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Soft Magnetic Properties of Annealed Co-Based Amorphous $Co_{66}Fe_4Ni_1B_{15}Si_{14}$ Alloy Ribbon

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The amorphous Co-based alloy $Co_{66}Fe_4Ni_1B_{15}Si_{14}$ (Metglas® 2714A) is a suitable magnetic core material for high frequency operation. Appreciable reduction of the coercive force can be achieved by proper heat treatment. In this study, samples annealed at wide temperature range were analyzed using differential scanning calorimetry, high frequency *B-H* loop tester, X-ray diffractometer and resistivity meter. The results show that coercive force at 10 kHz decreases with increasing annealing temperature up to 773 K, but dramatically increases above this temperature. The squareness shows that the magnetic anisotropy on longitudinal direction of the as-cast state remains up to 773 K. Above this temperature, it decreases down to 0.5 that represents random distribution of magnetic domains. The crystallization abruptly occurs between 781 K and 783 K.

1. Introduction

Metglas® 2714A with nearly zero magnetostriction has been widely used in switching mode power supply, high frequency transformer, high sensitive matching transformer, ultrasensitive current transformer, magnetic shielding [1] and magnetic field measuring sensor [2]. Hence high frequency properties and structure of Co-based metallic glass are very important for the basic research and the technological point of view. Several interesting magnetic properties of Metglas® 2714A have been reported [3-6]: (1) the anisotropy direction changes from longitudinal to transverse when sample is annealed just above Curie temperature T_c, (2) the magnetization occurs by the domain wall motion at magnetizing frequencies up to 50 kHz.

Generally they measure the high frequency magnetic properties using toroidal shape of sample. However the AC initial permeability is very sensitive to the winding method of the ribbons [7]. This implies that the AC magnetic properties of the sample with a toroidal shape may be different with a flat shaped sample. It is obvious that some of reported data have the value only for restricted cases.

In this work, the author studied the high frequency magnetic properties by using single sheet type high frequency *B-H* loop tracer to avoid the conflict [8]. High frequency magnetic hysteresis behaviors of a Co-based amorphous alloy annealed at different temperatures were measured and the macroscopic magnetic properties with annealing temperature were studied. From the results we briefly deduced the structural changes with annealing temperature.

2. Experimental details

The starting sample was the amorphous alloy, Metglas® 2714 A ($Co_{66}Fe_4Ni_1B_{15}Si_{14}$) produced by Allied Signal Co. with thickness of 20 μm and width of 50 mm. The devitrification phenomenon was measured using a differential scanning calorimeter (Seiko I DSC 2000) with silver pan using computerized data acquisition under argon atmosphere. The thermogram was taken in a continuous heating mode at a constant rate of 10 K/min from room temperature to 1123 K. Differential scanning calorimetry indicates that the two exothermic processes existed as shown in Fig. 1. The first crystallization peak maximum occurs at 821.8 K, the second at 929.5 K. It is important to notice that these two temperatures are not the static phase transition temperatures but the dynamic ones. Therefore the real equilibrium temperatures are somewhat lower than the measured values because of heating process.

The surface of ribbon sample of 20 μm × 5 mm × 90 mm were cleaned by chemical etching. The samples were then annealed during one hour at different temperature T_a, from 473 K to 813 K and in vacuum condition of 5 millitorr to investigate the properties of the high frequency *B-H* loops and the X-ray diffraction patterns with annealing temperature. Before and after the isothermal annealing, each sample

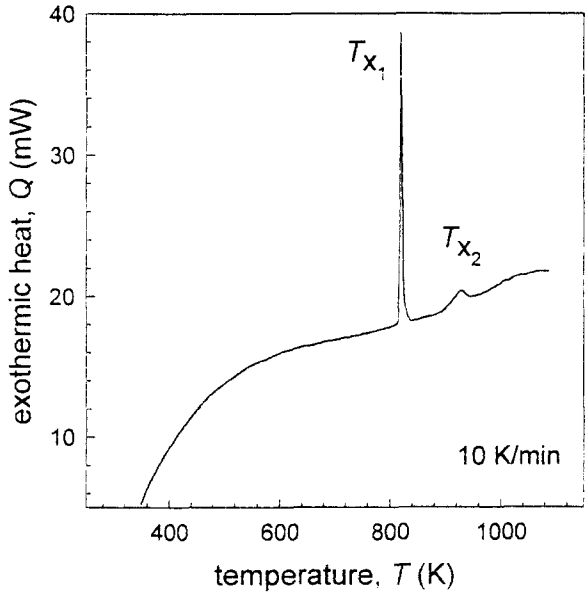

Fig. 1. Differential scanning calorimetry plot for as-cast state with constant heating rates of 10 K/min.

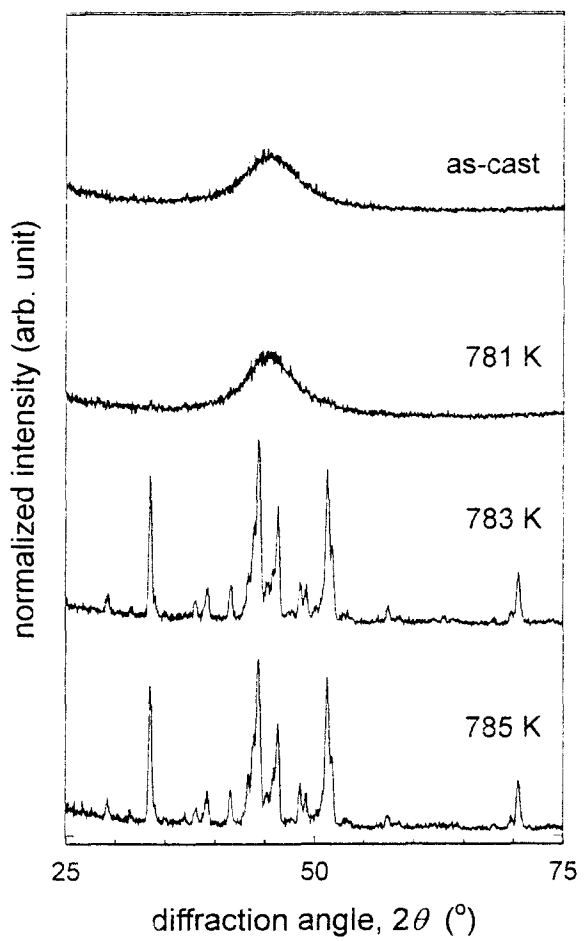

Fig. 2. Several selected X-ray diffraction patterns for the annealed samples: as-cast state (a), annealed at 781 K (b), at 783 K (c) and at 785 K (d).

was taken in a continuous heating and cooling modes at a constant rate of 10 K/min.

To obtain the structural information of as-cast and the annealed samples, X-ray diffractometer (12 kW, Rotaflex D/MAX -RB wide-angle goniometer) with CuKα was used, and the accelerating voltage and current were set to 50 kV and 100 mA respectively. Using θ-2θ reflection method with rotating sample, we measured X-ray intensity as a function of reflection angle, 2θ, between 20° and 130°. Several selected X-ray diffraction patterns of the samples in as-cast state and after annealing between 473 K and 785 K during 1 hour is shown in Fig. 2. X-ray diffraction patterns of annealed samples up to annealing temperature of 781 K are similar to that of as-cast amorphous alloy at around 2θ = 45°. However the spectra of samples annealed at above 783 K show obviously different patterns which implies that bulk crystallization occurs at the temperature between 781 K and 783 K.

In addition of X-ray diffraction measurements, we measured the resistivity of each sample by the conventional four-point probe method with inter-probe distance of 1 mm using Napson RT-8A-8 resistivity tester. The average resistivity is taken from several measurements for each ribbon.

In order to measure coercive force, remenance and saturation magnetic induction, we used a single strip *B-H* loop tracer operating up to 100 kHz magnetizing frequency. The *B*, *H* signals were digitized using 12-bit resolution of digital storage oscilloscope (Nicolet Pro32) and the digitized data were transferred to PC via IEEE-488 bus.

3. Results and discussion

The 10 kHz *B-H* loops for as-cast and several annealed ribbons are shown in Fig. 3. The as-cast sample has a square *B-H* loop shape with a low coercive force ($H_c \cong 0.14$ A/cm). This rectangular shape of *B-H* loop means that the magnetic structure of as-cast amorphous alloy consists of 180° domain structure. The hysteresis loops of annealed samples at temperature up to 769 K were similar to the as-cast state in shape, and it means that the as-cast domain structure reserved to annealed samples up to the temperature of 769 K as shown in Fig. 3(a). Annealing the sample at above 773 K, the shape of *B-H* loop changed from a rectangular shape to a round one. This implies that the magnetization direction changes from longitudinal direction. Another interesting point to note is that the shape of *B-H* loop changes temporarily from a rectangular type (*Z*-type) to a round type (*R*-type) [9] at 523 K that is near above Curie temperature T_c region as shown in Fig. 3 (b). It is known that the change of anisotropy direction at the annealing temperature near T_c is due to the internal stresses produced by different thermal expansion between the bulk and the surface layers [4]. Increasing the annealing temperature, however, this stress inhomogeneity disappears at above 573 K and the anisotropy direction is maintained the same distribution with the as-cast state.

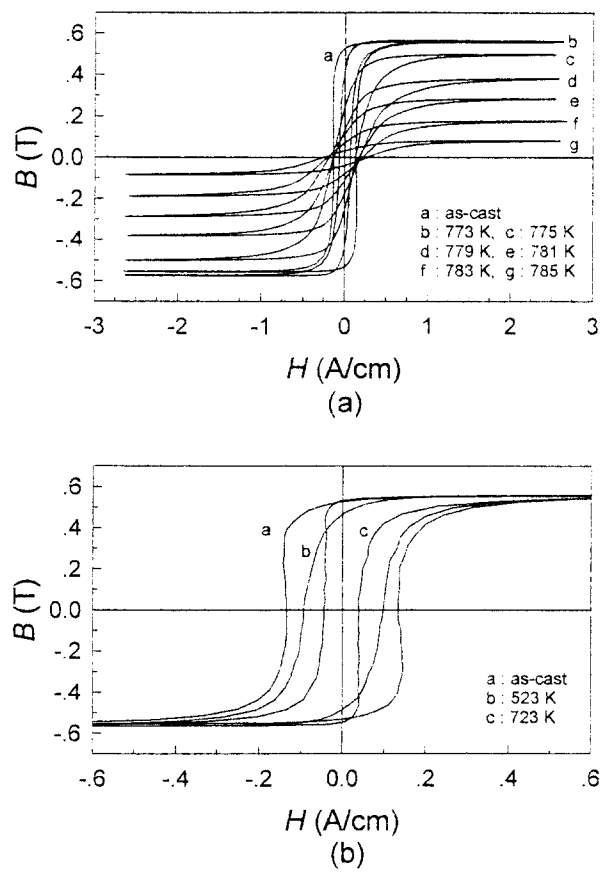

Fig. 3. Several selected AC B-H loops at the magnetizing frequency of 10 kHz for annealed samples: regions between 773 K and 785 K (a), and between 473 K and 773 K (b).

Fig. 4 shows the saturation magnetic induction as a function of annealing temperature. The saturation magnetic induction is nearly constant to a value of 0.56 T up to 773 K. However, it drops steeply, between 773 K and 785 K, with the slope of 0.09 T/K as the annealing temperature is increased. Decreasing saturation magnetic induction indicates that the total magnetic moment of sample decreases with increasing annealing temperature. Hence we can interpret the phenomenon that the chemical environment of Co atom changes from the state of random mixture to the state of having more non-magnetic atoms such as B and/or Si. Therefore it may be thought that the rearrangement of constituent atoms does not occur at annealing temperature up to 773 K, but proceed rapidly at above 773 K.

Thermal annealing leads the metastable microstructure of as-cast amorphous alloy towards more relax and stable atomic configuration. The degree of structural relaxation can be evaluated by studying the increase of remanence after different heat treatments. Thus, the squareness of a hysteresis curve (remanence-to-saturation magnetic induction ratio B_r / B_{max}) gives the information of the distribution of the magnetization direction of domains. The squareness with annealing temperature is represented in Fig. 5. The squareness of as-cast state is 0.98.

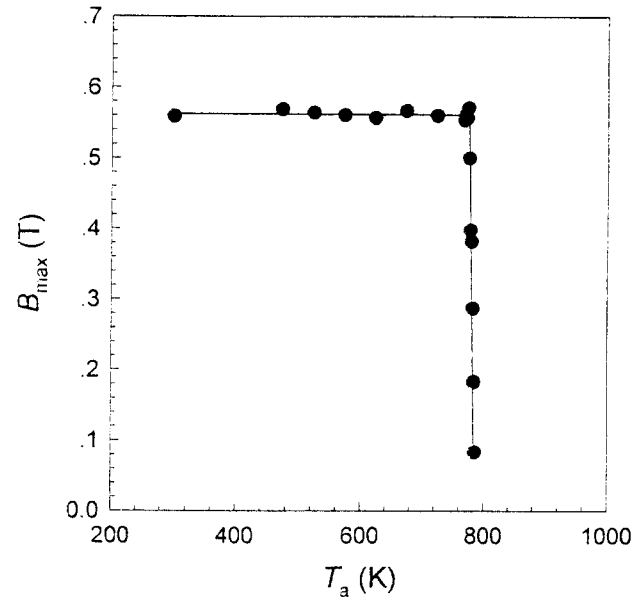

Fig. 4. Saturation magnetic induction B_{max} at the magnetizing frequency of 10 kHz for annealed samples.

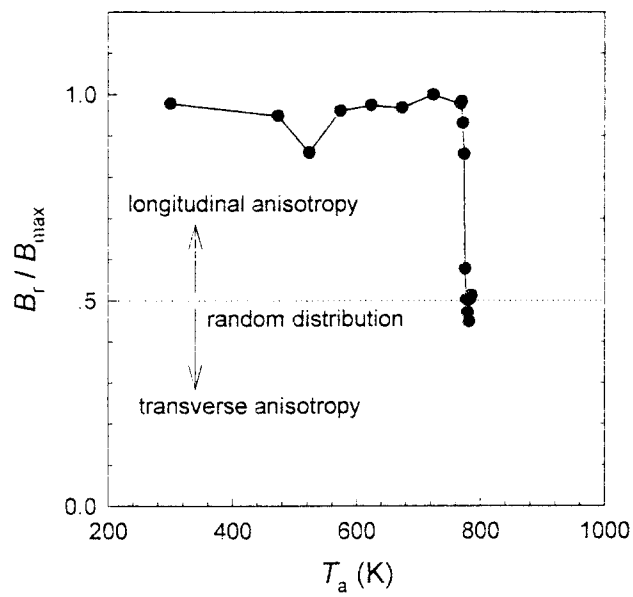

Fig. 5. Remanence ratios B_r / B_{max} at the magnetizing frequency of 10 kHz for annealed samples.

This high value of B_r / B_{max} means that all the magnetic domains are arranged in longitudinal direction as discussed above. In general magnetization is axially oriented after structural relaxation because of the shape anisotropy of ribbons. Fig. 5 illustrates that the longitudinal anisotropy of sample does not disappear by heat treatment up to the annealing temperature of 769 K for 1 hour. Beyond 769 K, the longitudinal anisotropy is not maintained to a constant value but sharply decreased, and disappear at 777 K with the squareness of 0.5. Above this temperature, the squareness was nearly constant. In Co-rich amorphous alloy, if B_r / B_{max} is

0.5, all the magnetic domains are randomly oriented. Thus, we can conclude that the magnetic domains are randomly distributed both the amorphous state just below 781 K and the crystalline state above 783 K.

The coercive force as a function of annealing temperature T_a at 10 kHz magnetizing frequency is shown in Fig. 6. The coercive force decreases as T_a increases from 473 K up to 767 K, where the coercive force reaches a minimum value of 0.037 A /cm. The coercive force does not change with annealing time between 673 K and 723 K. Beyond the annealing temperature of

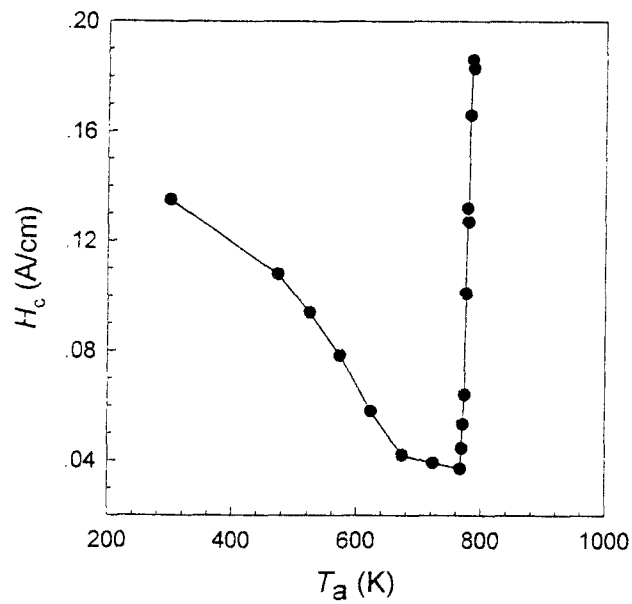

Fig. 6. Coercive force H_c at the magnetizing frequency of 10 kHz for annealed samples

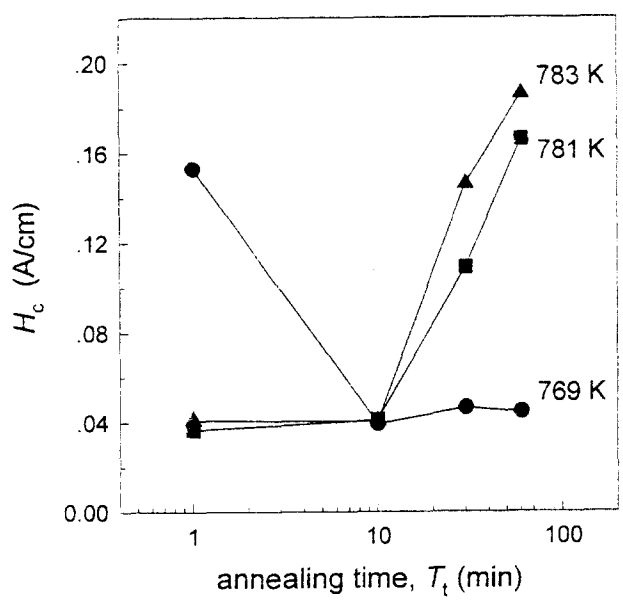

Fig. 7. Time dependency of coercive force H_c at the magnetizing frequency of 10 kHz for annealed samples.

767 K, the coercive force increases dramatically. It reaches 1.66 A/cm at 781 K where the sample is maintained the amorphous state as shown in Fig. 2. The coercive force increases further to 0.186 A/cm at 783 K. But the sample changes from amorphous to crystal.

An alternative way of demonstrating the initial reduction and later increase of magnetic hardness is to plot the coercive force against annealing time. One might expect that the thermal fluctuation on sample during annealing displaces atoms slightly and reduces free volumes. Such atomic rearrangements release internal stresses to some extent. As structural relaxation proceeds, internal stresses are progressively reduced and a subsequent reduction of number and strength of pinning centers results as the material becomes magnetically softer. Fig. 7 shows the coercive forces with increasing annealing time at the annealing temperature of 769 K, 781 K and 783 K. At 769 K, the magnetic softening proceeds between 1 minute and 10 minute, and reaches a plateau after 10 minutes. This implies that the internal stress releases to a great extent after 10 minutes. Therefore in the largely relaxed sample which has been annealed at below 769 K for 1 hour, the magnetization process consists predominantly of domain wall displacements. In this case, the coercive force has linear dependency on the product of the magnetostriction and the internal stress, but inverse dependency of the saturation magnetic induction. Assuming zero magnetostriction below 769 K, it could be concluded that the large decrease of coercive force (Fig. 6) results from the reduced strength of pinning centers for domain wall movement due to the small internal stress. However, Fig. 7 shows that the samples annealed at 781 K and 783 K softened very quickly before 1 minute. It is interesting that the coercive force increase for longer annealing time than 10 minutes at those temperatures. This cannot be explained by only stress-related anisotropy because the amorphous matrix is still stress relieved state. It might indicate that the internal structure is largely modified by topological and chemical redistribution of constituent atoms. The large redistribution of constituent atoms crystallizes the sample. The XRD experiment confirms the bulk crystallization at above 783 K. Annealed samples between 775 K and 781 K does not provide any evidence of crystallization on their XRD patterns but on their coercive force. The XRD cannot detect the crystallization of less a few percent in volume fraction. In order to investigate the crystallization, we measured the resistivity of each annealed sample. Fig. 8 shows the resistivity behavior with annealing temperature. Below the annealing temperature of 771 K, the resistivity increases slightly. Above 771 K, it decreases steeply as the annealing temperature become higher. This implies that the sample crystallizes at above 771 K.

From the above results, we concluded that the experimental data are co-related as follows: (1) Below 769 K, the structural rearrangement of constituent atoms does not occur, and the saturation magnetic induction has nearly constant value of 0.57 T. The coercive force decreases because of the reduced internal

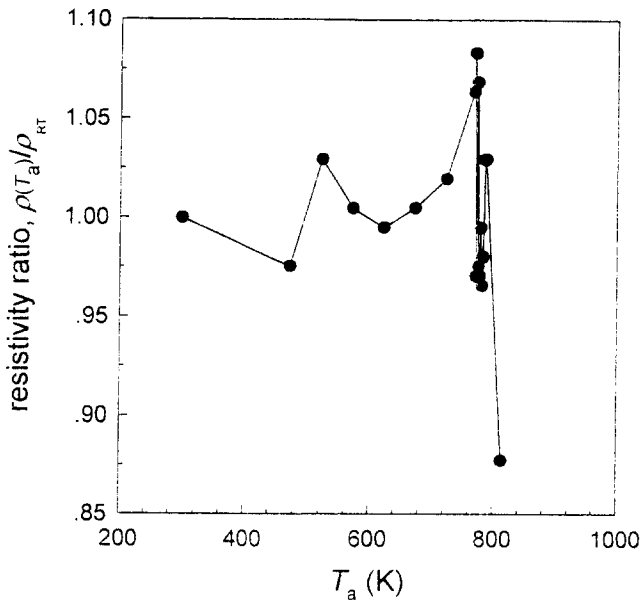

Fig. 8. Resistivity ratios $\rho(T_a)/\rho_{RT}$ for annealed samples.

stress. The uniaxial anisotropy maintains. (2) Above annealing temperature of 771 K, the saturation magnetic induction, squareness, and resistivity ratio decrease abruptly. The behavior of coercive force, however, increases abruptly. The coercive force increases due to the increase of domain wall pinning sites and decrease of resistivity by the crystallization. Furthermore the squareness decreases due to the relaxation of the uniaxial magnetic anisotropy.

4. Conclusions

The effect of annealing on the magnetic properties of a Co-based amorphous alloy (Metglas® 2714A) was studied. The two maximum exothermic process appear at 821.8 K and 929.5 K. Optimum high frequency properties were obtained between 673 K and 767 K. The coercive force decreased by annealing at temperature up to 767 K due to internal stress relaxation. But just below bulk crystallization occurs, the coercive force was sharply increased up to 781 K. For the annealing temperature of between 673 K and 723 K, the coercive force does not changes with annealing time up to 10 hour.

The bulk crystallization occurred at the temperature between 781 K and 783 K. The squareness was nearly constant of 1 at below 769 K. This implies that the magnetic anisotropy remains in longitudinal direction. Beyond 769 K, the squareness decreased to a limit value of 0.5. Annealing the sample at above 775 K, the maximum magnetic induction decreased with increasing annealing temperature due to the large redistribution of constituent atoms and/or products of very small nanocrystalline structure embedded in amorphous matrix. Finally, the optimal annealing temperature was between 673 K and 773 K during one hour.

Acknowledgment

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