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# Electrodeposition of Stress-Insensitive Ni-Fe and Ni-Fe-Cu Magnetic Alloys

The characteristics of Ni-Fe magnetic layers are of interest for use in magnetic components such as in high-performance stores or as nonlinear self-inductances for parametric cells. However, in order to take advantage of these characteristics and to obtain high quality components, it is desirable and often necessary that the characteristics of the magnetic layers be stress-insensitive.

We have attempted to obtain such layers by electrodeposition. Since magnetostriction depends on composition and since, as in the case of electrodeposition, composition is influenced by plating parameters, a thorough study of these parameters was made. This study enabled us to determine the conditions for preparing stress-insensitive deposits. In order to obtain such deposits more easily while still retaining low coercive force, we have also investigated some ternary deposits. The only suitable additive we have found is copper; other elements either increased the coercive force or made it more difficult to obtain stress-insensitive deposits. After showing the need for stress-insensitive magnetic layers, we shall analyze the influence of plating parameters on composition and on the stress sensitivity of the deposits; then we shall show the necessary tolerances for these parameters as used to obtain stress-insensitive deposits. In the last section we shall show that the addition of Cu to Ni-Fe permits wider tolerances.

### Need for stress-insensitive magnetic layers

It is known that the optimum characteristics of the alloys of the Permalloy type are obtained for low values of magnetostriction. On the other hand, if the magnetic materials are magnetostrictive, their characteristics will be sensitive to mechanical stresses and distortions,[1] and they will vary according to the extent of the strains. Components using magnetic layers are extremely sensitive to these factors. For the special needs of high-density arrays, the components generally have a very small cross section, hence a very slight rigidity. Therefore, even small applied forces cause large strains, accompanied by undesirable variations in the magnetic properties.

These components may be submitted to forces that might be either permanent, due to their connection in a cell or a memory (mostly through soldering), or accidental (vibrations, handling), or semipermanent, due to the action of temperature changes on materials with different expansion coefficients (component/component support, or even magnetic film/substrate). Of course, it is possible to avoid or to minimize as much as possible the occurrence of stresses and strains by taking many precautions, by selecting appropriate materials as substrates, and by adopting elaborate manufacturing procedures. In the process we have developed to make parametric cells, the plating of the magnetic films is the last step of the manufacturing operations;[2] this eliminates all handling of the magnetic components. However, to be sure to avoid all sources of degradation of the magnetic properties, it is preferable and often necessary to use nonmagnetostrictive magnetic alloys particularly since, in the manufacture of many components, it is not always possible to find a simple method to avoid the handling.

Moreover, because internal stresses in the deposits may be very high, it is not possible to know their intrinsic magnetic properties if they are stress-sensitive. Lastly, experience has proved that an aging of stress-sensitive deposits (change of magnetic properties with time) frequently occurs; presumably this phenomenon is mainly due to internal stresses (stress relief).

### Magnetostriction

Most ferromagnetic materials placed in a magnetic field undergo magnetostriction which is said to be positive when dimension $L$, parallel to the field, is increased by an amount $\Delta L$ ($\lambda = \Delta L/L > 0$) (e.g., Fe), and negative in the reverse case ($\lambda < 0$) (e.g., Ni).

Conversely, when a magnetic material is submitted to mechanical stresses, a change in its magnetic properties

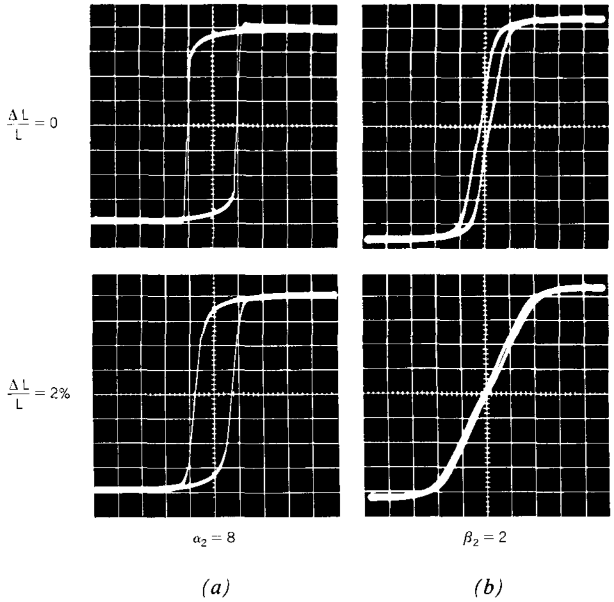



**Figure 1** Modification of shape of the hysteresis loops of magnetostrictive deposits when submitted to a 2% elongation, with $\lambda > 0$. (a) Circularly oriented deposit. (b) Longitudinally oriented deposit.

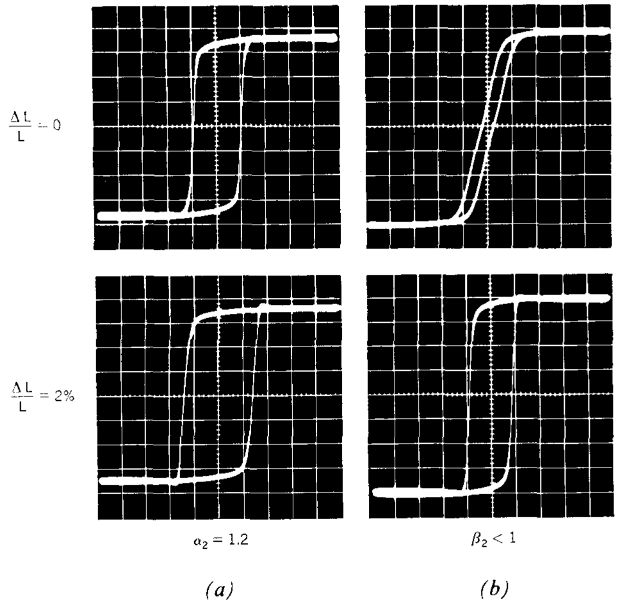



**Figure 2** Same as Figure 1 for case of $\lambda < 0$. (a) Circular orientation. (b) Longitudinal orientation.

(Villari effect) occurs. Thus, if a positive-magnetostriction material is subjected to a tensile stress lower than its yield strength, its hysteresis loop becomes squarer and its coercive force decreases.

• *Method for evaluating magnetostriction in electrolytic deposits*

Our measurement method is based on the Villari effect. In practice the relative variations of the coercive force are measured as a function of the elongation of the deposits. To ensure uniform stresses, and to facilitate their measurement, the material to be evaluated is deposited on copper wires.

If a tensile stress is applied to a copper wire plated with a positive magnetostriction Ni-Fe magnetic alloy, one finds, as a function of strain (Fig. 1):

(a) A decrease in coercive force $H_c$ for a circularly oriented deposit,
(b) An increase in anisotropy field $H_k$ for a longitudinally oriented deposit.

With a negative magnetostriction alloy, on the contrary, the following is found (Fig. 2):

(a) $H_c$ increases as a function of elongation,
(b) $H_k$ decreases slightly and the loop opens itself.

As the variations of $H_c$ and $H_k$ change signs at the same time as the magnetostriction $\lambda$, it is possible to evaluate $\lambda$ with a good accuracy by one of the ratios:

$$\alpha_n = \frac{H_c \text{ at } n\% \text{ elongation}}{H_c \text{ at } 0\% \text{ elongation}}$$

$$\beta_n = \frac{H_k \text{ at } n\% \text{ elongation}}{H_k \text{ at } 0\% \text{ elongation}}.$$

By making deposits with a variable magnetostriction factor on wires longitudinally and circularly oriented, the following approximate relationship was found (Fig. 3):

$$2\alpha_1 + \beta_1 = 3.$$

Since the measurement of $H_c$ is more precise than the measurement of $H_k$, we have adopted $\alpha_1$ to evaluate the stress sensitivity. Hereafter, we consider that a deposit is stress-insensitive if, after a 1% elongation, the change in the measured coercive force is not higher than $\pm 10\%$: $0.9 \leq \alpha_1 \leq 1.1$. In fact, this requirement is most severe, since it corresponds to a high permanent strain. Under normal utilization conditions, without other special care, the coercive force and the loop shape do not vary appreciably.

## Obtaining stress-insensitive Ni-Fe electrodeposits

The magnetostriction of the Ni-Fe alloys depends on the value of the magnetic field and on the composition, as

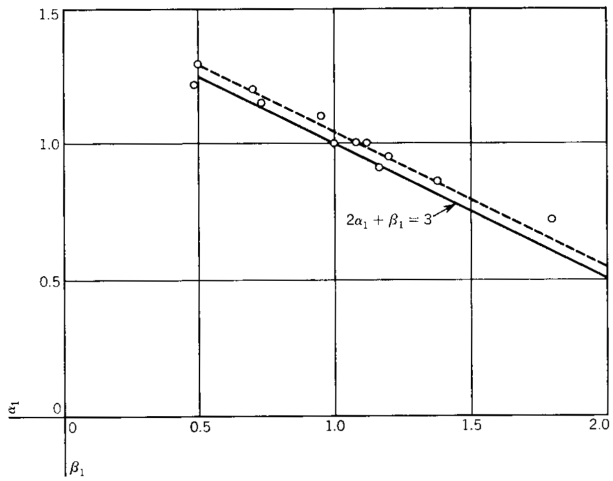



**Figure 3** Relationship between magnetization magnetostriction factor:

$$\alpha_1 = \frac{H_c \text{ at } 1\% \text{ elongation}}{H_c \text{ at } 0\% \text{ elongation}} \text{ and } \beta_1 = \frac{H_k \text{ at } 1\% \text{ elongation}}{H_k \text{ at } 0\% \text{ elongation}}$$

shown[3] by Fig. 4. It is shown that the nonmagnetostrictive composition of the Ni-Fe alloys of the Permalloy type is about 81% Ni-19% Fe. However, this Figure also shows a very steep slope of the magnetostriction curve as a function of composition, i.e., a very slight change in composition near the critical composition corresponds to a considerable increase in magnetostriction. We have observed that such slight changes in composition (as measured by means of an X-ray spectrometer) were very sensitive to changes in the plating parameters.

In order to obtain reproducible stress-insensitive deposits, it has, therefore, been necessary to study thoroughly the influence of the various parameters on composition in that narrow range of the best magnetic characteristics. The factors affecting the deposit composition are:

(1) Bath chemical analysis (Ni and Fe contents)
(2) Bath temperature
(3) Bath agitation degree
(4) Plating current density or voltage, and
(5) Cathode geometry (wire diameter).

For a well-fixed value of each of these parameters, a well-defined composition is obtained, and by varying only one parameter, a whole range of compositions can be obtained. However, the choice of precise values for these parameters was dictated not only by composition requirements but also by the need for well-oriented, low-coercivity deposits. In fact, all these requirements had already enabled us to determine with a good approximation the optimum values of the main parameters.

Precise information on the effects of these parameters on composition permitted us to specify parameter tolerances for the desired range of minimum magnetostriction. The results obtained are summarized here.

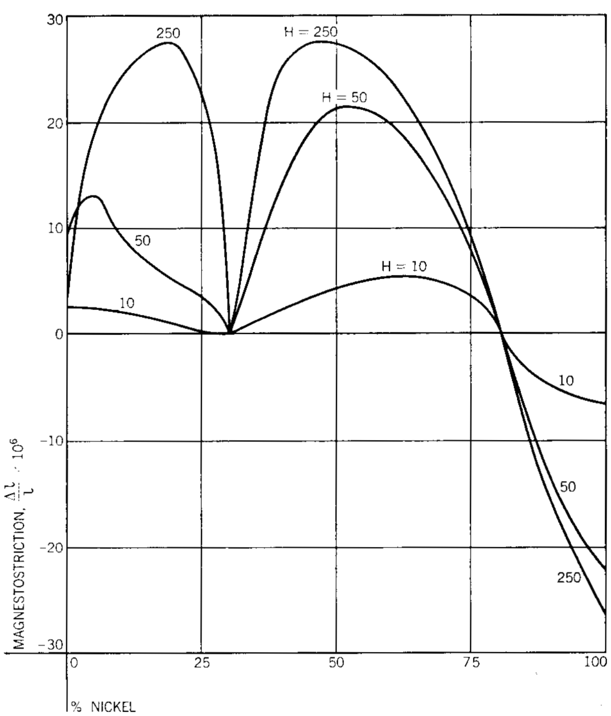
- *Bath composition*

The plating bath used is derived for Wolf's bath[4] (in turn derived from Watts' bath) and has the following composition:

| | | |
|---|---|---|
| Nickel sulfate | $SO_4Ni \cdot 7\,H_2O$ | See below |
| Iron sulfate | $SO_4Fe \cdot 7\,H_2O$ | See below |
| Boric acid | $H_3BO_3$ | 25 g/l |
| Saccharin | $C_6H_4CONHSO_2$ | 0.8 g/l |
| Sodium laurylsulfate | | 0.4 g/l |

The usual nickel sulfate content is 250 g/l. The iron sulfate content may range from 2 to 10 g/l for obtaining zero magnetostriction when plating conditions (temperature, potential, agitation) and substrate shape vary. We have determined that the content in these chemicals had to be kept within ±2% from bath to bath (see Fig. 5 for nickel). To obtain this result, it is necessary to check the nickel and iron content for each lot of nickel and iron sulfates we receive, and to gauge the stock solutions with a fairly great precision.

**Figure 4** Dependence of magnetostriction of Ni-Fe alloys on magnetic field and on alloy composition.



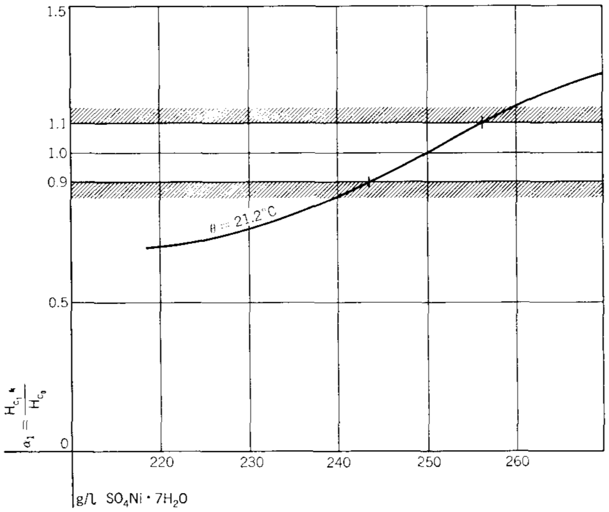



**Figure 5** Plot of $\alpha_1$ versus $SO_4Ni \cdot 7H_2O$ bath content. The content of $SO_4Fe \cdot 7H_2O = 4$ g/l.

• *Agitation*

To obtain uniform composition along the cathode, it is necessary either to agitate the bath strongly, or not to agitate it at all. Bath agitation is necessary when the bath is heated and may help to limit the composition gradient as a function of deposit thickness. But our bath operates at room temperature and besides, the thickness of the layer where there is a composition gradient is small compared with the total thickness of the deposit (10,000 to 20,000 Å). Moreover, a uniform agitation cannot be obtained with an intricately shaped cathode, and a strong agitation has to be avoided when the cathode is small to avoid deformation of the cathode. Therefore, it has been essential to avoid agitation.

•*Bath temperature*

Figure 6 shows that the bath temperature must be kept within $\pm 0.2\,°C$. Since the bath is not agitated, it is necessary that the bath temperature be about the same as the ambient atmosphere to avoid temperature gradients and convection currents in the bath. Temperature is stabilized by using a cooled water bath, a precision contact-thermometer, and a tank whose walls have a high thermal conductivity.

• *Plating current density and plating potential*

Composition of the deposit is actually governed by the plating current density. Since the actual cathode area is not known with sufficient accuracy (because of substrate roughness, difficulties of measuring the area of intricately shaped cathodes, area change during plating, etc. . .), it is difficult to determine the current density and, therefore,

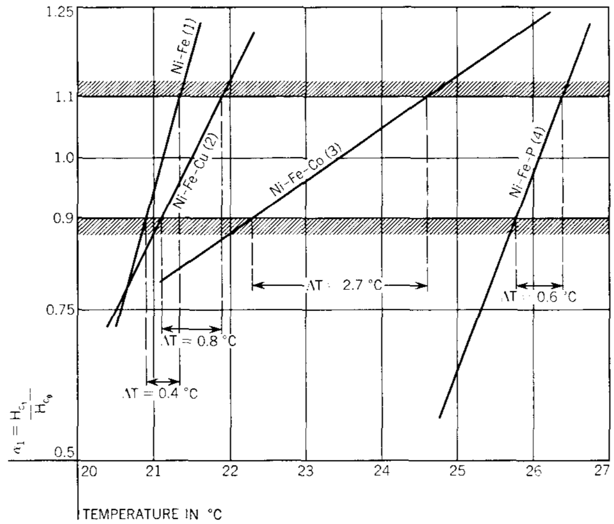
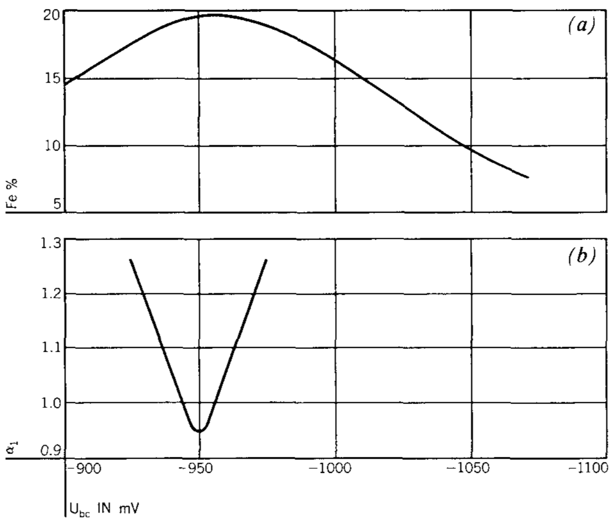



**Figure 6** Stress sensitivity versus bath temperature for Ni-Fe, Ni-Fe-Co, Ni-Fe-Cu, and Ni-Fe-P deposits.
(1) Bath containing 250 g/l $SO_4Ni \cdot 7H_2O$, 4g/l $SO_4Fe \cdot 7H_2O$
(2) Bath containing 250 g/l $SO_4Ni \cdot 7H_2O$, 4g/l $SO_4Fe \cdot 7H_2O$, 0.5g/l $SO_4Cu \cdot 5H_2O$
(3) Bath containing 250 g/l $SO_4Ni \cdot 7H_2O$, 4g/l $SO_4Fe \cdot 7H_2O$, 5g/l $SO_4Co \cdot 7H_2O$
(4) Bath containing 250 g/l $SO_4Ni \cdot 7H_2O$, 5g/l $SO_4Fe \cdot 7H_2O$, 0.2g/l $NaH_2PO_2$

**Figure 7** (a) Iron percentage of alloy versus plating potential for (a) $SO_4Ni \cdot 7H_2O = 250$g/l and $SO_4Fe \cdot 7H_2O = 4$g/l; (b) Stress sensitivity of the deposits vs plating potential for $SO_4Ni \cdot 7H_2O = 255$ g/l and $SO_4Fe \cdot 7H_2O = 4$g/l.




the plating voltage is used instead as a control. Figure 7a shows the deposit composition vs plating potential. For the bath studied, there is first an increase, then a decrease of the Fe content, the maximum being reached for $-950$ mV (about 5 $mA/cm^2$). Magnetostriction measurements corroborate these results: magnetostriction goes through a minimum ($\alpha_1 \simeq 0.9$) at $-950$ mV (Fig. 7b). It is obviously necessary to control the potential in the narrow range associated with the critical composition; to keep magnetostriction within permissible limits, the deposit potential cannot be allowed to vary more than $\pm 12$ mV. The use of a potentiostat enables us to control the voltage within $\pm 1$ mV.

• *Wire diameter*

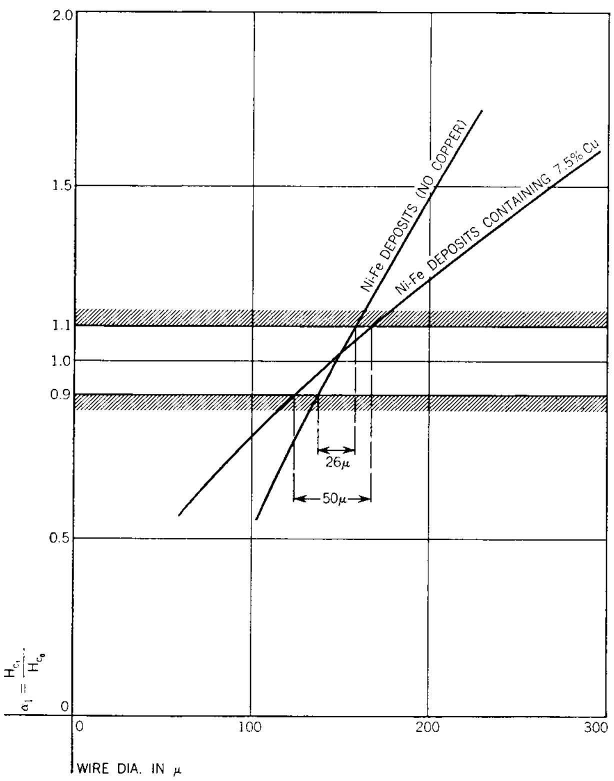
With either plating process that we can use (constant current or constant potential) the deposit composition varies with the wire diameter. Figure 8 shows that the maximum tolerance on the wire diameter is $\pm 13\ \mu$ for a wire diameter of 180 $\mu$. The wire is electropolished to control the diameter with a high degree of precision. In practice, after polishing, the desired diameter is attained within $\pm 3\ \mu$.

## Deposition of ternary alloys

We have just seen that by minutely controlling the value of the different parameters discussed above, it was possible to obtain stress-insensitive deposits. However, the required tolerances for these parameters are extremely narrow. This necessitates a very thorough checking at all levels: raw materials acceptance tests (chemicals, wires), preparation of the baths, of the wires, plating conditions, etc.

For these reasons it was desirable to broaden these tolerances while keeping low coercive force for the deposits and we have undertaken a study with this end in view. It was necessary to find a means either to stabilize the zero magnetostriction composition (by decreasing the slopes of the curves of the deposit composition as a function of the various parameters), or to decrease the slope of the magnetostriction curve as a function of composition, or else to decrease the modulus of elasticity of the plated alloy.

**Figure 8** $\alpha_1$ versus wire diameter for deposits containing copper and for copper-free deposits.




• *Nickel-iron-copper electrodeposits*

It is known that the presence of copper in bulk Permalloy makes heat treating less critical. Therefore, it might have been thought that copper would also make the plating conditions less critical. Besides, Randall[5] had reported, as far back as 1936, that the addition of copper to Ni-Fe alloys made them less sensitive to stresses.

Thus, we have been led to study Ni-Fe-Cu deposits. These deposits were obtained by adding a copper salt to the baths used for the Ni-Fe deposits.[6] Since we use a sulfate bath, we have added the copper in the form of copper sulfate, $SO_4Cu \cdot 5\ H_2O$.

• *Influence of copper on deposit stress sensitivity*

The relative variation of stress sensitivity of the deposits as a function of the variation of plating parameters will decrease when the copper sulfate content of the bath increases up to 0.5 g/l $SO_4Cu \cdot 5\ H_2O$ (0.002 M). Above that value the improvement is very slight. Figures 6 and 8 show that for a same variation of $\alpha_1$ (from 0.9 to 1.1), the addition of 0.5 g/l copper sulfate in the plating bath enables twice as great variation of the parameters that influence the composition. Indeed, for the examples given in Figs. 7 and 8, to keep $\alpha_1$ between 0.9 and 1.1 the following variations of temperature and wire diameter are permissible:

| | Bath containing no copper | Same bath $+ 0.5$ g/l $SO_4Cu \cdot 5\ H_2O$ |
|---|---|---|
| Temperature | 0.4 °C ($\pm$0.2 °C) | 0.8 °C ($\pm$0.4 °C) |
| Diameter | 26$\mu$ ($\pm 13\mu$) | 50$\mu$ ($\pm 25\mu$) |

It is, therefore, possible to double the tolerances within which these parameters may vary, which is a considerable advantage.

The copper percentage of the deposit has been plotted versus the copper sulfate contained in the bath (Fig. 9). It is seen in that Figure that the variation is linear. To 0.5 g/l copper sulfate in the bath corresponds a copper

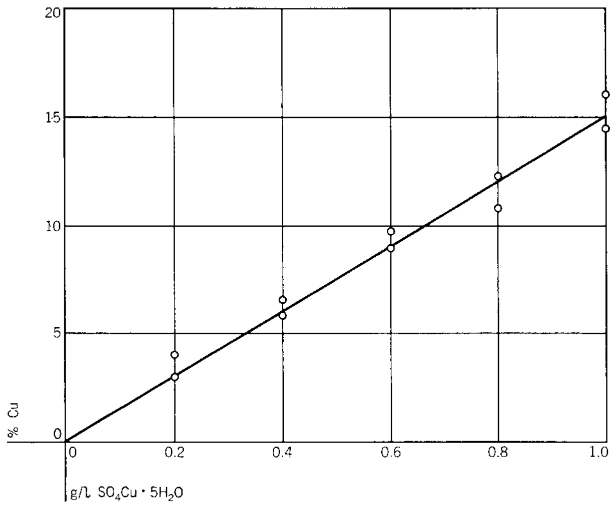



**Figure 9** Plot of percent copper in deposit versus copper sulfate content in the bath.

percentage of 7.5% in the deposits. For 1 g/l copper sulfate, the percentage is 15%. When the copper sulfate content in the bath exceeds this value, the deposit is black.

• *Influence of copper on the other characteristics of the deposits*

*Coercive force:* The deposits containing Cu have a slightly lower coercive force ($H_c \leq 0.4$ Oe) then the Ni-Fe deposits.

*Resistivity:* The Ni-Fe-Cu deposits (7.5% Cu) have a resistivity twice as great as the Ni-Fe deposits in the neighborhood of the composition having zero magnetostriction. Consequently, in very-high-frequency applications, the ternary deposits have definitely lower losses than the binary alloys.

## Example of application

We have employed this ternary alloy for magnetic deposits on wires used in parametric cells. These wires could be soldered, unsoldered, resoldered, bent, and submitted to mechanical tensile stresses without noticeably modifying the output voltage of parametric cells.

## Conclusion

A thorough knowledge and a very close check of the parameters affecting the characteristics of the deposits enable one to obtain zero Ni-Fe deposits having zero magnetostriction.

Addition of Cu to Ni-Fe deposits makes it possible to double the tolerances imposed upon these parameters and to improve the magnetic properties of these deposits, especially in very-high-frequency applications.

## Appendix

1. Among the other ternary elements investigated, some such as phosphorus and cobalt have a significant influence on relative variation of stress sensitivity of the deposits as a function of the variation of plating parameters:

   Phosphorus has little effect on magnetostriction (Fig. 6) but it is to be noted that Ni-Fe-P alloys have much lower coercive force and anisotropy field than Ni-Fe. But as P strongly increases internal stresses, it is highly desirable that the Ni-Fe-P deposits be stress-insensitive.

   Cobalt, on the contrary, has a very beneficial effect on magnetostriction (see Fig. 6), the more so as Co content is greater. The addition of Co to Ni-Fe, however, increases the coercive force and the anisotropy field of the deposits.
2. From a practical point of view, if for any reason the deposit is magnetostrictive, the knowledge of $\alpha_1$, on one hand, and of the variation of $\alpha_1$ versus bath temperature or composition, on the other hand, enables a rapid adjustment of the plating conditions to obtain a zero magnetostriction. The following table shows the corrections that must be made for some values of $\alpha_1$.

| | Parameters to be corrected | | | | | |
|---|---|---|---|---|---|---|
| | $SO_4Ni$, $7H_2O$ g/l | $SO_4Fe$, $7H_2O$ g/l | T, °C | $SO_4Ni$, $7H_2O$ g/l | $SO_4Fe$, $7H_2O$ g/l | T, °C |
| $\alpha_1 = 1.25$ | | +0.25 | −0.6 | | +0.5 | −1.2 |
| $\alpha_1 = 1.10$ | | +0.12 | −0.3 | | +0.25 | −0.6 |
| $\alpha_1 = 0.9$ | +10 | | +0.25 | +20 | | +0.5 |
| $\alpha_1 = 0.80$ | +20 | | +0.5 | +40 | | +1 |

From this table it is seen that it is possible to avoid controlling the Ni or Fe content of the sulfates by checking the magnetostriction of the deposit as soon as the bath is fabricated and by adjusting the plating conditions quickly.

## References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6. See also I. W. Wolf, "The Effect of Small Quantities of Copper on the Magnetic Properties of Electrodeposited Permalloys," Proceedings of the Leuven Conference, *Electric and Magnetic Properties of Thin Metallic Layers*, Brussels, 1961, p. 158.


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