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The influence of molybdenum concentration on the magnetic permeability and kinetics of order formation in molybdenum permalloys

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The initial magnetic permeabilities of molybdenum permalloys with a range of molybdenum concentrations have been measured as a function of isothermal annealing time in the temperature range 400 to 600° C. Annealing in the range from 400 to 460° C produces short-range ordering, leading to a maximum initial permeability when the magnetostriction is reduced to zero. From 460 to approximately 490 to 500° C it is suggested that microdomains of long-range order nucleate and grow in a short-range ordered matrix and these reduce the maximum initial permeability which can be obtained. Above about 490 to 500° C, long-range order does not form, but equilibrium values of short-range order are too small to produce initial magnetic permeabilities as large as in the lower temperature region. The rate of short-range order formation has been found to increase sharply at molybdenum concentrations of about 4 wt% (2.5 at. %) and the activation energy for short-range order formation falls sharply from about 180 kJ mol^{-1} to 140 kJ mol^{-1} at this molybdenum concentration. It is thought that different ordered structures and mechanisms of ordering occur below and above 4 wt% molybdenum. Quenching experiments suggest that quenched-in vacancies can increase the rates of short-range order production.

1. Introduction

In quaternary alloys of nickel–iron derived from binary alloys with compositions near to Ni_3Fe by additions of molybdenum and copper, an ordering heat-treatment in the temperature range of 400 to 500° C can produce material with very large initial magnetic permeabilities. These alloys can be conveniently referred to as molybdenum permalloys, although the ternary Ni–Fe–Mo alloys are often so named. The concentrations of the alloying elements which give the highest initial permeabilities can be calculated from a semi-empirical relationship discovered by Enoch and Fudge [1]. The ordering treatment alters the magnetocrystalline anisotropy and the magnetostriction constants of the material, and maximum initial permeabilities are obtained when the composition of the alloy is such that the anisotropy and magnetostriction both become zero, or very nearly zero, after the same ordering time [2, 3]. If this can occur, the magnetic domain walls are easily moved by very small magnetic fields and the initial magnetic permeability is consequently very large.

In the work reported in this paper, which forms part of a more general investigation of the effect of heat-treatment on the magnetic properties of molybdenum permalloys [4], the rates of ordering were investigated by measuring the changes in initial magnetic permeability on ordering at

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different temperatures for a series of alloys having a range of molybdenum concentrations. These measurements enable the activation energy for ordering to be determined and it is found, as discussed below, that there is a very pronounced change in the ordering rate and activation energy at a molybdenum concentration of about 4 wt% (2.5 at. %).

2. Materials and experimental technique

The compositions of the alloys used are given in Table I.

The alloys were commercially produced and, apart from basic alloying elements, they contained manganese to improve hot-workability. The main impurities were chromium, cobalt and magnesium. The material was in the form of cold rolled sheet, 375 μm thick, from which the specimens were punched in the form of annular rings with internal and external diameters of 17.5 and 25.4 mm respectively.

Prior to the ordering treatment, the permalloys require a high temperature anneal in hydrogen which produces a certain amount of purification, by the removal of interstitial impurities such as sulphur, nitrogen and oxygen, as well as beneficial structural changes. Investigation of the structural changes which occur on annealing showed that below about 500° C there is a slight improvement in magnetic properties which is thought to be due to the migration of excess vacancies to vacancy sinks, whilst above 500° C recovery occurs, the dislocations forming a cell structure. On annealing above about 700° C recrystallization occurs followed by grain growth and this produces a primary recrystallization texture of the cubic type, $\{100\}$ $\langle 001 \rangle$, which increases the initial permeability, although this increase is small in those specimens which have undergone ordering treatments which produce maximum permeabilities, and in which the anisotropy is presumably very small. Above 1130° C secondary recrystallization occurs and destroys the cubic texture, reducing the magnetic permeability. In view of these changes in structure occurring on annealing and their consequent effects on the initial permeability, it was found that maximum permeabilities were obtained if all the specimens were given the same high temperature anneal of 4 h at 1130° C in a constant flow of purified hydrogen with a dew point reduced to approximately $-60°$ C. The specimens were then either furnace-cooled to room temperature, the cooling rate in the ordering temperature range, 600 to 400° C, being about 2° C min^{-1} or quenched from above the ordering temperature range by withdrawing them into a water-cooled jacket, the quenching rate being estimated to be 125° C min^{-1}.

TABLE I Composition of the alloys (wt %)

Mo	Cu	Fe	Ni	Mn
3.65	5.05	13.8	75.6	0.34
3.85	5.1	13.8	75.6	0.50
3.95	5.0	13.9	75.5	0.40
4.17	4.94	14.1	76.1	0.70
4.36	4.90	13.4	76.65	0.69

The ordering heat-treatments were carried out at a fixed temperature in a hydrogen flow, the specimens being quenched after specified ordering times.

The initial permeability was calculated by measuring the inductance of a toroid whose core was formed from the permalloy specimens. A number of the annular ring specimens which had had the same heat-treatment were stacked in a perspex former and ten turns of PVC covered copper wire were wound on this to form the toroid. The inductance was measured at 40 and 60 Hz, and the mean taken to give the value at 50 Hz, using a Wayne–Kerr Universal Bridge. After investigating the variation of permeability with field strength, a value of 0.1 A m^{-1} was chosen as a sufficiently low field strength to give the initial permeability. The values quoted in this paper are initial relative permeabilities, but for convenience they are referred to throughout as initial permeabilities.

Magnetostriction measurements were made by using wire strain-gauges mounted on discs of the material. A dummy gauge mounted on a Cu–35% Zn sample, which has a similar expansion coefficient to permalloy, was used to compensate for temperature variations. It was possible to detect a magnetostrictive strain of 10^{-8} with the experimental arrangement used.

3. Results and discussion

3.1. The effect of molybdenum concentration on the rate of ordering

The very pronounced effect of molybdenum concentration on the rate of ordering in these alloys is demonstrated in Fig. 1, which shows the initial permeability μ_i of the alloys after cooling at different rates through the ordering temperature range, following the high temperature anneal.

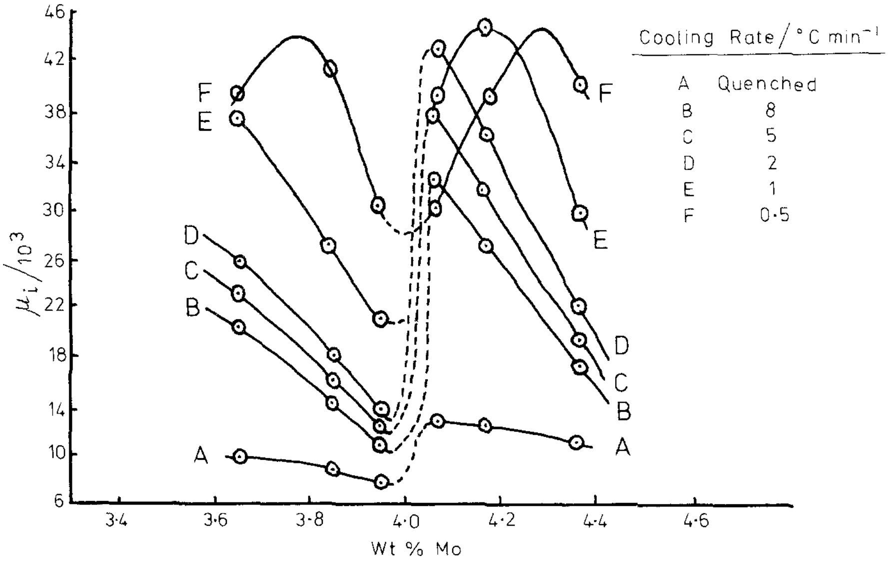

Figure 1 Variation of the initial permeability with Mo concentration for a series of cooling rates.

It can be seen that all the curves show a sharp break at about 4 wt% molybdenum, ordering proceeding much more rapidly in alloys with greater than 4 wt% molybdenum. The reasons for the shapes of these curves should become clear later.

Enoch and Fudge [1] have shown that with a fixed molybdenum concentration the ordering rate increases as the magnetic-nickel to iron ratio increases. The alloys used in this work had a range of magnetic-nickel to iron ratios but when these were taken into account it was found that the molybdenum concentration was the predominant factor determining ordering rates.

3.2. Isothermal annealing

Figs. 2 and 3 show the dependence of the initial permeability on the ordering time at different temperatures. These figures are for an alloy containing 3.65 wt% molybdenum and are typical of all the alloys listed in Table I, although the rates of ordering differ with molybdenum concentration. In Fig. 2 the specimens were furnace-cooled before the ordering anneals were carried out, and because of this the initial permeabilities were greater at the start of the anneals than those in Fig. 3, which were quenched before annealing. As the rate of ordering was being studied the permeability at the start was unimportant. Three

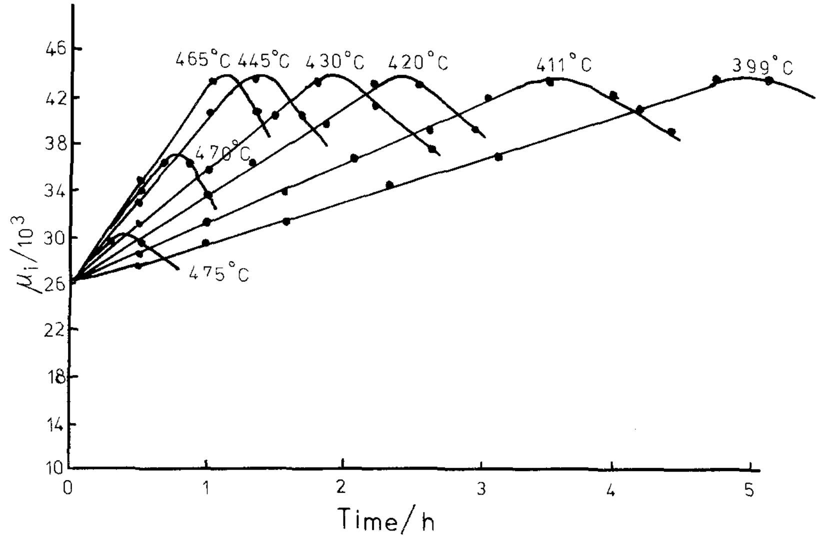

Figure 2 Variation of the initial permeability with annealing time for specimens with 3.65 wt% Mo.

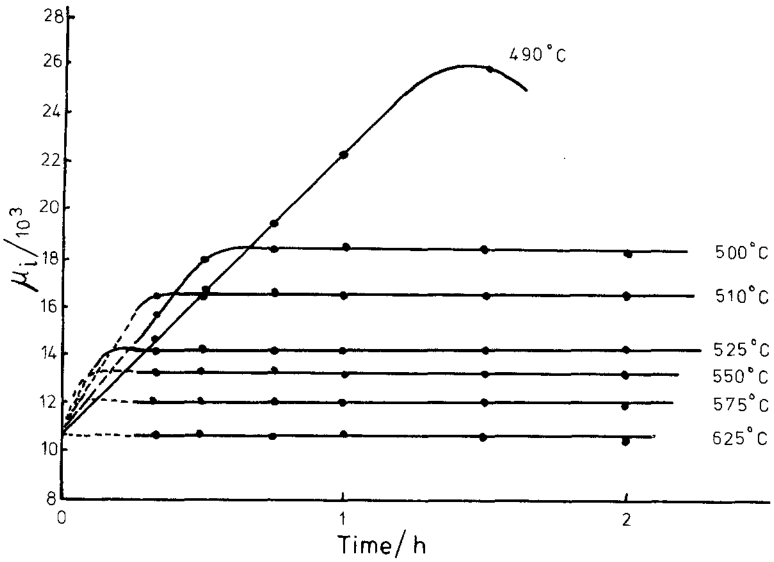

Figure 3 Variation of the initial permeability with annealing time for specimens with 3.65 wt % Mo.

temperature ranges can be distinguished in Figs. 2 and 3 by the different behaviour of the initial permeability with ordering time: (a) approximately 400 to 460° C, (b) 460 to about 490 to 500° C, and (c) above 500° C. These temperature regions are discussed separately below.

(a) The initial permeabilities of specimens which are isothermally annealed in the approximate temperature range 400° C to 460° C increase with time, at a rate which increases with increasing temperature, reach a maximum value which is independent of temperature and then fall with further increase in ordering time. The accepted reason for this behaviour is that it is due to the formation of short-range order on annealing. As the annealing temperature is increased. the rate of short-range order formation will increase, resulting in a similar increase in the rate of change of initial permeability with time, as is observed.

Fig. 4 shows the results of measurements of the saturation magnetostriction constant λ_s as a function of annealing time at different temperatures in specimens with a molybdenum concentration of 3.65 wt %. It can be seen that the magnetostriction decreases on annealing, leading to an increase in the initial permeability. The maxima in the permeability curves occur when the magnetostriction becomes zero and any further annealing reduces the permeability because the absolute value of λ_s increases, although λ_s has opposite sign. These results are in agreement with those of previous workers [3] on ternary molyb-

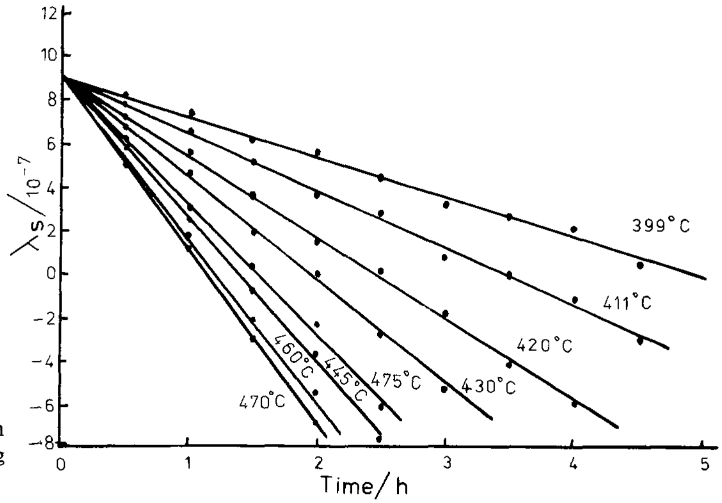

Figure 4 Dependence of the saturation magnetostriction constant on annealing time for specimens with 3.65 wt % Mo.

denum permalloys. It has also been shown [2] that at maximum initial permeability the anisotropy is also vanishingly small.

(b) In the temperature range of approximately 460 to 490–500° C the behaviour of the initial permeability on annealing differs in two respects from that at lower temperatures; firstly, the rate of increase of the permeability now decreases with increasing temperature and secondly, although the curves still show maxima, the maximum initial permeability decreases as the annealing temperature is raised, whereas the permeability at the maxima was constant in the lower temperature range. It is postulated, following other workers [1], that in this temperature range, as well as short-range order being produced, microdomains of long-range order are nucleated and grow. The production of short-range order increases the initial permeability, whereas microdomains will tend to pin the magnetic domain walls and reduce the permeability. When the microdomains of long-range order reach a critical size range they will tend to reduce the initial permeability and a permeability maximum will be reached which is less than can be achieved in the lower temperature range, where short-range order alone occurs.

The reason for the decrease in the rate of ordering with increasing temperature is that although diffusion rates will increase, the free energy of ordering will decrease and, unlike the case at lower temperatures, the latter will predominate and cause a decrease in the rate of order formation with increasing temperature. Similar reasoning is used to explain the shapes of the isothermal transformation curves for steels. The same phenomenon is observed in the case of the magnetostriction constant, as can be seen in Fig. 4. The measured magnetostriction constant is an average over the whole volume of the specimen and, therefore, will not be appreciably affected by the presence of microdomains of long-range order, unlike the permeability which can be very dependent on small volume fractions of impurities and imperfections. Therefore, the similar behaviour of both properties confirms that the microdomains of long-range order are not primarily responsible for the reduction in the rate of change of initial permeability with temperature, in this temperature range. This phenomenon will be discussed more fully in the section on ordering kinetics.

(c) Above approximately 490 to 500° C the curves do not show maxima, the initial permeability increases to a constant value, independent of annealing time, which decreases with increasing annealing temperature. From these curves it can be deduced that long-range order does not form above about 490 to 500° C, the order–disorder temperature lying in this temperature range. The formation of short-range order above 500° C leads to an increase in initial permeability but it appears that the equilibrium amount of short-range order is reached before the magnetostriction is reduced to zero. As the annealing temperature is increased above 500° C the equilibrium amount of short-range order decreases and the constant value of the initial permeability also decreases.

The observations in (a), (b) and (c) above are summarized in Fig. 5, which shows the maximum initial permeability which could be achieved on annealing at different temperatures. This figure is divided and labelled to show the ranges of temperature corresponding to (a), (b) and (c). To summarize the conclusions above: in region (a) the degree of short-range order to reduce the magnetostriction to zero and produce maximum initial permeability can be achieved on annealing, without the production of long-range order, in region (b) long-range order is nucleated and reduces the maximum permeability obtainable, in (c) the order–disorder temperature, of approximately 490 to 500° C, is exceeded and long-range order does not occur but equilibrium values of short-range order are achieved which are too small to produce maximum initial permeabilities. Further confirmation of these conclusions was obtained by annealing a specimen in temperature range (b) (Fig. 5) to its maximum initial permeability and then annealing it at a lower temperature in range (a), when the expected increase in initial permeability did not occur because the microdomains of long-range order remain to hinder the movement of magnetic domain boundaries. However, if this specimen after heat-treatment in range (b) was heated to a temperature in section (c) for a few minutes, and then ordered at a temperature in section (a), the initial permeability increased to its expected maximum. This is consistent with the long-range order being destroyed on heating above the order–disorder temperature. Exceptions to this behaviour were found in the case of specimens with 4.17% Mo and 4.36% Mo, which did not

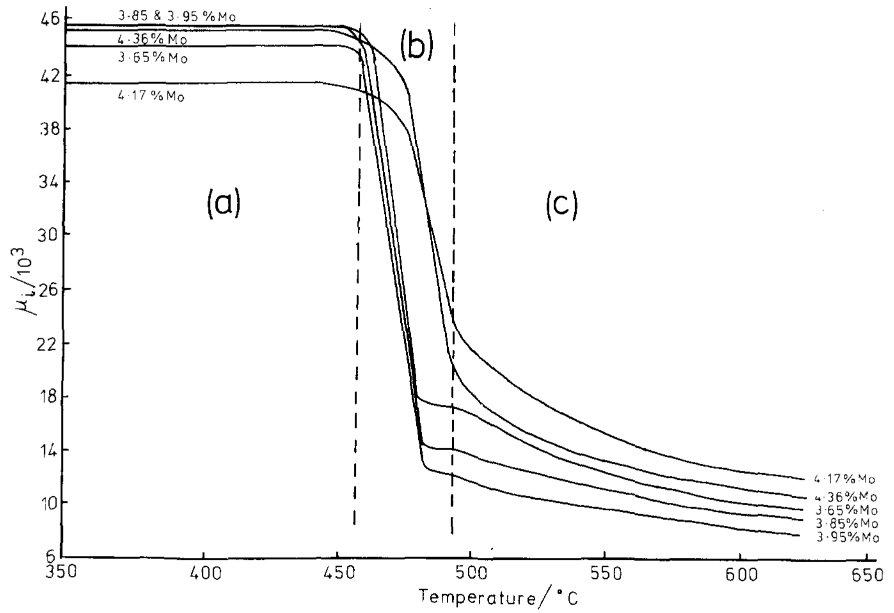

Figure 5 Variation of the maximum initial permeability with annealing temperature.

increase their permeabilities after heating in range (c) and then in range (a). This behaviour is not understood and will be investigated further, in particular by studying the times and temperatures required to destroy long-range order.

In an attempt to confirm the presence of long-range order, X-ray measurements were made, but even after annealing times of up to 35 h, superlattice lines could not be detected. This is probably due to the similarity in the X-ray scattering factors of nickel and iron, although superlattice lines have been detected by other workers using X-ray [5] and neutron diffraction [6] techniques, but annealing times of several weeks were required to produce sufficient long-range order. However, a decrease in lattice parameter due to the formation of short-range order did occur, as shown in Fig. 6.

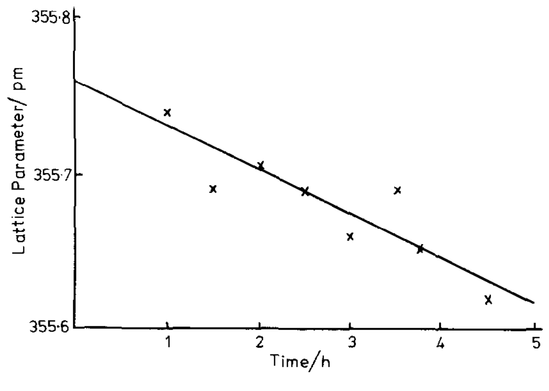

Figure 6 Variation of the lattice parameter with annealing time at 411° C for a specimen with 3.65 wt%Mo.

3.3. The kinetics of order formation

Figs. 2 and 3 show that on annealing at a temperature less than about 490 to 500° C the initial permeability rises with increasing annealing time, reaches a maximum and then falls. It is assumed that, before the maximum is reached, specimens of the same composition which have the same permeability have the same degree of short-range order, whatever the annealing time and temperature which produced it. Thus it is assumed that the variation of initial permeability with time represents the variation of the degree of short-range order with time, and hence the initial permeability can be used to estimate the activation energy for the formation of short-range order. The elementary analysis of the kinetics of short-range order formation considered in the Appendix suggests a means of plotting the time to reach a given initial permeability against temperature which will give the activation energy for short-range order formation.

Fig. 7 shows plots for material with 3.65 wt% Mo, where the times to reach the three different temperatures have been used. The values of T_c used were 490° C for compositions below 4%Mo and 500° C for compositions above 4%Mo.

Equally good straight lines were obtained for all the alloys with different molybdenum concen-

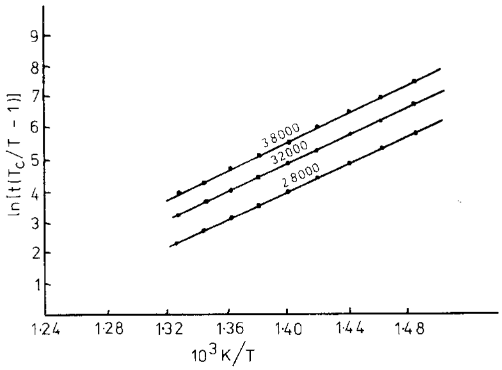

Figure 7 Graphical determination of the activation energy for short-range order formation in specimens with 3.65 wt% Mo.

trations. The activation energies, H, for the formation of short-range order obtained from such plots for the alloys with different molybdenum concentrations are listed in Table II.

A very sharp reduction in the activation energy occurs at concentrations above 4 wt% (2.5 at.%) Mo, in agreement with the results in Fig. 1.

Yeganyan and Selisskiy [7] noted the same effect in their study of the temperature dependence of Young's modulus in similar Ni–Fe–Mo alloys. They observed a drop in activation energy at 3 at.% Mo (4.9 wt%) from 176 to 134 kJ mol^{-1}, in very close agreement with the figures in Table II. They also observed the same effect with chromium and nickel instead of molybdenum, but the change in activation energy occurred at different compositions. These workers suggested that, in the ternary alloy, molybdenum takes part in the ordering process at concentrations above 3 at.%, the molybdenum atoms substituting for some of the iron atoms in the Ni_3Fe superlattice. Presumably the same process would occur in short-range order formation.

Gomankov *et al.* [6] have reported the results of neutron diffraction studies of ordering in Ni_3Fe with molybdenum additions. They showed that increasing concentrations of molybdenum tend to reduce superlattice formation and at molybdenum concentrations above about 4 at.% (6.5 wt%) long-range order no longer forms. Their results did not enable the positions of the molybdenum atoms in the superlattice to be determined directly, but from indirect evidence they suggested that molybdenum substitutes for iron atoms. They did not, however, observe any sudden change in ordering process at a particular molybdenum concentration, only a steady reduction in superlattice reflections with increasing molybdenum concentration.

TABLE II

Mo (wt%)	H(kJ mol^{-1})	Mo (wt%)	H(kJ mol^{-1})
3.65	186	4.17	136
3.85	182	4.36	138
3.95	178		

The observations in our work of an appreciable change in ordering rates and activation energies at 4 wt% (2.5 at.%) molybdenum suggest that different short-range ordered structures occur for alloys with compositions below and above this concentration. Differences in order–disorder temperature, T_c, deduced from Fig. 5, and quoted above, suggest that the same applies for long-range order. For all compositions studied, it was found that at annealing temperatures below about 460° C, where only short-range order occurs, approximately the same maximum initial permeability was obtained. This is difficult to understand if different short-range ordered structures occur below and above 4 wt% molybdenum and demonstrates that further work is required in order to fully understand the ordering processes occurring in these alloys.

3.4. Effect of quenched-in vacancies on ordering rates

Fig. 8 shows the initial magnetic permeabilities of specimens which were furnace cooled from the annealing temperature of 1130° C to a series of lower temperatures, and then quenched. It can be seen from the curves that below about 350° C no further ordering takes place. From approximately 350 to 600° C ordering takes place and the longer the time the specimen spends in this temperature range before quenching, the higher the permeability . These results are consistent with the results discussed in Section 3.2. Quenching temperatures above 600° C, however, lead to increased permeabilities, with a broad maximum at 800° C. This effect of quenching on ordering rates in similar alloys has been noticed previously in studies of the initial magnetic permeability [8], magnetostriction [9] and electrical resistivity [10], and is thought to be due to increases in ordering rates because of the presence of quenched-in vacancies. When specimens are quenched from about 600° C they spend only a very short time in the ordering temperature range 600 to 350° C and the resultant permeabilities are small, as shown in Fig. 8. It is

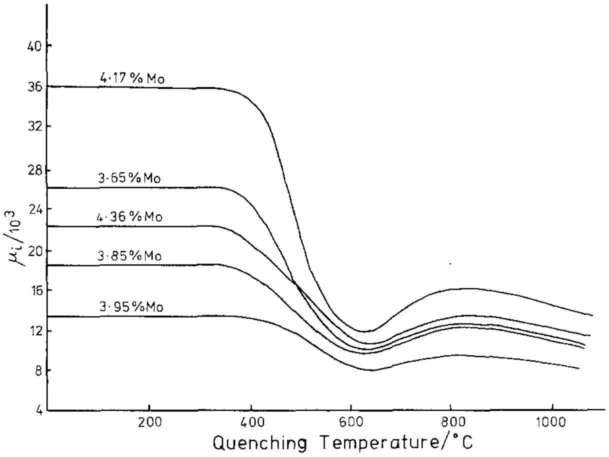

Figure 8 Variation of the initial permeability with quenching temperature.

envisaged, however, that on quenching from higher temperatures, say 800° C, an excess concentration of vacancies will remain in the specimens at lower temperatures and lead to an increase in the rate of ordering in the critical range 600 to 350° C and a consequent increase in permeabilities will occur.

The fall in permeability on quenching from above 800° C could be due to quenching strains having noticeable effects at these temperatures. In order to estimate whether sufficient vacancies would be expected to remain during the quench, the model of Kino and Koehler [11] for the annihilation of vacancies by dislocations was used. Using reasonable estimates of the activation energy for vacancy migration and the dislocation density, it was calculated that on quenching from 800° C about 3% of the vacancy concentration at 800° C would remain at 600° C, which is thought to be sufficient to lead to the required increase in ordering rate.

4. Conclusions

Isothermal annealing results suggest that in the temperature range of approximately 400 to 460° C short-range ordering occurs without the nucleation of long-range order and the initial magnetic permeability of molybdenum permalloy increases to a maximum value independent of annealing temperature. Magnetostriction measurements have shown that this maximum occurs when the magnetostriction is reduced to zero, further annealing increases the absolute value of the magnetostriction constant and the initial permeability decreases. In the temperature range from 460° C to about 490 to 500° C the initial permeability increases with annealing time to a maximum value which depends upon the temperature, and then decreases. These maximum values are less than that obtained in the lower temperature region. This behaviour is attributed to the nucleation and growth of microdomains of long-range order in a matrix in which short-range order is forming. It is envisaged that these microdomains will pin domain walls and this will reduce the initial permeability. On annealing above about 490 to 500° C long-range order does not form and the initial permeability increases at first and then levels out to a constant value. This constant value of initial permeability decreases as the annealing temperature is increased. It is concluded from this behaviour that equilibrium values of short-range order are reached before the magnetostriction is reduced to zero and the initial permeabilities are lower than can be obtained by annealing at lower temperatures.

Investigation of the rates of short-range order formation shows that alloys with greater than 4 wt % (2.5 at. %) molybdenum order more rapidly than those with less than 4 wt %. The activation energies for short-range order formation show a reduction from about 180 to 140 kJ mol^{-1} on increasing the molybdenum concentration through 4 wt %. It is suggested that different ordering processes and structures could be occurring in the ranges of molybdenum concentration above and below 4 wt %, but further work is necessary to confirm this.

Experiments on the quenching of material from above 600° C suggest that quenched-in vacancies can increase ordering rates in molybdenum permalloys.

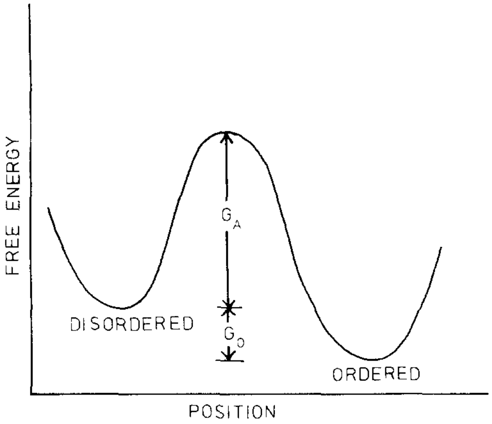

Figure 9 Change in the free energy on order formation.

Appendix. An elementary analysis of the kinetics of ordering

Consider an atom changing its position from a disordered to an ordered site where its free energy is lower by an amount G_o, as shown in Fig. 9. If in making this change the activation free energy is G_A, then in changing from an ordered to a disordered site the activation free energy will be $(G_o + G_A)$. The rate J_o at which atoms will tend to move from disordered to ordered sites will be [12]:

$$J_o \propto \exp\left[-(G_A + G_v)/kT\right],$$

where G_v is the free energy of a vacancy. G_v enters into this equation because the ordering rate depends on the probability of a neighbouring site being vacant, as well as on the atom having sufficient energy to surmount the free energy barrier. The rate J_D at which the opposite process will occur will be:

$$J_D \propto \exp\left[-(G_A + G_o + G_v)/kT\right].$$

The net rate of ordering, J, will therefore be

$$J = J_o - J_D \propto [1 - \exp(-G_o/kT)] \exp\left[-(G_A + G_v)/kT\right]$$

or

$$J \propto \exp(S/k)\exp(-H/kT)\,[1 - \exp(-G_o/kT)], \tag{A1}$$

where H and S are the activation energy, strictly enthalpy, and entropy for order formation, respectively. The experimental measurements were made in a temperature range where the amount of short-range order was small and close to the order–disorder temperature for long-range order and therefore G_o will be small and Equation A1 can be approximated to:

$$J \propto (G_o/kT)\exp(-H/kT). \tag{A2}$$

Writing

$$G_o = H_o - TS_o, \tag{A3}$$

we see that for long-range order G_o will be zero, and hence the ordering rate J will be zero, at the order–disorder temperature T_c given by

$$G_o = H_o - T_cS_o = 0 \tag{A4}$$

which, using Equations A2 and A3 gives the rate of long-range ordering as

$$J \propto \frac{S_o}{k}\left(\frac{T_c}{T} - 1\right)\exp(-H/kT).$$

Hence the time, t, required to produce a given state of long-range order will be given approximately by the relation:

$$t \propto \left(\frac{T_c}{T} - 1\right)^{-1}\exp(H/kT).$$

Hence

$$\ln\left[t\left(\frac{T_c}{T} - 1\right)\right] = \frac{H}{kT} + C, \tag{A5}$$

where C is a constant.

We make the assumption that if long-range order can be nucleated, the rates of growth of long-range and short-range order near the order–disorder temperature, T_c, will be very similar because the reason for both occurring is the same, that is the tendency for nearest neighbours to be different types of atom. This assumption appears to be justified by the experimental results in Figs. 2 and 3, where it can be seen that as the order–disorder temperature for long-range order is approached, the rate of production of short-range order, and its equilibrium amount, decreases.

Making the above assumption we can use Equation A5 as a means of plotting ordering times to obtain the activation energy H for short-range order formation. The fact that very good linear plots were obtained, as in Fig. 7, further justifies these assumptions.

Acknowledgements

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References

1. R. D. ENOCH and A. D. FUDGE, *Brit. J. Appl. Phys.* **17** (1966) 623.
2. R. D. ENOCH and A. WINTERBORN, *ibid* **18** (1967) 1407.
3. J. H. PHILLIPS and R. G. SHEPHARD, *J. Phys. D: Appl. Phys.* **3** (1970) 1017, 1605.
4. E. G. TAYLOR, Ph.D. Thesis, University of Leeds (1973).
5. R. G. TREUTING and B. W. BATTERMAN, *J. Appl. Phys.* **34** (1963) 2005.
6. V. I. GOMAN'KOV, I. M. PUZEY, A. A. LOSHMANOV and Ye. I. MAL'TSEV, *Phys. Met. Metallogr.* **28** (1969) 262.
7. I. L. YEGANYAN and Ya. P. SELISSKIY, *ibid* **27** (1969) 210.
8. R. E. S. WALTERS, Conference on Magnetism and Magnetic Materials (A.I.E.E., New York, 1956) p. 258.
9. R. C. JACKSON and E. W. LEE, *J. Mater. Sci.* **1** (1966) 362.
10. A. FERRO and G. GRIFFA, *J. Phys. Chem. Solids* **31** (1970) 2789.
11. T. KINO and J. S. KOEHLER, *Phys. Rev.* **162** (1967) 632.
12. C. ZENER, "Imperfections in Nearly Perfect Crystals" edited by W. Shockley (Wiley, New York, 1952) Ch. 11.

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