Serrated magnetic properties in metallic glass by thermal cycle*

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Fe-based metallic glasses (MGs) with excellent soft magnetic properties are applicable in a wide range of electronic industry. We show that the cryogenic thermal cycle has a sensitive effect on soft magnetic properties of $Fe_{78}Si_9B_{13}$ glassy ribbon. The values of magnetic induction (or magnetic flux density) $\boldsymbol{B}$ and coercivity $\boldsymbol{H}_c$ show fluctuation with increasing number of thermal cycles. This phenomenon is explained as thermal-cycle-induced stochastically structural aging or rejuvenation which randomly fluctuates magnetic anisotropy and, consequently, the magnetic induction and coercivity. Overall, increasing the number of thermal cycles improves the soft magnetic properties of the ribbon. The results could help understand the relationship between relaxation and magnetic property, and the thermal cycle could provide an effective approach to improving performances of metallic glasses in industry.

Keywords: amorphous soft magnetic materials, rejuvenation, aging, cryogenic thermal cycling

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1. Introduction

Owing to the small structural correlation length that is related to magnetic anisotropy constant, Fe-based MG materials are not only magnetically soft, but also mechanically hard at the same time and exhibit a high yield strength of around 3000 MPa.[1,2] The Fe-based metallic glasses are applicable in a wide range of electronic industry and power distribution systems. The transformers using the Fe-based amorphous ribbon have the advantage that their no-load core losses are 75%∼ 80% lower than that of Si-steel sheet. However, the Fe-based amorphous ribbons have a disadvantage, i.e., its magnetic saturation is lower than that of Si-steel.[3–5] A lot of attempts have been made to improve the soft magnetic properties of iron-based amorphous alloys.[6–10] The elimination of the stresses can improve the mobility of the Bloch wall of magnetic saturation under an applied field $\boldsymbol{H}$,[11] but this mobility of the Bloch wall of magnetic domain and reorientation of spin are subjected to restriction. Therefore, the magnetic saturation $\boldsymbol{B}_s$ is limited up to 1.56 T for $Fe_{78}Si_9B_{13}$ ribbon. The isothermal annealing is widely used to modify the magnetic properties of the soft magnetic properties of MGs but the annealing often induces the brittleness.

In metallic glasses, under lengthening time elastic loading, the macroscopic strain shows irreversible change, and the structural changes lead to the improvement of the mobility of the Bloch wall of the magnetic domain and then the change of the magnetic properties. Recently, Ketov *et al.*[12] reported the cryogenic-thermal-cycle- (CTC) induced rejuvenation of metallic glasses, which can reach less relaxed states of higher energy. The rejuvenation is related to applied stress by the CTC. Generally, the effective anisotropy constant is strongly dependent on stress.[13] The magnetic coercivity and saturation value can be possibly changed if the rejuvenation or aging occurs. Therefore, it is expected that the CTC could also induce the change of magnetic properties in soft magnetic amorphous ribbons. However, there is no study on the relationship between the magnetic properties and structural changes by the CTC treatment.

In this work, we investigate the changes of soft magnetic properties of Fe-based MG by the CTC. We show that the CTC treatment has a significant effect on the typical commercialized soft magnetic MG through inducing the rejuvenation and aging. The CTC treatment can induce the fluctuation of the properties such as Curie temperature (T_c), first crystallization temperature (T_{x1}), the magnetic induction $\boldsymbol{B}_m$ (maximum magnetic induction in the applied field) and coercivity $\boldsymbol{H}_c$ in the soft magnetic MGs. The structural origin for the serrated change of the magnetic properties induced by the thermal cycle is attributed to the competition between the aging and rejuvenation. The results are helpful for understanding the re-

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laxations and their relationship with the magnetic properties of the metallic glasses. The thermal cycle can be an effective approach to controlling and improving the performances of metallic glass in industry.

2. Experiment

The amorphous ribbons of $Fe_{78}Si_9B_{13}$ alloy (supplied by An Tai Inc. of China Iron & Steel Group) were prepared by melt-spun technique with a width of 10 mm and uniform thickness of 25 μm. To achieve the best soft magnetic properties due to the stress relief caused by structural relaxation, the specimens of $Fe_{78}Si_9B_{13}$ alloys for magnetic testing were pre-annealed at 390 °C for 2 h under Ar atmosphere.[14,15] To avoid thermally activated structural relaxation, all samples are thermally cycled from near room temperature (300 K) to liquid nitrogen temperature (77 K) (as shown in Fig. 1). The holding time of cycling is 1 min. The thermal cycling method can be readily used in industry. The amorphous nature of the after-cycling specimen was ascertained by x-ray diffraction (XRD) with Cu K_α radiation and differential scanning calorimeter (DSC, Perkin Elmer DSC8000). The structural relaxation behavior was explored using DSC,[11,15–17] in a purified argon atmosphere. The soft magnetic properties were evaluated by a ***B–H*** loop tracer (MATS 2010SD) under a maximum applied field of 800 A/m. We test the magnetic properties by performing single-sample CTC treatment with toroidal shape. There are no changes in XRD patterns after the CTC treatment, indicating that no crystallization occurs during the CTC.

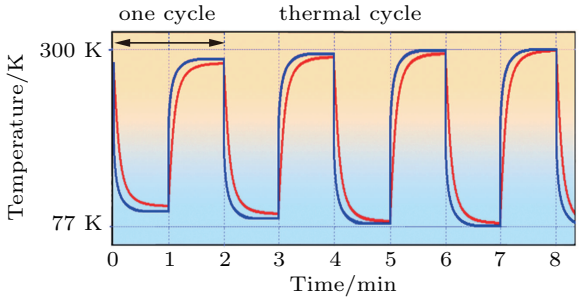


Fig. 1. (color online) Cryogenic thermal cycling procedure of metallic glass. Samples are cycled from near room temperature (300 K) to liquid nitrogen temperature (77 K). At each end the holding time is 1 min, so one cycle time is 2 min. Due to inertia of thermal energy the edge is not sharp. The degree of dullness and stabilization are different due to the sizes of samples

3. Results and discussion

Figure 2 shows the T_c and T_{x1} changes with CTC number. The T_c and T_{x1} of the ribbons exhibit obvious changes during the CTC treatment. The values of T_c and T_{x1} show the trend that they firstly rise and then go down, and again go up, and then again go down in general. With increasing the number of cycles, the T_c and T_{x1} are stochastically shifted toward higher temperature or lower temperature, showing a fluctuation or serrated behavior. However, they have an overall decreasing tendency with the increase of the CTC number. The change in the Curie temperature is associated with structural relaxation phenomena in the soft magnetic amorphous ribbons, and the shift toward the higher temperature of the T_c is due to the structural relaxation in the sample, and decreasing of the T_c is due to the structural rejuvenation in the sample.[16–18]

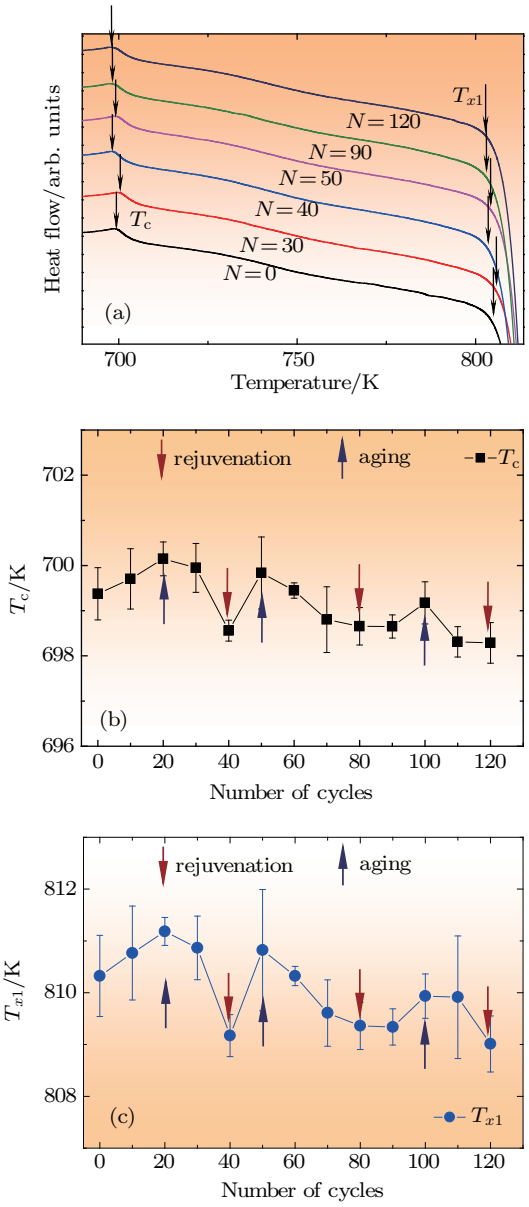


Fig. 2. (color online) Changes of (a) heat flow with temperature, (b) Curie temperature (T_c) and (c) the first crystallization temperature (T_{x1}) with the number of cycles. T_c and T_{x1} both show the serrated or fluctuation behavior by CTC, and the tendency of T_{x1} is similar to that of T_c.

The changes of induced properties present evidence that there are structural changes induced by CTC treatment, and the induced structural fluctuations are the competition between the aging and rejuvenation in the soft magnetic MG. The aging in metastable MG induces the lower enthalpy, smaller volume, and stable glassy state;[19–23] the rejuvenation is reversed

aging effect or a reduction in the degree of relaxation,[23–25] and the physical implication of structural rejuvenation is an increase in energy state of the glass and a decrease in density. The rejuvenation injects energy into the glass and some fraction of applied energy is stored in the glass. The increased stored enthalpy is a measure of rejuvenation and appears as an exothermic heat of relaxation on heating in the DSC curve of the metallic glass.

Figures 3 and 4 show the CTC-induced changes of magnetic induction $\boldsymbol{B}_{\rm m}$ and coercivity $\boldsymbol{H}_{\rm c}$. As illustrated, the magnetic induction and coercivity show the serrated or fluctuation behavior with the increase of the number of the CTCs. The values of magnetic induction $\boldsymbol{B}_{\rm m}$ change in a range of 1.365 T–1.435 T and the ones of $\boldsymbol{H}_{\rm c}$ change in a range of 6.7 A/m–15.0 A/m. The $\boldsymbol{B}_{\rm m}$ shows the trend that it first comes down and then rises, and once again and again in general, and so does $\boldsymbol{H}_{\rm c}$. The serrated changes of magnetic properties are attributed to the competition between aging and rejuvenation induced by the CTC treatment in the MG. During the CTC treatment, metallic glass undergoes the local structural change including the change of the topological short-range order (TSRO) or the number of nearest neighbors,[12] so the structural correlation length changes. As a consequence, the magnetic anisotropy fluctuates. The soft magnetic properties of amorphous materials can be described using magnetic anisotropy constant. According to the random anisotropy model,[26] magnetic coercivity and magnetic flux density (or magnetic induction) are described as follows,[1,13,27]

$$H_{\rm c} = p_{\rm c}\frac{\langle K\rangle}{J_{\rm s}}, \quad B = \mu_{\rm r}H, \tag{1}$$

where relative permeability $\mu_r = J_{\rm s}^2/2K_1$, $J_{\rm s}$ is the average magnetic saturation polarization of the material, K_1 is the local anisotropy constant, $\langle K\rangle$ is the averaged anisotropy constant, $p_{\rm c}$ is the dimensionless pre-factor of the order of unity. If in a material the exchange interaction tends to dominate, the magnetic coercivity $\boldsymbol{H}_{\rm c}$ can be represented by average anisotropy constant $\langle K\rangle$ of pure random anisotropies. For a real material with anisotropy randomly oriented on a scale smaller than a magnetic correlation length $L_{\rm ex}$, the average anisotropy constant $\langle K\rangle$ can be described by correlation length $L_{\rm ex}$, and the magnetic coercivity decreases with the local structural change of TSRO in the region less than basic ferromagnetic correlation length.[2,28–30] The magnetic correlation length $L_{\rm ex}$ is self-consistently related to the averaged anisotropy by $L_{\rm ex}=\sqrt{A}/K$ (A is the local exchange stiffness). Meanwhile, the relative permeability is inversely proportional to the anisotropy constant;[13,27] it is described that the magnetic flux density $\boldsymbol{B}$ increases with the local structural change of TSRO and decrease of anisotropy constant. So, contrary to the case of the early report,[31,32] the magnetic saturation change has behavior opposite to coercivity change, but the observed dependencies by CTC are explained as the fact that local order is metastable in soft magnetic MGs.

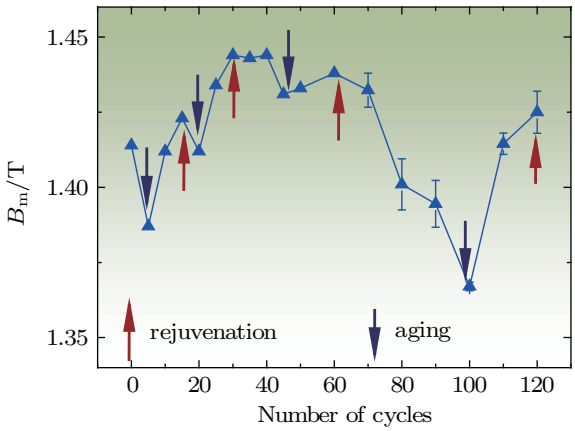


Fig. 3. (color online) CTC dependence of magnetic induction in $Fe_{78}Si_9B_{13}$ amorphous ribbons; magnetic induction also has a serrated or fluctuation behavior with the variation of the number of cycles. Magnetic inductions for more rejuvenated states are higher than for annealed state and aged state.

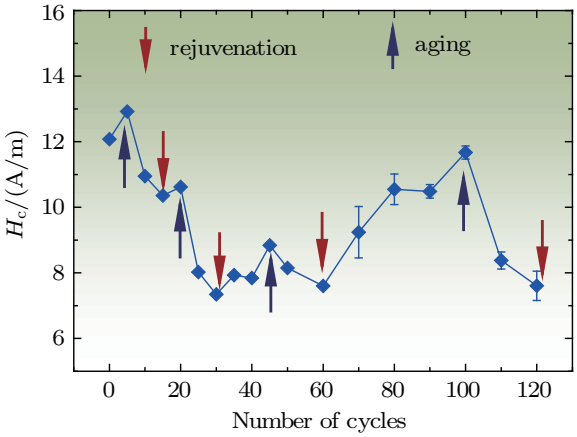


Fig. 4. (color online) CTC dependence of coercivity in $Fe_{78}Si_9B_{13}$ amorphous ribbons; magnetic coercivity also has a serrated or fluctuation behavior with the variation of the number of cycles, showing the contrary behavior to magnetic induction. Magnetic coercivities for more rejuvenated states are lower than for annealed state and aged state.

The CTC treatment can induce rejuvenations to reach less relaxed states of higher energy in MGs. With the increase of the energy, the MG becomes more unstable, and then the activation energy for aging the MG decreases and the aging gradually becomes dominant and the energy state of the MG decreases again. When the energy of the MG reaches a low enough state, CTC will induce rejuvenation and increase energy state of the MG again. That is, the CTC treatment induces the competition between rejuvenation and aging which behaves as the observed serrated dynamic phenomenon. The competition or fluctuation between rejuvenation and aging leads to the fluctuation changes of coordination number of atoms or topological short-range order, which is a typical characteristic of glass structure.[6,24,25] The rejuvenation reduces the structural correlation length and the average anisotropy

constant $\langle K \rangle$ and then $\boldsymbol{H}_{\rm c}$ will decrease (as shown in Fig. 5), whereas relative permeability $\mu_{\rm r}$ and magnetic induction $\boldsymbol{B}_{\rm m}$ will increase. In contrast, when aging becomes dominant, the aging increases the structural correlation length and causes the contrary phenomena. So magnetic inductions for more rejuvenated states are higher than for annealed state and aged state, magnetic coercivities for more rejuvenated states are lower than for annealed state and aged state. Overall, for Fe-based amorphous ribbons the CTC treatment results in rejuvenation and reaches more soft magnetic properties.

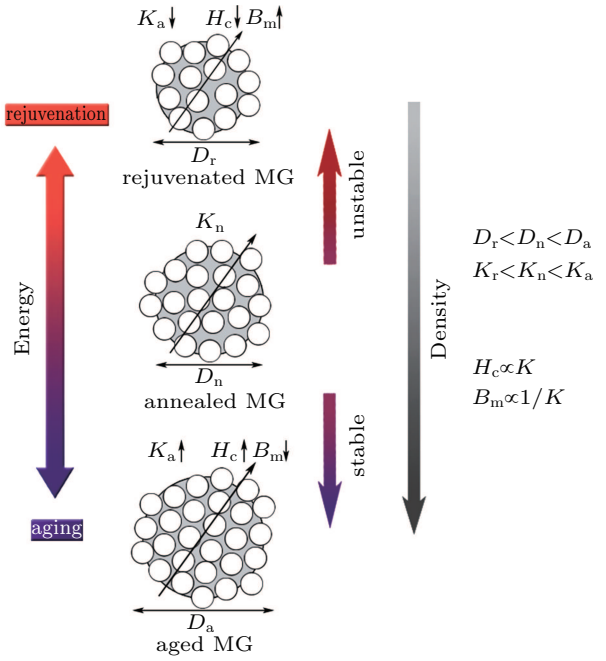


Fig. 5. (color online) Illustration of the relationships between rejuvenation, aging and structure, $\boldsymbol{H}_{\rm c}$, $\boldsymbol{B}_{\rm m}$ and density; the rejuvenation and aging cause the structure to change. The rejuvenation reduces structural correlation length and average anisotropy constant $\langle K \rangle$ and then $\boldsymbol{H}_{\rm c}$ will decrease, whereas magnetic induction $\boldsymbol{B}_{\rm m}$ will increase. The aging increases the structural correlation length and causes the contrary phenomena. K_i, D_i $(i = {\rm r}, {\rm a}, {\rm n})$ denote anisotropy constant and structural correlation length for i-th state, where r, a, n are rejuvenated, aged and annealed state, respectively.

4. Conclusions

The CTC treatment arises from structural changes of Fe-based amorphous ribbons and leads to the magnetic properties changing. The magnetic induction $\boldsymbol{B}_{\rm m}$ and coercivity $\boldsymbol{H}_{\rm c}$ have the serrated or fluctuation behavior with increasing the number of CTCs. These serrated phenomena are explained as cryogenic-thermal-cycle-induced stochastically structural aging or rejuvenation which randomly fluctuates magnetic anisotropy and, consequently, fluctuates the magnetic induction and coercivity. The thermal cycle could provide an effective approach to the improvement of performances of metallic glassy materials in industry, and the results could help in understanding the relationship between the relaxations and the magnetic properties of the MGs.

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