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Determination of diffusion in electrodeposited Cu–Ni compositionally-modulated multilayers based on magnetic measurements

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Abstract

The thermal stability in compositionally-modulated metallic multilayers (CMMs) is an important limitation towards their application. In the case of CMMs consisting of an alternation of magnetic and non-magnetic sublayers, the particular magnetic properties are destroyed by the diffusion between the sublayers.

A method for the study of the diffusion in magnetic CMMs, based on the decrease in magnetisation with time and temperature, is presented. Systematic measurements of the magnetisation after proper heat treatment, by means of a Curie–Faraday microbalance, allow a complete characterisation of the diffusion process within the CMMs. Experimental results are presented on electrolytic Cu–Ni CMMs with 100 nm thick sublayers. The value obtained for the activation energy agrees well with published data on diffusion of Cu in Ni obtained by radioactive measurements.

Keywords: Multilayers; Cu–Ni; Electrodeposition; Interdiffusion; Magnetic properties

1. Introduction

Improvements in magnetic materials are still the driving force for advances in related products. In that respect, recent developments in the information storage and magnetic head technology indicate a trend towards thin magnetic films and compositionally-modulated multilayers (CMMs) [1–3]. From an application point of view, CMMs have to be thermally stable to sustain elevated temperatures of a few hundred degrees celsius, as well as wear and corrosion resistant under the expected working conditions. Primarily, the thermal stability seems to be a matter of concern, since diffusion between the non-magnetic and the magnetic sublayers would annihilate the magnetic properties. Vacuum deposition techniques such as molecular beam epitaxy and sputtering are presently used almost exclusively for the production of CMMs. The synthesis of such materials by electrodeposition offers advantages such as a higher obtainable production rate, a lower cost price, a wider possible variation in shape and size of the sample, and a lower deposition temperature. Furthermore, the nucleation problem usually experienced in the electrolytic synthesis of thin films is not necessarily a disadvantage for the production of magnetic CMMs since the interface roughness can sometimes enhance the magneto-resistance [4].

The emphasis of this research was put on the determination of diffusion in electrodeposited magnetic CMMs. The diffusion between the sublayers in magnetic CMMs, which consist of an alternation of magnetic and non-magnetic materials, lowers the overall magnetisation. As such, this diffusion could also be derived from magnetic measurements [5]. The electrolytic Cu–Ni multilayer system was selected to serve this purpose. The method was applied to a multilayer with relatively thick sublayers.

2. Experimental

In order to obtain accurate data, magnetic measurements have been performed on foils. For this purpose,

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CMMs were electrodeposited onto stainless steel flat substrates (2×3 cm^2) mechanically polished to a mirror-like finish ($R_a \approx 0.08$ μm). The pre-treatment of the surface consisted of a degreasing step in an alkaline solution, a cleaning step in distilled water, a passivation step in 50% HNO_3 at 70°C for several minutes, and finally a cleaning step in distilled water. The passivation of the stainless steel was required to establish a low adhesion of the deposited multilayer onto the substrate due to the presence of an oxidised toplayer on the substrate. In this way the stripping by hand of the multilayer is facilitated.

The Cu–Ni CMMs were produced by the double-bath technique [6]. For the copper deposition, a bath containing 90 g l^{-1} $CuSO_4 \cdot 5H_20$ and 200 g l^{-1} H_2SO_4 was used. For the Ni electrolysis, a sulphamate bath containing 400 g l^{-1} $Ni(NH_2SO_3)_2$ and 30 g l^{-1} H_3B0_3 was preferred. The counter electrode in the copper plating cell consisted of electrolytic pure copper, the counter electrode in the nickel plating cell consisted of nickel. The deposition of Cu and Ni was performed galvanostatically at 2 A dm^{-2} and at room temperature. The thickness of the sublayers was calculated from Faraday's law, assuming a uniform coverage of the whole exposed substrate and a current efficiency of 100% for both the Cu and Ni deposition.

The structural characterisation was performed by scanning electron microscopy on cross-sections of the CMMs. Hereto, the foils were embedded in a cold-hardened epoxy resin, ground and polished. Chemical etching in a solution containing 1 g K_2CrO_7, 2 ml H_2SO_4 and 0.1 ml HCl was subsequently performed. This solution etches copper selectively, allowing the visualisation of the metallographic and layered structure of the Cu–Ni-multilayer.

The magnetic measurements were performed on a 5 μm thick Cu–Ni CMM having Cu and Ni sublayers of 100 nm thick. The magnetisation was measured for an applied field of 1260 Oe, by means of a Curie–Faraday microbalance.

The diffusion process was monitored isothermally, under high vacuum, for different time intervals. The diffusion was interrupted by fast cooling. The magnetisation was measured from about 100°C to the reference temperature of 30°C.

3. Results and discussion

The temperature dependence of the magnetisation of a Cu–Ni multilayer in an applied field of 1260 Oe is shown for successive heating and cooling runs in Fig. 1. A progressive lowering of the magnetisation for successive runs is noticed, the last one showing practically no magnetic moment. The decrease of magnetisation is associated with the annealing of the sample during the runs above 380°C. In all circumstances, the Curie point of Ni ($T_c = 360$°C) is detected

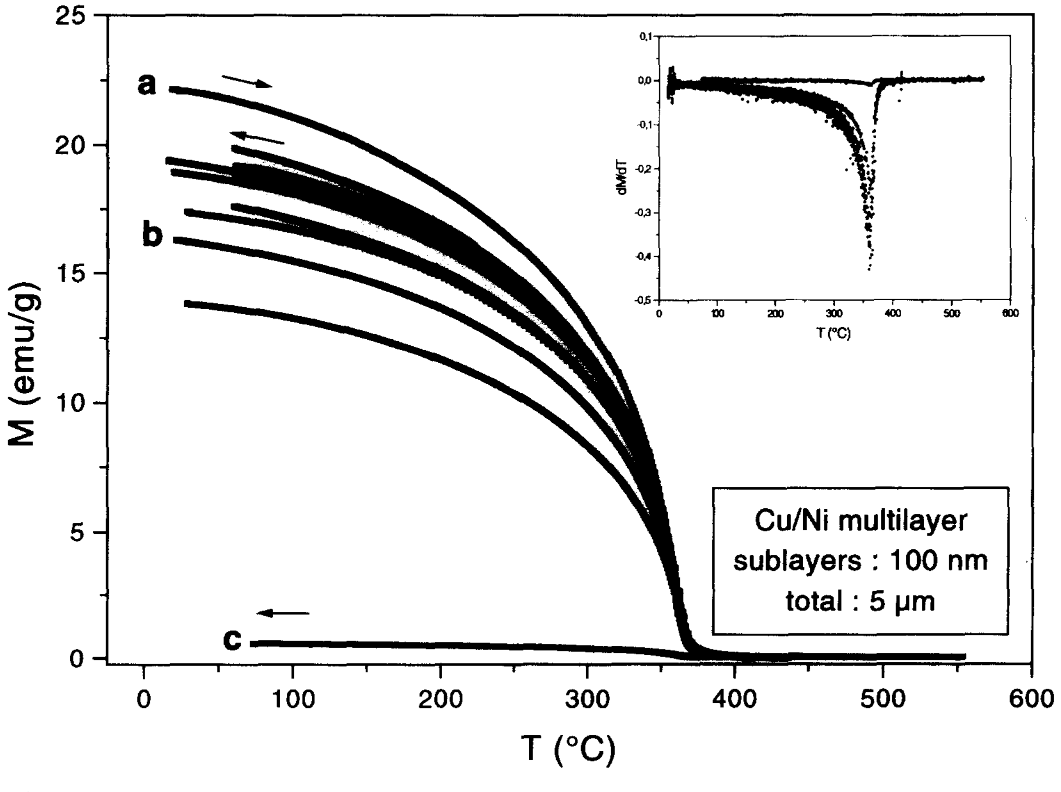

Fig. 1. Magnetisation of a Cu–Ni multilayer as a function of temperature for several consecutive runs. The insert gives for the respective curves the thermal derivative of the magnetisation.

in our measurements, as shown more clearly in the insert of Fig. 1 which plots the derivative of the magnetisation with temperature as a function of temperature. Moreover, this figure demonstrates the quality of the magnetic measurements, since the derivative, being quite sensitive to any scattering of the data mainly in the vicinity of the transition temperature, appears to be very smooth.

A metallographic investigation on cross-sections of the Cu-Ni CMMs was performed after different heat treatments. The as-plated Cu-Ni-multilayer microstructure (point (a), Fig. 1) has a uniform layered structure. After several heat treatments up to 430°C at a heating rate of 10°C $\min^{-1}$, such that at room temperature a smaller residual magnetic moment could still be measured (corresponding to point (b) in Fig. 1), the layering in the multilayer is not as sharp as in the as-deposited coating. After a thermal treatment in which practically no magnetisation is subsequently measured (point (c), Fig. 1), the multilayered structure is replaced by one uniform layer consisting of a Cu-Ni solid solution, as demonstrated by energy dispersive X-ray (EDX) analyses.

To quantify this diffusion in the magnetic CMMs, the magnetisation of the CMMs at a reference temperature well below the Curie temperature of Ni was determined first. Then, the influence of the heat treatment on the magnetic moment was derived.

The diffusion, besides affecting the typical multilayer structure, results from a solid-state thermal reaction between the completely miscible Cu and Ni [7]. In contrast, it is well known that, at room temperature, Cu-Ni solid solutions with Ni percentages below 43 at.% are non-magnetic and between 43 and 70 at.% are paramagnetic [7,8].

The term 'interface' is usually correlated with the surface of boundaries between different phases. In this work, however, the term is used to designate the boundary between magnetic and non-magnetic sublayers within the multilayered structure. During diffusion, this boundary will evolve into a diffusion zone consisting of a solid solution of Cu and Ni which can be considered as the interface. The simple problem of one-dimensional diffusion across a plane interface between semi-infinite sources is resolved as a solution of Fick's second law, which relates the concentration $C(x,t)$ to its initial value C_0 [9] by

$$C(x,t) = \frac{C_0}{2}\, erfc\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (1)$$

where erfc is the complementary error function and D is the diffusion coefficient.

The diffusion between semi-infinite sources can be related to the mechanism occurring in a multilayered sample, where each layer can be considered as an extended diffusion source. Exact solutions of the diffusion equations for real CMMs, where two phases may be reacting together under variable conditions, are complex, but approximate solutions may be obtained by a simple general argument. Diffusion is the overall result of random walks made by individual migrating particles. Statistical theory enables the average behaviour in a random walk to be analysed and shows that in a time t such a particle migrates on average a distance $(Dt)^{1/2}$ from its starting point. This is the distance over which the concentration can change substantially in a time t [10].

Taking this into account, the following model can be formulated to interpret the diffusion experiment:

(1) the magnetisation of the multilayer is solely due to the free Ni atoms;

(2) the boundary between the magnetic and non-magnetic sublayers varies with temperature and time. An interface, triggered by the diffusion between sublayers, will be formed. The resulting solid-state solution is assumed to be completely non-magnetic at room temperature, notwithstanding the fact that Cu-Ni solid solutions with Ni percentages above 30 at.% still exhibit ferromagnetic properties;

(3) the time rate of the increase of the thickness x of the interface dx/dt is proportional to $1/x$. This means that a parabolic law for diffusion through a planar layer is assumed ($dx/dt = K/x$);

(4) the activation energy for the reaction can be obtained from an Arrhenius plot.

The magnetisation per unit mass of the multilayer is therefore

$$\frac{M}{W} = m_{Ni}\frac{W_{Nif}}{W} \qquad (2)$$

where m_{Ni} is the magnetic moment per unit mass of Ni, W_{Nif} is the mass of the free Ni, and W is the total mass of the sample ($W = W_{Cu} + W_{Ni}$).

The actual mass of free Ni is the difference between the mass of Ni prior to the diffusion (W_{Ni}) and the mass of Ni in the interface of thickness x (W_{Nix}) due to diffusion:

$$W_{Nif} = W_{Ni} - W_{Nix} \qquad (3)$$

Therefore, before diffusion occurs, the quotient of the magnetic moment per unit mass of the Ni (m_{Ni}) and of the multilayer (M/W) is given by

$$\frac{m_{Ni}}{M/W} = 1 + \frac{W_{Cu}}{W_{Ni}} = 1 + \frac{At_{Cu}}{At_{Ni}} \qquad (4)$$

where At_{Cu} and At_{Ni} are respectively the atomic weights of Cu and Ni. The value calculated from this expression for $[m_{Ni}/(M/W)]$ is 2.08, which agrees well with the experimental value of 2.04 obtained by magnetic moment measurements. In addition, the transition temperature of the magnetic phase in the multilayer, as shown in Fig. 1, is precisely the Curie temperature of Ni. This supports point (1) of our model.

The mass of the interface formed during diffusion is given by

$$W_{\mathrm{Ni}x} + W_{\mathrm{Cu}x} = \rho SxN \tag{5}$$

where ρ is the average specific mass, S the cross-sectional area and N the number of layers. The equation valid for Cu–Ni CMMs relating the magnetisation per unit mass of the sample (M/W) to the thickness x of the diffusion interface can be written as

$$\frac{M}{W} = \frac{1}{1+F}\left(1 - \frac{\rho SxN}{W}\right)m_{\mathrm{Ni}} \tag{6}$$

where F is the ratio of atomic weights of Cu and Ni. The thickness of the diffusion interface x can be expressed as a function of the annealing time t, as $x = (Dt)^{1/2}$ where D is the diffusion coefficient. The time dependence of M/W is then expressed by

$$\frac{M}{W} = A - Bt^{1/2} \tag{7}$$

where $A = m_{\mathrm{Ni}}/(1+F)$ and $B = A(N/L)D^{1/2}$, $L = W/(\rho S)$ being the thickness of the sample.

If D follows an Arrhenius law $D = D_0\exp -(Q/RT)$, the activation energy Q associated with the diffusion process can easily be derived. Indeed, since

$$\frac{\mathrm{d}(\log B)}{\mathrm{d}(1/T)} = -\frac{Q}{2R} \tag{8}$$

where R is the gas constant; Q can be determined from the slope of the plot log B versus $1/T$.

To demonstrate the appropriateness of this model, diffusion studies were performed on five samples at temperatures of 388, 440, 455, 477 and 484°C. For each sample a heat treatment was done, and the time of diffusion, the temperature of diffusion and the magnetic moment after diffusion at a reference temperature (30°C) were measured, as mentioned in the previous section.

The time of diffusion was added up for each successive step of heating and the corresponding decrease in magnetisation was recorded, as shown in Figs. 2 and 3. The results are in good agreement with Eq. (7). The temperature dependence of the coefficient B is shown in Fig. 4. The calculated activation energy Q gives a value of 53.47 kcal mol^{-1}. This is in good agreement with the published diffusion data obtained by radioactive tracer for (bulk) Cu in Ni of 53.8 kcal mol^{-1} [11]. It is also in fairly good agreement with the value 64.5 kcal mol^{-1} obtained from the decay of X-ray diffraction satellite intensities on vapour-deposited Cu–Ni films with a composition modulation wavelength between 0.8 and 5.0 nm [12].

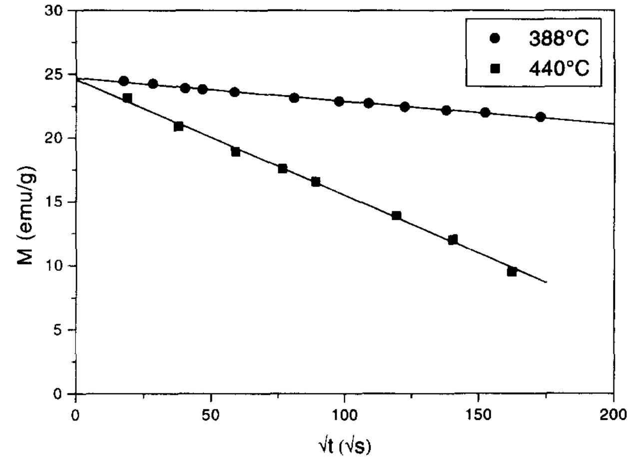

Fig. 2. Magnetic moment per unit mass at the reference temperature (30°C) of a Cu–Ni multilayer for an applied field H = 1260 Oe, as a function of the square root of the diffusion time. The diffusion took place at temperatures T = 388°C and T = 440°C.

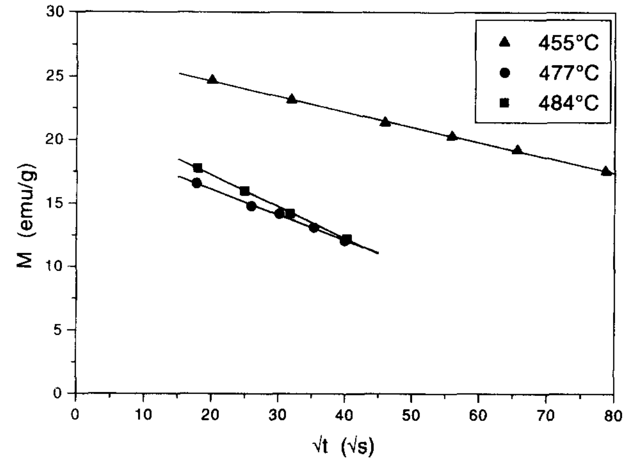

Fig. 3. Magnetic moment per unit mass at the reference temperature (30°C) of a Cu–Ni multilayer for an applied field H = 1260 Oe, as a function of the square root of the diffusion time. The diffusion took place at temperatures T = 455°C, T = 477°C and T = 484°C.

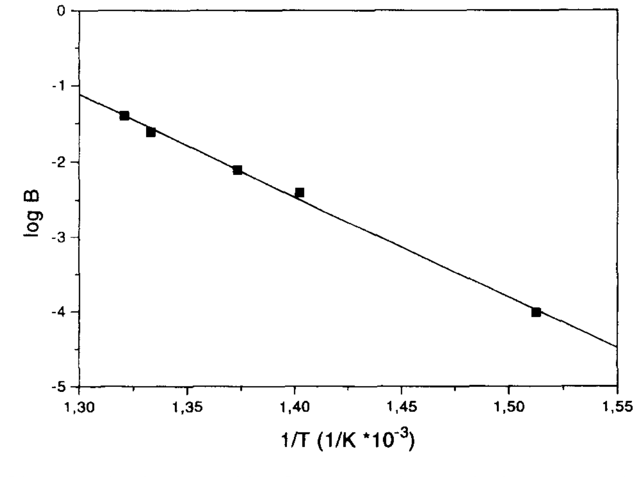

Fig. 4. Arrhenius plot of log B vs. $1/T$, where B is the slope of the lines shown in Figs. 2 and 3.

4. Conclusion

Magnetic measurements have been used to determine the diffusion in magnetic CMMs giving rise to a non-magnetic interface. The method is applicable to magnetic interfaces whose magnetic moment per unit mass is not zero, but is much smaller than that of the magnetic layer. The feasibility of this method was demonstrated for magnetic CMMs with sublayer thicknesses of 100 nm. Future work has to prove that this method can be elaborated for magnetic CMMs for which the remarkable magnetic properties appear, i.e. with sublayer thicknesses as small as several nanometers.

This method is a very useful alternative to radioactive methods used at present for the determination of the activation energy for thermal diffusion. This technique allows an accurate determination of the temperature dependence of homogenisation of CMMs. It opens the way to an indirect determination of the mixing at the interface between the magnetic and non-magnetic constituents of the CMMs.

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