. As a result, the mean grain size of the specimen very slightly in the low annealing temperature range. As the annealing temperature increases from 760 K to 780 K, the coarse cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites appear and become the major phase, and the amorphous phase disappears. This leads to a drastic increases of the mean grain size of the specimen. In the moderate temperature range, the mean grain size of the specimen increases gradually, and the fractions of the major cubic $(Fe, Ni, Mo)_{23}B_6$ phase and the minor fcc (Fe, Ni) solid solution phase change slightly. However, as the annealing temperature increases further into the high temperature range, the fraction of the fcc (Fe, Ni) solid solution increases noticeably. In the high temperature range, the cubic $(Fe, Ni, Mo)_{23}B_6$ phase decreases in fraction but increases drastically in grain size.

4. Conclusions

Depending on the annealing temperature, the nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens with different microstructure can be produced by annealing the amorphous alloy. The nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens prepared in the low temperature range have a microstructure of the 4–9 nm fcc (Fe, Ni) solid solution crystallites embedded in the residual amorphous matrix. The nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens prepared in the moderate temperature range show a polycrystalline microstructure of the major cubic $(Fe, Ni, Mo)_{23}B_6$ phase with average grain sizes from 20 nm to 40 nm and the minor fcc (Fe, Ni) solid solution crystallites of about 10 nm. The nanostructured $Fe_{40}Ni_{38}Mo_4B_{18}$ specimens prepared in the high temperature range represent a polycrystalline microstructure of the 12–25 nm fcc (Fe, Ni) solid solution crystallites and the 45–240 nm cubic $(Fe, Ni, Mo)_{23}B_6$ crystallites.

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