

Electro-deposition current density effect on Ni/PZT layered magnetoelectric composites performance

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Abstract

This paper considers the magnetoelectric (ME) effect in Ni/PZT layered ME composites that is related to the preferred crystallographic orientation of electro-deposited Ni layers. The Ni electro-deposition rate increases with applied cathodic current density. High (1 0 0) texture in the Ni layer was obtained at either low or high current densities, which improves the ME composite's performance. It is advantageous to increase the current density, while trying to avoid hydrogen evolution during electro-deposition to reduce the number of pinhole defects.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The magnetoelectric (ME) effect is characterized by an induced electric polarization in response to an applied magnetic field, or by an induced magnetization in response to an applied electric field [1]. The ME effect has stimulated continuous interest for dozens of years due to its unique multifunctionality and potential applications in devices such as sensors, actuators and energy converters [2]. Various kinds of ME materials have been investigated in recent years. They include some manganese perovskites, such as BiFeO₃ or BaMnF₄ [3, 4], bulk materials composed of both ferroelectric and ferromagnetic phases [5–7] and layered materials consisting of ferromagnetic and ferroelectric layers [8–12]. To achieve better ME properties, giant magnetostrictive material Tb_{1-x}Dy_xFe_{2-y} (Terfenol-D) was used in combination with piezoelectric materials, such as lead zirconium titanate (PZT) and polyvinylidene fluoride (PVDF), in a laminate structure [9, 10, 13–16].

Laletin *et al* reported ME interactions in layered transition metal/PZT samples synthesized by bonding slices of PZT and Fe, Co or Ni [17]. The maximum achieved ME voltage coefficient was 90 V cm⁻¹ Oe⁻¹. These results indicate that one can use transition metals as the piezomagnetic phase to improve the performance of layered ME composites. Transition metals can overcome some disadvantages of

Terfenol-D associated with its process and machinability. In our previous work Ni/PZT layered ME composites of varying geometries were made, including planar and cylindrical layered structures [18–22]. The ME voltage coefficient of the planar composites is comparable to that of the Terfenol-D/PZT composites with the same piezomagnetic/piezoelectric layer thicknesses. The cylindrical layered ME composites showed some novel ME properties that planar bonded layered composites do not possess. Our previous work focused on reporting the novel ME properties of structures prepared by electro-deposition.

The magnetic performance of electro-deposited nickel depends on its microstructure (grain size, surface morphology and crystallographic orientation), which in turn depends on electroplating conditions and the plating bath composition [23]. The effect of deposited Ni layer texture on the performance of ME composites has not yet been studied. In this work, the effect of electro-deposited Ni crystallographic orientation varied with the applied cathodic current density on the ME composite performance is studied.

2. Experimental details

The results of this paper rely on PZT-5H (PbZr_{0.52}Ti_{0.48}O₃) supplied by the Institute of Acoustics, Chinese Academy

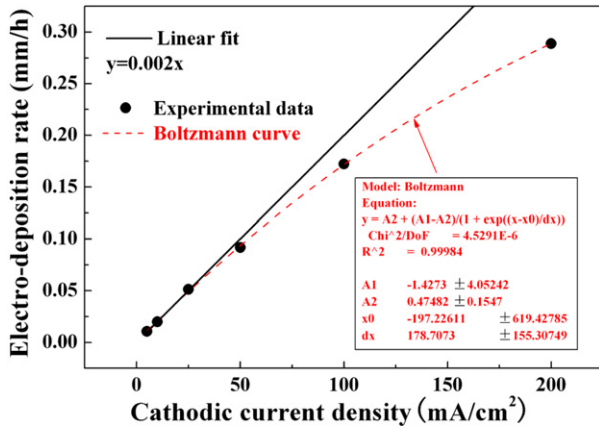


Figure 1. Ni electro-deposition rate dependence on the applied cathodic current density. The inset is the Boltzmann equation used for fitting the data.

of Sciences. The piezoelectric coefficient d_{33} is about 450 pm V^{-1} for the piezoelectric phase and electro-deposited Ni layers are the piezomagnetic phase. The PZT ceramics were cut into $10 \times 25 \times 0.8 \text{ mm}^3$ pieces. Sliced PZT samples with polarization through the thickness had Ni electrodes plated on both sides. PZT was polarized at 425 K in a $30\text{--}50 \text{ kV cm}^{-1}$ electric field. Following poling, the samples were bathed in nickel aminosulfonate plating solution, in which the cathodic current density was varied. Nickel aminosulfonate plating solution was used because of its stability, rapid plating rate and small resulting internal stress. The Ni electro-deposition process is described in detail elsewhere [18–22]. The applied cathodic current density was varied from 5 to 200 mA cm^{-2} . The total thickness of the Ni layers of all the samples was approximately 0.8 mm (0.4 mm for an individual layer). That is, the thickness of the Ni layers is equal to the PZT thickness in all electro-deposited ME composites. During the ME measurement, the bias (140 Oe) and the sinusoidal magnetic fields (22 Oe for 1 A ac current amplitude through the coil) are parallel to the length of the samples, and the generated voltage in PZT is along its thickness direction (perpendicular to the applied magnetic field). The ME voltage coefficient was measured in the ME measurement system discussed in detail in a previous publication [24]. X-ray diffraction (XRD) Rigaku D/max-RB, Cu $K\alpha 1$ source) analysis was performed to obtain the electro-deposited Ni layer crystal structure.

3. Results and discussion

The dependence of the Ni electro-deposition rate on the applied cathodic current density is shown in figure 1. At lower current density (below 25 mA cm^{-2}), the electro-deposition rate increases linearly with the current density (fitted solid line). The deposition rates are about 0.01 mm h^{-1} , 0.02 mm h^{-1} and 0.05 mm h^{-1} when the applied cathodic current density is 5 mA cm^{-2} , 10 mA cm^{-2} and 25 mA cm^{-2} , respectively. The electro-deposition rate initially increased linearly with the current density. However, the electro-deposition rate deviates from linearity at higher current density due to more hydrogen generation, which will be discussed further. This indicates that

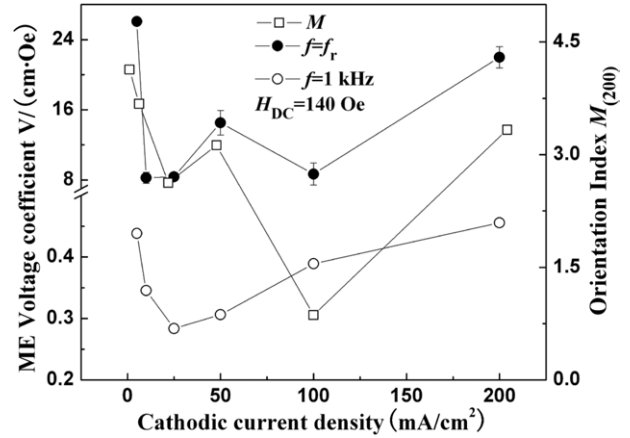


Figure 2. Cathodic current density effect on the ME voltage coefficient at resonant frequency and at 1 kHz (left) and on the orientation index $M_{(200)}$ (right).

the cathodic electro-deposition efficiency is lower at higher current densities. The linear fit does not do a good job of predicting the electroplating rate dependence on the current density, thus a Boltzmann function was used, which provides a better fit. The equation of the fitted Boltzmann function curve (dashed line) is shown in the inset of figure 1 ($R^2 = 0.99984$). From this fit, one can calculate the electro-deposition rate in the range between 0 and 200 mA cm^{-2} .

The ME effect dependence on the applied cathodic current density at resonant frequency and at 1 kHz is shown in figure 2. Initially, the ME voltage coefficient decreases and then increases subsequently with the current density rise when the applied frequency is 1 kHz. The ME coefficient behaviour at resonant frequency is similar to that at 1 kHz. The largest ME coefficient of $26 \text{ V cm}^{-1} \text{ Oe}^{-1}$ is obtained for the Ni layers deposited at 5 mA cm^{-2} . The ME effect at 50 mA cm^{-2} is larger than that at 25 and 100 mA cm^{-2} . The reason for this behaviour will be discussed next. This indicates that the ME effect depends on the applied cathodic current density used during Ni electroplating.

Figure 3 compares the XRD patterns of PCPDS: 65-2865 [25] and Ni layers electro-deposited at different cathodic current densities. This figure indicates that the electro-deposited Ni layers are formed of a single cubic phase for all current densities. The Ni layer texture varies with the current density. In order to evaluate quantitatively the preferred crystallographic orientation parallel to the substrate plane, the orientation index, M , was calculated as [26]

$$M_{(hkl)} = \frac{I_{(hkl)}}{\sum I_{(h'k'l')}} \cdot \frac{\sum I_{(h'k'l')}^0}{I_{(hkl)}^0}, \quad (1)$$

where $I_{(hkl)}$ is the XRD intensity from the experimental data, $I_{(hkl)}^0$ is the XRD intensity from PCPDS cards and $M_{(hkl)}$ is the calculated orientation index. $\sum I_{(h'k'l')}^0$ and $\sum I_{(hkl)}^0$ in this case are the sum of the intensities of four independent reflections: (1 1 1), (2 0 0), (2 2 0) and (3 1 1) for the PCPDS cards and the measured samples, respectively. Relative intensities obtained from the XRD data and the (2 0 0) orientation index $M_{(200)}$ of electro-deposited Ni layers are shown in table 1. Because of

the Ni layers preferred orientation, M is compared with the powder XRD data from PCPDS cards [25], therefore, $M_{(200)}$ of the PCPDS:65-2865 is 1. If M_{200} is larger than 1, it indicates that this layer has (100) preferred orientation, and the stronger the texture, the larger the M value is. The (100) reflection is forbidden for face-centred cubic Ni, both (200) and (400) reflections (at 122° 2θ angle, not shown) indicate (100) texture. Table 1 shows that the variation of $M_{(200)}$ is similar to that of the ME voltage coefficient, which varies with the cathodic current density (figure 2). This indicates that one can obtain (100) preferred orientation with low (5 mA cm^{-2}) and high (200 mA cm^{-2}) cathodic current densities, but (111) preferred orientation at 100 mA cm^{-2} . Moreover, it indicates that the ME effect is related to the preferred orientation of the Ni layers. For ME composites, the ME effect is directly related to the magnetostriction of the magnetostrictive phase. The magnetostriction of the [100] direction in cubic Ni is 45.9 ppm, which is larger than 24.3 ppm for the [111] Ni direction [27]. The (100) Ni preferred orientation has a larger ME effect than the (111) orientation of Ni/PZT layered composites along the same dimensions. Our experimental results are qualitatively in agreement with this theoretical prediction. For 25 mA cm^{-2} , 50 mA cm^{-2} and 100 mA cm^{-2} , the M_{200} index is 2.627, 3.125 and 0.865, respectively. At 50 mA cm^{-2} M_{200} is the largest for the three samples tested. That is why the ME effect at 50 mA cm^{-2} is larger than that at 25 and 100 mA cm^{-2} .

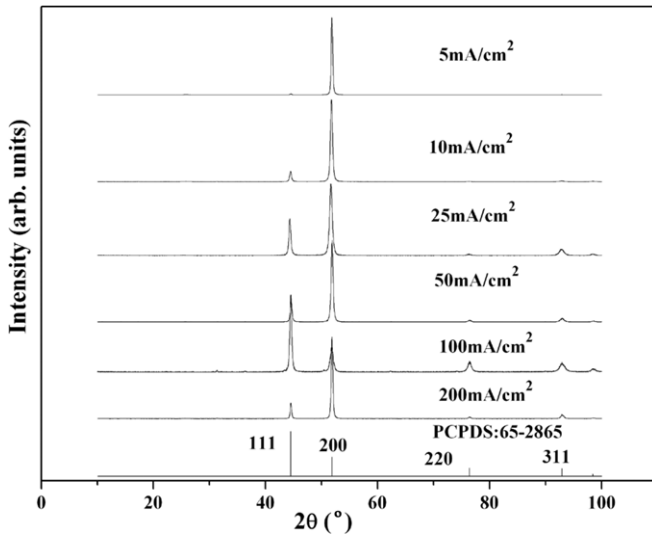
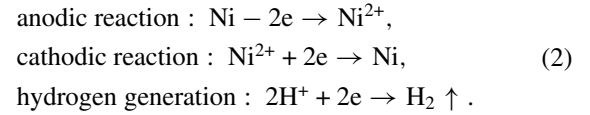


Figure 3. XRD patterns of Ni layers electro-deposited with different cathodic current density and PCPDS: 65-2865 [25].

Figure 4 shows optical images of electro-deposited Ni layers deposited at different cathodic current densities. This figure shows that the number of pinholes in the Ni layer is increasing with the current density. For 5 mA cm^{-2} current density, the Ni layer is smooth and no pinholes are present. However, when the applied current density is 200 mA cm^{-2} , the Ni surface topography degrades, exhibiting many pinholes. During electro-deposition, there is inevitable generation of hydrogen at the electrodes:



The pinholes in the Ni layer are related to hydrogen. With the rise in current density more hydrogen is generated. This can be proved by the Ni electro-deposition rate changing with different current densities discussed above (as shown in figure 1). The presence of hydrogen lowers the cathodic current efficiency at higher current density. Figures 1 and 4 indicate that the current density can increase the Ni deposition rate, but at the same time it increases the amount of hydrogen. Hydrogen generation should be suppressed as much as possible in electro-deposition, which can also reduce the ME effect [21]. It would be possible to obtain high performance ME composites using high current densities if one could control or suppress hydrogen generation. However, the 5 and the 200 mA cm^{-2} samples have the same ME coefficients, which indicates that there are some other factors affecting the ME performance, such as the internal stress state, Ni hardness and grain size. This requires a further study in order to fully explain the observed phenomenon.

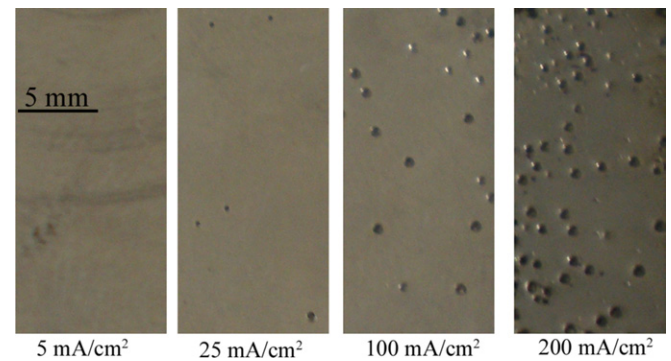


Figure 4. The optical images of the surface topography of Ni layers electro-deposited with different cathodic current density.

Table 1. XRD data and (200) orientation index M of electro-deposited Ni layer.

	Relative intensity $I_{(111)}$	Relative intensity $I_{(200)}$	Relative intensity $I_{(220)}$	Relative intensity $I_{(311)}$	Orientation index $M_{(200)}$
PCPDS:65-2865	999	427	185	173	1.000
5 mA cm^{-2}	10	999	0	1	4.133
10 mA cm^{-2}	125	999	3	8	3.678
25 mA cm^{-2}	490	999	15	85	2.627
50 mA cm^{-2}	273	999	21	43	3.125
100 mA cm^{-2}	999	322	127	107	0.865
200 mA cm^{-2}	188	999	19	47	3.332

4. Summary

In summary, the Ni electro-deposition rate increases with the current density. The cathodic current density affects the preferred crystallographic orientation of deposited Ni layers, and consequently it affects the layered composite ME performance. One can obtain (1 0 0) oriented Ni layers at either very low or high current densities applied to the cathode. The 1 0 0 Ni layer texture is beneficial and enhances the ME effect. More hydrogen is generated with increased current density. The electro-deposition process needs to be improved to increase the cathodic current density in order to obtain high (1 0 0) Ni layer preferred orientation to enhance the ME effect.

Acknowledgments

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References

- [1] Landau L D and Lifshitz E M 1960 *Electrodynamics of Continuous Media* (Oxford: Pergamon) p 169 chapter 4
- [2] Yang P, Zhao K, Yin Y, Wan J G and Zhu J S 2006 *Appl. Phys. Lett.* **88** 172903
- [3] Wang J *et al* 2003 *Science* **299** 1719
- [4] Scott J F 1977 *Phys. Rev. B* **16** 2329
- [5] van den Boomgaard J and Born R A J 1978 *J. Mater. Sci.* **13** 1538
- [6] van den Boomgaard J, Van Run A M J G and Van Suchetelene J 1976 *Ferroelectrics* **10** 295
- [7] Srinivasan G, DeVreugd C P, Flattery C S, Laletsin V M and Paddubnaya N 2004 *Appl. Phys. Lett.* **85** 2550
- [8] Srinivasan G, Rasmussen E, Gallegos T J, Srinivasan R, Bokhan I Yu and Laletin V M 2001 *Phys. Rev. B* **64** 214408
- [9] Wan J G, Wang X W, Wu Y J, Zeng M, Wang Y, Jiang H, Zhou W Q, Wang G H and Liu J-M 2005 *Appl. Phys. Lett.* **86** 122501
- [10] Mori K and Wuttig M 2002 *Appl. Phys. Lett.* **81** 100
- [11] Wan J G, Liu J-M, Chand H L W, Choy C L, Wang G H and Nan C W 2003 *J. Appl. Phys.* **93** 9916
- [12] Dong S, Li J F and Viehland D 2003 *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **50** 10
- [13] Ryu J, Priya S, Carazo A V and Uchino K 2001 *J. Am. Ceram. Soc.* **84** 2905
- [14] Nan C W, Liu L, Cai N, Zhai J, Ye Y and Lin Y H 2002 *Appl. Phys. Lett.* **81** 3831
- [15] Nan C W, Liu G and Lin Y H 2003 *Appl. Phys. Lett.* **83** 4366
- [16] Wan J G, Li Z Y, Zeng M, Wang H H and Liu J M 2005 *Appl. Phys. Lett.* **86** 202504
- [17] Laletin V M, Paddubnaya N, Srinivasan G, De Vreugd C P, Bichurin M I, Petrov V M and Filippov D A 2005 *Appl. Phys. Lett.* **87** 222507
- [18] Pan D A, Bai Y, Volinsky A A, Chu W Y and Qiao L J 2008 *Appl. Phys. Lett.* **92** 052904
- [19] Pan D A, Bai Y, Chu W Y and Qiao L J 2008 *J. Phys D: Appl. Phys.* **41** 02200
- [20] Pan D A, Lu J, Bai Y, Chu W Y and Qiao L J 2008 *Chin. Sci. Bull.* **53** 2124
- [21] Pan D A, Bai Y, Chu W Y and Qiao L J 2007 *Smart Mater. Struct.* **16** 2501
- [22] Pan D A, Bai Y, Chu W Y and Qiao L J 2008 *J. Phys.: Condens. Matter* **20** 025203
- [23] Kollia C and Spyrellis N 1993 *Surf. Coat. Technol.* **57** 71
- [24] Lu J, Pan D A, Bai Y and Qiao L J 2008 *Meas. Sci. Technol.* **19** 045702
- [25] Taylor A 1950 *J. Inst. Met.* **77** 585
- [26] Yoshimura S, Yoshihara S and Shirakashi T 1994 *Electrochim. Acta.* **39** 589
- [27] Chen C W 1977 *Magnetism and Metallurgy of Soft Magnetic Materials* (Amsterdam: North-Holland)