JOURNAL OF MATERIALS SCIENCE 1 (1966) 362–366

Magnetic and Electrical Properties of 77-14-5-4 Wt % Ni-Fe-Cu-Mo and Related Alloys

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Received 1 July 1966

A study has been made of a series of alloys centred on the composition 77 wt % nickel, 14 wt % iron, 5 wt % copper, 4 wt % molybdenum, in which the nickel-to-iron ratio has been varied. Measurements of electrical resistivity and magnetostriction show significant changes after heat treatment. These are ascribed to the formation of local atomic order. No definite evidence for long-range ordering has been observed.

1. Introduction

An alloy of composition 77–14–5–4 wt % Ni–Fe–Cu–Mo, manufactured under a variety of trade names, is widely used as a high-permeability magnetic material. When the starting material used is of appropriate purity, and care is taken to avoid contamination during alloying, this alloy exhibits an initial permeability in excess of 70 000. Moreover, this is achieved after cooling at about 100° C/h (a rate conveniently obtained by allowing a small electric furnace to cool freely), compared with the complicated, double heat treatment required to attain high initial permeabilities in binary Ni–Fe alloys; these, in any case, never exceed 10 000 [1].

The initial permeability of these quaternary alloys is known to depend on heat treatment. At first sight, this is to be expected since, as pointed out by Enoch and Fudge [2], if the action of Cu and Mo in these alloys is the same as it is in pure Ni, the quaternary alloys can be assumed to contain, not only magnetic Ni atoms, but also non-magnetic ones, whose magnetic moment has been annulled by the Cu and Mo. The ratio of these "magnetic" Ni atoms to Fe atoms is quite close to 3:1, and so the alloys might be regarded as Ni_3Fe with additions of, essentially, non-magnetic atoms. Ni_3Fe is known to exist in an ordered state with the formation of a well-defined superlattice [3]. Hence, it seems natural to explain the effects of heat treatment on the quaternary alloys in terms of ordering of Ni_3Fe.

Unfortunately, this interpretation is based upon an assumption which is untenable, namely, that only magnetic Ni atoms order. No case is known in which a significant amount of the ordering energy originates from magnetic interactions, and there are no grounds for believing the Ni–Fe alloys to be exceptional in this respect.

Owing to the presence of a total of about 7 at. % Cu + Mo, it is probable that such order as may exist in these alloys is extremely local, and the usual description of it in terms of a long-range superlattice is not very fruitful. A more appropriate description might be in terms of the nature of nearest and next-nearest neighbours, such as is employed in the theory of directional ordering [4]. On the other hand, the observation [5] of a kink in the resistivity-temperature curve for the quaternary alloy with 77 wt % Ni at about 490° C, and the very marked dependence of initial permeability on cooling rate through this temperature is strongly suggestive of a co-operative ordering of comparatively long range, such as occurs in Ni_3Fe at 498° C [3].

In Ni–Fe alloys, the highest permeability is attained after quenching, and this fact recently led Lewis [6] to suggest, as explanation, that the quenching stresses, combined with the magnetostriction constants, yield a magnetoelastic energy equal and opposite to the anisotropy energy. In this view, the high initial permeability would be a rotational permeability arising from an almost zero, net anisotropy. Evidence presented in section 6 and elsewhere [7] suggests that, in the quaternary alloys (and by implication, in the binary alloys too), domain wall displacements make the dominant contribution to the initial permeability, and that rotational processes are relatively unimportant.

Despite the large accumulation of experimental data on low-field magnetic properties of the quaternary alloys, little work has been carried out on other properties. The object of the investigation reported here was to study some of the more basic physical properties of a series of quaternary alloys in which the Ni/Fe ratio was altered, the subsidiary objective being to search for the presence of long-range order.

2. Materials and Experimental Methods

The materials were, in all cases, supplied by the Post Office Research Station, in the form of strip usually about 100 μm thick. The alloys were made by the methods of powder metallurgy and were estimated to have a total impurity content not greater than 0.03 wt %.

In most cases, the measurements were carried out on samples in two different states: (i) cold-rolled (CR) – reduced, usually by about 50%, in thickness by cold rolling from the annealed state but without subsequent annealing; (ii) annealed (A) – after the same cold rolling, annealed in hydrogen at 1050° C for 1 h followed by a furnace cool about 100° C/h. In certain alloys containing 77% Ni only (the standard composition), additional measurements were carried out on samples which were quenched (Q_T) – gas-quenched in hydrogen from a temperature T_Q° C.

The experimental techniques employed were quite standard and, except where necessary, will not be described.

3. Lattice Parameter

The lattice parameters determined by standard X-ray techniques are shown in fig. 1. The differences between the annealed and quenched samples are small and barely above the limit of accuracy of the method. However, the lattice parameters of the annealed alloys are, in all cases, less than those of the quenched alloys. This behaviour is similar to that observed in the binary alloys but the differences are smaller by a factor of about 10. For 85 wt % Ni, no difference was observed between the annealed and quenched conditions. This is in agreement with the observation [8] that lattice ordering in Ni–Fe alloys extends from the composition Ni_3Fe to Ni contents as low as 50 wt %, but that no ordering is observed when the Ni content exceeds about 82 wt %.

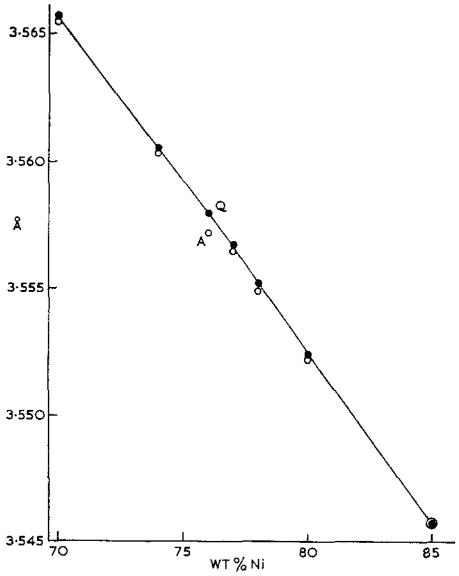

Figure 1 Lattice parameter as a function of Ni content.

The results suggest that the annealed alloys are in a more highly-ordered state than the quenched ones. A careful search with CoKα radiation failed to show any superlattice lines in the 77% alloy, even when it was maintained 10° C below its critical temperature for as long as 1 week. The X-ray evidence for superlattice formation is thus suggestive but by no means conclusive.

4. Electrical Resistivity

Measurements were made using a four-probe method. The distance between the potential terminals was measured with a travelling microscope. The thicknesses of the strips were measured by weighing a known area of sample and using the X-ray density. The uncertainty in the measured resistivity is about ± 1%.

The variation in room temperature resistivity with Ni content is shown in fig. 2. A feature common to all these alloys is that the resistivity of the cold-rolled alloy is increased by annealing. Fig. 3 shows the resistivity of the 77% Ni alloy

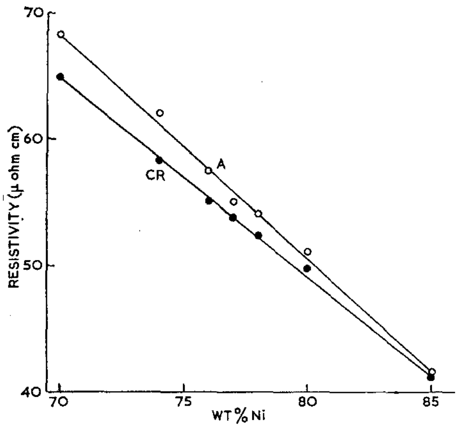

Figure 2 Electrical resistivity at 20° C as a function of Ni content.

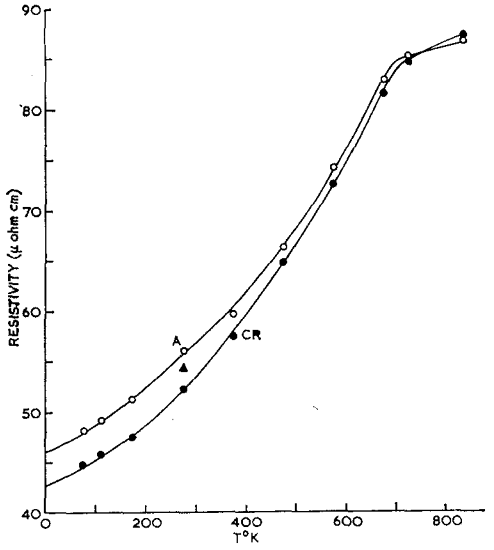

Figure 3 Electrical resistivity of the 77% Ni alloy as a function of temperature.

as a function of temperature. It can be seen that although the annealed sample has a larger residual resistance than the cold-rolled alloy, the combined phonon and magnetic resistivities at a given temperature are smaller. The isolated point at room temperature is for the cold-rolled alloy after having been cooled from 600° C in the measuring equipment. A significant amount of recrystallisation appears to have taken place. The change of slope in the vicinity of 700° K is due to the disappearance of ferromagnetic ordering.

The increase in electrical resistivity with annealing can hardly be due to superlattice formation, since this would have the opposite effect. It is possible that the normal decrease in resistivity associated with superlattice formation might be compensated and even outweighed by a change in band structure. However, although the band structure of certain alloys is known to be drastically changed by superlattice formation (e.g. Cu_3Au [8], Ni_3Mn [9]), these changes do not appear to increase the resistivity.

The increase in resistivity with annealing, although unusual, is not without precedent. It has been observed in an Fe–Co–V alloy [10] and in a number of Ni-rich alloys, notably in Ni–Cr alloys [11].

The most promising explanation seems to be that, although long-range order is absent, some degree of local ordering is promoted by annealing. This could account for the increase in resistivity [12] and would still be consistent with the absence of X-ray superlattice lines.

Further measurements were made on alloys quenched from 950° C. In all cases, the measured resistivities lay between those of the annealed and cold-rolled alloys. This suggests that the changes taking place occur quite rapidly, consistent with the early stages of order-formation in Ni_3Fe [13].

5. Saturation Magnetisation

Measurements were made at room temperature only using a vibration magnetometer [14] which measures the magnetic moment per unit volume, I_S. Fields up to 5000 Oe ensured complete saturation of the sample. The accuracy of the determinations was $\pm 2\%$.

The variation of I_S with Ni content is shown in fig. 4. Except for the 70% Ni alloy, the values

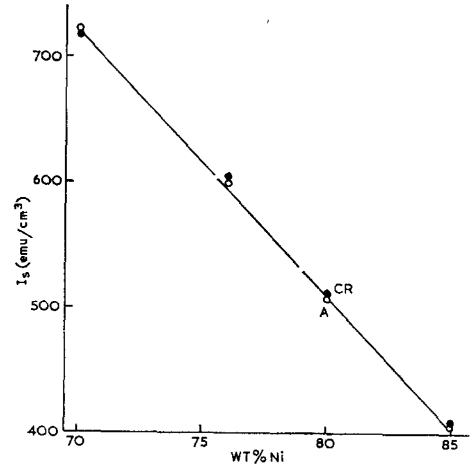

Figure 4 Magnetic moment per unit volume at room temperature as a function of Ni content.

of I_S for the annealed samples are always lower than for the cold-rolled samples. However, the differences are small and within the limits of accuracy of the method.

6. Magnetostriction

Determinations were made on discs using strain gauges. By measuring the strain at saturation as a function of the angle between the field and gauge, the isotropic magnetostriction constant is obtained independent of any uncertainties in domain orientation. This method does not eliminate possible errors due to crystal grain orientation. However, a careful search for preferred orientation using X-ray back-reflection methods showed that the crystal orientation in all samples was random. By observing the longitudinal and transverse strains as a function of field strength, the sign of the single-crystal magnetostriction constants, h_1 and h_2, can be inferred. In all cases, it was found that h_1 and h_2 have the same sign as λ_S. A typical example is shown in fig. 5. Table I shows the magnetostriction constants for three compositions. In all cases, the values are small and the measurements were difficult to carry out. In particular, different sets of measurements on the cold-rolled alloys often yielded somewhat different results. No such difficulty was experienced with the annealed alloys.

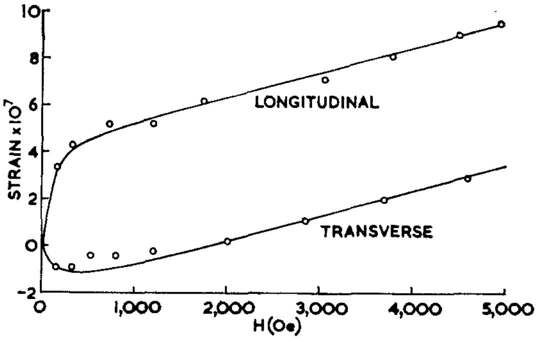

Figure 5 Magnetostriction of the annealed 77% Ni alloy at room temperature.

TABLE I Results of magnetostriction measurements.

Wt % Ni	$\lambda_S \times 10^7$		
	Cold-rolled	Annealed	
		Cooling rate 100° C/h	30° C/h
76	4.8	12.1	14.7
77	−12.7	4.0	2.6
78	− 8.3	−4.9	—

From table I, it can be seen that the minimum magnetostriction occurs between 77 and 78 wt % Ni for the annealed alloys. The initial permeability of these alloys is a maximum at 77% [15], and it can therefore be concluded, from the reasoning of Bozorth [1], that the dominant contribution to the initial permeability comes from domain boundary displacements. Also from table I, it appears that (i) there is no significant change in λ_S between the annealed and slow-cooled samples, and (ii) λ_S for the cold-rolled samples is algebraically less than that of the annealed samples.

A study of the magnetostriction of quenched alloys brought to light a totally unexpected result. After quenching from 850° C, a 77% Ni alloy was found to have $\lambda_S = -2.8 \times 10^{-7}$. This is different in sign from the value for the annealed alloy. Subsequent measurements on the same sample quenched from different temperatures produced the curve shown in fig. 6. It is clear that varying T_Q above the critical temperature for long-range order produces far greater changes in λ_S than varying the cooling rate below it. Fig. 6 also shows the initial permeability, μ_0, [5] as a function of T_Q. The two curves are almost exact mirror images, and show that the variation of μ_0 with T_Q is a consequence of a genuine change of λ_S with T_Q,

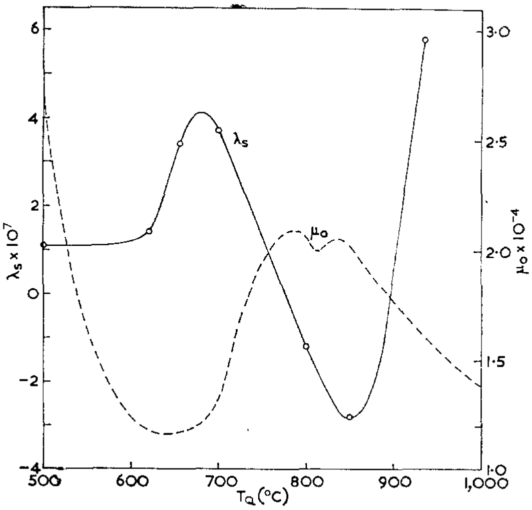

Figure 6 Magnetostriction constant, λ_S, of the 77% Ni alloy measured at room temperature as a function of quenching temperature, T_Q.

and is not due to a combined crystal and magnetoelastic anisotropy which sums to zero, as suggested by Lewis [6].

7. Discussion

This investigation failed to establish with certainty the existence of long-range order in these alloys. However, significant changes in many physical properties with heat treatment were observed, and it seems very probable that these are due to atomic rearrangements of some kind. The changes appear to be greatest for the 76 % Ni alloy. Of the greatest immediate relevance to the problem of high-permeability alloys is the observation that the magnetostriction constant can be significantly changed by quenching and depends in a systematic way on T_Q. Of all the physical properties studied, the magnetostriction is the one most likely to depend on the local environment of a given atom, since it is determined by short-range magnetic interactions. Therefore, it is suggested that atomic ordering takes place in these alloys on an extremely local scale. This is in agreement with the observation [3] that the superlattice lines observed in Ni_3Fe are very broad, indicating very small antiphase domains; they are likely to be even smaller in the quaternary alloys. It is also consistent with the interpretation of certain observations in the closely related Ni–Fe–Mo alloys [16]. This view does not in any way conflict with the statements that the order–disorder transformation is too slow to allow any appreciable degree of order to be formed in commercial alloys [3]. The degree of long-range order in the quaternary alloys is indeed quite small. Local order forms quite quickly, in agreement with Iida's observation [13] that the initial stage of order formation in Ni_3Fe is a comparatively rapid process. That it has such a profound effect on the magnetic properties of the 77 % Ni alloy is simply a consequence of the inverse relation between μ_0 and λ_s, and the fact that λ_s is itself very small.

The variation of λ_s with T_Q, although proportionately very large for the 77 % Ni alloy, is very small when viewed in the light of the magnetostriction of ordinary materials not having high initial permeability. The form of the variation of λ_s with T_Q suggests that two mechanisms may be involved. The continuation of the variation up to 930° C implies that lattice vacancies are involved, but the full explanation probably involves the number, size, and shape of the ordered regions, as well as the degree of order within them. For an alloy of given composition, these factors control the magnetostriction, the magnetic anisotropy (by implication), and hence the low-field magnetic properties.

Acknowledgement

It is a pleasure to acknowledge the benefit we have received from discussions with Mr R. D. Enoch.

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Note Added During Proofing

Collins, Jones, and Lowde (*J. Phys. Soc. Japan* **17** Suppl. B-III (1962) 19) have observed the presence of short-range order in 70 at. % and 60 at. % Ni-Fe alloys after quenching from temperatures as high as 1000°C.