Nanocrystalline structures obtained by the crystallization of an amorphous Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_4$ soft magnetic alloy

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Abstract

The kinetics of crystallization of a soft magnetic amorphous Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_4$ alloy was studied by TEM, EDX and resistivity methods. The kinetic parameters were measured from TEM studies and resistivity measurements. Nanocrystals of the fcc FeNi phase were found to crystallize by a primary crystallization mechanism followed by slow growth kinetics. The volume fraction measured by TEM matches well with that calculated from resistivity results and a TTT diagram was constructed. Quantitative measurements of the nucleation and growth rates as a function of temperature and time were performed. The nucleation rate was found to decrease with an increase in heat treatment time due to an increase in boron content in the amorphous matrix as the crystallization took place. The crystal growth was found to slow down considerably due to the presence of Mo. The crystal size was calculated according to the Michels model and compared to our experimental results. Molybdenum was found to dramatically alter the energetics of crystallization, the morphology of the crystals and particularly the kinetics of crystallization. These results offer a method of creating new families of nanostructured magnetic materials by suitable molybdenum addition.

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1. Introduction

The kinetics of crystallization of amorphous soft magnetic alloys such as Fe$_{40}$Ni$_{40}$B$_{20}$ has attracted considerable attention [1,2]. The crystallization products are generally large eutectic crystals [2]. However, a nanocrystalline morphology would be more favorable to for better soft magnetic properties, since the microstructure of the nanocrystalline crystals in an amorphous matrix can give rise to superior soft magnetic properties compared to the amorphous counterpart [3,4]. The crystallization processes are sensitive to alloy composition, the crystallization kinetics of amorphous materials is often described by the Johnson–Mehl–Avrami equation $y = 1 - \exp(-Kr^n)$ [5].

The difference in the composition of crystal and the amorphous matrix in nanocrystalline materials will affect the nucleation and crystal growth process, the crystal growth can be slowed down by the retarding force of suitable solute atoms. Thus, in this investigation, attention was focused on the effect of Mo on the nucleation and growth of a Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_4$ alloy. Mo is known to have a strong influence on growth kinetics and mechanism in many steels and the objective was to investigate if Mo could change the growth kinetics and mechanism to create a nanocrystalline morphology. The motivation of this work is to characterize and examine the properties of such a nanocrystalline morphology to see if superior magnetic properties are obtained as predicted by the Herzer model [3].

The counterpart alloy without Mo has been extensively studied [1,2], however, very little attention has been paid to evaluate the effect of Mo. The novelty of this work is that we wished to investigate if Mo could change the microstructure to that required by the Herzer model, as is the case for the effect of Nb in Fe–Si–B–Nb–Cu alloys. Interestingly, we find that Mo does indeed play a dramatic role in changing the nucleation and growth characteristics, the energetics of crystallization, crystal morphology and crystallization kinetics have been shown to be significantly altered by the presence of Mo. Significantly,
it is found that Mo is able to change the morphology to that of a high density of nanocrystals in an amorphous matrix, as required by the Herzer model as well as to change the mechanism of crystallization to the desired primary crystallization mechanism. In this paper the phase transformation kinetics of crystallization of an amorphous melt spun Fe40Ni38B18Mo4 alloy is reported, the magnetic properties have been reported elsewhere and have indeed shown that the magnetic properties can be improved. Initially amorphous samples were heat treated in the range of 350–450°C for a period ranging from 10 min to 24 h. The volume fraction of the crystallized phase was quantitatively measured by TEM analysis and also calculated from isothermal electrical resistivity measurements. This work extends the range of nanocrystalline soft magnetic materials and suggests that new families of such alloys may be created by suitable additions of Mo.

2. Experimental procedure

Amorphous Fe40Ni38B18Mo4 melt spun ribbon with a thickness of about 30 μm was supplied by Honeywell Electronics, USA. Isothermal electrical resistivity measurements at temperatures of 380, 400 and 420°C were conducted and the change in resistivity versus time was measured. The four point probe method was employed.

The resistivity can be used to calculate the volume fraction of crystallized phase by the Maxwell–Garnett relation: \[ \rho_x = \frac{\rho_c - \rho_a}{\rho_c - \rho_a + 2\rho(0)}(2\rho_a + \rho_c)(\rho_a + 2\rho(0)) \]
where \( t \) is the time, \( x \) stands for crystalline phase, \( a \) and \( c \) refer to the resistivity of crystalline phase, amorphous matrix and two phase microstructure alloy, respectively.

The amorphous ribbons were heat treated in vacuum furnace at temperatures of 350, 380, 400, 420 and 450°C for 10 min, 1 h, 4 h and 24 h, respectively. These temperatures were selected on the basis of our previous DSC results (as shown in Fig. 1). Quantitative study on the phase transformation kinetic parameters, i.e. volume fraction, crystal density and crystal size, were carried out by TEM analysis using JEM 2010, a 200 kV TEM. The samples were prepared by ion milling. Centered dark field image, as indicated in Fig. 2, was used to study the crystallization kinetics of heat treated melt spun specimens. To observe all crystals six areas (centered at the 2, 4, 6, 8, 10 and 12 O’clock positions) which cover the first ring of the diffraction pattern were selected. Some crystals appear more than once in the dark field image because of the symmetry of fcc crystals, these crystals were carefully eliminated before quantitative analysis, with appropriate corrections for thickness [7,8]. When the average particle diameter is smaller than the foil thickness the difference between the diameter measured in the projected plane and the real particle diameter can be estimated by the following equation [8]:

\[ D = \frac{dt}{1 - d + \frac{4A_\lambda}{E_\lambda}} \]

where \( A_\lambda \) is the projected area, \( t \) the foil thickness, \( L_\lambda \) the perimeter density (1/nm), \( d \) the projected diameter of the crystal and \( D \) is the real mean diameter.

The number of crystals per unit area, \( N_x \), was determined using the line intersection technique of quantitative metallography, the number of crystals per unit volume, \( N_v \), was calculated by the following equation:

\[ N_v = \frac{N_x}{L_\lambda} \]

The volume fraction of crystal, \( f_c \), can be calculated from the area fraction of the projected image, \( f_A \), by the equation:

\[ f_c = \frac{f_A}{1 + \frac{d}{L_\lambda}} \]

A large sample area compared with the crystal size was chosen to improve the accuracy of the data [9].

A convenient procedure for measuring specimen thickness is to use EELS and compare the area under the zero loss peak \( (I_0) \) with the total area under the whole spectrum \( (I) \). The thickness \( t \) can be given by

\[ t = \ln \left( \frac{I}{I_0} \right) \]

where \( \lambda \) is the total mean free path for all effective inelastic scattering. To obtain the thickness of the sample the value of the total inelastic mean free path is required. An estimate is given by \( \lambda \) in nm = 0.8E\text{eV_0} \), where \( E_0 \) is the incident electron energy in keV [10,11]. For materials of known composition, a more accurate mean free path can be obtained by using scattering theory to calculate \( \lambda \) using the collection semiangle \( \beta \), the incident energy \( E_0 \) and a mean energy loss \( E_m \) which depends on the chemical composition of the specimen [12]. In the present case for the Fe40Ni38B18Mo4 alloy, \( \lambda \) was calculated to be equal to 105.7 nm.
3. Results

Fig. 1 shows the DSC result of the alloy at different heating rates, the temperature for primary crystallization was obtained from this data and the heat treatment temperatures were chosen accordingly in the range of 350–450 °C. The amorphous melt spun alloys were heat treated at 350, 380, 400, 420 and 450 °C for 10 min, 1 h, 4 h and 24 h and studied by TEM. Fig. 3 shows an example of the results obtained from the sample heat treated at 350 °C for 10 min, 1 h and 24 h, crystals can be clearly observed. It is interesting to note that nanocrystals can be formed by primary crystallization in this alloy system. Statistics on the crystal size and volume fraction were measured using corresponding dark field TEM micrographs and EELS data. Fig. 4 shows the size distribution of the crystals, the average crystal size increased very slowly with an increase in heat treatment time for all the heat treatment temperatures studied. The sample thickness was measured by EELS. Kinetic data, such as size distribution, mean diameter of the crystals, number of crystals per unit volume and volume fraction of crystal, were determined from these experimental results.

Fig. 5 shows the isothermal resistivity results, it is clear that at higher temperatures the resistivity decreased with an increase in heat treatment time, which also confirmed the TEM result that substantial crystallization occurred during heat treatment. At 350 °C, the TEM results showed crystallization while the resistivity values showed little change. The data obtained can be used to calculate the volume fraction of crystallized phase by the Maxwell–Garnett relation and will be compared with the quantitative TEM results. Fig. 6 presents the volume fraction measured by isothermal resistivity at 380, 400 and 420 °C the corresponding value by TEM is also indicated. The values of volume fraction deduced by resistivity and TEM are very close for heat treatment time of 10 min. For the 1 h heat treatment time sample the volume fraction measured from TEM is higher than that from resistivity, the reason is that the Maxwell–Garnett relation which was used to calculate the volume fraction from resistivity were performed under two simplifying assumptions, which are not strictly valid in our case. The first one is that the resistivity of the amorphous matrix remains unchanged during crystallization and equal to the onset state, but in fact the change in composition during crystallization will definitely change the resistivity. In our data the relatively large deviation in the 1 h value compared with that of 10 min can be accounted for by the composition change during crystallization. The second assumption is that the electrons scattered at the interphase boundaries can be neglected which is not strictly valid because of the high crystal density [13]. Direct observation of microstructure by TEM is a more precise method, the advantage of employing electrical resistivity is that the incubation time can be easily measured, the incubation time is about 120, 60 and 40 s at 380, 400 and 420 °C, respectively. A TTT diagram was plotted according to the volume fraction measured by TEM results (Fig. 7). The unusual shape of the TTT diagram can be explained as due to the effect of molybdenum alloying additions. Specifically, in the temperature range of 350–390 °C a bay is observed in the diagram for 1% transformation. A similar bay has also been commonly observed in the case of steels containing Mo and it has been attributed to the strong effect of Mo on the nucleation and growth of the product phases [14]. This effect will
be temperature sensitive since the driving force for growth and particularly nucleation are extremely temperature sensitive. It is also expected to be sensitive to crystal volume fraction since the extremely high crystal density observed in the present system will lead to a rejection of solute to the matrix, altering the driving force and diffusional kinetics.

Fig. 4. Crystal size distribution of the Fe\textsubscript{40}Ni\textsubscript{38}B\textsubscript{18}Mo\textsubscript{4} alloy heat treated at (a) 350 °C, (b) 380 °C, (c) 400 °C, (d) 420 °C and (e) 450 °C.

The Johnson–Mehl–Avrami equation \((y = 1 - \exp(-Kt^n))\) was plotted on the basis of TEM data. The Avrami exponent \(n\) and kinetic constant \(K\) for the heat treated samples at different time is listed in Table 1, the average Avrami exponent is 0.39. The kinetic constant \(K\) obeys the Arrhenius law: \(K = K_0 \exp(-Q/kT)\), ln \(K\) was plotted against \(1/T\), \(Q\) was obtained
as $3.20 \pm 0.77 \times 10^{-19}$ J/atom (or $2.00 \pm 0.48$ eV/atom). Here, the $Q$ reflects the activation energies for both nucleation and growth [15].

The variation of number of the crystals per unit volume with heat treatment time at different temperatures is shown in Fig. 8. Interestingly, the average crystal size increased initially with an increase in heat treatment time and then reached a constant value. Fig. 9 indicates the average crystal size as a function of heat treatment time, initially the growth rate is high followed by a marked slowing down in the growth as the crystallization proceeded.

EDX using the TEM was carried out to study the elemental distribution after heat treatment. The measurement may be not precise due to the spot size of the electron beam but the results generally reflect the distribution of elements. Three spots on a TEM micrograph were selected for study, the crystal, the crystal:matrix interface and the matrix (as shown in Fig. 10). Several crystals were selected for analysis, Table 2 lists typical EDX results of elemental content at the crystal interface and the amorphous matrix. The Mo content at the crystal interface is higher than in the amorphous matrix, thus accumulation of Mo at the interface was observed experimentally. Note that the Mo content in the crystal is very small, clearly, a rejection of Mo takes place during growth.
4. Discussion

This study of the crystallization of the Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_{4}$ alloy showed that nanocrystallization took place at the heat treatment temperatures and times studied in this investigation. We have previously reported that this is a fcc taenite phase of Fe–Ni [16,17]. The TEM results suggested an average value of Avrami exponent $n$ equal to 0.39, which is very small compared with classic nucleation and growth theory, which suggests that it should be in the range from 1 to 4. The Avrami exponent was earlier reported to be close 1.0 by XRD [18] and 1.08 by ferromagnetic resonance spectroscopy (FMR) [19], but these experimental methods are indirect methods and many assumptions were made to arrive at these values. The well-studied alloys with the composition, Fe$_{40}$Ni$_{40}$B$_{20}$ and Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$, have very different crystallization behavior compared to the Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_{4}$ alloy used in this investigation due to the effect of Mo. The Avrami exponent of the Fe$_{40}$Ni$_{40}$B$_{20}$ alloy has been measured to be close to 3 [2] and between 2.3 and 3.3 by several researchers [1], and for the Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ alloy the Avrami exponent is 4 [20]. It has been found that the Fe$_{40}$Ni$_{40}$B$_{20}$ and the Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ alloys crystallize by the eutectic crystallization mechanism, on the other hand, the Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_{4}$ alloy forms by primary crystallization.

A low value of Avrami exponent has been reported in the primary crystallization of many amorphous alloys and in several cases abnormally low value was found [21,22]. This phenomenon can be explained by the model of diffusion controlled growth with soft impingement [23,24]. The composition of the crystals is different from that of the matrix, this results in the presence of gradients of concentration at the crystal:matrix interface, as crystallization proceeds the overlapping of the diffusion profiles of neighboring crystals decreases the growth rate [25]. Other researchers [26] evaluated the Avrami exponent when soft impingement was taken into consideration, and could explain the low value of Avrami exponent (below 1) in primary crystallization of amorphous alloys. Another common reason is that one or more elements can retard the growth by piling up at the interface, due to the partitioning of alloying element. Such reasoning has been used to explain the effect of Nb in the commercial Fe–Si–B–Nb–Cu alloys referred to as Finemet alloys. In the case of steel, Mo possessing a bcc crystal structure, prefers not be in the fcc austenite, thus Mo can severely reduce growth. In our case, as well, the experimental observation of enhanced composition of Mo at the matrix:crystal interface showed that Mo is rejected by the fcc taenite crystal and is piled up at the interface, severely retarding the growth of the crystal. Thus our experimental observations are consistent with a model similar to that prepared for Nb in Finemet alloys.

The activation energy of the Fe$_{40}$Ni$_{38}$B$_{18}$Mo$_{4}$ alloy calculated from kinetic constant $K$ is 2.00 ± 0.48 eV/atom compared to 4.24 eV/atom obtained by Kissinger analysis of our DSC results [17] and it was reported by other researchers to be 3.66 eV/atom [19]. The activation energy deduced from kinetic constant $K$ is much lower than the value by other experimental methods, because the calculation is based on the JMA model of nucleation and growth, which assumes a diffusion controlled phase transformation, but our reaction is interface controlled (as will discussed later). For related alloy compositions, the corresponding activation energy of the Fe$_{40}$Ni$_{40}$B$_{20}$ alloy is 3.0 eV/atom and for the Fe$_{40}$Ni$_{40}$P$_{14}$B$_{6}$ alloy, the activation energy is 350 kJ/mol (3.6 eV/atom) [27].
4.1. Effect of boron on the nucleation process

Phase transformation from the amorphous to crystalline phase requires nucleation of the crystalline phase. It is believed that the initial nucleation depends on the quenched-in pre-existing nuclei formed during melt spinning procedure [28,29]. There is a high volume fraction of the crystalline phase as it is also observed in the Fe–Si–B–Nb–Cu Finemet alloy [30]. The variation of crystal number density with heat treatment time at 350, 380, 400 and 420 °C is shown in Fig. 8. The sample heat treated at 450 °C was not included in the calculation because of the second phase (FeNiMo)23B6 formed at this temperature and it is not practical to separate this phase from that of the primary crystallization phase in either bright field or dark field image because the diffraction rings of these two phases are very close to each other. The crystal number density is in the range of $10^{22}$ m$^{-3}$, this is a reasonable value for amorphous-crystallized samples, nucleation density in amorphous aluminum alloys was reported to be $10^{21}$ m$^{-3}$ [31], other researches reported the nanocrystal densities range from $10^{21}$ to $10^{23}$ m$^{-3}$ [32] and even higher up to $10^{24}$ m$^{-3}$ [33]. The crystal number density increased with an increase in heat treatment time and reached a steady state, this steady state value increases with increasing heat treatment temperature.

The nucleation rate was calculated from the slope of the crystal number density curve. As shown in Fig. 11, nucleation rate decreased with an increase in heat treatment time and finally reaches zero, the higher the heat treatment temperature the faster it reaches zero. This statistical analysis of crystal size distribution in partially transformed specimens was compared to theoretical calculation. Calculation of crystal size distribution has been studied by other researchers [34,35] for the case of homogeneous nucleation, homogenous transient nucleation, quenched heterogeneous nucleation and heterogeneous and transient nucleation. When these calculations are compared with our experimental size distribution measurements, it is found that the nucleation mode is heterogeneous and transient nucleation.

4.2. Effect of molybdenum on growth

The kinetics of crystal growth in nanocrystalline materials can be different from that of coarse grained polycrystalline materials. Fig. 9 indicates that the average crystal size (measured from TEM micrographs) of isothermally heat treated samples as a function of heat treatment time, the crystal size was found not to follow the traditional power law and the growth eventually stagnated. Other researchers observed similar crystal growth stagnation in nanocrystalline materials [39,40]. As explained earlier, Mo was found to cause transformation stasis in Fe–C–Mo
Mo accumulates at the crystal:matrix interface because of its slow diffusion rate and slows the crystal growth. Take into account the effect of partitioning Michels [42] developed a model to explain the phenomenon, we have modified this model to better suit our alloy system.

Hillert’s theory on normal crystal growth in pure and single phase materials yields the parabolic growth law for the mean crystal size as a function of time:

$$\frac{dR}{dt} = \frac{A}{R} \Rightarrow R^2(t) - R^2(0) = 2At$$

where \(A\) is a temperature and material dependent parameter and \(R(0)\) is the initial mean crystal size at \(t = 0\).

Other researchers modified Eq. (5) [43] to obtain:

$$R^{-1/m}(t) - R^{-1/m}(0) = \frac{A}{m}t$$

but it is difficult to understand the crystal growth mechanism from the value of \(m\). As discussed above, molybdenum piled up at the crystal interface and caused an increase in molybdenum concentration. When we take the partitioning effect into account the stagnation of crystal growth observed experimentally can be seen to be equivalent to a drag force exerted on the crystal, hence the differential equation for \(R(t)\) is given by:

$$\frac{dR}{dt} = A \left( \frac{1}{R} - \frac{1}{R_{\text{max}}} \right)$$

Integrating this equation we obtain:

$$\frac{A}{R_{\text{max}}^2} t = \frac{R(0) - R(t)}{R_{\text{max}}} + \ln \left( \frac{R_{\text{max}} - R(0)}{R_{\text{max}} - R(t)} \right)$$

For the Fe\(_{40}\)Ni\(_{38}\)B\(_{18}\)Mo\(_4\) amorphous system \(f\) is not a constant during isothermal heat treatment. Consider the composition change during crystallization, when Fe–Ni crystal formed within Fe\(_{40}\)Ni\(_{38}\)B\(_{18}\)Mo\(_4\) amorphous matrix, molybdenum was expelled by crystal growth and piled up at the interface, hence the molybdenum expelled by Fe–Ni should be equal to the amount of molybdenum increased in boundary. Assume the average concentration of molybdenum at crystal boundary is \(C_{Mo}^0\) and the thickness of the concentration gradient is \(L\). The overall concentration of molybdenum can be written as:

$$C_{Mo}^0 V^x = (C_{Mo}^0 - C_{Mo}^0)A^B L$$

where \(C_{Mo}^0\) is the original concentration of Fe\(_{40}\)Ni\(_{38}\)B\(_{18}\)Mo\(_4\) amorphous ribbon, \(V^x\) the volume of the crystal, \(A^B\) is the area of the crystal boundary and

$$V^x = \frac{4}{3}\pi R^3$$

the following relation is obtained:

$$RC_{Mo}^0 = 3L(C_{Mo}^B - C_{Mo}^0)$$

or,

$$C_{Mo}^B = \left( 1 + \frac{R}{3L} \right) C_{Mo}^0$$

Assuming that the drag force \(f\) is proportional to the difference in the concentration of solute in the crystal boundary and the crystalline region:

$$f \propto \Delta C = C_{Mo}^B - C_{Mo}^0$$

$$f = \beta C_{Mo}^B = \beta C_{Mo}^0 \left( 1 + \frac{R}{3L} \right)$$

where \(\beta\) is a constant.

The differential equation can be written as:

$$\frac{dR}{dt} = \frac{A}{R} - \beta C_{Mo}^0 \left( 1 + \frac{R}{3L} \right)$$

considering the boundary condition that crystal growth stops at \(R_{\text{max}}\),

$$\frac{dR}{dt} = 0, \quad R \rightarrow R_{\text{max}}$$

\(\beta\) can be calculated as:

$$\beta = \frac{3LA}{C_{Mo}^0 R_{\text{max}}(R_{\text{max}} + 3L)}$$

Finally, we achieve the differential equation as:

$$\frac{dR}{dt} = \frac{A}{R} - \frac{AR}{R_{\text{max}}(R_{\text{max}} + 3L)}$$

\(L\) can be estimated as:

$$L = \sqrt{\frac{2\pi A t}{3}}$$

at the early stage of phase transformation \(3L \ll R\), Eq. (19) can be written as:

$$\frac{dR}{dt} = A \left( \frac{1}{R} - \frac{1}{R_{\text{max}}} \right)$$

which is same as the equation deduced by Michels.

Integrating Eq. (21), yielding

$$R(t) = \left( \frac{R_{\text{max}}^2 - (R_{\text{max}}^2 - R^2(0)) \exp \left[ -\frac{2At}{R_{\text{max}}^2} \right] }{2A t} \right)^{1/2}$$

Fig. 9 shows the calculated average radius as a function of heat treatment time, the values of fitting parameter \(R_{\text{max}}, R(0)\) and \(A\) are listed in Table 3. Generally the calculated curve fits the experimental results well. The value of \(R(0)\) corresponding to crystallization taking place during heating to the heat treatment temperature.

The value of parameter \(A\) at 450°C is much larger than the value at other temperatures. Consider the effect of diffusion of
molybdenum on the crystal interface, the thickness of molybdenum rich layer, \( L \), will increase for long time heat treatment. \( L \) can be estimated as \( L \approx \sqrt{D t} \) [44], diffusion coefficient, \( D \), of molybdenum in α iron can be calculated as,

\[
D = D_0 \exp \left( \frac{-Q}{kT} \right)
\]

where \( D_0 = 45.9 \text{ cm}^2/\text{s} \) and \( Q = 67.97 \text{ kcal/mol} \) [37].

The diffusion coefficient at different temperature and \( L \) at 24 h is listed in Table 4. The criteria of \( 3L \ll R \) is not satisfied for long time and high temperature (420 and 450 °C) heat treatment, this may cause the anomalous value of \( A \) at 450 °C.

5. Conclusions

The crystallization of amorphous Fe\(_{40}\)Ni\(_{38}\)B\(_{12}\) alloy was studied mainly by TEM, EDX and isothermal resistivity measurements, the crystallization was modeled from the experimental measurements. Mo was found to play a significant role in determining the crystallization mechanism, nucleation and growth kinetics and crystal morphology. A nanocrystalline morphology was successfully produced in this alloy system and the magnetic properties were shown to improve after selected heat treatment [44]. The following results were obtained.

1. It is interesting to note that nano scale fcc Fe–Ni crystals formed in the amorphous matrix by a heterogeneous and transient nucleation followed by very slow growth. This strong inhibition of growth is due to the presence of molybdenum in the alloy.

2. The volume fraction measured by TEM is higher than that calculated from resistivity measurements. A TTT diagram was plotted according to the TEM results. The average Avrami exponent \( n \) is calculated to be 0.39 which is very low compared with alloy compositions which do not contain Mo. Activation energy was calculated from kinetic constant \( K \) to be \( 3.20 \pm 0.77 \times 10^{-19} \text{ J/atom} \).

3. Due to the effect of B and Mo, the free energy change and the driving force for nucleation decreases during crystallization, resulting in a decrease in nucleation rate. The crystal number density increased with increase in heat treatment time and reached a steady state, this steady state value increases with increasing heat treatment temperature. The crystal number density is in the range of \( 10^{12} \text{ m}^{-3} \).

4. The well-studied alloys with close composition, Fe\(_{40}\)Ni\(_{40}\)B\(_{20}\) and Fe\(_{40}\)Ni\(_{40}\)P\(_{14}\)B\(_{6}\), have very different crystallization behavior compared to the Fe\(_{40}\)Ni\(_{38}\)B\(_{12}\)M\(_{0}\) alloy. The Fe\(_{40}\)Ni\(_{40}\)B\(_{20}\) and the Fe\(_{40}\)Ni\(_{40}\)P\(_{14}\)B\(_{6}\) alloys crystallize by the eutectic crystallization mechanism while the Fe\(_{40}\)Ni\(_{38}\)B\(_{12}\)M\(_{0}\) alloy was found to crystallize by primary crystallization.

5. The EDX results showed that the Mo content at the crystal interface is higher than in the amorphous matrix, and is negligible within the crystal thus accumulation of Mo at the interface due to solute rejection by the crystal was observed experimentally.

6. The average crystal size increased initially with an increase in heat treatment time, and reached a constant value to the Mo partition and segregation at the crystal:matrix interface.

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