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Formation of the K-state in a Ni-Fe-Mo-Cu alloy

R. J. WILLEY*
Department of Metallurgy, University College, Swansea, UK

The electrical resistivity, magnetic saturation and Vicker's hardness of the alloy 79 wt% Ni–16 wt% Fe–4.3 wt% Mo–0.7 wt% Cu have been measured as a function of heat treatment in the range 300 to 500° C. These properties have also been measured on a binary 75 at. % Ni–25 at. % Fe alloy heat treated in the same temperature range so as to produce atomic order. An increase in resistivity in the quaternary alloy has been found and, by comparison with the binary alloy, this has been associated with short range atomic order.

1. Introduction

The magnetic properties of Ni–Fe alloys with compositions close to 75 at. % Ni depend markedly on their thermal history. Very high permeabilities can be obtained by heat treatments below 600° C and this has been associated with atomic order and the development of the super-lattice Ni_3Fe. Alloys with small additions of Cr, Cu or Mo, at the expense of the iron, have superior magnetic properties, although heat treatment in the range 300 to 600° C is still required. Because of the similarities in the heat treatments of the alloy systems, the properties of the more complex alloys have also been considered to depend on atomic order.

In general the resistivity of an alloy decreases with the formation of atomic order. However, in the alloy 77 wt% Ni–14 wt% Fe–4 wt% Mo–5 wt% Cu the resistivity was found to increase when given a heat treatment such as to increase the degree of atomic order [1]. This phenomenon has been noted in a number of different ternary alloy systems including Ni–Fe–Mo and Ni–Fe–Cr [2] and is commonly known as the "K-effect". Davies [3] and Starke [4] have tabulated a series of different alloys in which this effect has been found. The mechanism involved appears to differ with the alloy investigated and proposed explanations of the resistivity increase have involved short range order [5, 6], long range order [7, 8] and the formation of Guinier–Preston zones [4].

In the present investigation the existence of the K-state has been established in an alloy of 79 wt% Ni–16 wt% Fe–4.3 wt% Mo–0.7 wt% Cu. By simultaneously heat-treating the quaternary alloy and a binary 75 at. % Ni–25 at. % Fe alloy, the changes in resistivity, magnetic saturation and hardness of the former have been compared with a system known to undergo atomic ordering and whose ordering kinetics are relatively well known.

2. Specimen preparation and heat treatment

Specimens of both alloy systems were machined to dimensions 7 cm × 0.15 cm × 0.06 cm from vacuum-melted polycrystalline strip material. They were then annealed for 2 h at 1000° C in pure dry hydrogen. The purpose of this was two-fold: firstly, to relieve the stress in the specimens; secondly, since long range order is destroyed above 500° C and short range order can only persist up to 600° C, to produce a completely disordered matrix. From the work of Bozorth [9] and Enoch [10], it may be inferred that to maintain the disordered state at room temperature the specimens must be quenched at a rate greater than 10^5° C h^{-1} through the ordering range 600 to 300° C. This was accomplished by suspending the specimens in a vertical furnace and quenching into an oil bath held at room temperature. To minimize complications due to quenched-in vacancies [3], the specimens were furnace-cooled to 700° C and then quenched.

*Present address: Department of Mathematics and Physics, Glasgow College of Technology, Glasgow, UK.

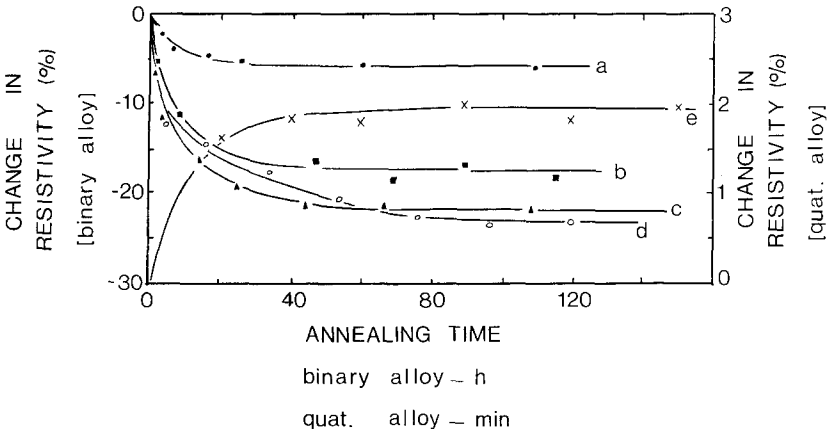

Figure 1 Change in resistivity as a function of annealing time at: (a) 350° C (binary alloy), (b) 400° C (binary alloy), (c) 480° C (binary alloy), (d) 465° C (binary alloy), (e) 450° C (quaternary alloy).

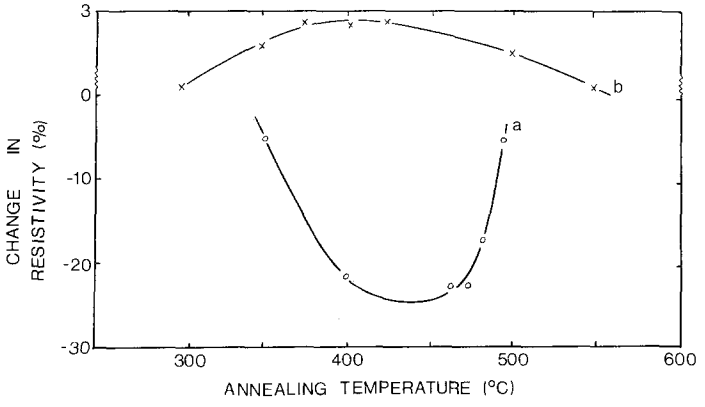

Figure 2 Change in resistivity as a function of annealing temperature: (a) binary alloy – 100 h at each temperature; (b) quaternary alloy – 3 h at each temperature.

Different states of order were produced by annealing for various periods in the ordering range and then quenching to room temperature.

3. Experimental techniques and results

3.1. Resistivity

The electrical resistivity was measured at a constant temperature of 20° C using a Diesselhorst potentiometer with an overall accuracy of ±0.2%. The resistivity was firstly measured on a disordered specimen of the binary alloy and the value of 16.49×10^{-8} Ω m is in good agreement with the published data [11–13]. The resistivity was subsequently measured as a function of annealing time for specimens heat treated at different temperatures. The results show that, for the binary alloy, the change in resistivity is always completed after about 80 h annealing. This is in good agreement with the formation of order observed in an alloy of this composition using neutron diffraction methods [14]. Also, by comparing these results with the ordering kinetics of Ni–Fe proposed by Iada [15–18], it is clear that resistivity depends on both short range order and long range order. In the quaternary alloy, the resistivity was measured on a specimen in the disordered state as a function of annealing time and temperature. The resistivity increases with annealing time, in marked contrast with the binary alloy. This increase is very rapid and is completed after about 30 min at the annealing temperature, further annealing for periods as long as 90 h having no effect. The change in resistivity is always positive for all annealing temperatures in the range investigated.

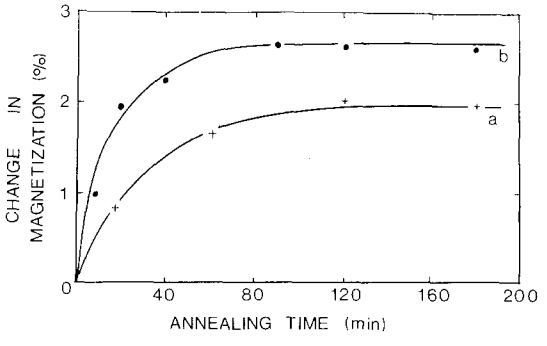

Figure 3 Change in magnetic saturation as a function of annealing time at: (a) binary alloy – 440° C; (b) quaternary alloy – 450° C

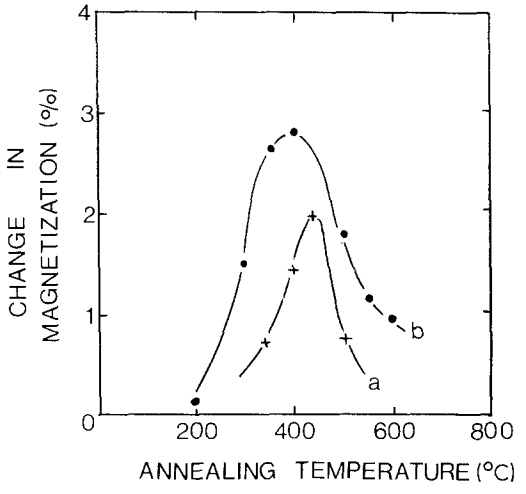

Figure 4 Change in magnetic saturation as a function of annealing temperature: (a) binary alloy – 5 h at each temperature; (b) quaternary alloy – 3 h at each temperature

3.2. Magnetic saturation

This was measured at room temperature by a ballistic technique with an accuracy of ±0.6%. To ensure saturation, measurements were made with an applied field of 8×10^3 A m^{-1}. In all cases a specimen was tested in the disordered state, and then at various stages while being taken through the ordering cycle. The same specimen was used for both resistivity and saturation measurements.

The magnetic saturation of the binary alloy in the disordered state was found to be 1.15 T, in very good agreement with published data [12, 19, 20]. The saturation rises sharply with annealing time and is constant after about 2 h. The general shape of this curve is in good agreement with the work of Taoko [12], the rise times of the graphs being very similar. However, that author reported a change of about 4% on annealing at 490° C. In the present work the maximum change was approximately 2%, and this occurred at an annealing temperature of about 440° C. The maximum change in resistivity also occurred well below the published critical ordering temperature. In view of the high purity materials used in this study, it is unlikely that the critical ordering temperature was affected by impurities. However, if the definition of critical temperature is taken as "that temperature above which the alloy, if already in the disordered state, remains in that state" [11], then both resistivity and saturation results indicate a critical temperature of about 490° C, in accordance with the published data.

The magnetic saturation of the quaternary alloy also increases on annealing, and in a manner very similar to the resistivity. Saturation increases rapidly, attaining its maximum value after about 40 min, further anneals having no effect. The change in saturation is always positive and its maximum value occurs at about 400° C. This appears contrary to the work of Jackson and Lee [1], where the saturation of a cold-rolled alloy was decreased by annealing. However, the experimental errors in their work were quite large (±2%) and they pointed out that the total change was within these limits.

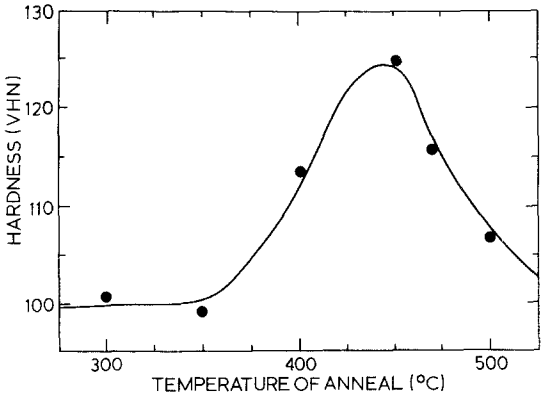

Figure 5 Hardness of the binary alloy as a function of annealing temperature (5 h at each temperature).

3.3. Hardness

Hardness values were measured using a Vicker's Hardness Machine with a load of 20 kg. By taking adequate care over the measurements, testing each specimen at ten different positions along its length and then finding the mean value, the reproducibility was found to be ±2 VHN, i.e. about ±2%.

The hardness was initially measured on a quenched specimen of the binary alloy, and then on specimens which had been annealed for 5 h at various temperatures. The maximum change in hardness was about 25% and occurred after annealing at a temperature between 440 and 450° C. This is in good agreement with the previous resistivity and saturation results.

In the quaternary alloy hardness was measured at three stages in the heat treatment cycle: (a) after the initial quench, (b) after a 3 h anneal at 400° C, and (c) after a subsequent disordering heat treatment, i.e. the "annealed" specimen was further heat treated for 2 h at 1000° C and then quenched

through the ordering range, as described earlier. The value of the Vicker's Hardness in each case was: (a) 111 VHN, (b) 143 VHN, and (c) 107 VHN. The hardness is observed to increase by about 30% on annealing, in good agreement with the results for the binary alloy. Also, considering the reproducibility of these tests, the hardness appears to return to its original value after the re-quenching heat treatment.

4. Discussion

The resistivity results have shown conclusively that the "K-effect" does occur in this alloy of Ni–Fe–Cu–Mo; the resistivity increases by about 2% in marked contrast to the 23% decrease found with the binary alloy after a comparable heat treatment. Pfeifer [21] has shown that the K-state in a Ni–Fe–Mo alloy is due to atomic ordering and he suggests that the drop in resistivity normally accompanying order is masked by some other effect.

It has been reported that the annealing atmosphere may have some effect on the formation of order in Ni–Fe [22–24] and, therefore, on magnetic properties. Consequently, some of the resistivity experiments were repeated on the binary and quaternary alloys, but with the specimens annealed under vacuum. No difference was found between vacuum-annealed specimens and those annealed under pure dry hydrogen. Also, a careful investigation was carried out using metallographic and X-ray diffraction techniques. No evidence was found of any phase change, precipitates, or any other metallurgical changes in the quaternary alloy after the formation of the "K-state". It would thus appear that the masking referred to by Pfeifer is not some simple metallurgical factor.

The hardness of quenched specimens of the quaternary alloy was found to increase after annealing at 400° C, and returned to its original value after a further high temperature heat treatment. This is characteristic of the behaviour found with the binary alloy on the formation of Ni_3 Fe and seems to suggest that the change in the quaternary alloy is basically due to the formation of atomic order. The reversible nature of this change is a further indication of an order–disorder phenomenon. The magnetic saturation of the quaternary alloy increased by a maximum of about 2.7% after annealing and this is very similar to the change in saturation in the binary alloy. The maximum changes do not occur at the same temperature, but the temperature ranges over which a change in saturation occurs are clearly very similar. Also, the temperature ranges over which resistivity changes occur correspond closely.

Apart from Figs. 2 and 4, the similarity between the two sets of results is quite marked. It is suggested, therefore, that the basic phenomenon occurring in the quaternary alloy is the same as that in the binary alloy, i.e. the formation of atomic order. Slight differences in the results for the two alloys, such as the temperature of maximum change, may then be explained as a change in the critical ordering temperature due to compositional differences [25]. Iida [15–18] has pointed out that relatively long times (>10 h) are necessary for the formation of long range order, as observed in Figs. 1a to d. The changes which produce the "K-state" occur in substantially shorter periods and can, therefore, only be associated with short range order. Work carried out on the temperature dependence of the magnetic saturation of Ni–Fe–Mo alloys has shown that two different Curie temperatures can exist [2, 26]. One is associated with the disordered state and the other, 100° C higher, with the ordered state. It was proposed that the order existing in this alloy was entirely short range and that in the solid solution there exist "complexes", i.e. very small regions of short range order. These regions of highly localized order would be separated by large boundaries of disorder, giving a net long range order of zero, in accordance with results of neutron diffraction experiments [27]. It is now proposed that this model be extended to the quaternary alloy at present under investigation.

The coefficient of thermal expansion is different for solid solutions in various states of order [2]. Thus the "complexes" should give rise to regions of internal stress. These would be randomly distributed over the matrix and should not affect the magnetic saturation. They could, however, cause an increase in resistivity. It is possible that these "complexes" are the source of the residual internal stress (and consequent anisotropy) said to prevent the development of infinite permeability in alloys near this composition [28]. If this interpretation is correct then it should theoretically be possible to detect the resultant internal stresses by the broadening of X-ray diffraction lines. This work was attempted using a CoK_α radiation source, the Debye–Scherrer diffraction method and a Wooster

Microdensitometer. No consistent variation was found in the half-widths of the lines after annealing in the range 350 to 520° C. The internal streses (σ) constitute an effective anisotropy of magnitude $\frac{3}{2}\lambda_s\sigma$, where λ_s is the saturation magnetostriction [28]. This effective anisotropy has been estimated to be of the order of $10\,J\,m^{-3}$ for a quaternary alloy similar to that used in this work [10], while $\lambda_s \simeq 3 \times 10^{-7}$ [1]. These values give a calculated internal stress of approximately $2.2 \times 10^7\,N\,m^{-2}$. In practice the limits of error in measurement of internal stress by the X-ray techniques reported here are of the order of $\pm 6 \times 10^7\,N\,m^{-2}$ [29]. The observed lack of line broadening may thus be due to a lack of sensitivity of the apparatus used and is not necessarily an indication that the internal stresses were not being developed.

5. Conclusions

Resistivity measurements have shown the existence of the "K-state" in the alloy 79 wt% Ni–16 wt% Fe–4.3 wt% Mo–0.7 wt% Cu. By comparing the changes in resistivity, magnetic saturation and hardness of the quaternary alloy and a binary 75 at. % Ni–25 at. % Fe alloy, both annealed in the temperature range 200 to 550° C, it is concluded that the "K-state" is associated with short range order. No evidence has been found to suggest the increase in resistivity is due to any metallurgical change in the alloy and it is proposed that the model for the ternary Ni–Fe–Mo alloy, involving small regions of highly developed order, be extended to this quaternary alloy.

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