Preparation and Study of the Crystallization Behavior of the Fe$_{87}$Zr$_7$B$_{5-x}$ Nanocrystalline Soft-Magnetic Alloys

Nagantié Kone$^1$ and Tu Guo Hua$^2$

$^1$Malian Agency of Radiation Protection (AMARAP), Building A3, Complexe of Ex-CRES, PO Box 1872, Hill of Badalabougou, Bamako, Mali

$^2$Nanging Normal University, Nanging, People’s Republic of China

Abstract: A series of materials of composition Fe$_{87}$Zr$_7$B$_6$, Fe$_{87}$Zr$_7$B$_7$Ag$_1$, Fe$_{87}$Zr$_7$B$_7$Cu$_1$ have been prepared by the melt spinning method for different cooling speed to get completely or partly amorphous ribbons. It is proved that the crystallization process is composed of 2 steps. The first step is the precipitation of &-Fe only and the second step is the phase separation of &-Fe, Fe$_2$Zr and Fe$_2$B.

All our own made materials have been used in the library monitoring system. Most of them showed a capability of trigging the alarm of the system. The trigging sensitivity at different positions and different sample geometry were investigated and the physical mechanisms were analyzed.

Key words: Fe-based, amorphous, alloys, crystallization, nanocrystalline, magnetic, quenching.

1. Introduction

Fe-based amorphous alloys show a great interest for their soft magnetic properties, i.e. with their high magnetic flux density [1, 2]; or from a theoretical view, a magnetic material is to be said soft if it shows:

- Low effective magnetic anisotropy;
- Small magnetostriction, when it is used in AC (alternating current) field, it needs low electrical conductivity and small domain width to reduce the magnetic losses. The magnetostriction always happens in all magnetic materials.
- The magnetostriction, in the case of saturation magnetization is characterized by a coefficient noted $\lambda_8$ which is a characteristic of a magnetic material. The magnetocrystalline anisotropy is characterized by a coefficient $K$ which shows the different energy of different directions of magnetization with respect to the crystal orientation.
- It is the mechanical deformation along the substance (dimensions changes) with the changing of the magnetical situation, the magnetostriction free energy is nothing but the interaction between mechanical stress and magnetostriction.

- The magnetic domain is a local region in the material where all the local magnetic moments are aligned in the same direction because of the exchange interaction between spins [1, 2]. The domain structure of a material plays an important role in the magnetic behavior of the material.
- In 1960, a new method of producing amorphous materials was reported by Graham et al. [5]. From that time, most of the research work and industrial interest have been concentrated on this method. It consists of producing amorphous (short range atomic order) alloy ribbons by rapidly quenching liquid melt on to a rotating wheel.
- During the rapid cooling, the atoms do not have enough time to arrange themselves before solidifying and results in random arrangement. Therefore, better soft magnetic properties related to the very small magneto-cristalline anisotropy result from the absence of atomic long range order. In the case of domain wall motion, due to structural uniformity, high flux density

---

Corresponding author: Nagantié Kone, Dr., master of conference, research field: radiation physics.
is also obtained. So, during the later years, many research efforts are made to use Fe-based soft magnetic alloys for high frequency applications such as high frequency transformer and choke cores. Since the report of Yoshizawa et al. in 1988 [3], particular attention has been accorded to the Fe-based amorphous nanocrystalline alloys to minimize magnetic core losses annealing procedure.

- In fact, a (Fe-based) nanocrystalline alloy is crystallized often from an amorphous matrix, containing many methods such as single roller spinning combined with after annealing or by consolidation of mechanical alloyed (using ball mill) powder by hot pressor. The magnetic properties of such materials produced, depend on many factors like the grain size, the Fe-B-M (M = Mo, Nb, Zr…) alloys with nanocrystalline structure showing a large interest.

- Many reports have been published about improving Fe-based nanocrystalline structure showing a large interest.

- Many reports have been published about improving Fe-based nanocrystalline amorphous materials. In a general way, they can be summarized as follows.

1.1 Aim
- Fabrication of amorphous soft magnetic materials using spinning procedure combined with after annealing;
- Investigation of the effect of cooling speed after the end of annealing;
- Annealing temperature and time effect.

1.2 Experimental Procedure

The magnetic properties have been measured:
- Ms: by vibrating sample magnetometer $\mu_i$, $\mu_{\text{max}}$, $\mu_e$; by a BH loop tracer;
- $H_c$: by impedance analyzer;
- $\lambda_\gamma$: by capacitance bridge or strain guage;
- $\rho$: by DC four-point probe method;
- Bs: by SQUID (super conducting quantum interference device);

- The structure of sample: by super X-ray diffractometre using CuK & radiation and TEM;
- The surface structure: by SEM and AFM;
- The mean grain size and the volume fraction of residual amorphous phase evaluated: from the peak width of the X-ray diffraction spectrum and $^{57}\text{Fe}$ Mossbauer study respectively;
- the density: by Archimedian method;
- the mechanical and thermomechanical analysis: by TMA.

1.3 Results

During these studies, it has been found that:
- Very good soft magnetic properties can be obtained for grain size less than 15 nm, amorphous phase less than 35%, the zero crystalline anisotropy does not correspond necessarily to the highest permeability [4];
- A decrease in the ribbon thickness which is related to higher quenching speed was very effective in improving the permeability as well as the core loss in high frequency range [5].
- To reach good results, many ways are used to treat the raw material as well as in the spinning and annealing processes [6, 7].

It has been reported that high cooling speed after the end of annealing is very effective to lead to zero crystalline anisotropy, minimize amorphous phase and achieve small grain size. Hence, the initial permeability $\mu_i$ and the saturation magnetic flux density Bs are improved and the magnetostriction coefficient $\lambda_\gamma$ lowered [8].

But the most impressive improvement of grain size has been related to adding small amount of impurity (Cu, Ag ..., with only 1 at.% in the best case) [6, 8]. In the Fe-Zr-B-M (M = Ag, Cu...), the effect of the impurity has been explained as Cu, Zr, Ag rich regions around the b-c-c Fe cannot grow in the region. So, the grain size becomes very small and the alloy will show excellent properties [8].
Through the analysis of several reports mentioned above, it seems that the best composition in Fe-B-M alloys is between 92% and 93% of Fe-B with at least 80% of Fe and 7% to 8% additive elements M. This may be due to the fact that for more than 75% of the Fe there will be no completely amorphous phase.

2. Experimental Procedures

2.1 Preparation of Three Alloys: Fe$_{87}$Zr$_7$B$_6$, Fe$_{87}$Zr$_7$B$_5$Ag$_1$, Fe$_{87}$Zr$_7$B$_5$Cu$_1$

2.1.1 Description and Principle (Fig. 1)

The samples can be melt either by an arc furnace or by a copper “boat” tube. We will be using this later.

It is composed of a quartz tube of about 50 cm long and 35 mm of diameter containing a copper tube water cooled and carrying the “boats” in which samples are melted. A high frequency current was produced by radio frequency magnetic field in the winding coil. The raw materials placed in this field will induce a high frequency eddy current because of the low resistivity of the material which will create a high power. The power will generate a heat to melt the samples in the “boat”.

Several melting will give homogenous alloy ingot. The boat tube presents more advantages than the arc furnace. With the former, there is no too high temperature and no spread of the sample will occur during the heating process. Also, because of the limited volume of the quartz tube, there will be much less oxidation for the sample and the composition of the sample will be accurately maintained.

Our samples have been melted between 2 kV and 3 kV of the plate voltage under a pure Argon pressure of 0.6 atm.

Three types of ingot of composition Fe$_{87}$Zr$_7$B$_6$, Fe$_{87}$Zr$_7$B$_5$Ag$_1$, Fe$_{87}$Zr$_7$B$_5$Cu$_1$ with respective masses of 1.5 g, 3.0 g and 15.0 g have been prepared by three different ways.

The original materials were: Fe, Zr, B, Ag and Cu with respective purities of: 99.9%, 99.5%, 99.5%, 99.99% and 99.999%.

(1) Direct combination of the elements Fe, B, Zr: In this case we met some difficulty in getting a good ingot because the B has quite high melting point and takes a long time to dissolve into the alloy completely. During this long period, the Zr has more chance to be oxidized.

(2) Precombination of Fe and B to form Fe$_{80}$B$_{20}$ by using this way, melting became easier then Fe$_{87}$Zr$_7$B$_6$, Fe$_{87}$Zr$_7$B$_5$Cu$_1$ were prepared without difficulty. But a serious problem of evaporation occurred during the Ag melting and Ag seemed not well dissolved. To solve this problem, we tried another way of preparation.

(3) Precombining Ag and Zr to form AgZr alloy

No evaporation occurred during the melting of AgZr. But, when it came to combining AgZr with Fe$_{80}$B$_{20}$, additive iron and Zirconium, problem of silver evaporation still remained, although the evaporation is not serious, it does affect the precise composition of the final ingot.

Fig. 1  Copper boat.
2.2 The Spinning

Description and principle (Fig. 2): The spinning chamber is a cylindrical iron tube of 30 cm height and 33 cm diameter containing a copper wheel of 120 mm in diameter droved by an electrical motor of variable speed. The heat generator is also a radio frequency furnace.

About 3 to 5 g of the raw material broken in suitable sizes is melted in a quartz tube with an orifice of 0.6 mm in diameter and known ejection angle. The molten solution was pouched in jet on the copper wheel (good thermal conducting) rotating at a defined speed, the ribbon produced collected in the collecting tube.

Fourteen samples have been prepared in the following conditions:

- The chamber pressure: 0.7 atm;
- Ejection gas pressure: 1.1 atm;
- RF furnace PC = 2 amp, PV = 3 kV;
- The copper wheel speed varied from 25 m/s to 45 m/s.

2.3 Annealing

Description (Fig. 3): A very efficient annealing furnace was made with a ceramic tube carrying heater wire with thermal isolation layer of glass wool. But ends of the ceramic tube were closed with heat choke made of refractory material and carrying small openings for the thermocouple and the evacuating sample tube. A thin wall stainless steel tube was prepared to keep vacuum around the sample to be annealed. The temperature control was assumed by an automatic temperature controller using a chromel-alumel thermocouple.

Such system has shown a very reliability since very light oxidation has been observed on the samples and the temperature fluctuation was very close to zero.

The three samples of composition Fe$_{87}$Zr$_7$B$_{6}$, Fe$_{87}$Zr$_7$B$_6$Ag$_1$, Fe$_{87}$Zr$_7$B$_6$Cu$_1$ spun at a copper wheel speed of 45 m/s have been successively annealed at 200 °C, 400 °C and 500 °C during a time period of 1 h, 50 min, 40 min and 30 min.
The samples have been annealed under a vacuum of 104 mmHg produced by a diffusion pump.

2.4 Measurement

A new device based on the automatic display of hysteresis loop has been built. It is using a single strip ribbon instead of toroid. With such device, the measurement becomes easier and rapid. The details of the measuring device as well as the measures will be described elsewhere.

3. Experimental Results and Discussions

3.1 Samples Preparation and Crystallization

3.1.1 Sample Preparation

Their densities have been measured by the Archimedian method and the cross section deduced from the density which was in average 7.4 g/cm³. The permeability and coercive field of the samples have been measured in a quenched state. Three samples of composition respectively Fe₈₇Zr₇B₆, Fe₈₇Zr₇B₅Ag₁, Fe₈₇Zr₇B₅Cu₁ annealed at 200 °C (1 h), 300 °C (40 min) and 500 °C (30 min) have been measured.

The Fe₈₇Zr₇B₅Ag₁ reached a maximum permeability at 300 °C but did not show the drastic increase as in the reference paper [5]. The two others reached their maximum permeability at 400 °C. Before annealing the samples, the X-ray analysis showed an amorphous state as can be seen in Fig. 4. From the DTA (differential temperature analysis) data (Figs. 10 and 11), it appeared that:

(a) All the samples were either completely amorphous (ideally amorphous for those spun at 45 m/s) or partly amorphous (lower spun speed).

(b) The crystallization behavior in our case was different from that of the reference paper report [3]. All the samples showed two steps of crystallization as shown by their DTA curve in Fig. 10 except that spun at 25 m/s for which the DTA curve is shown in Fig. 11.

3.1.2 Crystallization Behaviour of the Samples

The two steps of crystallization can be clearly explained by the X-ray data in Figs. 5 and 7 where we can see the gradual passage from partly amorphous Fig. 5 to totally crystallized Fig. 7 with very sharp peaks, through the intermediate state Fig. 6.

Fig. 5 shows the XRD (X-ray diffraction) pattern of Fe₈₇Zr₇B₆ ribbons annealed at 500 °C when the first crystallization peak rises and the ribbon still keeps very ductile and cannot be powdered, the X-ray pattern reflects more about the surface situation. We can see apart from &-Fe peaks of Fe₃O₄ and ZrO.

Fig. 6 shows the pattern of the same ribbon heated in DSC system just after the first crystallization peak is over than rapidly cooled down. The sample became brittle and ready to be powdered. Here, we can see more perfect &-Fe lattice, oxidation products and only a trace of ZrO.

Fig. 7 shows the same sample heated at 710 °C which is after the complete crystallization. Here, we can see the sharpest peak with whole set of &-Fe peaks.
as well as Fe₃O₄, ZrO, ZrFe₂ and Fe₂B which perfectly agree with the known phase diagram of Fe-Zr and Fe-B binary system. From these analyses we can conclude that the material crystallized firstly through the precipitation of α-Fe, then with the increasing density of Zr and B in amorphous matrix, finally crystallized completely through a phase separation. This crystallization will give us some hint in controlling the microstructure of the material through annealing.

In Figs. 8 and 9, we have also plotted the onset, the peak and the crystallization enthalpy versus the quenching rate.

![X-ray diffraction pattern](image1)

**Fig. 4** X-ray diffraction pattern.

![X-ray diffraction curve (after 500 °C)](image2)

**Fig. 5** X-ray diffraction curve (after 500 °C).
Fig. 6  X-ray diffraction curve (after 610 °C).

Fig. 7  X-ray diffraction curve (after 710 °C).
Preparation and Study of the Crystallization Behaviour of the Fe$_{87}$Zr$_7$B$_{5-x}$
Nanocrystalline Soft-magnetic Alloys

Fig. 8 DTA.

The feature is as follows:

- ΔH curves:
  The larger ΔH corresponds to higher quenching rate. A latent heat means a larger difference between the amorphous structure and the crystalline structure, which means the more complete amorphousness. Increasing the quenching rate, the degree of randomness increases correspondingly. The curve also reflects the sample with lower rate being only partly amorphous.

- The DTA peak and onset in Fig. 8 show:
  The higher crystallization temperature corresponds to the higher quenching rate or more stability of the amorphous state because more complete amorphous structure will be more difficult to form crystalline nuclei within the amorphous matrix.

  The materials with smaller quenching rate are not completely amorphous, so, the crystalline nuclei already exists in the sample, only the crystalline nuclei growth can cause the crystallization of these samples as
Preparation and Study of the Crystallization Behaviour of the Fe$_{87}$Zr$_7$B$_{5-x}$ Nanocrystalline Soft-magnetic Alloys

Fig. 10  DTA curve.
we know nucleation needs more energy than simple growth.

As far as we know for various ferromagnetic amorphous materials, this series of material has quite high crystallization temperature and hence better stability in the practical purpose that is one of the advantages of these materials.

4. Conclusion

(1) Our materials can be made perfectly amorphous or partly amorphous by changing the quenching speed.

(2) Almost all the samples will be crystallized through two steps:

• the first step is the precipitation of \( \alpha \)-Fe;

• the second step is the phase separation of \( \alpha \)-Fe, \( \text{Fe}_2\text{Zr} \) and \( \text{Fe}_2\text{B} \).

References

[1] Choi, J. S., et al. 1995. “Nanoscale Size Effect of Magnetic Nanocrystals and Their Utilization for Cancer Diagnosis via Magnetic Resonance Imagin.” J. of Korean Magn. Soc. 5 (5): 47.

[2] Freeman, M. R., and Smyth, J. F. 1996. “Picosecond Time-resolved Magnetization Dynamics of Thin-Film Heads.” Journal of Applied Physics 79 (8): 5898-900.

[3] Yoshizawa, Y. A., Oguma, S., and Yamauchi, K. 1988. “New Fe-based Soft Magnetic Alloys Composed of Ultrafine Grain Structure.” Journal of Applied Physics 64 (10): 6044-6.

[4] Chaudhari, P., and Turnbull, D. 1978. “Structure and Properties of Metallic Glasses.” Science 199 (4324):
11-21.

[5] Graham, C. D., et al. 1995. “HTTLPR-environment Interplay and Its Effects on Neural Reactivity in Adolescents.” J. of Korean Magn. Soc. 5 (5): 579.

[6] Hermando, A., et al. 1995. J. of Korean Magn. Soc. 5 (5).

[7] Chikazumi, S., and Graham, C. D. 2009. Physics of Magnetism. Oxford: Oxford University Press.

[8] Kim, B. G., et al. 1995. “Structure and Magnetic Properties of Nanocrystalline Soft Ferromagnets.” Journal of Applied Physics 77 (10): 5298.