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Microstructure Evaluation of Fe-based Amorphous Alloys Investigated by Doppler Broadening Positron Annihilation Technique

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Abstract: Microstructure of Fe-based amorphous and nanocrystalline soft magnetic alloy has been investigated by X-ray diffraction (XRD), Transmission electronic microscopy (TEM) and Doppler broadening positron annihilation technique (PAT). Doppler broadening measurement reveals that amorphous alloys (Finemet, Type I) which can form a nanocrystalline phase have more defects (free volume) than alloys (Metglas, Type II) which cannot form this microstructure. XRD and TEM characterization indicates that the nanocrystallization of amorphous Finemet alloy occurs at 460℃, where nanocrystallites of α-Fe with an average grain size of a few nanometers are formed in an amorphous matrix. With increasing annealing temperature up to 500℃, the average grain size increases up to around 12 nm. During the annealing of Finemet alloy, it has been demonstrated that positron annihilates in quenched-in defect, crystalline nanophase and amorphous-nanocrystalline interfaces. 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. This study throws new insights into positron behavior in the nanocrystallization of metallic glasses, especially in the presence of single or multiple nanophases embedded in the amorphous matrix.

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

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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 nanocrystallization is required for a detailed understanding of their excellent soft magnetic properties.

Positron annihilation spectroscopy (PAS) is a non-destructive spectroscopy technique to study voids and defects in solids and 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

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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 intensity 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.

Therefore, in this paper, the Doppler broadening positron annihilation technique is used to study the microstructure in Fe-based amorphous and nanocrystalline soft magnetic alloys. We will investigate the difference of interfacial defects (or free volume) 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℃ to 580℃.

Figure 1 shows the schematic diagram of Doppler broadening measurement. 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.

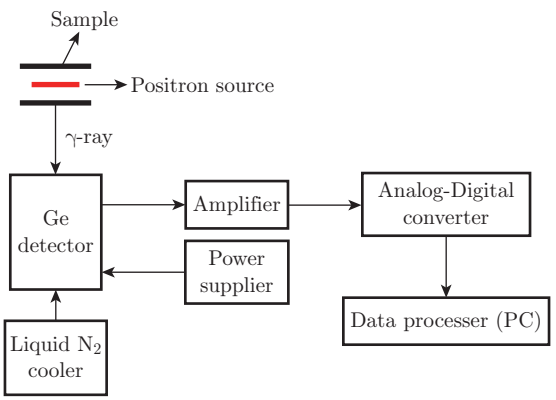

Fig. 1 Schematic diagram of Doppler broadening measurement.

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 $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_2V_1Si_{13.5}B_9$, $Fe_{73.5}Cu_1Nb_2Mo_1Si_{13.5}B_9$ and $Fe_{78}Si_9B_{13}$, $Fe_{78}Si_5B_{17}$, $Fe_{76}Si_{15}B_9$, respectively. The amorphous state of these alloys is confirmed by XRD technique. The first three alloys (Type I) can form a mixed 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 measured from Doppler broadening spectroscopy are shown in Table 1. From the results, it can be seen that the S parameters of type I alloys are higher than that of Type II. This means that although there is a little difference in the composition of these two type of alloys, there are more defects in Type I alloys than in Type II alloys after quenching to amorphous state. Obviously, the different amount of defects is strongly related to the addition of Cu, Nb, V and Mo elements. Generally, the defects will

Table 1 Line shape parameter S of different amorphous alloys.

No.		Composition	Parameter S
Finemet Type I	1	$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$	1.231
	2	$Fe_{72.5}Cu_1Nb_2V_2Si_{13.5}B_9$	1.191
	3	$Fe_{73}Cu_1Nb_{1.5}Mo_2Si_{13.5}B_9$	1.174
Metglas Type II	4	$Fe_{78}Si_9B_{13}$	1.041
	5	$Fe_{78}Si_5B_{17}$	1.046
	6	$Fe_{76}Si_{15}B_9$	1.054

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 I amorphous alloys.

Change of structural defects in amorphous Finemet alloy during annealing

The dependence of S on annealing temperature for amorphous Finemet ally is shown in Fig. 2. The measured line-shape parameter S decreases from as-quenched state (20℃) to 300℃ and increases significantly between 300℃∼500℃, then it becomes stable after nanocrystallization (above 500℃).

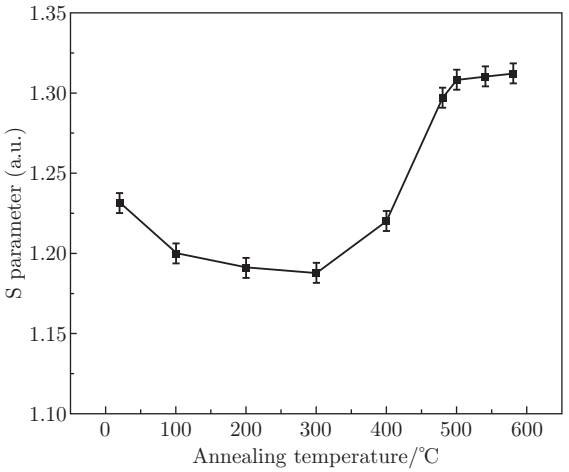

Fig. 2 Dependence of S on annealing temperature for amorphous Finemet ally.

The decrease of line-shape parameter S below 300℃ 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℃. In the range of 300℃∼400℃, the line-shape parameter S has a slow increasing. In present case this can be explained by 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 in 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℃ and lower than 500℃ 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 the 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 makes 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℃∼580℃), the structure of nanocrystallized Finemet alloy becomes stable and does not change with the annealing temperature due to the obstruction of Nb atoms in the phase boundaries, then caused a stable grain boundaries and free volumes in interfaces, which result in a stable S value in the nanocrystallized Finemet alloy.

Conclusion

The structural defects in Fe-based amorphous and nanocrystalline soft magnetic alloy has been investigated by Doppler broadening positron annihilation technique in present paper. Results show that 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. The nanocrystallized Finemet alloy has more defects than the as-quenched amorphous Finemet alloy and the nanocrystallization process introduces

additional defects into the structure. 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, present experiment 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.

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