2) The fact that you plot relaxation times for the magnetic annealing process implies that you have followed the magnetic annealing anisotropy as a function of time. What is the form of the curve of K_u *vs.* time, and is the form the same at all temperatures and for all films?

S. METHFESSEL: 1) The reproducibility of our results is indicated by the scattering of the measured values in the diagrams which I have shown.

2) We followed the anisotropy during the annealing treatment and derived from this measurement the relaxation time for turning the easy axis by an angle of 90°. However, the accuracy of the H_K values obtained from the measurements of the initial susceptibility in the hard direction is not very high, and small deviations from exponential law in the K_u *vs.* time curve cannot be detected in ultrahigh vacuum films.

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Influence of Minor Constituents in Ferromagnetic Films

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Studies have been made on the effect of minor constituents, especially oxygen, in permalloy thin films. A model is proposed in which a columnar structure is formed during deposition. The oxygen is assumed to diffuse upwards from the substrate between the columns to form iron oxide and nickel-rich regions. This model is supported by electron photomicrographs of thin-film cross sections which have been prepared by etching. The model permits an interpretation of the origin of M-induced anisotropy. Other experiments which have been carried out to test this model are discussed.

Introduction

The manner in which the uniaxial anisotropy is produced in permalloy thin films has been the subject of much controversy. Recently, evidence has been presented which indicates that this anisotropy is M-induced rather than field induced[1,2,3]. It has been suggested[4] that the elongation of the crystallites produces an easy axis which specifies the direction of the magnetization M. Models of this nature are not entirely convincing inasmuch as the mechanism producing this elongation is not considered.

We have re-examined this question and have arrived at a different model for the origin of the M-induced anisotropy[5]. The two main features of this model are first, the assumption that the growth proceeds from the substrate in the form of columns, and secondly, that the oxygen originally on the substrate diffuses between the columns and reacts to form iron oxides and stressed nickel-rich regions. We have been led to this model by studies of oxidation processes in bulk permalloy, nickel, and copper.

Proposed model

In the oxidation study of bulk permalloy, the more reactive element (in this case iron) is oxidized first by an internal oxidation mechanism. Iron oxide is formed within the metal matrix until a nickel-rich phase (almost pure nickel) remains at the metal surface to be subsequently oxidized[5]. When the cross sections of oxidized alloy samples are examined with the metallurgical microscope, the presence of the iron oxide along the grain boundaries is clearly evident. This indicates that the oxygen has diffused into the alloy along the grain boundries. It is well established that the presence of oxygen has an important effect on the magnetic properties of bulk permalloy. For example, it has been reported[6] that alloys containing less than $10^{-4}\%$ oxygen do not respond to magnetic anneal treatment.

The effect of oxygen on anisotropy in normal permalloy films can be understood by reference to a proposed model[7]. Alloy crystals nucleate at random on the substrate surface and grow normal to the surface in a columnar array (Fig. 1-a and 1-b). The oxygen present on the substrate prior to the deposition diffuses up from the substrate along the sides

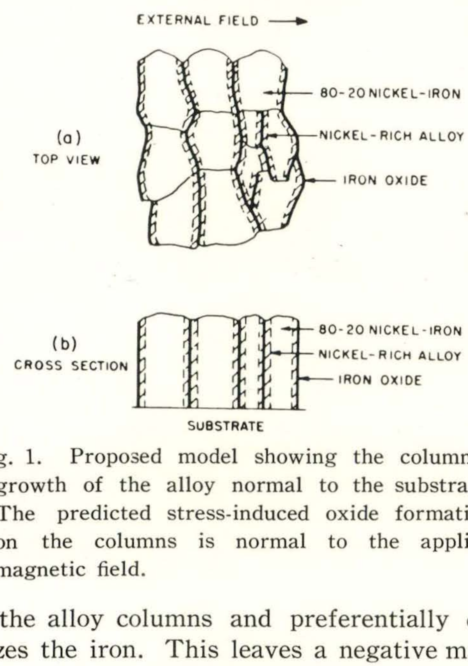

Fig. 1. Proposed model showing the columnar growth of the alloy normal to the substrate. The predicted stress-induced oxide formation on the columns is normal to the applied magnetic field.

of the alloy columns and preferentially oxidizes the iron. This leaves a negative magnetostrictive nickel-rich layer along the column surface.

In essence, this model states that the most important oxygen is that present on the substrate prior to the deposition and this oxygen diffuses into the film along the column boundaries. No detailed experiments are known in which the grain boundary diffusion coefficient for oxygen in nickel or permalloy has been determined. However, we can reason from the self-diffusion experiments on nickel that it is possible for the oxygen to diffuse up from the substrate in the time that the film is deposited. The self-diffusion coefficient for nickel[8] extrapolated to the substrate temperature is about $10^{-24}\,cm^2\,sec^{-1}$. On the other hand, the activation energy for grain boundary self-diffusion is expected to be about half as large[9] leading to a coefficient 10^{-12} to $10^{-14}\,cm^2\,sec^{-1}$. Assuming the diffusion of oxygen along the grain boundaries to be equally fast, the average oxygen diffusion distance along the columns is comparable to the deposited thickness when deposition rates are 10 to 100 Ångstroms per second.

By analogy with the oxidation study of copper[10], it is believed that stress plays an important part in controlling the oxidation. The sides of the columns normal to the magnetic field oxidize more readily because they are under tension (see Fig. 1). This tension arises from two causes. First, there is a difference in thermal expansion coefficients between the alloy and the oxide so that when the temperature changes due to radiation, stresses are created. Secondly, the magnetization of the nickel-rich phase will lie along the direction of the imposed field and will create a stress because of the magnetostriction. Thus, a self-regenerative process is envisioned in which the tension enhances oxidation and the oxidation increases tension. Evidence has been presented by Heidenreich, et al.[11], identifying the presence of iron oxide in permalloy films. Furthermore, they show that this oxide has a preferred orientation whether the anisotropy is produced by angle evaporation or by an applied field. The oxidation occurring under stress as proposed in this model could give rise to the oriented oxide.

Finally, we propose that the magnetization would tend to lie perpendicular to the columns. It has been demonstrated by the results of Neugebauer[12] that when a nickel film has a thin oxide layer the magnetization tends to lie normal to this layer. In our model the oxide layer lies on the surfaces of the columns normal to the magnetic field. Thus, there will be an easy axis along the direction of the applied field. This is not in contradiction to the iron-pair model since the iron oxidation would enhance unidirectional diffusion of the iron atoms and even promote dislocation alignment normal to the columns.

Again by analogy with bulk permalloy oxidation studies, NiO will be formed in thin films if sufficient oxygen is present during the deposition process. NiO has been identified by electron diffraction of permalloy films which possess "rotatable anisotropy" since these films are prepared under high oxygen conditions[13]. "Rotatable anisotrory" films show marked irreversible changes in their magnetic characteristics when heated above 350°C; these are assumed to be a result of changes in the nature of nickel oxide structure. Bulk nickel oxidation studies show that the oxidation is a nickel diffusion process below the Curie temperature for nickel (350°C)[14] while above 650°C[15] a double diffusion process is involved. A study of single crystal nickel films[16] indicates that oxygen diffusion into the nickel lattice begins abruptly at 350°C. This diffusion removes the stress between the nickel oxide layer and the permalloy film in "rotatable anisotropy" films and markedly changes the magnetic properties.

Experimental results and discussion

The effect of the oxygen present in the substrate prior to deposition has been dramatically demonstrated in a series of experiments. First, when a substrate with a high affinity for oxygen (such as glass or silicon monoxide) is saturated with oxygen just prior to deposition, "rotatable anisotropy" films will be formed[13]. Second, under normal deposition conditions (i. e., using a glass substrate which has been cleaned, ion scrubbed, and heated to about 300°C during deposition with a vacuum of 10^{-5} to 10^{-7} Torr) uniaxial anisotropy films are formed. Third, where oxygen is eliminated from the substrate prior to deposition, isotropic films are formed. This condition can be obtained in several ways; for example, a crystal of sodium chloride has little affinity for oxygen especially when it is heated. Deposition on such a substrate will produce isotropic films[11]. We have performed another experiment designed to eliminate the substrate oxygen while at the same time show that anisotropic films are formed if the oxygen is not eliminated. In this experiment, several substrates are covered with a thick copper (or aluminum) film while several others are shielded from the copper with a shutter. Immediately after depositing the copper, two shutters are opened simultaneously, one to start the permalloy deposition and the other to expose the shielded substrates. The results of this experiment are shown in Fig. 2. All the films deposited over the copper undercoat are isotropic presumably because the copper film has depleted the substrate oxygen. The films deposited directly on glass are normal anisotropic films.

Cross section electron micrographs have been taken to show the columnar growth and the position of the oxide or stress present. In order to do this, the films were mounted in bakelite, polished, and etched with acid ferric chloride. A deep etch was necessary to bring out the desired details. This leaves a concave surface as the film etches below

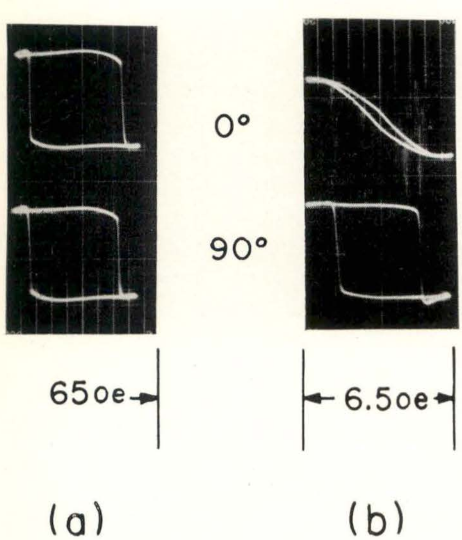

Fig. 2. Hysteresis loops are shown here for a permalloy film deposited (a) over a newly formed copper undercoat, and (b) directly on the glass substrate.

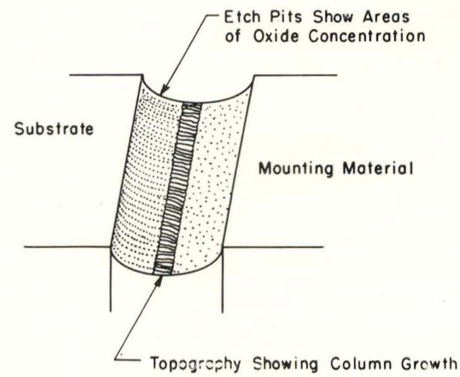

Fig. 3. Graphic representation of the surface showing the concave contour obtained when etching the cross section with acid ferric chloride etch solution.

the polished bakelite surface. This is graphically represented in Fig. 3.

The Parlodion replica and the carbon film used to study this surface will follow the concave surface. Thus, when the carbon replica is spread out for examination, the apparent film thickness differs from that measured interferometrically. Along the bottom of this concave trough, the normal topography of the film can be seen and the columnar growth is strongly in evidence (see Fig. 4).

Fig. 4. Cross section electron micrograph showing evidence for the columnar growth in the central portion of the picture and the lines of etch pits toward the substrate marking the high energy regions of the film.

A second striking feature is seen along the slope of the trough toward the substrate surface. Here prominent, deep etch pits (some as deep as 1700 Å) appear to lie in lines along the substrate and appear to lie along the edges of grains or columns. Since this etchant should preferentially attack high energy areas such as strain centers, chemical inhomogeneities, or dislocation clusters, this is taken as strong evidence to support the model of columnar growth with oxides aligned in sheets normal to the preferred magnetization direction. Likewise, the stress between the oxide and alloy would enhance this etch picture.

Research on the influence of stress on the oxidation of bulk permalloy and deposited thin films is currently in progress. In the studies on the thin films, tension is mechanically induced by bending the film during the deposition. Although these studies indicate that stress does contribute to the control of anisotropy, it has not been possible to completely control the direction of easy magnetization by mechanically induced stress. It can be reasoned that the mechanically induced stress is overshadowed by the stress which would result from the surface oxidation of the particles. However, stress orientation may well occur in normal deposition as a result of differential substrate heating and in this way could greatly affect the uniformity of easy axis alignment.

The model presented here is not expected to be complete in all detail. However, it is consistent with most of the work published to date and has allowed us to predict the results of several experiments. In addition it presents a means for forming uniaxial anisotropy in pure iron and nickel films. One of the tests for this model will be the study of these films.

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References

1 D. O. Smith: J. Appl. Phys. **30** (1959) 264S.
2 J. B. Goodenough and D. O. Smith: "Magnetic Properties of Metals and Alloys" (American Society for Metals, Cleveland, Ohio, 1960), Chapter 7.
3 W. Andra, Z. Malek, W. Schupper, and O. Stemme: J.Appl. Phys. **31** (1960) 442.
4 D. O. Smith: J. Appl. Phys. **32** (1961) 70S.
5 S. Kennedy, L. D. Calvert, M. Cohen: Trans. Am. Met. Eng. **215** (1959) 64.
6 R. D. Heidenreich, E. A. Nesbitt, R. D. Burbank: J. Appl. Phys. **30** (1959) 995.
7 R. J. Prosen: DP 61-601, AIEE Great Lakes District Meeting, April (1961).
8 R. E. Hoffman, F. W. Pikus, and R. A. Ward: AIME Trans. **206** (1956) 483.

9 C. E. Birchenoll: Metallurgical Review **3** (1958) 267.
10 J. A. Sartell, R. J. Stokes, S. H. Bendel, T. L. Johnston, C. H. Li: Trans. Am. Inst. Met. Eng. **215** (1959) 420.
11 R. D. Heidenreich, F. W. Reynolds: "Structure and Properties of Thin Films", Wiley (1959), Page 402.
12 C. A. Neugebauer: Private Communication.
13 R. J. Prosen, J. O. Holmen, B. E. Gran: J. Appl. Phys. **32** (1961) 91S.
14 H. Uhlig, J. Pickett, J. MacNairn: Acta. Met. **7** (1959) 111.
15 J. A. Sartell, C. H. Li: J. Inst Met. (in print).
16 E. I. Alessandrini, J. F. Freedman: ACA Meeting, August (1961) Boulder, Colorado.

DISCUSSION

E.P. WOHLFARTH: Could we please have a few details of Neugebauer's results referred to in your talk? Also, what do you think is the relation of your results to those just reported by Graham?

R.J. PROSEN: Neugebauer deposited some very pure nickel films and upon increasing the pressure in the vacuum chamber, a thin oxide layer was produced (20–30 Å). He found that the magnetization showed a tendency to point out of the plane of the film. The only written source of information has been an abstract of an Air Force Contract Report.

It may very well be that when we do torque measurements on the samples which appear to be isotropic, we may find anisotropy as well. If this is the case, these are indeed inverted films with $H_c \gg H_k$.

F.B. HUMPHREY: I would like to point out that it is very difficult to determine that a film is isotropic by looking at the hysteresis loop as you do in your last slide. We have looked at films with isotropic hysteresis loops that are very anisotropic when looked at with a torque balance.

R.J. PROSEN: Again, I am sorry that we had not seen Dr. Graham's paper before this meeting. Had we seen it, we would certainly have checked our films deposited on copper for anisotropy with torque measurements.

J.M. BROWNLOW: Is it possible that the first oxidation product is a Ni-Fe spinel rather than simply iron oxide? If such is the case, a magnetic inclusion would have to be considered. Strong oxidation of iron rich Ni-Fe alloy films show spinel according to our experience.

R.J. PROSEN: The work by Kennedy and co-workers does not show spinel to be present. The only actual electron diffraction we have done to date was on "Rotatable Anisotropy" films. These are produced with high oxygen content and show NiO to be present.