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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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Keywords: Nanocrystal formation; Soft magnetic materials; Alloying effects; Crystallization

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 $y = 1 - \exp(-Kt^n)$ [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,

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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 $Fe_{40}Ni_{38}B_{18}Mo_4$ 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 $Fe_{40}Ni_{38}B_{18}Mo_4$ 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: [6] $x(t) = ((\rho(t) - \rho_a)/\rho_c - \rho_a))((2\rho_c + \rho_a)/(\rho_c + 2\rho(t)))$, where t is the time, x stands for crystalline volume fraction and ρ_c, ρ_a and ρ 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

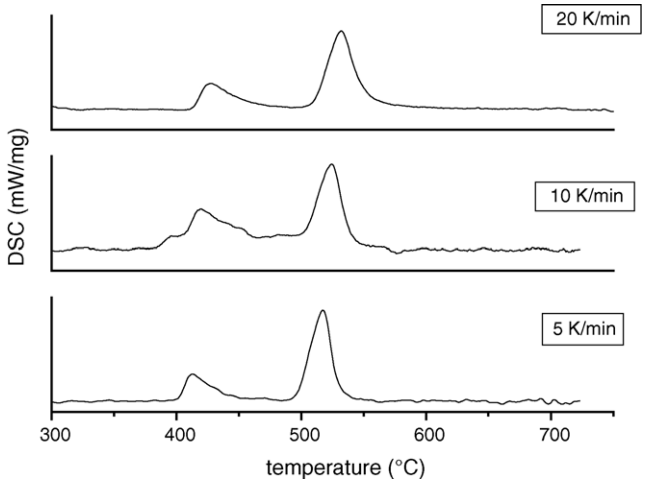

Fig. 1. DSC measurement curves of the $Fe_{40}Ni_{38}B_{18}Mo_4$ samples heated linearly at different heating rates: 5, 10 and 20 K/min.

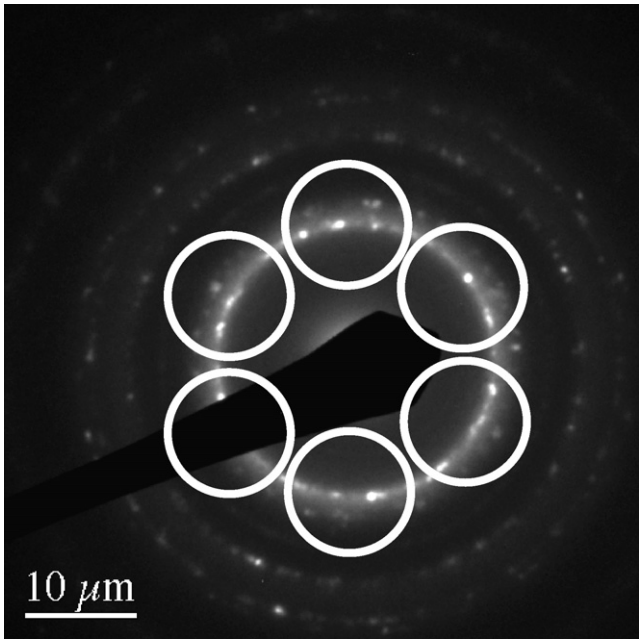

Fig. 2. Aperture selection for dark field image.

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]:

$$D = \frac{dt}{t - d + \frac{\pi A_A}{L_A}} \tag{1}$$

where A_A is the projected area, t the foil thickness, L_A the perimeter density (1/nm), d the projected diameter of the crystal and $\bar{D}$ is the real mean diameter.

The number of crystals per unit area, N_A, 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:

$$N_v = \frac{N_A}{t + \bar{D}} \tag{2}$$

The volume fraction of crystal, f_v, can be calculated from the area fraction of the projected image, f_A, by the equation:

$$f_v = \frac{f_A}{1 + \frac{3t}{2\bar{D}}} \tag{3}$$

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_t). The thickness (t) can be given by

$$\frac{t}{\lambda} = \ln\left(\frac{I_t}{I_0}\right) \tag{4}$$

where λ 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 λ (in nm) = $0.8E_0$, 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 λ using the collection semiangle β, 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 $Fe_{40}Ni_{38}B_{18}Mo_4$ alloy, λ was calculated to be equal to 105.7 nm.