Giant magneto resistance for CuCoNi granular films prepared by electrode position

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Abstract. CuCoNi granular films were prepared by electrodeposition, and the magnetoresistance were measured. The results show that the content of Ni is favorable for separation of more magnetic particles in the films. More Ni addition would decrease the concentration of magnetic particles. XRD analysis showed that the addition of Ni is in favor of magnetic particles of layer depositing. Excessive Ni added in the film but reduced concentration of magnetic particles. The layer complete phase separation after 600 °C annealing, corresponding to the copper diffraction peak intensity reaches the maximum; There is a clear satellite peaks at the between Co and Ni diffraction peak. Vacuum annealing make superparamagnetic particles into ferromagnetic particles, improve the coercivity. The GMR results show that 450 °C heat treatment to achieve the best film structure, with a maximum GMR, higher temperatures will form a ternary alloy phase in making the film, the GMR value is the lower.

1. Introduction
The researchers have been constantly exploring direction to improve the performance of giant magnetic resistance material. According to the two elements granule membrane materials, adding a third phase elements will influence the structure of the film, furthermore change its performance. The addition of magnetic elements can provide scattering centre for the new film, adding non-metallic elements may have some impact on the crystallization process of granule membrane, structure and other factors, thus improve the GMR effect [1-8] On the other hand, the formation of three element alloy, the film of crystallization kinetics and process can change because of forming three element alloys; The formation of a new equilibrium influence on the microstructure of the particles film.

This paper studies the use of electrode position adding Ni element into CuCo granule membrane material in order to improve the GMR effect film. Select Ni as the third phase the reason for: 1) Ni as a ferromagnetic element, which is slightly lower than the magnetic susceptibility of Fe, Co, also can improve proportion of iron magnetic particle of the granule membrane material, provide the new scattering center, is expected to enhance the film GMR value; 2)Researchers have found that: alloying Fe, Mn and other elements can’t improve the GMR, and the amount of Ni can improve the GMR value of CuCo alloy.3) Using electro deposition method to add Ni is convenient and simple, which can be adjusted Ni element ratio in the film plating by changing the Ni ion concentration in the plating solution.
At present already reported in the literature [7-10], using rapidly quenching method to add an appropriate amount of Ni element in the CuCo can improve the effect of the film GMR. The use of preparing CuCoNi ternary alloy particles films have not been reported in China; the effect of doping Ni in the electrode position preparing film on structure and magnetic properties didn’t in-depth research both at home and abroad. First, this paper studies the condition of electrode position preparing CuCoNi ternary alloys, analysis the relationship between the concentration of Ni ion in plating solution and the content of Ni in the film; Further alloy films of the different composition ratios annealed, so as to achieve the best structure, measured GMR values.

2. Experimental

2.1. Electrodeposition process
After degreasing and hydrofluoric acid corrosion, the specimen of silicon was carried out electrodeposition. A thin film is annealing in a vacuum at temperature of 300-600 °C, holding time 1 h, cooled to room temperature after the end of heat preservation. Plating solution composition and process parameters is shown in Table 1.

| Reagent and processing parameters | concentration /g·L⁻¹ |
|----------------------------------|---------------------|
| CuSO₄·5H₂O (AR)                  | 6                   |
| CoSO₄·7H₂O (AR)                  | 18                  |
| sodium citrate (AR)              | 80                  |
| Na₂SO₄(AR)                       | 16                  |
| Anode mate                       | Inert anode, 1Cr18Ni 9Ti stainless steel plate |
| Bath temperature (°C)            | 60                  |
| pH                               | 6.0 (Dilute H₂SO₄ or Dilute NaOH to adjust) |
| Current density                  | 45mA/cm²            |

2.2. Coating performance test
Surface morphology was observed by SHIMADZU SSX-550 scanning electron microscope, the composition analysis using EDS, take a five-point averages. The measuring of Magnetoresistance is used to conventional four-probe method, the maximum plus magnetic field is 1.0T, current flows in the film plane and perpendicular to the magnetic field direction. Magneto resistive MR is defined as MR=(R₀– RH)/R₀, R₀, RH the resistance of external magnetic respectively are zero and H. XRD analysis using HUBER Company Huber D8211 X-ray diffractometer, Analysis conditions is: Cu target, the tube voltage 40Kv, tube current 40mA, step length of 0.03.

3. Experimental results and discussion

3.1. Study on electrodeposition preparing CuCoNi ternary alloy
Figure 1 is cathodic polarization curve of after adding Ni in the solution. The deposition potential of Co-deposition of copper and cobalt approximately is E_c = -0.95~1.15V, deposition current is about I_c = 0.0041~0.010A / cm². After adding Ni, the polarization of cathodic polarization curves is prolongation, deposition potential changes E_c1 = -1.20~1.7V, deposition current is about I_c1 = 0.0125~0.075A / cm², added Ni ions to improve the conductivity of the solution, reduce the concentration polarization, improve cathodic polarization effects.
Figure 1. Cathodic polarization curves of plating solutions for alloys

Table 2. EDS analysis of CuCo film with Ni addition

|     | INTENSITY | WEIGHT% | AT%  | KVALUE | Z     | A       |
|-----|-----------|---------|------|--------|-------|---------|
| CO  | 1.496     | 14.662  | 15.667 | 0.10538 | 0.99158 | 1.00311 |
| Ni  | 0.149     | 5.120   | 5.276 | 0.01347 | 0.95583 | 1.00048 |
| Cu  | 22.054    | 80.218  | 79.057 | 0.30371 | 1.00126 | 1.49209 |
| TOTAL | 100      | 100   |       |        |        |         |

Figure 2. EDS of CuCo film with Ni addition

The table 2 is EDS analysis of CuCo film with Ni addition, the Figure 2 is corresponding mapping, at this time adding the amount of NiSO₄ was 22g / L in the bath. The energy peaks of Ni obvious appear in the figure, due to the content of Ni is low, the peak is also low, and the quantitative analysis results are shown that the film is about Cu₈₀Co₁₅Ni₅.
3.2. Effect of Ni addition on the granule membrane structure

Figure 3 is the XRD of Cu80Co15Ni5 before and after heat treatment. Doped Co and Ni elements in the coating to form fine particles dispersed in the Cu matrix. The theory of alloy electrodeposition thinks that during the electrodeposition process, a variety of metal ions coexist in plating, due to the presence of multiple metal ion reduction reaction, prone to electrochemical polarization, the grain refinement effect is obvious. Can be seen from the XRD pattern of the coating, the main diffraction peak is broadening significantly, indicating that the film is very dense grain.

According to the formula Sherrer calculated, the grain size is about 3nm. But also there is still slight Co, Ni particles in the film, the diffraction peak position of three elements is close, leading to the (111) diffraction peak broadening, position shifting to the wide-angle. The film is thermodynamic steady, annealing treatment will cause the change of the film structure. After annealing treatment, with the increase of temperature, due to the solubility of Co in Cu is low, Co element continuously precipitated from the copper base and continues to grow, therefore the diffraction peak position and intensity is continuous change. The similar of intensity of two the diffraction peaks is appeared at near 43.3° in XRD spectra after 450 °C heat treatment, corresponds to the rich Cu phase and rich Co phase, both of them are face-centered cubic structure (fcc) structure. The position of the two diffraction peaks is near, and the difference of strength is not big. There is lower intensity small peak in the vicinity of the main peak, which should be Ni diffraction peak of (fcc) structure. Cu3Ni compound phase appeared in 500 °C vacuum film, therefore corresponding to the diffraction peak positions of copper left shift, strength increase.

The layer complete phase separation after 600 °C annealing, corresponding to the copper diffraction peak intensity reaches the maximum; There is a clear satellite peaks at the between Co and Ni diffraction peak. The analyses of appearing the hexagonal close packed (hcp) structure of Co particles indicated that at this moment the grain size has exceeded the scope of nano, the grain growth make the diffraction peaks become sharp.

Visible, accession to the Ni in the CuCo granular films, improving the vacuum annealing temperature, the changes of XRD patterns of granular films is larger, changes of phase of film inside is more obvious.
3.3. Surface morphology of the film after adding Ni particles

![SEM photographs and element distribution of Cu80Co15Ni5 film before heat treatment](image1)

**Figure 4.** SEM photographs and element distribution of Cu80Co15Ni5 film before heat treatment

![SEM photographs element distribution of Cu80Co17.3Ni2.7 film after 450℃ annealing in vacuum](image2)

**Figure 5.** SEM photographs element distribution of Cu80Co17.3Ni2.7 film after 450℃ annealing in vacuum

SEM photographs element distribution of Cu80Co15Ni5 film after 450℃ annealing in vacuum as shown in figure 5. After heat treatment, the surface of the film deposited tiny crystal grains.

Elemental analysis showed that the Co, Ni distribution of the film surface is more compact, uniform. Heat treatment can be considered to promote the precipitation of Co, Ni in the film, while Ni element solid solution in Cu and Co, so that distribution of Ni element is more uniform.

Fig 6 is surface morphology of Cu80Co15Ni5 coating. The grain of film surface is refinement. Surface brighter place by EDS analysis, Co element content is slightly higher than the matrix. After vacuum annealing treatment due to the grain of membrane layer is shrinkage, appearing a certain number of holes.
Figure 6. Surface morphology of Cu80Co15Ni5 coating

3.4. Effect of adding Ni on Giant Magnetoresistance of particle film
The relation of Ni content and GMR in as-deposited films is shown in figure 7. For plated state samples, when the nickel content is about 5% GMR, the maximum value is about 1.5%, which is higher than state GMR of the sample without addition of nickel plated Cu80Co20.

Figure 7. Relation of Ni content and GMR in as-deposited films

Figure 8. Relation of Ni content and GMR in films after annealing

In plated alloys, the film exists in tiny Co; Ni particles are distributed in the Cu matrix. The two kinds of magnetic particle interaction is strengthening spin scattering of matrix interface, also improving the GMR value.

In two kinds of Co, Ni elements, magnetic Co as the center of the scattering particles of GMR effect is the largest. When Ni content increased while reducing the Co content, GMR is also reduced, but still higher than the film without adding Ni GMR value.
The relation of Ni content and GMR in films after annealing is shown as figure 8. After vacuum annealing, the GMR film which the nickel content is 2.7% reaches a maximum about 2.4% lower than under the same conditions without addition of the nickel plating GMR. Continue to improve the coating of nickel content, GMR decreases.

The properties of the magnetic particles are the main factors affecting the particle film GMR values, which contains particle size, particle type, particle concentration, inter-particle interactions and so on. After the addition of Ni, the performance of Ni has a certain difference in Cu and Co.

After adding a certain amount of Ni element in the electrodeposited CuCo particles film, tiny particles of Ni and Co particles dispersed in the coating film state, which occurs ferromagnetic coupling, increases the number of scattering centers in the film, improve the value of the GMR film.

When nickel content is higher, ternary alloy phase will form in granular films, Cu electronics will enter the 3d electronic shell internal of Co, reduce the density of magnetic phase in the film, also reduce the spin scattering center [8], therefore, the film GMR of higher Ni content decreased.

4. Conclusion
CuCoNi ternary granular films was prepared by electrodeposition method, XRD analysis showed that the addition of Ni is in favor of magnetic particles of layer depositing. Excessive Ni added in the film but reduced concentration of magnetic particles. Vacuum annealing make superparamagnetic particles into ferromagnetic particles, improve the coercively. 450 °C heat treatment to achieve the best film structure, with a maximum GMR, higher temperatures will form a ternary alloy phase in making the film, the GMR value is the lower.

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