11 The composition of the films measured generally about a 1000 Å thick, varied between 77 and 83% Ni. This includes several films kindly provided by A. Noreika, Philco Corp. D. O. Smith, Lincoln Laboratory and M. Prutton, I. C. T.

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DISCUSSION

E. P. WOHLFARTH: For the specimen you describe the rotational hysteresis W_r vanishes below h about 0.16. This leads to a reduced cylinder radius $S=2.6$. The rotational hysteresis integral for this specimen is quoted as 2.6 which, on using the Shtrikman-Treves' results, leads to $S=2.5$. Hence the quantitative agreement is here excellent.

D. O. SMITH: What relation do you think there is between the theoretical noncoherent switching of an infinite cylinder and the labyrinth switching experimentally observed in thin films?

S. SHTRIKMAN: I really do not know. We did not study labyrinth switching. I want to stress, however, that I do not claim to attach any physical meaning to an infinite cylinder in connection with a thin film.

I think however that it is clear enough why the Kondorsky and Stoner-Wohlfarth models yield good approximation to the behaviors in low and high fields respectively. The infinite cylinder behaves in a similar way and therefore describes formally the experimental behavior for the whole field range reasonably well.

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Effect of Pressure During Evaporation on the Magnetic Properties of Nickel Films

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Nickel films have been evaporated over a range of pressures from 10^{-5} to 2×10^{-10} mm Hg and at two widely different evaporation rates to determine the effect on the magnetic properties. Under the best conditions, with a liquid helium finger present in the system, all the glass surfaces which are exposed to impinging nickel atoms previously metal-coated, a pressure of 2×10^{-10} mm Hg and a deposition rate of 400 Å/min, the maximum calculated concentration of trapped gas atoms in the film is less than 10 parts per million. All the films tested, including those made under the best vacuum conditions, show a uniaxial anisotropy of 1 to 3×10^3 erg/cm^3 which can be reoriented by annealing in a field. We therefore conclude that trapped impurity atoms such as oxygen are not responsible for the uniaxial anisotropy in nickel films.

Introduction

A major unsolved problem in the behavior of ferromagnetic thin films is the origin of the uniaxial anisotropy (usually denoted by K_u) which occurs in films evaporated or electrodeposited in a magnetic field. Similar phenomena in bulk alloys are generally attributed to directional ordering[1], but this explana-

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tion cannot be sufficient for thin films because films of pure metals still show uniaxial anisotropy.

When the present work was begun, there were two results which suggested that impurity atoms (especially oxygen) trapped in the film during deposition might greatly influence the magnetic properties. Neugebauer[2] had found that nickel films deposited in vacuums below 10^{-9} mm Hg have normal bulk values of saturation magnetization and Curie temperature down to thicknesses of 30Å, whereas very thin films made at normal bell-jar system pressures of 10^{-5} to 10^{-6} mm Hg have abnormally low saturation and Curie temperatures. Nesbitt and Heidenreich[3] had reported that no uniaxial anisotropy could be developed by magnetic annealing in bulk Ni-Fe and Ni-Fe-Co alloys if the oxygen content was below some limiting value near 10 parts per million.

Our experiments were designed to reduce the concentration of trapped impurity atoms in nickel films to very low levels by improving the vacuum conditions during evaporation, and to determine the effect of this procedure on the magnetic properties of the films, with particular attention to the uniaxial anisotropy.

Experimental Procedure

Films were evaporated and measured in the vacuum system shown in Fig. 1. The pumping system comprises a rotary mechanical pump, followed by a liquid nitrogen trap, two single-stage mercury diffusion pumps, and another liquid nitrogen trap. The Bayard-Alpert type ionization gage also acts as a pump at low pressures. There are no joints or valves on the high-vacuum side of the diffusion pumps, and this portion of the system can be baked at 350° to 450°C. The ultimate pressure of the system is about 10^{-10} mm Hg.

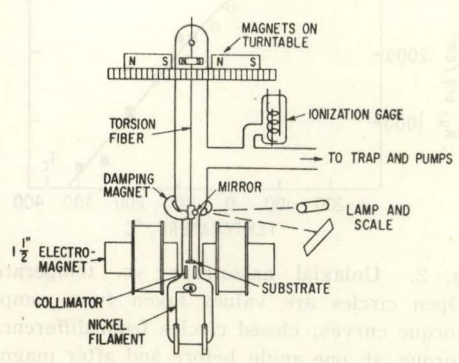

Fig. 1. Vacuum system and measuring equipment.

Only pure nickel films were made, so that there could be no contribution to the measured anisotropy from directional ordering of alloy constituents. Nickel was chosen rather than iron or cobalt since nickel has no phase changes in the solid state and has a reasonably low Curie temperature. Substrates were pyrex glass disks, generally held at room temperature but in a few cases heated to 300° or 400°C during deposition. Substrates were degreased and rinsed before being mounted in the vacuum system, and were baked in the system at 450°C before the nickel was deposited. Nickel was deposited either by sublimation from a solid wire (deposition rate about 1 atom layer/min) or from a liquid drop in an Al_2O_3-MgO crucible with an imbedded tungsten heater (about 150 layers/min). The films were from 400 to 3000Å thick, as measured by *X*-ray fluorescence analysis and by torque measurements of the kind described by Neugebauer[2], and were deposited at pressures from 2×10^{-10} to 10^{-8} mm Hg; a few films were also made at 10^{-5} mm Hg to extend the measurements into the range of normal bell-jar vacuum systems. All the films were deposited with a field of 1000 Oe applied along a diameter.

In the final experiments of the series, a finger containing liquid helium was present in the system, and all glass surfaces exposed to impinging nickel atoms (including the substrate) were previously coated with nickel, molybdenum, or copper to prevent the liberation of oxygen or other foreign atoms from the glass. In the best of these runs, the pressure during evaporation was 2×10^{-10}, the substrate was coated with copper and a film of 1350Å was deposited in $3\frac{1}{2}$ minutes from a molten nickel source.

The magnetic measurement was of the torque exerted on the film by a magnetic field. The sample was hung on the end of a tungsten torsion fiber 1/2 mil (12.7μ) in diameter and about 15 cm long, giving a sensitivity of 4×10^{-4} dyne-cm, or about 50 erg/cm^3 for a film 1000Å thick and 1 cm in

diameter. The magnetic field, which could be rotated to lie along any direction in the plane of the film, was supplied by a pair of Helmholtz coils at low fields and by a small electromagnet at high fields; the range of fields available was 10 to 2500 Oe. Measurements were made with the film in the vacuum, and could be carried out from liquid nitrogen temperature to 400°C by cooling or heating the section of the system which contained the film. After completion of the measurements on each film as deposited, the film was heated to 300° or 400°C and cooled in a field of 1000 Oe to see if the easy direction could be reoriented.

Considerable care was necessary to eliminate or correct for background torques in the substrate and its holder. In some cases, there were anisotropies in the films which could not be reoriented completely by annealing in a field. These were determined by annealing the sample in two mutually perpendicular directions and taking half the difference in the resulting torque curves as the true magnetic annealing anisotropy. These fixed anisotropies were probably the result of an angle of incidence effect or possibly a crystallographic texture in the sample.

Results

The general form of the torque results as a function of field has been given in an earlier paper[4]; at low fields, the torque vs. azimuth curve is of the form $L=K_r \sin\theta$, corresponding to a fixed remanent magnetization M_r interacting with the applied field according to $L=M_r \times H$. This torque is proportional to the applied field up to some maximum field H_p. The value of H_p is a measure of the coercive force of the film, although H_p will be substantially smaller than H_c as measured conventionally. At intermediate fields, the $\sin\theta$ torque diminishes and the rotational hysteresis becomes large. At high fields (500 to 2500 Oe), the rotational hysteresis approaches zero and the torque vs. angle curve is of the form $L=K_u \sin 2\theta$, where K_u is the uniaxial anisotropy constant.

All the nickel films measured showed the following properties:

1. A limiting field H_p (which is a lower limit for the coercive force) generally near 50 Oe, with occasional films as low as 10 Oe and as high as 100 Oe.

2. A uniaxial anisotropy, deduced from high-field torque measurements, of 1000 to 3000 erg/cm^3. These values correspond to anisotropy fields $H_k=2K_u/M_s$ of 4 to 12 Oe; the films were therefore "inverted", with $H_c>H_k$. Such films when measured in a conventional hysteresis loop tracer appeared isotropic, which illustrates the danger of relying on hysteresis measurements in studies of anisotropy.

3. A uniaxial anisotropy which could be reoriented by annealing the film with a magnetic field applied along any diameter. The magnitude of the anisotropy at room temperature was generally changed somewhat by the first one or two anneals, but then remained constant.

Therefore we find an induced anisotropy of normal magnitude present in all our films, including those made under vacuum conditions near the limit of present technology. The residual gas in our vacuum system was probably almost all carbon monoxide[5]. If we assume that every CO atom which strikes the substrate during deposition is trapped in the film, then for our best films the final CO content would be about 8 parts per million by weight. If the CO dissociates to C and O in the film, the result would be $4\frac{1}{2}$ ppm 0. We believe that these results eliminate oxygen, or any trapped impurity atom, as the source of induced anisotropy in nickel films.

Several of our related observations may be pertinent in determining the origin of the uniaxial anisotropy. The "stable" uniaxial

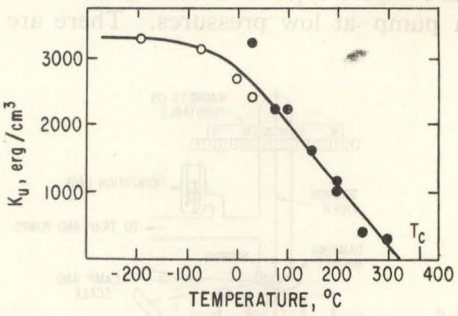

Fig. 2. Uniaxial anisotropy vs. temperature. Open circles are values taken from complete torque curves; closed circles from difference in torque at one angle before and after magnetic annealing.

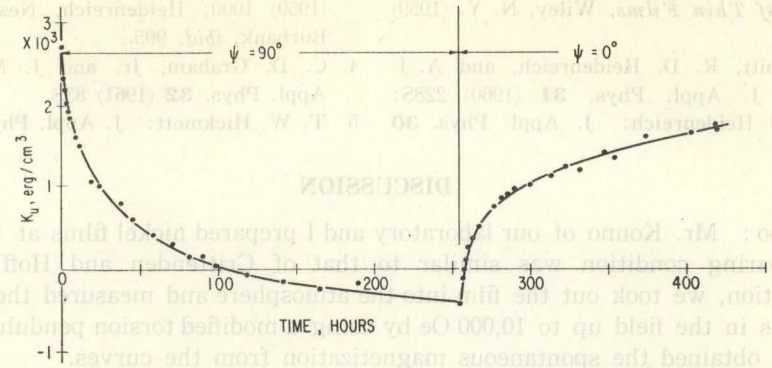

Fig. 3. Uniaxial anisotropy vs. time during magnetic annealing at 300°K. At $t=0$, a field of 1000 Oe was applied in the hard direction ($\psi=90°$); at $t=255$ hours, the field was rotated back to the original easy direction ($\psi=0°$). The change in sign of K_u at $t=100$ means that the easy direction has shifted.

anisotropy obtained after the first few annealing treatments was measured as a function of temperature for two films. One set of results is shown in Fig. 2; the nearly linear decrease in K_u above room temperature is unlike the temperature dependence of the crystal anisotropy, of the saturation magnetization, or of the magnetostriction.

Extensive measurements of the kinetics of the magnetic annealing process have been made. One series of measurements is shown in Fig. 3. Much of our data can be represented fairly well by an empirical equation of the form $1-f=\exp(-t/\tau)^{1/3}$, where f is the fraction of the annealing process completed, and τ is a relaxation time of the no order of 100 hours at 300°K.[4] We attach great significance to the forms of this equation; the important point is that the magnetic annealing process clearly does *not* follow any simple first- or second-order kinetic law.

Especially in the films prepared in the best vacuums, there was evidence of structural change occuring in the films even after repeated annealing treatments. In one case a 4θ component of the torque suddenly appeared, and in another case there was a sudden change in the rate of annealing. These effects made the kinetic data uncertain.

The films were undoubtedly in a state of severe strain, at least in the as-deposited condition. Very thick films tended to crack and peel away from the glass, and one film deposited onto a substrate 3 mils thick (76μ) produced a curvature in the glass which led to a calculated strain in the film of the order of 0.1%.

In related experiments, we have looked for magnetic annealing in foils of nickel prepared in other ways. Foils about 14,000Å thick were rolled directly from bulk nickel, and pieces averaging 6000Å thick were electropolished from the rolled material. The foils were annealed in dry hydrogen or in argon, reheated to 400°C in vacuum, and cooled in a field of 1000 Oe. No magnetic annealing anisotropy within the experimental error of about 20 erg/cm³ could be detected. Foils of nickel 560 and 700Å thick were prepared by electroless chemical deposition and cooled 400°C in a field of 1000 Oe. Again no magnetic annealing anisotropy was detectable within the experimental error of 100 erg/cm³. These results indicate that something inherent in the structure of evaporated films is responsible for their magnetic annealing rather than their small thickness *per se*.

Electron microscope observations of the films and foils showed in all cases a grain size comparable to the film thickness, with some twins within individual grains. No directional structures were evident.

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DISCUSSION

Y. GONDO: Mr. Konno of our laboratory and I prepared nickel films at 10^{-5} mm Hg. This preparing condition was similar to that of Crittenden and Hoffman. After the deposition, we took out the film into the atmosphere and measured the magnetization curves in the field up to 10,000 Oe by using a modified torsion pendulum magnetometer and obtained the spontaneous magnetization from the curves.

We have observed no thickness dependence of spontaneous magnetization at room temperature at least down to 20Å thick. This result is in accord with that of Neugebauer, in spite of the difference of vacuum condition during evaporation. We agree with Dr. Graham; that is, the pressure during the evaporation has no effect on the spontaneous magnetization in the range of pressure from 10^{-5} to 10^{-9} mm Hg.

C. D. GRAHAM, JR.: To what do you attribute the difference between your results and those of Crittenden and Hoffman?

Y. GONDO: Most of nickel films are not saturated in the field of less than about 3000 Oe, even applied within the film plane. I guess, the field used by Crittenden and Hoffman may be too weak to saturate their nickel films.

K. KUWAHARA: I would like to suggest that the substrate has an effect on the nature, especially the magnetic annealing, of the film.

According to our experiment, the films which were deposited on a usual glass substrate clearly have an effect of magnetic annealing. But we could not find such an effect in the films deposited on a quartz glass.

C. D. GRAHAM, JR.: I am afraid our experimental results do not agree. We have used pyrex, quartz, and pyrex coated with Cu or Mo as substrates, with no difference in results outside the usual experimental scatter. However, in our case the substrates were baked at 450°C for several hours in high vacuum before the films were deposited.

S. METHFESSEL: The purity of the film prepared in ultra high vacuum is not only given by the residual gas pressure. There are other sources of impurities, which must be considered; the evaporation source, the film substrates.

C. D. GRAHAM, Jr.: I agree. Our calculated gas content is based on the simplest assumptions, and may be in error. However, from the behavior of our system when the source is heated (after thorough outgassing), we do not believe that there is much gas coming from the nickel source.