ELSEVIER

Journal of Magnetism and Magnetic Materials 215–216 (2000) 463–465

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Saturation magnetization and amorphous Curie point changes during the early stage of amorphous–nanocrystalline transformation of a FINEMET-type alloy

A. Lovas[a,b,*], L.F. Kiss[b], I. Balogh[b]

[a]Department of Mech. Eng. Techn., Technical University of Budapest, H-1111 Bertalan L. utca 2., Budapest, Hungary
[b]Research Institute for Solid State Physics and Optics, HAS, P.O.B. 49, H-1525 Budapest, Hungary

---

Abstract

Saturation magnetization and thermomagnetic curves were determined on FINEMET-type glassy precursors after different heat treatments below the nanocrystallization temperature. Saturation magnetization (M_s) shows a maximum at the early stage of nanocrystallization, then it drops to below the M_s characteristic for the as-quenched state. Curie temperature of the amorphous phase (T_c^{am}) increases continuously due to structural relaxation up to the beginning of nanocrystallization. The results are interpreted on the basis of irreversible structural relaxation as well as Si redistribution between the Fe(Si) nanograins and the intergranular amorphous shell. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nanocrystalline alloys; Low-temperature properties; Thermomagnetic measurements

---

The nanocrystalline structure of Fe(Si)-based (FINEMET-type) soft magnetic alloys is formed via the primary crystallization of BCC Fe(Si) solid solution from the amorphous precursors according to the basic scheme characteristic to the hypo-eutectic glasses [1]: $\mathbf{am_1 \rightarrow Fe(Si)+am_2}$, ($am_1$ and am_2 are the initial amorphous precursor and the remainder amorphous phase, respectively). Though this reaction takes place within a few seconds as thermal effect, the excellent soft magnetic properties do evolve only gradually, until the final volume fraction and the concentration distribution of the components between the nanograins and the intergranular amorphous shell is reached (usually isothermal heat treatments at around 520°C are used). The addition of nucleating element (Cu) ensures the evolution of homogeneous grain size and a sufficient separation between the two stages of crystallization. The nucleation process starts already well below the temperature of the nanocrystalline grain formation [2].The structural features and the soft magnetic properties of these alloys have been thoroughly investigated in the final nanocrystalline state [3,4]. On the contrary, relatively few data are available from the early stage of nanocrystalline grain formation, especially as far as the low-temperature properties like saturation magnetization, M_s, or coercive force are concerned [5]. In this paper the field dependence of M_s after structural relaxation, nucleation, and the early stage of crystallization will be compared with those in the fully nanocrystalline state. The measurements were carried out at 12 and 300 K.The Curie temperature of the remainder amorphous phase was determined by thermomagnetic measurements. Finally, a possible structural background of the structural relaxation and nucleation process in these alloys will be discussed.The FINEMET-type amorphous ribbons ($Fe_{73.5}Nb_3Si_{13.5}B_9Cu_1$) were prepared by Vacuumschmelze. The isothermal heat treatments were carried out at 400°C, for 30 min (structural relaxation), at 450°C, for 15 and 30 min (nucleation process together with pronounced structural relaxation without any nanocrystalline Fe–Si formation) and at

---

[*] Correspondence address. Department of Mech. Eng. Techn., Technical University of Budapest, H-1111 Budapest, Bertalan L. utca 2., Hungary. Fax: + 36-1-463-3467.

E-mail address: lovas@kgtt.bme.hu (A. Lovas).

0304-8853/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0304-8853(00)00189-X

525°C, for 4 min as well as 60 min (initial stage and completed nanocrystallization). The magnetic measurements were performed by a Quantum Design SQUID magnetometer of the type MPMS-5S with a maximum field of 5 T. Thermomagnetic measurements (using 20 K/min heating rate) have been performed with a home-made testing system based on AC susceptibility measurements as a function of temperature. The values of saturation magnetization and coercive force (measured at 12 and 300 K after the heat treatments) are collected in Table 1. Structural relaxation (400°C, 0.5 h) causes a definite increase in M_s. A similar effect was found after the nucleation heat treatment (450°C), however, it strongly depends on the measuring temperature. The maximum in saturation magnetization is reached at the early stage of nanocrystallization (525°C, 4 min). Note that an increase in M_s due to structural relaxation has been detected in Fe-based glasses [6]. It was interpreted as a result of varying degrees of chemical disorder in the glass influenced by the thermal history. On the contrary, M_s definitely decreases below that of the as-quenched value in the fully nanocrystallized state (especially if it is measured at low temperatures). With the exception of data obtained on the fully nanocrystallized sample, our observations apparently contradict the trend published in Ref. [5], where a gradual decrease in M_s was observed with increasing temperature of the isothermal heat treatments. The possible reason of this contradiction is the difference in duration and temperature of the heat treatments applied.The non-monotonic behaviour of M_s with annealing (Table 1) indicates that irreversible structural relaxation and nanocrystallization influence the Fe atomic moment in qualitatively different ways. The increase in M_s is evidently caused by the irreversible relaxation. The irreversible structural relaxation in amorphous materials can be satisfactorily interpreted in terms of annihilation of compressed (p-type defects) and stretched (n-type defects) regions (with respect to an average density) [7] where the latter process dominates, resulting in a slightly more compact structure. The atomic volumes of Fe atoms in the p-type defects become greater during annihilation leading to the increase of their magnetic moments whereas the contrary occurs to the Fe atoms in the n-type defects. However, theoretical calculations for FCC and amorphous iron [8,9] show that there exists a threshold Fe atomic distance where the atomic moments rapidly decrease with compression whereas a moderate increase is obtained for dilatation. This can result in the increase in M_s in spite of the higher weight of the n-type annihilation. It is supposed that only short-range atomic rearrangements are required for the p-type annihilation. This takes place already in the first period of the heat treatment, leading to the increase in M_s and T_c^{am}. As part of the irreversible relaxation, it also contributes to the well known decrease in H_c^{am} (see the increase in T_c observed after the heat treatment at 400°C in Fig. 1 and the appropriate H_c data in Table 1). The surprising fact that nanocrystallization causes a decrease of the average Fe magnetic moment is in line with literature reports [5]. As it is evident from the increased coercive field of the (525°C/4 min) sample (Table 1), nanocrystallization has already started at this treatment, in agreement with the literature [10]. In spite of the low volume fraction of the grains (not detected by X-ray measurements), its effect can be observed on the saturation magnetization. When the nanocrystallized fraction reaches detectability, the magnetization decreases.The Fe moment decrease with annealing can be interpreted by the continuous Si diffusion into the BCC grains as well as the ordering of the Fe(Si) phase as the isothermal heat treatment proceeds. This diffusion results in the enrichment of Si in the nanograins. The redistribution of Si atoms requires diffusion at least over a 10 nm distance. This new distribution will be completed only after the formation of the BCC nanograins. Therefore, the role of the dissolved Si becomes dominant in lowering the M_s only during more prolonged nanocrystallization heat treatments. On the other hand, it is well known that the

Table 1
Saturation magnetization (M_s) and coercive force (H_c) measured at 12 and 300 K after isothermal heat treatments

Annealings	M_s (emu/g) 12 K	M_s (emu/g) 300 K	H_c (mOe) 12 K	H_c (mOe) 300 K
As-quenched	153.1	131.3	—	102
400°C/0.5 h	154.6	135.0	83	36.6
450°C/15 min	155.1	135.5	154	38.7
525°C/4 min	159.4	138.2	165.5	67.2
525°C/1 h	145.9	134.1	67.2	< 20

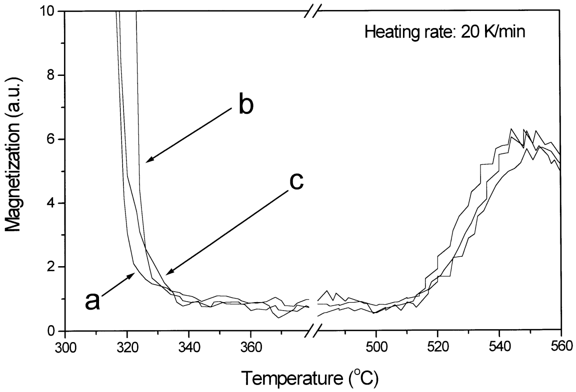

Fig. 1. Thermomagnetic curves for different isothermally annealed samples. (a) as-quenched, (b) relaxed (400°C, 0.5 h) (c) early stage of nanocrystallization (4 min. 525°C).

Fe_3Si phase forms an ordered DO_3 phase in the FINEMET alloys [11]. Since the Fe atoms in the ordered phase have lower magnetic moments than in the disordered phase [12], this can also be associated with the decrease of M_s in the optimal nanocrystallized state with respect to the underannealed ones. As nanocrystallization proceeds, the influence of Nb enrichment in the amorphous matrix on reducing M_s cannot be excluded either.

Cu as nucleating element acts through the enhancement of p-type annihilation as it is qualitatively described in Ref. [1]. As the activation energy of diffusion for Cu in the amorphous precursor is lower than that of the self-diffusion of Fe in the same matrix, the p-type defects can easily collapse after the precipitation of Cu. Therefore, the temperature for the onset of primary α-Fe crystallization will be lowered. This kind of nucleation enhancement of α-Fe precipitation due to Cu addition is supported by several experimental findings concerning the crystallization mechanism of eutectic and hypo-eutectic binary Fe–B glasses [13].

The thermal annihilation of p-type defects can also play a role in the T_c^{am} increase during relaxation ("*b*" curve in Fig. 1) and after nucleation. (The curve referring to the latter is similar to the *b* curve, so it is not plotted in Fig. 1.) After the onset of the nanograin crystallization, the thermomagnetic curve for the partially decomposed amorphous phase is already more complicated, and a small shoulder begins to develop near the Curie temperature of the amorphous phase. ("*c*"curve in Fig. 1)

This work has been supported by the Hungarian Scientific Research Fund (OTKA) through Grants T022124 and T025707.

References

[1] A. Lovas, L.F. Kiss, B. Varga, P. Kamasa, I. Balogh, I. Bakonyi, J. Phys. IV J. Inst. Met. France 8 (1998) 291.
[2] K. Hono, Y. Zhang, A. Inoue, T. Sakurai, Mater. Trans. J. Inst. Met. 36 (1995) 909.
[3] K. Hono, K. Hiraga, Q. Wang, A. Inoue, T. Sakurai, Acta. Metall. Mater. 40 (1992) 2137.
[4] G. Herzer, Scripta Metall. Mater. 33 (1995) 1741.
[5] D. Holzer, I. Pérez de Albéniz, R. Grössinger, H. Sassik, J. Magn. Magn. Mater. 203 (1999) 82.
[6] A.E. Berkowitz, J.L. Walter, K.F. Wall, Phys. Rev. Lett. 46 (1981) 1484.
[7] D. Srolovitz, T. Egami, V. Vitek, Phys. Rev. B 24 (1981) 6936.
[8] U. Krauss, U. Krey, J. Magn. Magn. Mater. 98 (1991) L1.
[9] I. Turek, J. Hafner, Phys. Rev. B 46 (1992) 247.
[10] V. Franco, C.F. Conde, A. Conde, J. Magn. Magn. Mater. 185 (1998) 353.
[11] X.Y. Zhang, J.W. Zhang, F.R. Xiao, J.H. Liu, R.P. Liu, J.H. Zhao, Y.Z. Zheng, Mater. Lett. 34 (1998) 85.
[12] S.J. Pickart, R. Nathans, Phys. Rev. 123 (1961) 1163.
[13] É. Kisdi-Koszó, A. Lovas, Key Eng. Mater. 81-83 (1993) 209.