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ARTICLE

Piezomagnetic Properties and Negative Piezomagnetic Effect of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ Amorphous Alloy Films

Chen Jie[1], **Zhu Zhenghou**[1], **Lin Qianying**[1], **Bai Ruru**[1], **Zhao Hui**[2]

[1] *School of Materials Science & Engineering, Nanchang University, Nanchang 330031, China;* [2] *Institute of Space Science and Technology, Nanchang University, Nanchang 330031, China*

Abstract: The piezomagnetic properties and negative piezomagnetic effect in $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy films were investigated. The results show that the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy film has a significant positive piezomagnetic property in its quenched state. Furthermore, the inductance of the alloy film decreases substantially in the 0~0.66 kPa pressure range, whereas the compressive stress, σ, increases. When σ=0.66 kPa, the piezomagnetic effect value, S_1, reaches 5.5%. The ambient temperature has a significant influence on the sensitivity of the piezomagnetic property. The films show the optimal piezomagnetic properties and sensitivity stability in the temperature range of 20~30 °C. Increase in ambient temperature leads to decrease in the piezomagnetic property and sensitivity values, and the inner stress state of the film changes after annealing treatment. At an annealing temperature of 350 °C, the piezomagnetic effect of the film changes from "positive" to "negative". Furthermore, as the internal stress decreases, the value of $|S_1|$ decreases, and the piezomagnetic property of the film becomes less sensitive to the change in ambient temperature. At an annealing temperature of 555 °C, the value of $|S_1|$ is 0.59% (σ=0.44 kPa). When the annealing temperature reaches the crystallization temperature, the piezomagnetic property of the film becomes less sensitive to the changes in ambient temperature.

Key words: amorphous alloy films; piezomagnetic effect; inner stress

Fe-based amorphous (nanocrystalline) alloys are new materials that are prepared using a special metallurgical technique known as the "rapid quenching method". These alloys have been the subject of recent attention[1-6] due to their excellent magnetic properties. The $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy ribbon[7-9] is typically representative of Fe-based amorphous alloy ribbons.

Fe-based amorphous alloy films are widely used in the fields of thin film inductors[10] and force sensitive sensors[11-14]. However, when used as inductive materials, $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ series alloys are very sensitive to stress due to a phenomenon called "positive piezomagnetic effect". Their magnetic permeability therefore decreases significantly even under relatively small stresses, eventually resulting in a decline in the performance and stability of the products. Fe-based amorphous alloy films are nevertheless widely used in the chips of current piezomagnetic sensitive film sensors due to their high piezomagnetic effect values, high linearity, and large linear range. They are therefore the focus of research about force-sensitive sensors.

At present, research on the piezomagnetic effect of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy film mainly focuses on the phenomenon itself[15-21]. However, there are two gaps in the research of the characteristics of this phenomenon: the values of the piezomagnetic effect and its sensitivity, along with its environmental influence and its sensitivity to different values of internal stress.

This study focuses on the characteristics of the piezomagnetic effect of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy film, and the effect of internal stress on the piezomagnetic effect. The results are expected to improve the understanding of the phenomenon of the piezomagnetic effect, leading to the development of better thin film inductors and force-sensitive thin film sensors.

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Corresponding author: Zhu Zhenghou, Ph. D., Professor, School of Materials Science & Engineering, Nanchang University, Nanchang 330031, P. R. China, E-mail: z00708@sina.com

Furthermore, $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy films may also exhibit a “negative piezomagnetic effect” under appropriate internal stress conditions. This “negative piezomagnetic effect” can improve not only the force-sensitive characteristics of Fe-based amorphous alloy films, but also improve the stability of the inductor products. Research on this effect is therefore of great significance.

1 Experiment

Amorphous alloy films were prepared by rapid solidification, as shown in Fig.1 and Fig.2. In a vacuum intermediate frequency furnace, pure iron, pure niobium, pure copper, and ferrosilicon were compounded according to a certain composition ratio, and then smelted into a master alloy. The resulting alloy was then printed onto a high-purity copper plate at 1350 °C to form $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy thin films, with a width of 10 mm and thickness of 25~30 μm.

The film was then annealed in a vacuum annealing furnace. The annealing process was as follows: (150~500) °C/1 h and 555 °C/2 h. The film was then cooled in the furnace.

The phase composition of the film was investigated via X-ray diffraction (XRD, D8 Advance, Bruker-axe, Germany) using Cu Kα radiation. Experiments were performed under a tube pressure of 40 kV, a current of 40 mA and steps of 0.02°.

Thermal analysis of the film was performed via differential scanning calorimetry (DSC) using a synchronous thermal analysis instrument (Q-600 DSC-TGA, America). The crystallization temperature of the amorphous alloy film was determined by measuring the power difference between the sample, the reference material, and the temperature. The heating rate was 10 °C/min, argon was protective gas, and the temperature range of heat treatment was 20~800 °C.

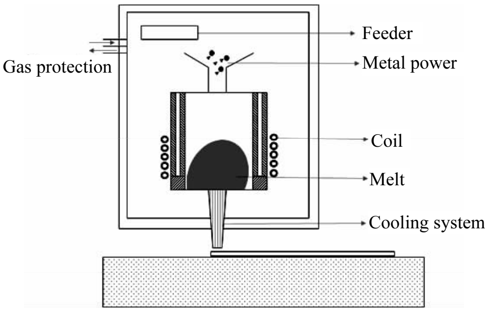

Fig.1 Schematic diagram of preparation of amorphous alloy films by rapid solidification

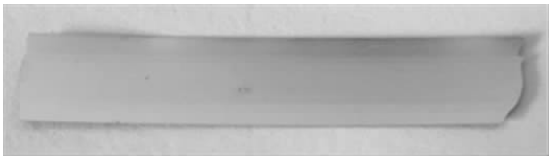

Fig.2 Amorphous alloy film samples prepared by rapid solidification

The internal stress distribution of the amorphous alloy film was analyzed by a Huayun HK21B residual stress detector, using a traditional single channel stress detection method.

The piezomagnetic properties were tested using an inductive measuring device (the test principle is shown in Fig.3). This device has some special merits such as high sensitivity, fast response, strong anti-interference, non-contact testing, and accurate test data. The results can more intuitively and accurately reflect the piezomagnetic property of the ribbons. The temperature was varied by the temperature control box. During the experiment, the thermocouple was used to monitor the ambient temperature in real time. Each heating was held for 20 min to ensure the accuracy of the test results. In order to minimize the hysteresis effect of the measurement, the weights were added intermittently in the experiment, and the inductance, L_s, was collected using a TH-2816B digital bridge. The testing frequency, f, was 1 kHz, the testing voltage was 0.3 V, the pressure range was 0~0.1 MPa, and the no-load inductance, L_s, was 655.452 μH.

The piezomagnetic effect was characterized using L_s-σ curves. The piezomagnetic effect value S_I is defined as follows:

$$S_I = \frac{\Delta L_s}{L_s} = \frac{L_s(\sigma) - L_s(\sigma_0)}{L_s(\sigma_0)} \times 100\% \qquad (1)$$

where L_s is coil inductance value, $L_s(\sigma)$ is coil inductance when the compressive stress is equal to σ, and $L_s(\sigma_0)$ is the inductance value with no compressive stress.

2 Results and Discussion

2.1 Piezomagnetic properties of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy films

The phase composition of the ribbon was investigated by

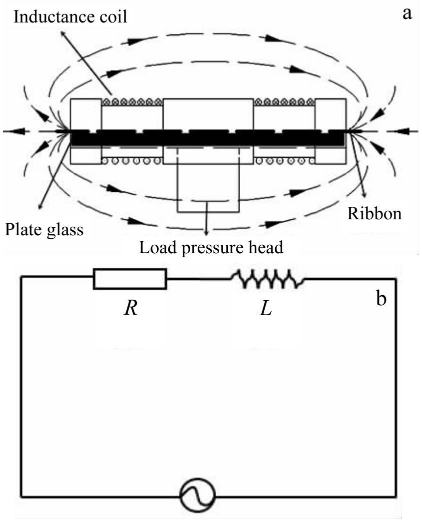

Fig.3 Schematic diagram (a) and equivalent circuit (b) of the testing device

XRD, as shown in Fig.4. According to the results, the diffraction angle is 10°~90°, and there are no obvious crystallization peaks during the entire process of diffraction. In the vicinity of 2θ=45°, a diffuse peak appears in the XRD patterns, which indicate that the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy ribbon in quenched condition is a single amorphous structure. DSC analysis (Fig.5) shows a crystallization peak at 522 °C. When the annealing temperature exceeds 491 °C, the amorphous alloy films begin to crystallize.

Fig.6 shows the curves of piezomagnetic property of quenched $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous ribbon, and the analysis highlights three key results as follows. (1) In 0~0.66 kPa pressure range, the inductance of the quenched $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy film increases significantly with increasing the σ. In other words, it is a "positive piezomagnetic effect". When σ=0.66 kPa, the S_I value is 5.5% (Fig.6b). (2) The slope, K, of the "S_I-σ" curve reflects the sensitivity of the piezomagnetic effect. The R-squared value is a linear regression coefficient, and the closer the value to 1, the higher the fitting degree. The ambient temperature has an influence on the sensitivity. Within the test temperature range of 20~60 °C, increase in the test temperature leads to decrease of the S_{Imax} and slope K, indicating that the sensitivity and the pressure magnetic effect value both decrease (Table 1). (3) The piezomagnetic effect and the sensitivity stability are optimal within the test temperature range of 20~30 °C.

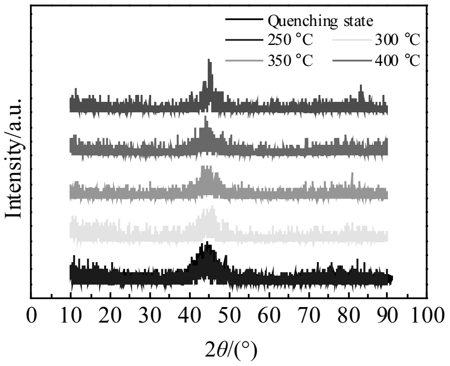

Fig.4 XRD patterns of as-quenched $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy films

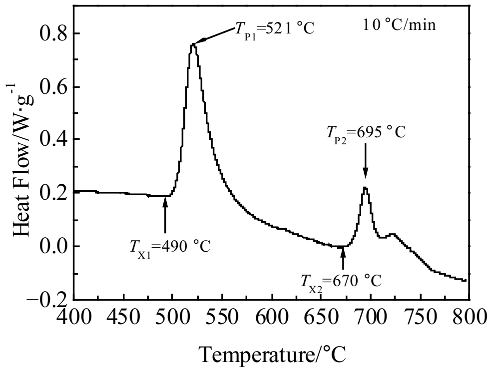

Fig.5 DSC curve of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy film

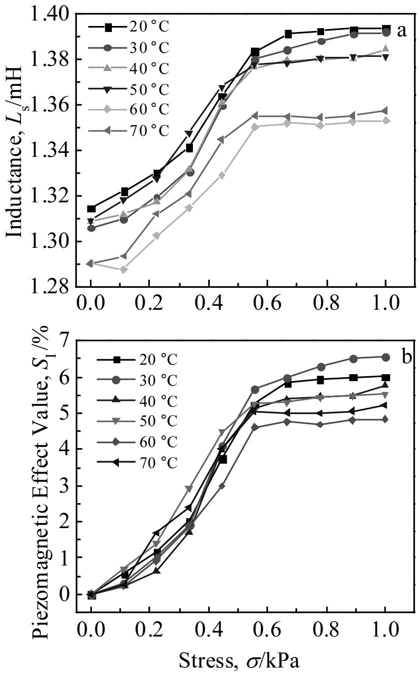

Fig.6 Curves of piezomagnetic property of quenched $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous ribbon: (a) L_s-σ and (b) S_I-σ

The internal stress of the film changes after the annealing process, and the characteristics of the piezomagnetic effect also change significantly (Fig.7). When the annealing temperature is less than 350 °C, the K value is positive, i.e. the phenomenon of the "piezomagnetic effect" is exhibited. When the annealing temperature exceeds 350 °C, the K value is negative, i.e. the phenomenon of "negative piezomagnetic effect" appears. At the same time, as the compressive stress increases, the L_s value of the film decreases. Furthermore, when the annealing temperature is less than 350 °C, increase in the annealing temperature causes positive S_I values; the S_I value is 0.29% when σ=0.66 kPa, which is significantly lower than the quenching value (5.5%). The S_I value is negative at annealing temperatures larger than 350 °C. At σ=0.66 kPa, $|S_I|$=1%~1.8%, and the value of $|S_I|$ decreases slowly as the annealing temperature increases. At an annealing temperature of 555 °C, the value of $|S_I|$ is 0.59% under σ=0.44 kPa (Table 2). When the annealing temperature reaches the crystallization temperature, the piezomagnetic property of the film is minimally affected by ambient temperature (Fig.8).

Table 1 Fitting results of S_I -σ standard curves

T/°C	20	30	40	50	60	70
Slope, K	10.36	10.22	9.44	9.03	8.07	8.66
R-square	0.97	0.94	0.92	0.95	0.95	0.96

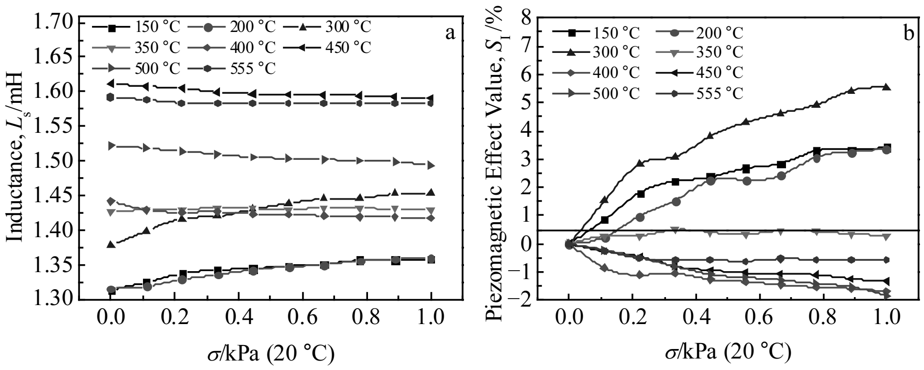

Fig.7 Curves of L_s-σ (a) and S_I-σ (b) of the films with different annealing temperatures tested at ambient temperature of 20 °C

Table 2 Piezomagnetic property parameters of films after heat treatment tested at 20 °C

T/°C	Quenched state	150	200	300	350	400	450	500	555
$\lvert S_{I\max}\rvert$/%	5.5	3.43	3.37	5.54	0.29	1.68	1.34	1.84	0.59
K	10.36	4.09	4.05	6.57	0.53	−1.78	−1.68	−2.05	−0.77
Sensitive range/kPa	0~0.66	0~0.78	0~0.78	0~1.0	a	0~1.0	0~1.0	0~1.0	0~0.44

a: there is no obvious sensitivity range

2.2 Negative piezomagnetic effect and its mechanism for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous thin film

The film under quenching state exhibits the most stable piezomagnetic property at the test temperature of 20 °C, so this situation was selected as the research objective.

Based on the previous studies about ferromagnetics, the piezomagnetic effect can be qualitatively explained by the skin effect. The stress applied to the amorphous alloy ribbon can lead to corresponding strain, and the equivalent permeability within the materials will change due to magnetoelastic coupling, thereby affecting the skin depth of the material. This can be expressed as follows:

$$\delta = \sqrt{\rho / \pi f \mu_{\mathrm{eff}}} \tag{2}$$

where f is current frequency, ρ and μ_{eff} are the resistivity and effective permeability of the materials, respectively.

The impedance, Z, of the ribbon can be expressed as follows:

$$Z=(k\rho l/2w)\coth(kt/2) \tag{3}$$

where l, w, and t are the length, width, and thickness of the ribbons, respectively.

This indicates that Z is related to the skin depth, while the skin depth is also dependent on the effective permeability of the material, and the effective permeability directly affects the inductance of the material.

According to the mechanism of the piezomagnetic effect, the main factor affecting the piezomagnetic effect of the Fe-based amorphous film is the internal stress during the stress process. The $S_{I\max}$ (Fig.9) and the internal stress (Fig.10) of different heat-treated films were therefore analyzed at room temperature. The results show that there is a certain correlation between the characteristics of the piezomagnetic effect of the amorphous films and their internal stress. The greater the internal stress of the material, the more pronounced the piezomagnetic effect.

The heat treatment process can release the internal stress and improve the soft magnet properties of the films. However, when the annealing temperature is too high, the magnetic anisotropy inside the films will be destroyed and the soft magnetic properties will be crippled. In this statement, there must be different optimal annealing temperatures for different films. Our results agree well with the description.

When the annealing temperature reaches 350 °C, the internal stress of the film drops rapidly to a minimum of 375.24 Pa. Meanwhile, the piezomagnetic effect is the weakest, and the $S_{I\max}$ value decreases significantly. The piezomagnetic properties of the amorphous alloys are therefore not only related to the magnitude of internal stress, but also affected by its distribution.

Different internal stress distribution states and sizes correspond to different piezomagnetic properties. During the preparation of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy film, a large number of internal stress and uneven internal stress distribution will occur due to the influence of the cooling rate. The internal stress decreases with increasing the annealing temperatures, but the internal stress distribution only changes slightly. The films begin to crystallize at an annealing temperature of 491 °C (Fig.5). The amorphous phase crystallizes into a nanocrystalline phase, and the structural stability is greatly improved. The distribution of internal stress also changes significantly during the crystallization process; at ambient temperatures of 500 and 555 °C, piezomagnetic effect is the smallest and sensitivity to ambient temperature in the film is the lowest.

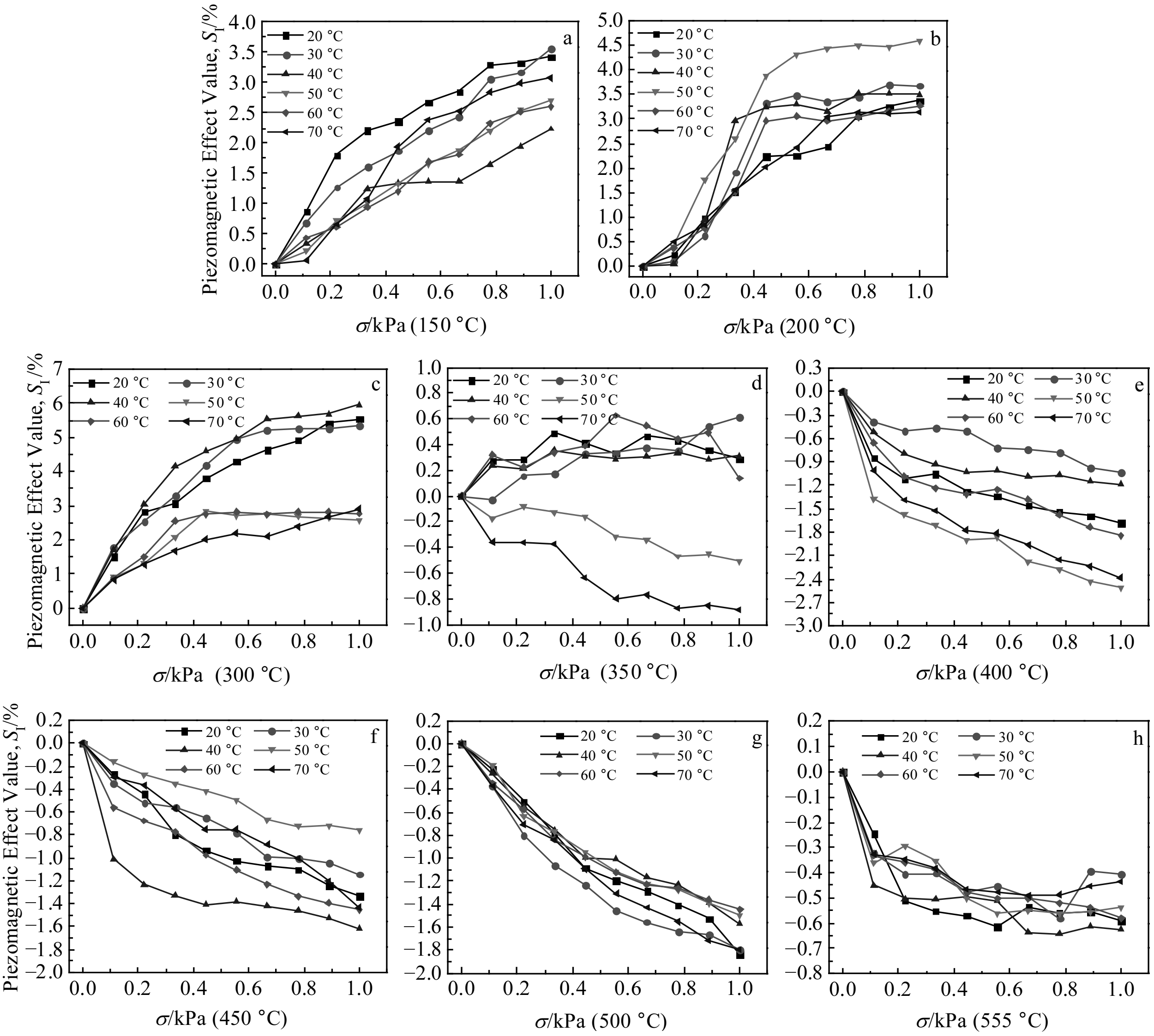

Fig.8 Piezomagnetic properties of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ ribbon under different annealing treatments: (a) 150 °C, (b) 200 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C, (f) 450 °C, (g) 500 °C, and (h) 555 °C

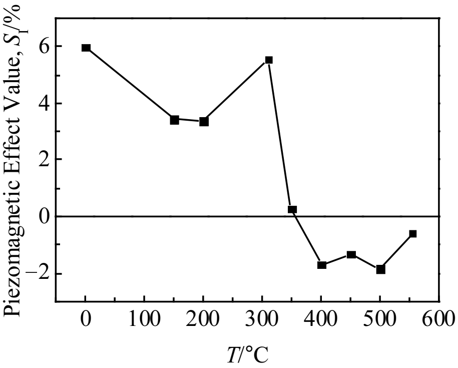

Fig.9 Piezomagnetic property as a founction of heat treatment temperature of the film

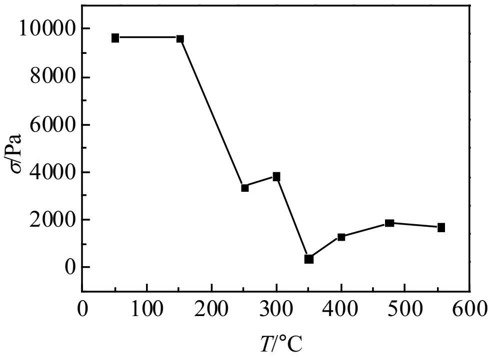

Fig.10 Curve of internal stress and heat treatment temperature of the film

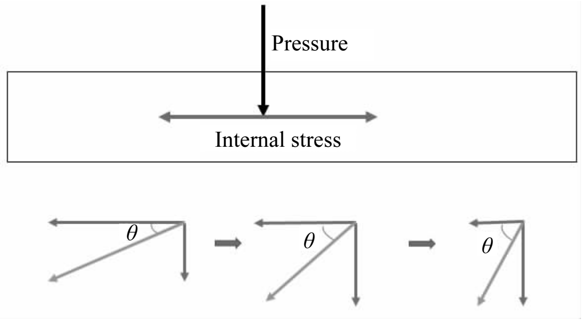

Fig.11 Internal stress state of the film

The internal stress in the film is equal to the tensile stress along the length of the film. As the annealing temperature increases, the internal stress value decreases significantly, but the direction remains the same. The external pressure forms compressive stress distributed along the thickness of the film (perpendicular to the length of the film). When the annealing temperature exceeds 350 °C, the tensile stress of the film decreases before reaching a relatively stable value. The resultant force of the tensile stress and the compressive stress in the direction θ increases to the maximum values (Fig.11). At this time, the internal stress of the film is dominated by the compressive stress, and the film exhibits a negative piezomagnetic effect, i.e. the inductance value declines to different degrees when the compressive stress increases.

3 Conclusions

1) In the pressure range of 0~0.66 kPa, the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy films in the quenched state exhibit a significant positive piezomagnetic property. The inductance of the alloy film decreases substantially with increasing the compressive stress. Under the compressive stress σ=0.66 kPa, the piezomagnetic effect value S_I reaches 5.5%. The ambient temperature can greatly influence the sensitivity of the piezomagnetic property. The films show optimal piezomagnetic properties and sensitivity stability in the range of 20~30 °C. Increase in the ambient temperature leads to obvious decrease in the piezomagnetic property and the sensitivity value.

2) The internal stress state of the film changes after the annealing treatment. The characteristics of the piezomagnetic effect are also altered significantly. When the annealing temperature reaches 350 °C, the type of piezomagnetic effect of the film changes from “positive” to “negative”. As the compressive stress increases, the inductance of the film decreases. As the internal stress in the film decreases, the value of $|S_I|$ also decreases. At the annealing temperature of 555 °C, the value of $|S_I|$ reaches 0.59% under σ=0.44 kPa. When the annealing temperature reaches the crystallization temperature, the piezomagnetic properties of the film become minimally affected by the ambient temperature.

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$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$非晶合金薄膜压磁效应的特征及负压磁效应

陈　杰[1]，朱正吼[1]，林前英[1]，白茹茹[1]，赵　辉[2]

(1. 南昌大学 材料科学与工程学院，江西 南昌 330031)

(2. 南昌大学 空间与技术研究院，江西 南昌 330031)

摘　要：以 $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ 非晶合金薄膜作为研究对象，研究了其压磁效应的特征及其负压磁效应现象。结果表明，淬态下的 $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ 非晶合金薄膜在 0~0.66 kPa 压力带具有显著的正压磁效应，随着压应力增大，薄膜电感值下降。当压应力 σ=0.66 kPa 时，压磁效应值 S_I 达到 5.5%；环境温度对压磁效应灵敏度有影响，在 20~30 ℃范围内，压磁效应和灵敏度稳定性最好，随着环境温度升高，薄膜灵敏度和压磁效应值均降低；薄膜经过退火处理后，薄膜内应力状态会发生变化，当退火温度≥350 ℃时，薄膜的压磁效应类型由“正压磁效应”转变为“负压磁效应”，且随着薄膜中内应力降低，$|S_I|$值下降，且薄膜的压磁效应受环境温度影响减小。当退火温度为 555 ℃，σ=0.44 kPa 时，$|S_I|$值仅为 0.59%；当退火温度达到薄膜的晶化温度时，薄膜的压磁效应受环境温度影响最小。

关键词：非晶合金薄膜；压磁效应；内应力

作者简介：陈　杰，女，1991 年生，博士生，南昌大学材料科学与工程学院，江西 南昌 330031，E-mail: chenjiepaper@sina.com