Influence of Annealing Processes on Piezomagnetic Property in Fe73.5Cu1.5Nb3Si13.5B9 Amorphous Alloy Strips

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ABSTRACT

It is researched the influence rule on piezomagnetism property of Fe73.5Cu1.5Nb3Si13.5B9 amorphous alloy with technology for heating processing. Result shows that the piezomagnetism property of Fe-based amorphous alloys appears favorable property at frequency of 1 KHz. Elevating the temperature of heating processing is in favor of promoting the piezomagnetism effect. In the condition of frequency at 1KHz, and continuous upload/offload stress applying process, the piezomagnetism property of Fe73.5Cu1.5Nb3Si13.5B9 amorphous alloy is enhanced with increase of heating treatment temperature. When the temperature rise at 550 ℃, stress impedance (SI) effect value SI(%)=1.402 (relevant applying stress σ=0.612MPa). SI effect of Fe-based amorphous alloy is more sensitive under the stress of 0.2 MPa than above.

INTRODUCTION

Since its unique organization, inexistence crystal defect and heterogeneous organization or composition, Fe-based amorphous alloys have excellent soft magnetic properties, highly intension, corrosion resistance, abrasive resistance and hardness. In recent years, the piezomagnetism of Fe-based amorphous alloys have been widely researched on. Applying stresses such as pressure and stretching on amorphous alloys which have been magnetized will induce changes of its inner state of magnetization. This is so called piezomagnetism, but its essence is the changes between magnetic system and mechanical system in ferromagnetic material. Utilizing the piezomagnetism property of Fe-based amorphous ribbon can make stress sensitive elements which are used in most kinds of sensors. And the sensors are widely used in information technology, automatic control,
transportation, power electronics and medical instruments etc areas, which also perform a decisive role on modern industry.

In this paper, it is preliminary worked on the piezomagnetism property of quenching amorphous ribbon with constant pressure. The highlight of this paper is technology for heating processing to the influence of piezomagnetism in Fe73.5CulNb3Si13.5B9 ribbon. Results show that, when the temperature rise to 500 ℃, Fe73.5CulNb3Si13.5B9 amorphous ribbons begin to crystallize. And while rise to 550 ℃, the inner structure of ribbon is absolutely crystallized. Because of prolonging the time of quenching up to over 1h, which has nothing to do with property of ribbons. In this paper, it is researched piezomagnetism of Fe73.5CulNb3Si13.5B9 amorphous ribbon with quenching temperature from 300–550 ℃ for 1h.

Experiment:

Ribbons of Fe73.5CulNb3Si13.5B9 in the experiment is prepared by rapid quenching. The composition of ribbon is Fe73.5CulNb3Si13.5B9, and the size is 45mm×20mm×(25~30)mm. The whole process of quenching is in a vacuum tubes furnace with a vacuum degree of 6.67×10^-2Pa and a quenching temperature of 330–550 ℃, soaking for 1h.

Crystallization temperature is measured by means of DSC, and testing equipment is made in America of Q-600DSC-TGA thermal analyzer. Heating rate is 10 ℃/min from 20~800℃ with argon atmosphere protection.

In addition, phase analysis of amorphous ribbon is measured by Bruker D-8X X ray diffractometer of German. Test parameters: Cu Kα radiation, diffraction angle (2θ) range from 10° to 90°, graphite monochromater, and scanning step with 0.02°. Changes of crystal phases in the side of amorphous ribbon is observed by HX-100 3D high depth of field microscope.(Model:MEF3 of Cambridge Corporation).

![Figure 1. Skeleton drawing of the non-contact measuring apparatus.](image)

Figure 1 is the schematic diagram of inductance type piezomagnetic effect. Ribbon lies flat on a plastic pipe which internally installed a magnetic core. Coil inner diameter is 3mm, outer diameter is 20.13mm, testing frequency is 1KHz, and unload inductor value Ls=1.76139mH. Pressure applied on the ribbon controlled by a compression-testing machine with a 10mm×10mm pressure head. Stress applying process is a constant upload from 0 to 1MPa and offload from 1 to 0MPa with a displacement velocity of 0.1mm/min. The inductance value of coil is measured by TH-2816B digital electric bridge.
RESULTS AND DISCUSSION

Figure 2. DSC curves of quenched Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ amorphous alloy strip.

Figure 2 is the curve of as-quenched Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ribbon. The process of heating up to 800°C, in the beginning, the sample has been in a state of heat absorption, and curve descended gradually. There is a small exothermic process at 490°C and an endothermic process at 521°C, both of which form the crystallization peak. The temperature TP1 at 521°C with ferromagnetic phase α-Fe(Si) separated out. Therefore, Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ribbon can be estimated that it begins to crystallization at 490°C, and crystallization rate riches to maximum at 521°C. When temperature over TP1, the grain growth occupied the leadership. The second exothermic peak in curve is the second crystallization peak which TP2 is 695°C. Surplus amorphous phase is crystallized forms Fe-B compound, which correspond to the second crystallization peak, and the initial temperature of crystallization is 670°C. In the two exothermic peaks, the intensity of first crystallization peak is stronger than the second. The corresponding initial crystallization temperature of these two peaks Tx1 and Tx2 are 490°C and 670°C separately. $\Delta$Tx=Tx2-Tx1=180°C. Between $\Delta$Tx, there is only α-Fe(Si) crystallization phase. Because, to ensure the ribbon has a crystallization and nanocrystalline compound phase, choose a reasonable heat temperature Tp1~Tc, that is 521~565°C±10 °C.
Figure 3. Annealing temperature and phase change.

Figure 3 is X-ray atlas of amorphous ribbon after annealing (soaking time 1h). Between the soaking temperature 300℃ and 400℃ for 1h, there is not any crystal structure peak. Because the main structure of ribbon still an amorphous state, when the temperature rise at 500℃, it appears some crystallization peak. It indicated that the inner structure of ribbon has being changed from amorphous into crystallization. When temperature rise at 550℃, it appears a strong crystallization peak. This because, the ribbon has absolutely changed into crystallization.

Figure 4. Metallographic photos of \( \text{Fe}_{71.5}\text{Cu}_{1.5}\text{Nb}_{3}\text{Si}_{13.5}\text{B}_{9} \) amorphous alloy strip.
Figure 4 is the phase images on the side of Fe73.5CuNb3Si13.5B9 ribbon. It reveals that the thickness of ribbon is 25~30μm, as-quenched state, and shiny surface between 300°C and 400°C. Since, between the temperatures, the structure of ribbon is amorphous. After 500°C, the surface turns dark, because it begins to crystallize at 500°C. The surface appears gloomy at 550°C. Because the grain boundary of nanocrystalline has been corrupted and crystallization has accomplished.

Figure 5. $f=1\text{kHz}$, The curves of loop inductance $L_s$ and stress of ribbon change with the time (The curves with 1st, 2nd, and 3rd are the serial number of repeat experiments). When $f=1\text{kHz}$, the curves of $L_s$-t and $\sigma$-t about the ribbons with 300°C, 400°C, 500°C and 550°C anneal for 1h that all have favorable repeatability. The variation of curves with different annealing temperature are the same. Inductance value of inductive coil rise with enhancement of stress. Analysising the curve of 300°C, in which the time from 0 to 120s and stress from 0 to $\sigma_{\text{max}}$ 1MPa. When stress apply to $\sigma_{\text{max}}$, $L_s$ has not reach its maximum value, but remain keep rising trend. Until the stress offload and the time at 200s, $L_s$ reaches a maximum value 1.91616mH. This shows that the change of $L_s$ behind pressure stress. The reason of this phenomenon is related to elastic after effect and hysteresis in the ribbon. Elastic after effect can be described that the stress applied on elastic materials, deformation of offloaded process will slower than uploaded process. $\Delta L_{s\text{max}}$ can be defined $\Delta L_{s\text{max}}=L_{s\text{max}}-L_{s\text{min}}$. The ribbon with 300°C heat treatment, $\Delta L_{s\text{max}}$ of inductive coil 15.20μH. With 400°C heat treatment, $L_{s\text{min}}=1.921076\text{mH}(t=0\text{s}, \sigma=0\text{MPa})$, $L_{s\text{max}}=1.939137\text{mH}(t=154.28\text{s}, \sigma=0.975\text{MPa})$, $\Delta L_{s\text{max}}=18.06\mu\text{H}$. With 500°C heat treatment, $L_{s\text{min}}=1.915846\text{mH}(t=0\text{s}, \sigma=0\text{MPa})$, $L_{s\text{max}}=1.941207\text{mH}(t=155\text{s}, \sigma=0.619\text{MPa})$, $\Delta L_{s\text{max}}=25.36\mu\text{H}$. And with 550°C heat treatment, $L_{s\text{min}}=1.92589\text{mH}$, $L_{s\text{max}}$
=1.952115\text{mH}(t=175.56s, \sigma=0.501\text{MPa}), \Delta Ls_{\text{max}}=26.22\mu\text{H}. From these data above, it draws a conclusion that the value of \Delta Ls_{\text{max}} enhanced with the increment of heat treated temperature.

Using software of matlab to matching Ls-\sigma functions in each experiments by means of Gaussian function fitting method. Afterword, by functional relationship of Ls-\sigma, we can get the value of Ls to specified \sigma value, and calculate the SI(\%).

Piezomagnetism SI(\%) can be defined as:

\[
SI(\%) = \frac{\Delta Ls}{Ls} \times \% = \frac{Ls(\sigma) - Ls(\sigma_0)}{Ls(\sigma_0)} \times \%
\]  

(1)

Where, Ls is inductance value of coil, Ls(\sigma) is inductance value of coil with applying stress \sigma, Ls(\sigma_0) is inductance value of coil without any stress.

Figure 6. \(f=1\text{kHz}\). The curves of piezomagnetic property of ribbon at different annealing temperature.

Figure 6 is the piezomagnetism curve of different ribbons with \(f=1\text{KHz}\). As show in the figure, the SI(\%) enhanced with stress increasing. These four figure reveal a common phenomenon, that is, in a tiny applied stress (\sigma<0.2\text{MPa}) condition, the value of Ls appears a sharp rise. It can be deduced that SI value is more sensitive with tiny stress than that of normal stress. In stress offloading process, the SI value have not any obvious change. The maximum value of SI(\%) appears in the offloaded process, which also induced by elastic after effect and hysteresis. With heat treatment temperature at 300\^\circ\text{C}, the maximum value of SI(\%)_{\text{max}} appears at stress offload process (\sigma_{\text{offload}}=0.29\text{MPa}) and SI(\%)_{\text{max}}=0.845. 400\^\circ\text{C}, SI(\%)_{\text{max}}=1.012 (\sigma_{\text{offload}}=0.605\text{MPa}). 500\^\circ\text{C} SI(\%)_{\text{max}}=1.318 (\sigma_{\text{offload}}=0.614\text{MPa}). And 550\^\circ\text{C}, SI(\%)_{\text{max}}=1.402 (\sigma_{\text{offload}}=0.612\text{MPa}). When frequency at 1KHz, the value of SI(\%) in Fe73.5CuNb3Si13.5B9 ribbon enhanced with increasing of heat treatment temperature.
Figure 7. \(f=100\text{kHz}\), The curves of loop inductance \(L_s\) and stress of ribbon at different annealing temperature with loading and unloading time.

Figure 7 is the curve of \(f=100\text{KHz}\), \(L_s\) and \(\sigma\) change with the time in the ribbons which are treated in 300°C, 400°C, 500°C and 550°C for 1h separately. It can be known from the curves of inductance and stress with heat treatment in 300°C, that the sensitive of \(L_s\) enhanced with increasing of \(\sigma\). When uploaded stress to 0.376MPa, the inductance value of coil from original value 1.78659mH rise to 1.7998mH. The whole stress upload process with inductance value change is increases at the beginning, decreases in halfway and then appears a tiny increasing in the end. \(\Delta L_s_{\text{max}}=13.0\mu\text{H}\). 400°C, 500°C and 550°C heat treatment ribbons, values of \(L_s\) appear sharp enlargement in the beginning, a small increasing in halfway and sharp decrease in the end. In the offload process of 400°C treatment ribbons, \(L_s\) changes from initial value 1.808368mH (\(t=0s, \sigma=0\text{MPa}\)) to 1.828851mH (\(t=227s, \sigma=0.28\text{MPa}\)), \(\Delta L_s_{\text{max}}=20.49\mu\text{H}\). 500°C, \(L_s\) changes from 1.820646mH to 1.841718mH (\(t=157.32s, \sigma=0.599\text{MPa}\)), \(\Delta L_s_{\text{max}}=21.07\mu\text{H}\). 550°C, \(L_s\) changes from 1.835369mH to 1.856706mH (\(t=161.12s, \sigma=0.547\text{MPa}\)), \(\Delta L_s_{\text{max}}=21.34\mu\text{H}\). Draw a conclusion that, the initial value of induction coil and \(\Delta L_s_{\text{max}}\) enhanced with increasing of heat treatment temperature.
Figure 8. $f=100$kHz. The curves of piezomagnetic property of ribbon at different annealing temperature.

Figure 8 is amorphous ribbon’s curve of piezomagnetic property in different annealing temperature with $f=100$KHz. As shown in the figure, SI(%) enhanced with increasing of pressure stress in upload, and with a tiny pressure stress ($\sigma<0.2$MPa), the value of Ls appears a sharp increasing. The ribbon with 300°C heat treatment, which SI(%) curve’s maximum value $SI(\%)_{max}=0.814$ appears on offload process and the corresponding stress $\sigma=0.386$MPa. The same with 400°C, SI(%)$_{max}=0.711$ (corresponding stress $\sigma=0.733$MPa), 500°C, SI(%)$_{max}=1.081$ (corresponding stress $\sigma=0.733$MPa), And 550°C, SI(%)$_{max}=1.123$ (corresponding stress $\sigma=0.558$MPa).

**TABLE 1. THE FUNCTION OF $Ls-\sigma$ STANDARD EQUIVALENT CURVES.**

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>$Ls-\sigma$ standard equivalent functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-quenched</td>
<td>$y=0.4706\exp(-((x-1.052)/0.6983)^2)+0.1356\exp(-((x-0.5526)/0.2584)^2)+0.118\exp(-((x-0.3716)/0.1553)^2)+0.1163\exp(-((x-0.2743)/0.07111)^2)+0.2251\exp(-((x-0.1641)/0.07111)^2)+0.03958\exp(-((x-0.2544)/0.05454)^2)$</td>
</tr>
<tr>
<td>300°C</td>
<td>$y=35.39x^9-163.1x^8+310.6x^7-314.2x^6+179.7x^5-56.58x^4+8.48x^3-0.3508x^2+0.02423x+1.901$</td>
</tr>
<tr>
<td>400°C</td>
<td>$y=-24.43x^9+115.8x^8-230.3x^7+248.8x^6-156.6x^5+56.55x^4-10.08x^3+0.2242x^2+0.1807x+1.921$</td>
</tr>
</tbody>
</table>
500°C \quad y=1.941\exp\left(-((x-0.9458)/23.15)^2\right)-0.04368\exp\left(-((x+0.1347)/0.1455)^2\right)+0.07131\exp\left(-((x-0.09057)/0.09109)^2\right)+0.0007494\exp\left(-((x-0.2009)/0.04185)^2\right)
+0.0006606\exp\left(-((x-0.2497)/0.03525)^2\right)

550°C \quad y=1.952\exp\left(-((x-0.9957)/23.63)^2\right)-0.02242\exp\left(-((x+0.02508)/0.06594)^2\right)+0.00727\exp\left(-((x-0.07141)/0.06034)^2\right)-0.001837\exp\left(-((x+0.1088)/0.1936)^2\right)+0.0002833\exp\left(-((x-0.2101)/0.01974)^2\right)+7.575\times10^{-5}\exp\left(-((x-0.2394)/0.1808)^2\right)

We use software matlab to fitting functions in which stress σ as independent variable and Ls as function value. Matlab use different repeat experiment results to fitting Ls-σ standards equivalent functions (Table1) by means of error analysis in fitting functions. Where “adjrsquare” is called multiple correlation coefficient, which is used to measure the performance of the regression equation fitting. The “adjrsquare” can represent as R, and |R| ≤ 1. The bigger the absolute value of R, the performance of fitting is better. In our experiment, the value of R>95%. So the standard equivalent functions are effective, which will approximately and truly reflect the relationship of Ls-σ. Then, according equation 1 to calculate effective SI(%) and draw figure 9.

### TABLE 2. ERROR ANALYSIS OF THE FUNCTION.

<table>
<thead>
<tr>
<th>Heat treatment temperature</th>
<th>sse</th>
<th>rsquare</th>
<th>dfe</th>
<th>adjrsquare</th>
<th>rmse</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-quenched</td>
<td>0.09027</td>
<td>0.98877</td>
<td>377</td>
<td>0.98826</td>
<td>0.015474</td>
</tr>
<tr>
<td>300°C</td>
<td>0.0001052</td>
<td>0.98762</td>
<td>359</td>
<td>0.98731</td>
<td>0.00054132</td>
</tr>
<tr>
<td>400°C</td>
<td>0.00059518</td>
<td>0.9519</td>
<td>456</td>
<td>0.95095</td>
<td>0.0011425</td>
</tr>
<tr>
<td>500°C</td>
<td>2.2086e-05</td>
<td>0.99821</td>
<td>243</td>
<td>0.99811</td>
<td>0.00030148</td>
</tr>
<tr>
<td>550°C</td>
<td>0.00010145</td>
<td>0.99522</td>
<td>369</td>
<td>0.99497</td>
<td>0.00052434</td>
</tr>
</tbody>
</table>
Figure 9. $f=1$kHz, Comparison of piezomagnetic property curve of ribbon at different annealing temperature under the loading process.

Figure 9 is the comparison chart of piezomagnetic property in ribbons with different heat treatment temperature at $f=1$KHz. It emphasizes analysis of the process of upload. In the figure, with enhancement of heat treatment temperature, the piezomagnetic property SI(%) increased. The SI($%$)$_{max}$ of as-quenched ribbon is 0.4781. In 300°C heat treatment condition, the SI($%$)$_{max}$ is 0.8102, 400 °C is 0.9578, 500°C is 1.2905, and 550°C is 1.3874. The fastest ascending velocity of the curves is in 550°C. Since, on the one hand, the residual stress of FeCuNbSiB ribbon have been eliminated in higher temperature, and on another hand, the soft magnetic properties have been improved, which enhanced the changes of magnetic induction ability in the ribbon with a certain stress. So the piezomagnetic property is in direct proportion to the heat treatment temperature.

CONCLUSION

(1) When pressure stress less than 0.2MPa, the value of $L_s$ in the coil has a sharp enhancement with increasing of pressure. Fe-based amorphous alloy has a more sensitive piezomagnetism effect in tiny stress.

(2) The piezomagnetism effect is better with $f=1$KHz than $f=100$KHz, and the maximum value of SI(%) is 1.3874, which appears in upload process with $f=1$KHz and heat treatment temperature at 550°C for 1h.

(3) Heat treatment technology will effectively change the piezomagnetism effect of Fe73.5Cu13.5Si13.5B9 amorphous ribbon with testing frequency at 1KHz, and continuous upload/offload stress. The SI(%) value enlarged with increasing of heat treatment temperature. And the maximum value of SI(%) is 1.402 with temperature at 550°C for 1h and offload stress $\sigma=0.612$MPa.

REFERENCES


[5] Fu Yuan, Zhu Zhenghou, Li Xiaomin, et al. The tiny stress impedance effect of Fe73.5Cu1Nb1.5Si13.5B9Mo1.5 powder/ silicon rubber composite film film and Fe73.5Cu1Nb3 Si13.5B9 amorphous ribbon with lamellar structure.