NON-MAGNETIC FILMS OF NICKEL

By L. R. Ingersoll and S. S. De Vinney

Abstract

Properties of sputtered nickel films.—(1) *Magnetic.* These films, prepared by sputtering in hydrogen on to a cooled surface, with a 1000 volt d.c. generator, are initially non-magnetic, showing neither magneto-optic rotation nor tractive effects in a magnetic field. After heating to 300° or 400°C, however, they become strongly magnetic and exhibit both these effects. Films much thicker than $120 m\mu$, or those sputtered with an induction coil, are likely to be magnetic from the start. (2) *Crystal structure.* X-ray spectrograms by the powder method show for the heat-treated (magnetic) film the face-centered cubic lattice as for ordinary nickel, but prove that the original non-magnetic film is amorphous. These facts suggest that *ferro-magnetism* in nickel, at any rate, is not a property of the individual atom as customarily supposed, but of the crystalline aggregate. A number of possible objections to this point of view are taken up and discussed. (3) *Electric.* The gain in magnetic properties on heat-treatment is accompanied by a decrease of *resistance* to a fraction (a fifth in one case) of its initial value. The original film also gives only about 1 percent of the *Hall effect* that it does after heat-treatment. (4) *Color.* Some films, particularly those deposited on a surface at liquid-air temperatures, display remarkable colors. On examination of the reflected light with a spectroscope, only a narrow spectral region is seen to be absent. If the nickel films are thin, covering with an optically dense liquid completely destroys the colors.

SOME years ago one of the writers noticed that most films of nickel sputtered in hydrogen showed little or no Faraday or Kerr magnetic rotation. On taking up the matter later it was found that these films which gave no magneto-optic rotation also *showed no tractive effects* when suspended in a magnetic field, although after heating to a few hundred degrees for a short time both magneto-optic and tractive effects appeared.

As this "non-magnetic nickel," if such it can be considered, has seemed of more than passing interest, and the change to the magnetic form produced by heating is so striking, considerable study has been devoted to it and the results will be described briefly.

Preparation of films. These were deposited with the apparatus described in a recent paper,[1] the chief novelty of which was the arrangement for keeping the surface (microscope cover-glass) on which the film was sputtered, cooled by running water or even liquid air. The cathode was a 32 mm disk cut from a plate of very pure nickel furnished by the International Nickel Co., through the kindness of Dr. Paul D. Merica. The

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[1] L. R. Ingersoll, J. Opt. Soc. Amer. & R. S. I. **8**, 493 (1924)

analysis was given as: nickel, 99.48 percent; cobalt, 0.40 percent; iron, 0.10 percent; copper, 0.02 percent.

While an induction coil was used in some cases, the fifty or more best films were deposited with a direct-current generator at about 900 to 1000 volts. The cathode was 15 to 18 mm from the glass and the vacuum such that the dark space extended almost to its surface, the current being 15 to 20 milliamp. Save for a few experiments with nitrogen, the residual gas in all cases was hydrogen.

Magnetic tests were admittedly very primitive but quite satisfactory for the purpose. After sputtering, the film was cut into strips about 5×25 mm and one of these was suspended by a thread so as to swing freely between the poles of an electromagnet giving a field of some 12,000 gauss. The tractive effects when the current was turned on were observed and estimated on a scale of 1 to 100, the former representing the smallest observable motion and the latter about the magnitude one would expect for ordinary nickel; that is, an effect such that the film would instantly be drawn to one of the pole pieces. In making these estimates account had to be taken of the width and relative thickness of the film, factors which would make really accurate measurement a difficult problem.

Heat treatment was carried on at various temperatures between 100° and 450°C or higher, generally in a fairly good vacuum or low pressure (0.1 mm) hydrogen, although a few tests in hydrogen at atmospheric pressure and also in hot oil gave essentially the same results. The time element is quite secondary to temperature; a few minutes at 400° were much more effective than hours at 250°, while a few seconds in a Bunsen flame in air produced a large effect, although this was not easily controllable. A number of nickel films were sputtered over with a layer of gold and then heated. The surface then generally showed little blisters, indicating that the heat treatment involved an escape of gas (hydrogen) as would be expected. Some experiments were also tried on alloying with gold by sputtering this metal along with the nickel from a small strip across the cathode. The general characteristics were the same save that the gaining of magnetic properties upon heating was somewhat slower and not so marked. No substitute for heating, for bringing about magnetic properties, has been found. Ageing in a dessicator for six months or more produced little if any effect. Tests on ageing in a vacuum are not yet conclusive—3 months in vacuum seem to yield no results—although some effect might well be expected here from the experiments of Koller[2] on ageing platinum films in a vacuum. A trial of burnishing with a

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[2] L. R. Koller, Phys. Rev. **18**, 221 (1921).

rounded glass rod, which might be expected to compact anything like a loose powder, brought about no magnetic effect.

Resistance measurements. The work of[3] Richtmyer and others shows that the resistance of a sputtered film generally decreases rapidly upon heating, so a like effect was to be expected for these nickel films. A test of a film the ends of which had been sputtered with gold to insure good contact, gave the following results:

Heat treatment	Resistance	Magnetic intensity
Original film	30.6 ohms	0
17 hr at 100°C	26.8	2
19 hr further at 150°	24.1	4
18 hr further at 200°	19.4	12
4 hr further at 250°	16.7	16
1.5 hr further at 300°	16.6	25
0.5 hr further at 350°	10.6	50
0.1 hr further at 400°	7.0	60
0.5 hr further at 450°	6.0	80

Other films showed qualitatively the same effects. If the heating at the higher temperatures was prolonged the film began to crack and the resistance rose. The change in resistance and in magnetic properties of the film tabulated above was probably almost complete.

Crystal structure. The powder method (G. E. apparatus, molybdenum tube) was used. The film was scraped from the glass with a sharp knife—it was usually strongly adherent and the scrapings resembled a fine black powder—and packed into the capillary tube. This was then tested in the magnetic field and showed no tractive effects. A 12 to 24 hr exposure was then made on it, after which it was heated to 400° for a short time and another exposure made. It was strongly magnetic after heating. Check films were also made on filings of metallic nickel and on a blank glass tube. The comparison substance in all cases was aluminum.

The photographs for the nickel filings and *heat-treated film* were practically identical and showed the face-centered cubic lattice as found by Hull[4] for this metal. *The original untreated nickel film, however, showed an amorphous character.* A second test, in which the nickel films used were especially carefully selected for their absence of any magnetic tractive effects, gave particularly conclusive evidence on this point.[5] Only the line produced by the (111) planes was present, indicating the presence of small groups containing only a few molecules each—not enough to produce interference of a higher order.

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[3] F. K. Richtmyer and L. F. Curtiss, Phys. Rev. **15**, 465 (1920 ; L. F. Curtiss, Phys. Rev. **18**, 255 (1921); L. R. Koller, loc. cit.,[2] and others. See also F. W. Reynolds, Phys. Rev. **24**, 523 (1924).

[4] A. W. Hull, Phys. Rev. **17**, 571 (1921).

[5] Dr. Hull, who obligingly examined the x-ray films, considers that they prove beyond question that these nickel films are amorphous.

Other experiments. The films were ordinarily deposited in about half an hour and were usually almost opaque. Measurements by the interference method on an average film gave a thickness of about 120mμ. When the thickness was greatly in excess of this the film generally showed some magnetic properties from the start. In one case when the sputtering was continued for 20 hr the film was apparently as magnetic as ordinary nickel. This indicates that it would be difficult, if not impossible, to obtain this amorphous nickel in bulk form.

A number of films were sputtered with an induction coil, with varying results as regards magnetic characteristics. The rule seemed to be that the higher the potential used in sputtering the more likely the film was to turn out somewhat magnetic. A few films were sputtered in nitrogen but the results were unsatisfactory. The idea gained, on very little evidence, however, was that films deposited in this gas were likely to be magnetic.

Professor Alpheus W. Smith, who obligingly tested samples of both treated and untreated films for the Hall effect, reports that, while the measurements he was able to make left much to be desired in the way of accuracy, the indications were that the original film showed hardly more than 1 percent as much effect as the heat-treated one.

Color effects. Microscopic structure. In many cases, particularly when the surface on which the film was sputtered was kept at liquid-air temperatures, brilliant surface colors appeared. On examining the reflected light with a spectroscope it was found that only a narrow spectral region was absent, and that this absorption band moved towards the red with increasing film thickness. This duplicates almost exactly the observations of Wood[6] on sodium and potassium films. It is possible, however, to try certain things with nickel films which cannot be done with sodium and potassium and one of these is to cover with water or other liquid. It was found on trying this that, with thin films, liquids of low refractive index such as water dulled the color, while optically denser liquids like carbon bisulphide or mono-bromnapthaline completely destroyed it, although the color returned when the liquid was washed off. This might be construed in favor of Wood's theory that this absorption is a type of resonance phenomenon taking place in the interstices between the particles.

The matter of film color, however, is far from simple. In the thicker films the effect of the liquid was not as definite as explained above. Such films also occasionally showed evidence under the microscope of being double or triple in character after heat-treatment. In general an original film showed no trace of structure, while a heat-treated one frequently

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[6] Phil. Mag. **38,** 105 (1919)

showed a very complicated structure when examined with oil-immersion objective, although no connection could be clearly traced between this and the color effects. The colors were almost invariably changed by heating, sometimes disappearing and sometimes appearing when they did not exist before.

DISCUSSION OF RESULTS; CONCLUSIONS

Undoubtedly the most important conclusion to be drawn from this work is that, on the evidence of these films, *ferromagnetism in nickel requires a crystalline structure and is therefore not a property of the individual atom, but of the crystalline aggregate.* Whether or not this means that the Amperian currents must circulate in orbits wider than the ones of atomic size customarily supposed, becomes a matter of interpretation, but the evidence would certainly seem to point in this direction.

There is a possible escape from this conclusion that the original film is non-magnetic because amorphous. As already mentioned, scrapings from such a film resemble a fine black powder. If this film, as originally deposited, could be regarded as a loose aggregate, its lack of magnetic properties might then be at least partially attributed to this fact rather than to its amorphous character. There are several reasons which have caused this point of view to be rejected: (a) The original film is tough and resistant, hard to rub off or scrape off. (b) Its optical properties are not at all such as one would associate with a loose powder. In appearance the film is bright and metallic-looking. The change produced by heating is small; it is slightly darker afterwards and has a faint golden tinge. (c) Its electrical resistance, while lessened by heat-treatment, is not high and indicates a coherent metal structure. Moreover, it cannot be assumed that the film is a compressed, rather than a loose powder, since the work of Speed and Elmen[7] on the magnetic properties of compressed powdered iron show a value of the permeability up to several hundred for this material.

Another possible suggestion, namely that the nickel as originally sputtered might be in an oxidized state and that the heat-treatment—usually carried out in hydrogen—involved a reduction of this to metallic nickel, may be answered at once by pointing out that heat-treatment could be effectively carried out in the oxidizing part of a Bunsen flame. Furthermore, great care was taken to secure pure hydrogen for sputtering and the slightest air leak always meant a ruined film.

The fact that there was apparently an escape of hydrogen during the heating process is not taken to have any particular significance. It is true

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[7] Speed and Elmen, Trans. Am. Inst. Elect. Engineers, **40**, 1321 (1921).

that occluded hydrogen modifies[8] somewhat fundamentally the magnetic characteristics of some metals. But it is hard to see how this fact can be used to explain the non-magnetic character of these nickel films, when, as already stated, thicker ones, or, for that matter, films deposited with an induction coil, may turn out strongly magnetic.

The absence of Hall effect in the unheated films is not unreasonable in view of their amorphous character. The fact that they show no magneto-optic rotation, however, is probably a purely magnetic phenomenon and due to the lack of high internal magnetic fields in the non-magnetic specimen.

While no evaporated films have been tested as yet in connection with the present experiments, one of the writers found, a few years ago, that evaporated nickel films showed magneto-optic rotation. This doubtless means that such films are ordinarily magnetic[9] and therefore crystalline, as was found by Steinberg[10] to be the case for evaporated silver and iron.

In conclusion, the writers accept the common view of the sputtered film as an aggregate which is brought into a greater degree of coalescence by heating. As the present work shows, this aggregate may be initially amorphous in some cases, if temperature and voltage conditions during deposition are properly controlled. Whether the sputtered particles are single atoms, as assumed by some investigators, or actual granular crystals, as believed by Kahler,[11] is a much-discussed question on which this work perhaps throws a little light. For the amorphous film must be built up either of single atoms or of exceedingly small groups, while, on the other hand, the apparent effect of higher voltages in producing crystalline films would be in accord with the view of such voltages giving larger sputtered particles, crystalline in character—although, of course, there are other possible explanations, such as local heating accompanying the higher voltage.

Cobalt and iron films are now being investigated to see to what extent they bear out these conclusions for nickel, particularly as regards the connection between magnetization and crystal structure.

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[8] A. E. Oxley, Proc. Roy. Soc. **101**, 264 (1922).

[9] On this point see A. J. Sorensen, Phys. Rev. **24**, 658 (1924).

[10] J. C. Steinberg, Phys. Rev. **21**, 22 (1923).

[11] H. Kahler, Phys Rev. **18**, 216 (1921).