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Unusual grain growth during annealing process: from amorphous to nanocrystalline

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The relationships between grain size and annealing temperature for nanocrystalline soft magnetic alloys were investigated, an improved model based on the crystallization kinetics was proposed, and the unusual phenomenon that the grain size firstly increases, then decreases, and finally increases again with the increasing annealing temperature was explained by using this model. Theoretical analysis results are in excellent agreement with the existing experimental data.

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1. Introduction

Nanocrystalline soft magnetic alloys have attracted considerable attentions in the field of condensed matter physics and material engineering because of their excellent soft magnetic properties, such as low coercivity H_c and high permeability μ, which make these materials promising for technological applications [1-3]. It is known that these alloys are generally prepared by annealing and partial nanocrystallization from rapidly quenched amorphous ribbons [4], and their magnetic behaviors depend highly on the microstructure, especially the grain size, of the partially crystallized alloys [5-8]. Also it has been found that the minimum grain size would lead to the lowest coercivity as well as the highest permeability [9-10]. Therefore, it is essential to investigate how grain size evolves during the annealing process, to get nanocrystalline alloys with optimal soft magnetic properties. The grain size was suggested to increase monotonously with the increasing annealing temperature for nanocrystalline soft magnetic alloys according to most previous investigations [4, 11]. At the same time, an abnormal phenomenon that the grain size firstly decreases and then increases was also observed [12, 13], however, it has drawn little attention and can not be explained satisfactorily by the existing theories up to now.

In the present work, an improved theoretical model concerning the grain growth based on the crystallization kinetics was proposed and a corresponding formula was obtained. Moreover, the theoretical results were compared with experimental ones to verify our model.

2. Theoretical considerations

Amorphous alloys are thermodynamically unstable and have a tendency to transit to crystallites by the annealing treatment, and nanocrystalline soft magnetic alloys are mainly composed of crystalline phases and residual amorphous matrix. The crystallization process mainly consists of two elementary processes: nucleation of embryos (crystallization centers) and the following growth of crystallites from these centers. For the nucleation process [14, 15], the nucleation rate I expressed in the crystallization kinetics is

$$I \approx \frac{N_v kT}{3\pi a_0^3 \eta} \exp(-\frac{\Delta G_r^*}{RT}) \times \exp(-\frac{E_n}{RT}) \qquad (1)$$

where N_v is the Avogadro constant, k the Boltzmann's constant, η the viscosity, a_0 the atomic diameter, ΔG_r^* the critical free energy, T the annealing temperature, R the ideal gas constant, and E_n the nucleation activation energy.

Meanwhile, the variation of free energy [16] taking into account both of the volume free energy and the surface free energy is given by

$$\Delta G_r = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \Delta G_V \qquad (2)$$

with r the radius of the crystallites, σ the crystal-amorphous interfacial energy, and ΔG_V the volumetric change of free energy upon crystallization. The first part in Eq. (2) is the surface free energy, which usually has a positive value, when the phase transformation takes place from amorphous to crystalline; while the second part is the volume free energy which usually has a negative value. The variation of free energy with radius of the crystallites was shown in Fig. 1.

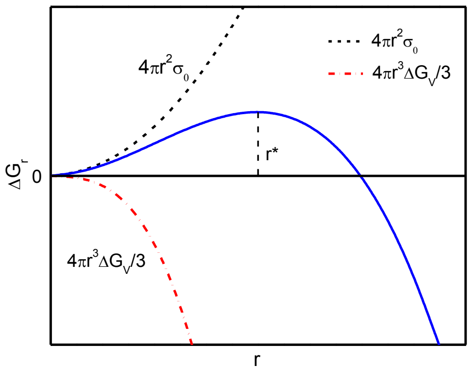

Fig. 1. Schematic drawing of the variation of free energy with crystallite radius.

It can be seen from Fig. 1 that $\Delta G_r = f(r)$ has an extreme value. Assuming that r^* is the critical radius of crystallites and ΔG_r^* the corresponding critical free energy, then r^* can be obtained from $d(\Delta G_r)/dr = 0$ that

$$r^* = -2\sigma / \Delta G_V \tag{3}$$

Substitute Eq. (3) to Eq. (2), we obtain

$$\Delta G_r^* = 16\pi\sigma^3 / 3(\Delta G_V)^2 \tag{4}$$

In addition, the volumetric change of free energy upon crystallization can be expressed as follows based on the crystallization kinetics [17]

$$\Delta G_V = \frac{\Delta H_{\mathrm{m}}(T_m - T)}{VT_m}\frac{T}{T_m} \tag{5}$$

where ΔH_{m} is the latent heat of nanocrystallization, V the molar volume, and T_m the melting point of nanocrystalline soft magnetic alloys.

Thus, the relationship between the nucleation rate and annealing temperature can be drawn from Eqs. (1) - (5) that

$$I \approx \frac{N_{\mathrm{v}}kT}{3\pi a_0^3\eta}\exp\left[-\frac{16\pi\alpha^3\beta T_m^5}{3(T_m - T)^2T^3}\right]\times\exp\left(-\frac{E_n}{RT}\right) \tag{6}$$

where $\alpha = \frac{(N_V V^2)^{1/3}\sigma}{\Delta H_{\mathrm{m}}}$ is the reductive surface tension,

and $\beta = \frac{\Delta H_{\mathrm{m}}}{RT_{\mathrm{m}}}$ the reductive dissolution enthalpy.

Meanwhile, the grain growth rate U can be expressed as [14, 15]

$$U \approx \frac{fkT}{3\pi a_0^2}\left[1-\exp\left(-\frac{\Delta G}{RT}\right)\right]\exp\left(-\frac{E_g}{RT}\right) \tag{7}$$

with ΔG the free energy difference between crystalline phases and residual amorphous matrix, and E_g the growth activation energy. Since $\Delta G >> RT$ in the annealing process [15], thus Eq. (7) can be simplified as

$$U \approx \frac{fkT}{3\pi a_0^2}\exp\left(-\frac{E_g}{RT}\right) \tag{8}$$

The microstructures of the nanocrystalline soft magnetic alloys were affected by the nucleation rate I and the grain growth rate U during annealing simultaneously, and the grain size can be written as [18]

$$D \approx \sqrt[4]{\frac{U}{I}} \tag{9}$$

With $D_0 = \left(\frac{fa_0\eta}{N_{\mathrm{v}}}\right)^{1/4}$, $\gamma = \frac{16}{3}\pi\alpha^3\beta$, the dependence of grain size on the annealing temperature for nanocrystalline soft magnetic alloys can be further expressed as

$$D \approx D_0\sqrt[4]{\exp\left[\frac{\gamma T_m^5}{(T_m - T)^2T^3}\right]\times\exp\left(-\frac{\Delta E}{RT}\right)} \tag{10}$$

where $\Delta E = E_g - E_n$, which is the difference between the crystal nucleation and the growth activation energy. It can be seen that the grain size increases with the increasing annealing temperature if the value of ΔE was very large; while the grain size would firstly decrease and then increase with the increasing temperature if ΔE was very small.

It is known that the nucleation and growth process both involve two styles: atoms jumping to the crystallites and ordered clusters combination (ordered clusters shearing deposition) [19]. By assuming E_{jn} and E_{cc} as the activation energy for atoms jumping and the ordered clusters combination in nucleation respectively, then the total activation energy in nucleation is [20]

$$E_n = A_n E_{jn} + B_n E_{cc} \tag{11}$$

where A_n and B_n are the respective weight factors for atoms jumping and ordered clusters combination in nucleation, with $A_n + B_n = 1$.

Similarly, the growth activation energy can be expressed as [20]

$$E_g = A_g E_{jg} + B_g E_{cd} \tag{12}$$

where E_{jg} and E_{cd} the activation energy for atoms jumping to the crystallites and the ordered clusters combination in growth process respectively, A_g and B_g their respective weight factors, with

$A_g + B_g = 1$. The crystal nucleation and growth activation energy on atoms jumping and ordered clusters combination can be schematically shown in Fig. 2.

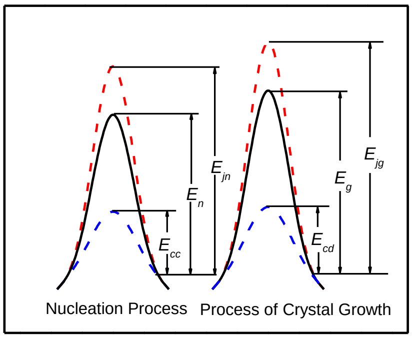

Fig. 2. Schematic drawing of the nucleation and growth activation energy.

It is generally known that the amorphous alloys do not begin to crystallize when annealed below their primary crystallization temperatures T_x, and the atoms of amorphous alloys were assumed to jump in amorphous matrix depending on the hot fluctuations. However, numerous ordered clusters in amorphous matrix would be produced when amorphous alloys are annealed above their primary crystallization temperatures. As a consequence, the nanocrystallization process was suggested involving two cases as follows:

2.1 Annealed below T_x

When annealed below T_x, the dependence of activation energy on ordered clusters combination can be ignored and the atom jumping governs the crystallization process, that is $B_n \to 0$, $A_n \to 1$, and $B_g \to 0$, $A_g \to 1$, thus we can obtain $E_n \approx E_{jn}$ and $E_g \approx E_{jg}$ from Eqs. (11) - (12). Moreover, $\alpha \to 0$ ascribed to the rapid increase of ΔS in the disordered state after annealed below T_x [16]. So Eq. (10) can be further simplified as:

$$D \approx D_0 \exp(-\frac{\Delta E}{4RT}) \tag{13}$$

2.2 Annealed above T_x

When annealed above T_x, however, the ordered clusters combination plays a leading role rather than the atom jumping, then $B_n \to 1$, $A_n \to 0$, and $B_g \to 1$, $A_g \to 0$, thus we can obtain $E_n \approx E_{cc}$, $E_g \approx E_{cd}$ from Eqs. (11) - (12). Also, because ordered clusters diffusion can lower the free energy of system by reducing their surface energy and lead to the nucleation activation energy approximately equal to growth activation energy ($E_n \approx E_g$) in this process [21]. Therefore, in this case, Eq. (10) can be simplified as:

$$D \approx D_0 \exp[\frac{0.25\gamma T_m^5}{(T_m - T)^2 T^3}] \tag{14}$$

3. Results and discussion

3.1 Theoretical analysis

When annealed below T_x, the change of the grain size with annealing temperature can be drawn from Eq. (13) that

$$\frac{\partial D}{\partial T} \approx D_0 \frac{\Delta E}{4RT^2} \exp(-\frac{\Delta E}{4RT}) \tag{15}$$

In general growth process, the atoms must diffuse a certain longer distance to reach the surface of crystallites, so it requires more activate energy than the formation of nucleation [16], so, $E_g \approx E_{jg} > E_{jn} \approx E_n$, and $\Delta E = E_g - E_n > 0$. Therefore, we can draw from Eq. (15) that $\partial D / \partial T > 0$, which suggests that the grain size would increase with annealing temperature.

However, when annealed above T_x, the change of grain size for nanocrystalline soft magnetic alloys with annealing temperature obtained from the Eq. (14) is

$$\frac{\partial D}{\partial T} \approx 0.25\gamma T_{\mathrm{m}}^5 D_0 \exp[\frac{0.25\gamma T_{\mathrm{m}}^5}{(T_{\mathrm{m}} - T)^2 T^3}] \times [\frac{5T/T_{\mathrm{m}} - 3}{(1 - T/T_{\mathrm{m}})^3 (T/T_{\mathrm{m}})^4}] \tag{16}$$

It can be seen from Eq. (16) that the grain size decreases with the increasing annealing temperature below about $0.6T_m$ ($\partial D / \partial T < 0$) and increases with the increasing annealing temperature above about $0.6T_m$ ($\partial D / \partial T > 0$), which means the grain size would have a minimum value when annealed near 0.6 times that of melting point T_m.

From Eqs. (13) - (14), we can also obtain the schematic relationship of the grain size as a function of the annealing temperatures, as shown in Fig. 4. It can be seen that the grain size increases gradually up to T_x until attains a limiting value when annealed below T_x; on the contrary, when annealed above T_x, the grain size decreases with increasing annealing temperature to the minimum at about $0.6T_m$, and then increases again when annealed at higher temperature.

3.2 Experimental verification

In order to verify the improved theoretical model, comparisons between the theoretical values and the experimental data of the grain size with annealing temperature for $Fe_{73.5}Cu_1Ta_3Si_{13.5}B_9$ [22] and $Fe_{74.5}Nb_3Si_{13.5}B_9$ [23] alloys were shown in Figs. 3 - 4, respectively.

It can be seen from Figs. 3 - 4 that the grain size firstly increases with annealing temperature. However, when annealed at higher temperatures, the grain size of $Fe_{73.5}Cu_1Ta_3Si_{13.5}B_9$ alloy begin to decrease to the minimum until about 823K, and it begin to decrease to the minimum until about 875K for $Fe_{74.5}Nb_3Si_{13.5}B_9$ alloy, and then increases with increasing annealing temperature. At temperatures about 823K for $Fe_{73.5}Cu_1Ta_3Si_{13.5}B_9$ alloy and 875K for $Fe_{74.5}Nb_3Si_{13.5}B_9$, the nucleation and grain growth rate may occur at temperatures higher than the maximum of the nucleation rate. So it is obvious that the microstructure with the minimum grain size can be formed at certain temperature. The improved theoretical model is more consistent with the experiments [22-24] than previous model [11].

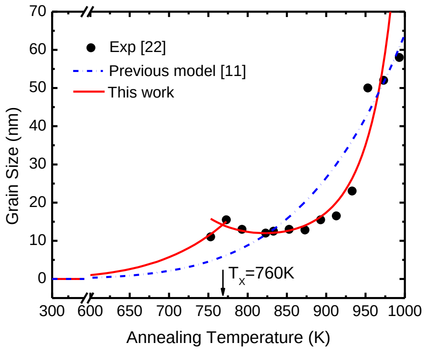

Fig. 3. Comparisons of experiments and theoretical calculations of the grain size in $Fe_{73.5}Cu_1Ta_3Si_{13.5}B_9$ alloy with annealing temperature for 1 h.

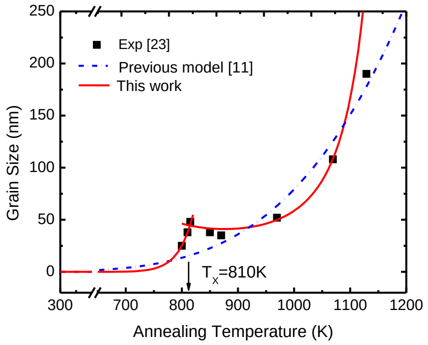

Fig. 4. Comparisons of experiments and theoretical calculations of the grain size in $Fe_{74.5}Nb_3Si_{13.5}B_9$ alloy with annealing temperature for 1 h.

4. Conclusions

An improved model concerning the grain growth in annealing process for nanocrystalline soft magnetic alloys was proposed in this paper, and it can be summarized as follows:

(1) The atoms of amorphous alloys were jumped in amorphous matrix depending on the hot fluctuations when annealed below their primary crystallization temperatures T_x, and numerous ordered clusters in amorphous matrix would be produced when amorphous alloys are annealed above their primary crystallization temperatures.

(2) The grain size of nanocrystalline soft magnetic alloys firstly increases then decreases and finally increases with the increasing annealing temperature.

(3) The physical mechanism that the negative grain growth can be explained by this improved model satisfactorily.

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References

[1] S. A. Ciureanu, Optoelectron Adv Mater. – Rapid Commun. **4**, 714 (2010).
[2] A. Makino, C. T. Chang, T. Kubota et al J Alloys Compd **483**, 616 (2009).
[3] A. Grujic, T. Zak, V. Cosovic et al Optoelectron Adv. Mater. – Rapid Commun. **3**, 477 (2009).
[4] Z. Stokłosa, J. Rasek, P. Kwapuliński et al J Alloys Compd **509**, 9050 (2011).
[5] G. Herzer, J. Magn Magn Mater **294**, 99 (2005).
[6] G. Herzer, IEEE Trans Magn **26**, 1397 (1990).
[7] P. Sovák, P. Petrovič, P. Kollár et al J. Mater. Sci. **33**, 3197 (1998).
[8] K. Suzuki, J. M. Cadogan Phys. Rev. B **58**, 2730 (1998).
[9] A. Hirata, Y. Hirotsu, E. Matsubara et al Phys. Rev. B **74**, 184204 (2006).
[10] K. Hono, Prog Mater Sci **47**, 621 (2002).
[11] X. Y. Zhang, F. X. Zhang, J. W. Zhang et al J Appl. Phys. **84**, 1918 (1998).
[12] H. Hermann, N. Mattern, S. Roth et al Phys. Rev. B **56**, 13888 (1997).
[13] L. T. M. Hoa, J Alloys Compd **420**, 50 (2006).
[14] M. T. Clavaguera-Mora, N. Clavaguera, D. Crespo et al Prog. Mater. Sci. **47**, 559 (2002).
[15] K. Lu, Acta Metall Sin. **30**, B1(1994).
[16] Y. C. Guo, Z. X. Wang, Amorphous State Physics, Science Press, Beijing 1984.
[17] Y. H. Wang, Y. S. Yang, Amorphous Alloys, Metallurgical Industry Press, Beijing 1989.
[18] V. V. Bzazhkin, V. I. Larchev, S. V. Popova et al Phys Scripta **39**, 338 (1989).
[19] P. Klugkist, K. Rätzke, S. Rehders et al Phys Rev. Lett. **80**, 3288 (1998).
[20] K. Lu, J. T. Wang J Cryst. Growth **112**, 525 (1991).
[21] K. Lu, J. T. Wang Sci. China Ser **A 4**, 555 (1992).
[22] A. Hernando, T. Kulik, Phys. Rev. B **49**, 7064 (1994).
[23] G. Herzer, Handbook on Magnetic Materials **10**, 415 (1997).
[24] M. A. Hakim, S. M. Hoque J Magn Magn Mater **284**, 395 (2004).

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