



(Proceedings of 2011 Shanghai International Nanotechnology Cooperation Symposium, SINCS 2011, Published online 10 January 2012)

Microstructural Defects of Fe-based Amorphous and Nanocrystalline Soft Magnetic Alloys Investigated by Doppler Broadening Positron Annihilation Technique

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Abstract: The structural defects in Fe-based amorphous and nanocrystalline soft magnetic alloy has been investigated by Doppler broadening positron annihilation technique. Amorphous alloys (Type I) which can form a fixed microstructure with amorphous and nanocrystalline phases after traditional annealing have more defects than alloys (Type II) which cannot form this microstructure after the same heat treatment Also, the nanocrystallized Finemet alloy has more defects than the as-quenched state and the nanocrystallization process introduce more defects. The change of line shape parameter S with annealing temperature in Finemet alloy is mainly due to the structural relaxation, the pre-nucleation of Cu nucleus and the nanocrystallization of α -Fe (Si) phase during annealing. In addition, Nanocrystalline Finemet alloy has good thermal stability at temperature range of 500°C~580°C and good aging stability at room temperature.

Keywords: Positron annihilation; Defect; Amorphous alloy; Nanocrystalline alloy

Citation: Wei LU*, Biao YAN and Renjian Tang, "Microstructural Defects of Fe-based Amorphous and Nanocrystalline Soft Magnetic Alloys Investigated by Doppler Broadening Positron Annihilation Technique", Proceedings of Shanghai International Nanotechnology Cooperation Symposium, 68-71 (2011). <http://dx.doi.org/10.3786/sincs2011.17>

Introduction

Iron-based amorphous and nanocrystalline alloys exhibit excellent soft magnetic properties, such as very low coercivity, high permeability, and high saturation magnetization [1]. These soft magnetic materials are normally prepared by thermal annealing of an amorphous ribbon. Such heat treatments lead to a mixed structure consisting of nanocrystalline ferromagnetic particles embedded in an amorphous ferromagnetic matrix [2]. Since the excellent soft magnetic properties of Fe-based amorphous and nanocrystalline alloys depend closely on their specific structure, a profound knowledge regarding the two-phase structure is required for a

detailed understanding of their excellent soft magnetic properties.

Positron annihilation spectroscopy (PAS) is based on the ability of the positrons to seek open-volume imperfections in the solid, where they become localized and eventually are annihilated by nearby electrons [3,4]. Its sensitivity covers a wide spectrum of defect types and concentrations, often encompassing regions not within the applicable ranges of other techniques. The lifetime of positron provides direct information about the size of the free volume voids space, while the intensity of positron annihilation correlates with the amount of the free volume. The techniques of Doppler broadening spectroscopy provide the information about the inten-

sity of positronium and thus the amount of free volume in a sample. In the past, positron annihilation lifetime spectroscopy was used to study the microstructure in many different amorphous and nanocrystalline alloys [5~9]. But, to our knowledge, few papers describing the microstructure in Fe-based amorphous and nanocrystalline alloys using Doppler broadening positron annihilation technique could be found in the literature.

So, in this paper, the Doppler broadening positron annihilation technique is used to investigate the microstructure in Fe-based amorphous and nanocrystalline soft magnetic alloys. It is hoped that the present investigation would shed additional insight into the microstructure of Fe-based amorphous and nanocrystalline alloys.

Experimental

The as-quenched Fe-based amorphous alloy ribbons with 10 mm wide and about 30 μm thick were produced as the raw material by means of the melt-spinning technique on a single copper roller. X-ray diffraction (XRD) confirms that the as-quenched ribbon is in the amorphous state. The isothermally annealing was achieved in a vacuum furnace (10^{-5} Torr) at a set of temperatures from 20°C to 580°C.

The Doppler broadening measurements (with a total count of 10^6 for each spectrum) were performed at room temperature using a solid-state detector (pure Ge). After background subtraction the line shape parameter S was determined by the ratio of the central area over 20 channels to the sum of two side areas over 16 channels. Sandwiched samples were used in the Doppler broadening measurements. Each stack has five layers of ribbons with six pieces in each layer, so that the total thickness was sufficient to contain, within the sample, even the most energetic positrons.

Results and Discussion

Typically the Doppler broadening spectroscopy results are reported in terms of the line shape S parameter. Discussed in detail below, the S parameter can be thought of as essentially a bulk property of the sample, like density or porosity, and is a way of characterizing the average density and amount of defects (or free volumes) in the sample. The higher the density or amount, the larger is the value of S. By analyzing the line-shape parameter S, the microstructure about defects (or free volumes) can be studied.

Structural defects of different Fe-based amorphous alloy

Six amorphous ribbons with different compositions

were prepared by the melt-spinning technique. They are $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$, $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_2\text{V}_1\text{Si}_{13.5}\text{B}_9$, $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_2\text{Mo}_1\text{Si}_{13.5}\text{B}_9$ and $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$, $\text{Fe}_{78}\text{Si}_5\text{B}_{17}$, $\text{Fe}_{76}\text{Si}_{15}\text{B}_9$, respectively. The amorphous state of these alloys is confirmed by XRD technique. The first three alloys (Type I) can form a fixed microstructure with amorphous and nanocrystalline phases after thermal annealing of an amorphous ribbon. The latter three (Type II) cannot form this microstructure after the same heat treatment.

The results of line shape parameter S tested by Doppler broadening spectroscopy are shown in Table 1. From the results, we can see that the S parameters of type I alloys are higher than that of Type II. This means that although there is a little different in the composition of these two type alloys, but after quenching to amorphous state, there are more defects in Type I alloys than in Type II alloys. Obviously, the different amount of defects is strongly related to the addition of Cu, Nb, V and Mo elements. Generally, the defects will act as nucleus and restrain the growth of grains. The more defects will result in more nucleus and strongly restrain the growth of grains, thus lead to the nanocrystallization of Type II amorphous alloys.

Table 1 Line shape parameter S of different amorphous alloys.

No.	Composition	Parameter S
1	$\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$	1.231
2	$\text{Fe}_{72.5}\text{Cu}_1\text{Nb}_2\text{V}_2\text{Si}_{13.5}\text{B}_9$	1.191
3	$\text{Fe}_{73}\text{Cu}_1\text{Nb}_{1.5}\text{Mo}_2\text{Si}_{13.5}\text{B}_9$	1.174
4	$\text{Fe}_{78}\text{Si}_9\text{B}_{13}$	1.041
5	$\text{Fe}_{78}\text{Si}_5\text{B}_{17}$	1.046
6	$\text{Fe}_{76}\text{Si}_{15}\text{B}_9$	1.054

Change of structural defects in amorphous Finemet alloy during annealing

The dependence of S on annealing temperature for amorphous Finemet alloy is shown in Fig. 1. The measured line-shape parameter S decreased from as-quenched state (20°C) to 300°C, increased significantly between 300°C~500°C, and became stable after nanocrystallization (above 500°C).

The decrease of line-shape parameter S before 300°C may be attributed to the elimination of the free volumes formed during quenching. This is a structural relaxation process. This structural relaxation can be explained as follows: According to the model proposed by Egami et. al. [10], in as-quenched amorphous alloys there exists equal amount of dilated regions (n-type defects) and compressed regions (p-type defects). These defects which are characterized as thermal defects can annihilate each other during heating giving a more defect free amorphous structure. Positron trapping at

room temperature takes place mainly in the interior of dilated regions, where the free volumes act as deep trap. The heat treatment to this alloy reduces the concentration of both n- and p- type defects (because of the annihilation of both type of defects). So, there is a decrease of line-shape parameter S before 300°C.

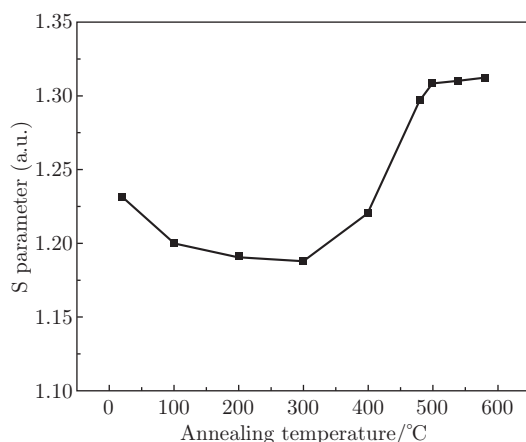


Fig. 1 Dependence of line-shape parameter S on annealing temperature for amorphous Finemet alloys.

In the range of 300°C~400°C, the mean lifetime has a slow increasing. In present case this can be explained by indicating short-range ordered (SRO) atomic clusters, which are formed and grow as the temperature increases. These boundary-like regions will induce interfacial defects and trap positrons and result an increase in S value, which represents the pre-nucleation process of Cu nucleus.

The significant increase at the temperatures which are higher than 400°C and lower than 500°C is clearly related to the nucleation and growth of nanocrystalline α -Fe (Si). In this stage, nanocrystalline α -Fe (Si) grains begin to nucleate and precipitate within the amorphous matrix, while the atoms Nb and B which are not soluble in the α -Fe (Si) phase are excluded from the crystallized regions. Hence, two phases are formed, namely the nanocrystalline α -Fe (Si) and the Nb- and B-enriched residual amorphous phase. Due to the small size of nanocrystallites, the phase boundaries between grains and the residual amorphous phase appear to prevail in the nanocrystalline alloys. As the ultrafine crystallites scarcely contain defects, it may be considered that the residual free volumes in the original amorphous phase were excluded from the regions of perfect nanocrystallites into the boundary regions during transformation of the amorphous phase into the nanocrystalline. All the free volumes scattered over the transformed amorphous matrix are concentrated on the boundary regions. At the same time, owing to the preferential interaction of the Nb and B, they probably would interact to form relatively stable clusters [11]. The Nb-B clusters enriched in the phase boundaries may hinder the migration of the

crystallized boundaries, thus make the growth of α -Fe (Si) phase become difficult, in addition, the agglomerates of the Nb-B clusters may contribute to the interfacial defects. Another origin of the extra defects may be the intersections of several crystallites, e.g., tripple junctions, suggested by Palumbo [12]. Thus, more defects are induced in the microstructure of crystallized alloys and S parameter increases rapidly.

At high annealing temperature (500°C~580°C), the structure of nanocrystallized Finemet alloy become stable and do not change with the annealing temperature due to the obstruction of Nb atoms in the phase boundaries, then caused a stable S value in nanocrystallized Finemet alloy. Accordingly, we can see that the results from positron annihilation lifetime are well consistent with the results from Doppler broadening spectrum.

In addition, the S parameter of samples annealed at high temperature (above 480°C) is bigger than that of the as-quenched alloy, which indicates that the nanocrystallized Finemet alloy has more defects than the as-quenched amorphous Finemet alloy and the nanocrystallization process of amorphous Finemet alloy introduce many defects into the structure.

Aging characterization of nanocrystalline Finemet alloy at room temperature

Generally, components which are made from nanocrystalline materials will be working at room temperature for a long time (up to several years). So the aging characterization of these nanocrystalline materials are very important. In the following, we give a detailed study on the aging characterization of nanocrystalline Finemet alloy at room temperature by Doppler broadening spectroscopy.

Table 2 shows the relative changes of line shape parameter S (ΔS) during 250 days' aging in nanocrystalline Finemet alloy which was annealed at 540°C for 30 mins. From the results we can see that there are nearly no changes in ΔS during aging for 250 days. This result indicates that nanocrystalline Finemet alloy has good aging stability.

Table 2 Relative changes of line shape parameter S (ΔS) during aging in nanocrystalline Finemet alloy.

Aging time (Days)	0	20	50	100	150	200	250
ΔS	0.091	0.089	0.092	0.090	0.091	0.091	0.089

Conclusion

The structural defects in Fe-based amorphous and nanocrystalline soft magnetic alloy has been investigated by Doppler broadening positron annihilation

technique. And the summary can be concluded as follows:

1. Alloys (Type I) which can form a fixed microstructure with amorphous and nanocrystalline phases after traditional annealing have more defects than alloys (Type II) which cannot form this microstructure after the same heat treatment.

2. Nanocrystallized Finemet alloy has more defects than the as-quenched amorphous Finemet alloy and the nanocrystallization process introduces additional defects into the structure.

3. The change of line shape parameter S with annealing temperature in Finemet alloy is mainly due to the structural relaxation, the pre-nucleation of Cu nucleus and the nanocrystallization of α -Fe (Si) phase during annealing.

4. Nanocrystalline Finemet alloy has good thermal stability at temperature range of 500°C~580°C and good aging stability at room temperature.

In addition, this work shows that positrons are very sensitive to the variation of defects associated with different amorphous alloys and can be applied as a useful tool to the investigation of their structural changes during annealing.

References

- [1] A. Makino, T. Bitoh, A. Inoue and T. Masumoto, *J. Appl. Phys.* 81, 2736 (1997).
- [2] A. Makino, K. Suzuki, A. Inoue, Y. Hirotsu and T. Masumoto, *J. Magn. Magn. Mater.* 133, 329 (1994).
- [3] P. Schultz and K. G. Lynn, *Rev. Mod. Phys.* 60, 701 (1988).
- [4] M. J. Puska and R. M. Nieminen, *ibid.* 66, 841 (1994).
- [5] H. E. Schaefer, R. Wurschum, R. Birringer and H. Gleiter, *Phys. Rev. B* 38, 9545 (1988).
- [6] X. D. Liu, J. T. Wang, D. H. Ping and D. X. Li, *J. Appl. Phys.* 74, 4501 (1993).
- [7] H. Y. Tong, B. Z. Ding, J. T. Wang, K. Lu, J. Jiang and J. Zhu, *J. Appl. Phys.* 72, 5124 (1992).
- [8] X. Y. Zhang, Y. Guan, J. W. Zhang and *J. Appl. Phys.* 92, 6933 (2002).
- [9] D. Suh, P. A. Kumar and R. H. Dauskardt, *Acta Materialia* 50, 537 (2002).
- [10] T. Egami, K. Maeda and V. Vitek, *Phil. Mag. A* 41, 883 (1980).
- [11] H. S. Yang, G. C. Tu, X. Y. Xiong, Z. X. Zu and R. Z. Ma, *J. Magn. Magn. Mater.* 138, 94 (1994).
- [12] G. Palumbo, S. J. Thorpe and K. T. Aust, *Scripta Metall. Mater.* 24, 1347 (1990).