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Nanocrystalline Deposition for Developing High Permeability Ferromagnetic Materials

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ABSTRACT - A nanocrystalline deposition method for developing high permeability ferromagnetic materials in composite wire sensing element of magnetic field sensors is investigated in this study. The method is based on material coercivity or permeability in relation to the crystalline grain sizes of the material. Composite wire samples made by electroplating of various recipes which resulted in different crystalline grain sizes of the plated material are developed, and magnetic properties of the plated material in terms of the magnetoimpedance (MI) effect ratio of the composite wires are measured and analyzed. The results show that nanocrystalline permalloy at different grades in terms of the crystalline grain sizes at nanoscales can be developed by electroplating using DC plating without saccharin, DC plating with saccharin, and pulse plating at different level of duty cycles. The MI effect ratios of the composite wires having the nanocrystalline permalloy of different grades varied in an increasing trend with the decrease of the nanocrystalline grain size of the plated permalloy material. Such a relation is analyzed using Alben et al's Random Anisotropy Model [1].

Keyword: Nanocrystalline Deposition, Magnetic Permeability, Giant Magneto-impedance Effect

I. INTRODUCTION

Composite wires, such as electroplated $Ni_{80}Fe_{20}/Cu$ composite wires, can be used as micro sensing elements of high sensitivity sensors for detecting weak magnetic field [2]. To increase the sensitivity of such sensors, one of the key issues is to increase the magnetic permeability of the ferromagnetic coating material of the composite wire element.

It was shown [3] that for some Fe-based nanocrystalline materials the magnetic permeability largely increased as the crystalline grain size was reduced from 100 nm to 10 nm. The permeability, however, showed an increasing trend in variation with grain size decreasing as the grain size was larger than 100 nm. This decreasing trend was also showed for permalloy with the grain sizes ranging from 10 μm to 100 μm. In view of the trend change of permeability in variation with the grain size at about 100 nm for Fe-based materials, it can be expected that for permalloy there may be a permeability increase as the grain size is reduced at nanoscale.

It has been shown [4] that in pulse electroplating of some alloys, including permalloy, the crystalline grain size of the plated material varies with the plating parameters, especially varies with the pulse plating duty cycle. It was also showed [5] that in electroplating of permalloy the crystalline grain size of the plated material was significantly reduced by adding saccharin into the electrolyte solution.

In the present study, for developing high permeability ferromagnetic coating layer of the composite wire magnetic sensing elements, $Ni_{80}Fe_{20}/Cu$ composite wires with a range of nanocrystalline grain sizes for the plated layer are developed, and the permeability of the plated materials in terms of magnetoimpedance (MI) effect ratios of the wires are measured. The increasing trend of permeability in variation with the crystalline grain size in nanoscale is analyzed

II. EXPERIMENTAL SETUP

The electrodeposition setup consists of a water bath, a cylindrical stainless steel plating cell and an electrical power source (Advantest R6145 DC Voltage Current Source) that is capable of generating DC current and pulsed current.

As the plating procedure, 20 μm copper wire specimens were placed into diluted hydrochloric acid and then distilled water to cleanse the wires before the electrodeposition process. A layer of permalloy was deposited onto copper wires when a current was passed through the wires in an electrolyte solution consisting of $FeSO_4.7H_2O$, H_3BO_3, $NiSO_4.6H_2O$, $NiCl_2.6H_2O$ and saccharin. The electrolyte solution was immersed in a water bath and heated and maintained at a temperature of 55°C. The pH value of the solution was maintained at about 3.4 for the whole duration of the electrodeposition process. For the specimens, the peak current density used in the electrodeposition process was $2A/dm^2$. For the purpose of measuring the grain sizes under X-ray Diffraction, a layer of permalloy was electrodeposited onto copper plates of area $4cm^2$ under the exact same conditions as specified for the copper wire specimens. For pulse plating, the peak current used was at $2A/dm^2$ and the period of the pulsed current was 1000ms. In this experiment, the duty cycle (the ratio of on-time to the total plating time) of the pulsed current was varied at 20%, 30% and 40%. The total on-time was fixed at 3 minutes in order to compare the pulsed plated samples with the DC plated samples. The thickness of the permalloy coating was about 1.4 μm. The effect of the addition of saccharin to the electrolyte solution was also investigated. The wire specimens were placed under Scanning Electron Microscope (SEM) to observe the surface of the specimens and also placed under Energy Dispersive X-Ray (EDX) to obtain the composition of the permalloy coating on each specimens. An SEM picture of a pulsed plated wires specimen was given in Fig. 1. The plate specimens were placed under X-ray Diffraction (XRD) to obtain the grain sizes on the permalloy coating.

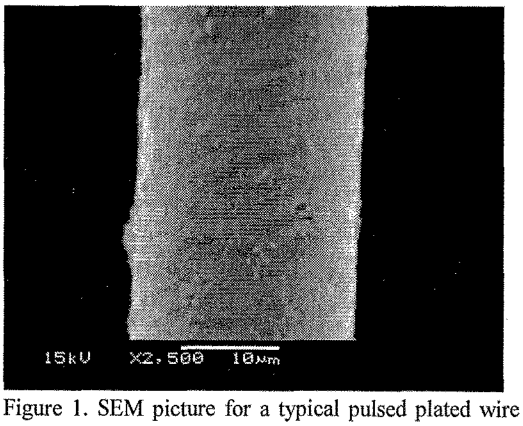


Figure 1. SEM picture for a typical pulsed plated wire specimen.

The wire specimens were later mounted onto a PCB and placed in a Helmholtz coil. An alternating driving current of 10mA was passed through the specimen at a range of frequency from 100 kHz to 50 MHz. The external field was varied by varying the direct current through the Helmholtz coil and the impedance changes through the wire specimen were observed by means of the Agilent 4294A Precision Impedance Analyzer. The relative change of impedance ratio is defined as:

$$\Delta Z/Z = [Z(H_{ex}) - Z(H_{max})] \,/\, Z(H_{max}) \ (\%) \qquad (1)$$

where $Z(H_{ex})$ and $Z(H_{max})$ are the impedance values of a composite wire in MI effect testing under an arbitrary and maximum intensity of external magnetic field H_{et}, respectively.

III. RESULTS AND DISCUSSION

3.1. Nanocrystalline Deposition of Permalloy

Three kinds of electroplating methods were used to generate nanocrystallne permalloy of different grain sizes, namely DC plating without saccharin added, DC plating with saccharin added and pulse plating with saccharin added. In pulse plating, the relationship between the duty cycle and the grain size of the plated materials was investigated.

In order to produce the permalloy of right composition by pulse electroplating, the effect of pulse plating duty cycle on the Fe percentage in the plated material was firstly investigated. The results are shown in Fig. 2. It was found that the Fe percentage decreases almost linearly with the decrease in the duty cycle. To maintain the right composition ration of $Ni_{80}Fe_{20}$ in pulse plating with varying the duty cycle, the $FeSO_4$ content in the plating solution has to be varied accordingly. In keeping the composition of $Ni_{80}Fe_{20}$, the relationship between the $FeSO_4$ content and the duty cycle was studied. The results are shown in Fig. 3. As the duty cycle decreased from 40% to 20%, the need in increasing $FeSO_4$ tended to be higher and higher.

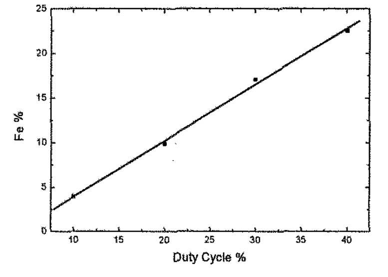


Figure 2. Effect of duty cycle on the Fe percentage of the plated layer.

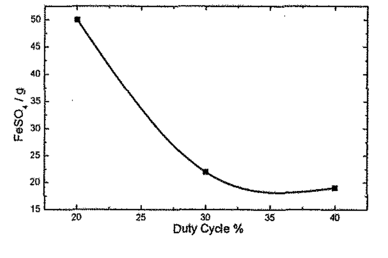


Figure 3. Variation of $FeSO_4$ with pulse plating duty cycle in the plating solution for permalloy.

In order to compare the effect of pulse plating duty cycle on the plated composite wire magnetic properties in terms of MI ratio, the thickness of the plated layers has to be consistent for wires plated at different duty cycles. This was achieved by varying the plating time for each plating such the total plating on-times for all the wire samples are equal. Under this arrangement, the plated thickness remained constant as the duty cycle varied from 50% to 10%, as shown in Fig. 4. Having controlled the $FeSO_4$ in plating solution for the right composition ratio and the plating time for equal plated layer thickness, the crystalline grain sizes of the materials plated by DC plating without and with saccharin added, and by pulse plating with saccharin added were measured from the plated samples. The results are shown in Fig. 5. DC plating without saccharin added produced the largest grain sizes, about 50 nm. Pulse

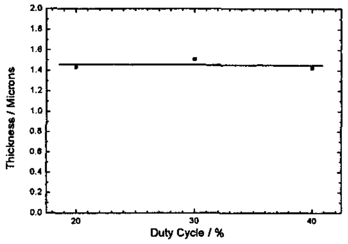


Figure 4. Effect of pulse plating duty cycle on plated layer thickness.

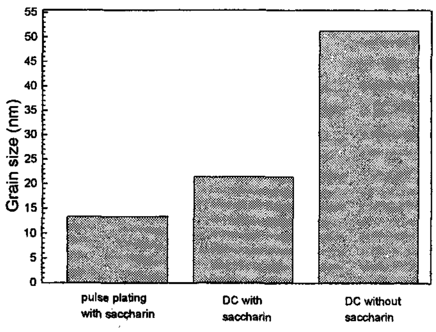


Figure 5. Variation of crystalline grain size with DC plating without saccharin, DC plating with saccharin and pulse plating with saccharin.

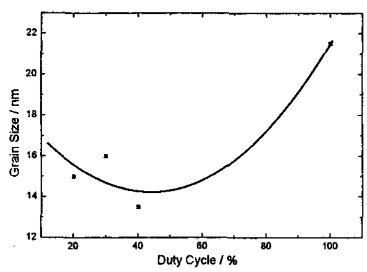
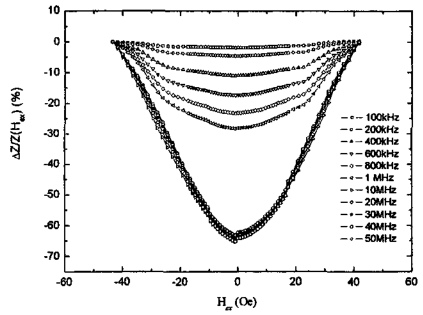


Figure 6. Variation of the grain size with pulse plating duty cycle.

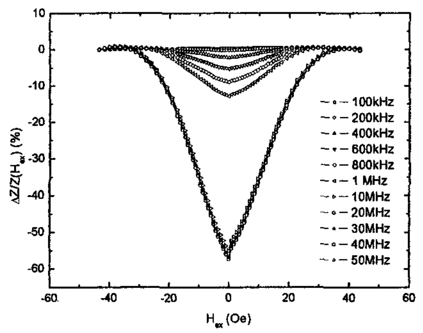
plating with saccharin added produced the smallest grain sizes, about 13 nm. In pulse plating, the grain size of the plated material was found to be dependent on the duty cycle, as shown in Fig. 6. It seems that there was an optimum value for the duty cycle at which the grain size reached the minimum.

3.2. Relationship between Nanocrystalline Grain Size and the MI ratio

The magnetic permeability of the plated materials of different nanocrystalline grain sizes in the composite wires was estimated through measuring the MI ratios of the wires. The MI ratios of the wire samples of different nanocrystalline grain sizes were measured at the current frequency varying from 100 kHz to 50 MHz. To ensure



(a)



(b)

Figure 7. MI ratio curves at different testing frequencies for wire sample made DC plating without saccharin added (grain size of 52 nm); (a) on sample 1, (b) on sample 2.

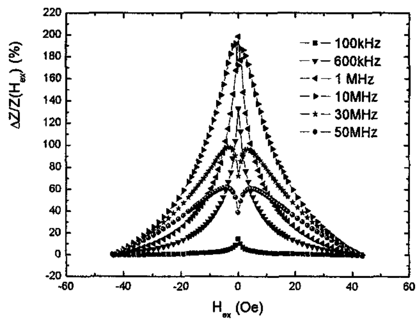
the repeatability, for each level of the grain size at least two wire samples were measured. The results are shown in Figs. 7 – 11.

For the wire samples with permalloy made by DC plating without saccharin, having the grain size about 52 nm, Fig. 7 shows at the testing frequencies ranging from 100kHz to 50MHz the variation of MI ratios of the wire samples with external magnetic field H_{ex}. The maximum MI ratio was about 60 at the testing frequencies ranging from 20MHz to 50MHz. The anisotropy of the plated permalloy was so large that the MI could not reach saturation within the tested range of external field, $H_{max} = \pm 43$ Oe.

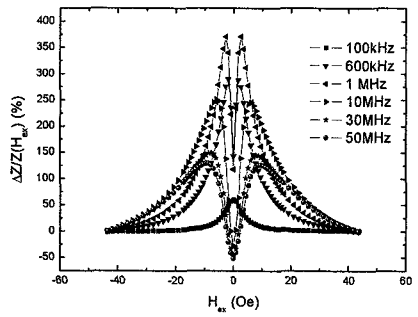
For the wire samples with permalloy made by DC plating with saccharin, having the grain size about 22 nm, Fig. 8 shows at the testing frequencies ranging from 100kHz to 50MHz the variation of MI ratios of the wire samples with external magnetic field H_{ex}. The maximum MI ratio was about 300 at the testing frequencies ranging from 10MHz to 40MHz.

For the wire samples with permalloy made by pulse plating of 20% duty cycle with saccharin, having the grain size about 15 nm, Fig. 9 shows at the testing frequencies ranging from 100kHz to 50MHz the variation of MI ratios of the wire samples with external magnetic field H_{ex}. The maximum MI ratio was about 320 at the testing frequencies ranging from 800kHz to 1MHz.

For the wire samples with permalloy made by pulse plating of 30% duty cycle with saccharin, having the grain size about 16 nm, Fig. 10 shows at the testing frequencies ranging from 100kHz to 50MHz the variation of MI ratios of the wire samples with external magnetic field H_{ex}. The maximum MI ratio was about 420 at the testing frequencies ranging from 800kHz to 1MHz.

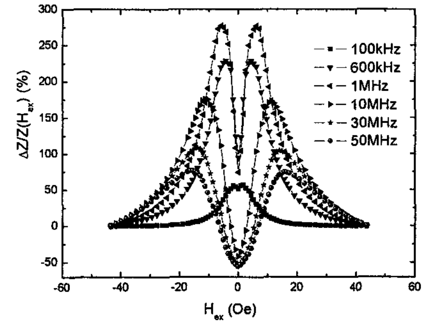


(a)

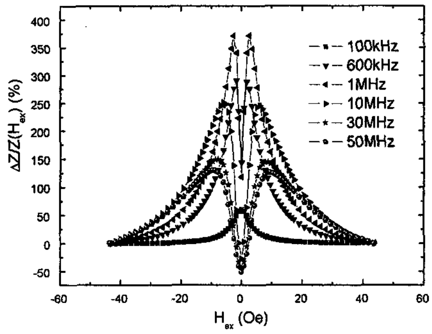


(b)

Figure 8. MI ratio curves at different testing frequencies for DC plating with saccharin added (grain size of 22 nm); (a) on sample 1, (b) on sample 2.



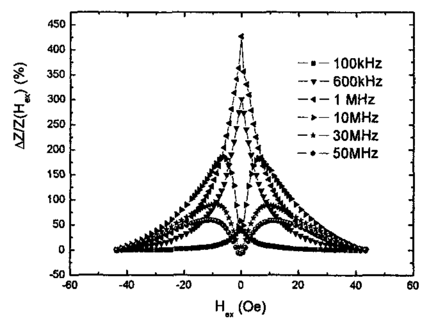
(a)



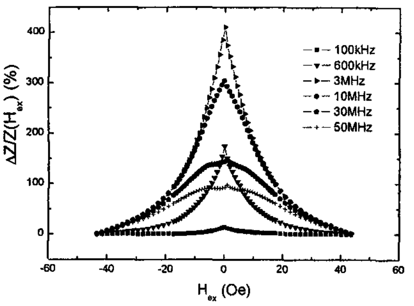
(b)

Figure 9. MI ratio curves at different testing frequencies for pulse plating with 20% duty cycle (grain size of 15 nm); (a) on sample 1, (b) on sample 2.

For the wire samples with permalloy made by pulse plating of 40% duty cycle with saccharin, having the grain size about 16 nm, Fig. 11 shows at the testing frequencies ranging from 100kHz to 50MHz the variation of MI ratios of the wire samples with external magnetic field H_{ex}. The maximum MI ratio was about 340 at the testing frequencies ranging from 1MHz to 3MHz.

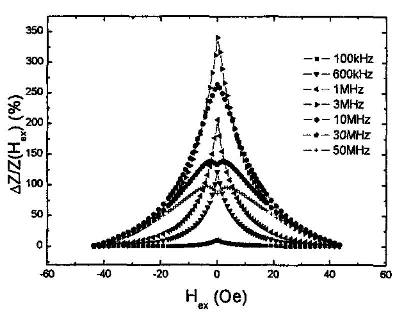


(a)

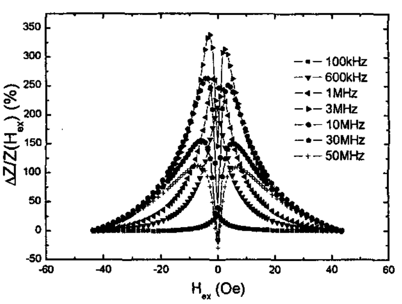


(b)

Figure 10. MI ratio curves at different testing frequencies for pulse plating with 30% duty cycle (grain size of 16 nm); (a) on sample 1, (b) on sample 2.



(a)



(b)

Figure 11. MI ratio curves at different testing frequencies for pulse plating with 40% duty cycle, (grain size of 13 nm); (a) on sample 1, (b) on sample 2.

In summary, there was a significant trend showing that the maximum MI ratio (MI%) of the wire increases as the nanocrystalline grain size decreases. This is presented in Fig. 12, the absolute value is used for the sample made DC plating without saccharin added.

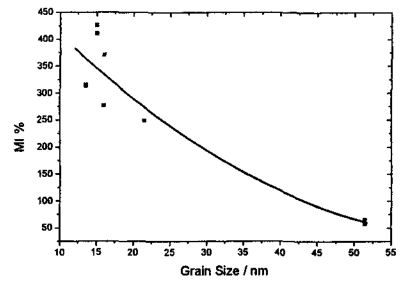


Figure 12. Variation of the maximum MI ratio (MI%) with crystalline grain size of the permalloy coating.

3.3 Discussion

The results as shown in Fig. 12 indicate that the permeability of nanocrystalline permalloy increases as the grain size decreases. This can be explained by the random anisotropy model [1] for small grain size ferromagnetic materials, in which the grain sizes are smaller than the ferromagentic exchange interaction length,

$$L_{ex} = \sqrt{A/K_1} \qquad (2)$$

where A denotes exchange stiffness, K_1 is the magneto-crystalline anisotropy constant. As analyzed by Herzer [3], in ferromagnetic materials with large grains (the grain size larger than the exchange interaction length), the magnetization can follow the easy magnetic directions in the single grains and domains can be formed within the grains. The magnetization process is thus determined by the magneto-crystalline anisotropy K_1 of the crystallites. In ferromagnetic materials with very small grains, the ferromagnetic exchange interaction more and more forces the magnetic moments to align parallel, thus impeding the magnetization to follow the easy directions of each individual grain. As a consequence the effective anisotropy for the magnetic behavior is an average over several grains,

$$K_e = \frac{K_1}{\sqrt{N}} \qquad (3)$$

where K_e is the effective anisotropy and N is the number of grains included by the exchange interaction length,

$$N = (L_{ex} / D)^3 \qquad (4)$$

where D is grain size. When D is smaller than L_{ex}. N is larger than 1, then $K_e < K_I$, and the smaller the D the smaller the K_e compared to the K_I. The magnitude of the effective anisotropy is thus reduced.

For permalloy $Ni_{80}Fe_{20}$, $K_1 = 0.35 \times 10^3 J/m^3$, A = 26×10^{-12} J/m, then the exchange interaction length L_{ex} is about 270 nm. For the nanocrystalline permalloy tested in the present study, the grain sizes were all below 270 nm, therefore, the permeability increased with the grain size decrease.

It should be noted that for normal permalloy in which the crystalline grain size is larger than the exchange interaction length, the permeability normally decreases with the grain decrease [3], as shown in Fig. 13. Therefore, to produce high permeability permalloy, one of the approach could be reducing the crystalline grain size to nanometer scale and well below the exchange interaction length. The present nanocrystalline deposition for permalloy can be one of the methods for developing high permeability permalloy.

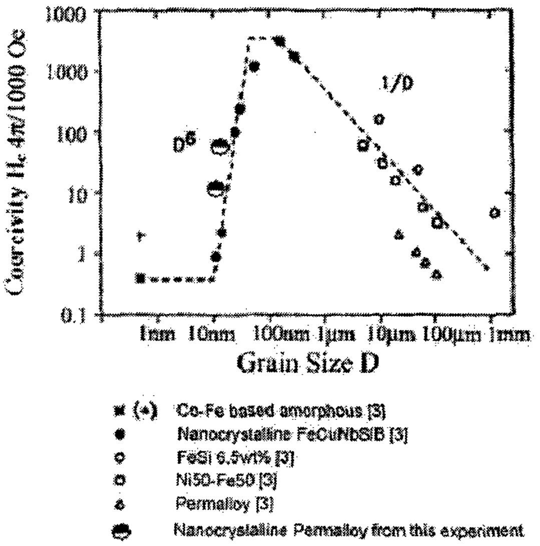


Figure 13. Variation of coercivity with crystalline grain size for different soft magnetic materials.

IV. CONCLUSIONS

- Nanocrystalline deposition of permalloy can be achieved by DC or pulse electroplating with and without saccharin added. The crystalline grain size can be reduced by adding saccharin into the electrolyte solution and by pulse plating with a proper duty cycle.
- In pulse plating of permalloy there is a optimum duty cycle that makes the crystalline grain size reach the minimum.
- In pulse plating of permalloy the duty cycle does not affect the thickness of the plated layer. However, the Fe percentage of the plated material decreases with decreasing the percentage of the duty cycle. A compensation corresponding to reduction in the duty cycle by increasing the $FeSO_4$ content in the electrolyte solution is needed.
- As the nanocrystalline grain size increased from 13 nm to 52 nm, the MI effect ratio of the composite wire showed a significant decreasing trend, which indicated that within the range of nanocrystalline grain sizes, the permeability of the permalloy increases with increasing the crystalline grain size.
- A nanocrystalline deposition method has been developed for producing NiFe/Cu composite wires with large MI ratios, in which the MI ratio depends on the nanocrystalline grain size of the plated materials, and grain size can be controlled by electroplating recipes.

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