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Magnetic hardening and anomalous behaviour of Vicalloy

I. JOFFE*
Department of Physics, University of Sheffield, Sheffield, UK

Thermomagnetic and X-ray measurements in the range $77K \leq T \leq 320K$ were made on an alloy in the Fe-Co-V system. It is shown that on quenching this alloy from 1050°C, bcc particles having diameters about 400 Å form martensitically. Ageing at 634°C stabilizes the particles and causes an ordering reaction to occur within them. Cooling this material below room temperature produces an appreciable increase in the saturation magnetization, and a large decrease in the coercivities H_c and H_R. The magnetic hardening and the anomalous behaviour are interpreted in terms of a model requiring the presence in the particles of ordered bcc cores surrounded by disordered bcc shells. At room temperature, the ordered regions are ferromagnetic, whereas the Curie temperature falls continuously as a function of increasing radius in the surrounding shells.

1. Introduction

High coercivity alloys belonging to the Co-Fe-V system have been the subject of considerable attention in the past, where attempts have been made to determine the factors and mechanisms responsible for the magnetic hardness. For classification purposes, this alloy system has been divided into two basic groups, depending upon the V-content: Those containing less than 11% V, known as the Vicalloy I alloys, and those consisting of 11 to 20% V, known as Vicalloy II.

Earlier workers found that a marked improvement in the magnetic hardness was obtained if severe cold-working preceded the final heat-treatment of Vicalloy. The phase diagram of these alloys was investigated by Martin and Geisler [1] who concluded that the ferromagnetic bcc phase could occur either in an ordered phase (α') or a disordered phase (α), and that these could co-exist under certain circumstances both with themselves and with the high temperature fcc γ-phase. It was implied that the magnetic properties could be due to the presence of fine particles of α'. Work done by Fountain and Libsch [2] showed that increasing additions of V to Fe-Co alloys lowered the α-γ transformation temperature, thus promoting the formation of the non-magnetic γ-phase at room temperature. Vanadium also decreased the rate of the α-ordering reaction. A later re-examination of the phase diagram of Co-Fe-V alloy systems enabled Köster and Schmid [3] to report the occurrence of a $\gamma \rightarrow \alpha$ martensitic transformation on quenching alloys containing less than 10% V from 1300°C, and Henkel [4] concluded that magnetic hardening of all Vicalloy alloys depends normally on the occurrence of a martensitic transformation. The magnetic behaviour of Vicalloy II was interpreted by Baran *et al* [5] in terms of the formation of fine particles of the magnetic bcc phase, having diameters of the order of 500Å and with a uniaxial anisotropy probably due to strains associated with the γ-α transformation. Replica electron micrographs of the precipitate structure confirmed the presence of small spheroidal particles.

The present work describes thermomagnetic measurements of an alloy in the Co-Fe-V system for which the behaviour of the magnetic properties as a function of the measurement temperature was anomalous. An attempt is made in the discussion of Section 4 to explain the observed anomalies in terms of a simple phenomenological model.

2. Experimental

Cylindrical specimens of length 9 mm and diameter 2 mm, having rounded ends, were

*Present address: Physics Department, University of the Witwatersrand, Johannesburg, South Africa.

made from an alloy with atomic composition 52.1% Co, 35.2% Fe and 12.7% V. These were homogenized in a small pressure of argon for 360 h at 1050° C, after which they were quenched in cold water. Cumulative ageing at 634°C in argon then followed, each ageing period being followed by a water quench.

Magnetic measurements were made mainly over the temperature range 80K $\leqslant T \leqslant$ 300K, although the upper limit was extended occasionally to 340K to check on higher temperature behaviour. The properties measured were the saturation magnetization (σ_S), the coercivity (H_C), being the reverse field required to reduce the magnetization to zero and the remanent coercivity (H_R), being the reverse field which, when removed, produces a zero remanent magnetization state. The remanence (σ_R) is the magnetization found at zero applied field after having previously saturated the sample. σ_R values were not corrected for demagnetizing effects. For convenience of presentation, cgs units are used. Conversions to S.I. are: 1 Oe = 79.6 Am^{-1}, 1 emu = $4\pi \times 10^{-7}$ Wb.m.

Magnetic measurements were made using a ring balance. The maximum applied field was 3.2 kOe and σ_S was taken to be the magnetization at this field value. A plot of σ versus 1/H showed that this agreed to better than 1% with the true saturation magnetization.

X-ray diffractometer measurements were made with filtered Co$K\alpha$ radiation, using a flat slab of the alloy having dimensions 2 mm × 1 mm × 20 mm. This sample was given heat-treatments similar to the magnetic test-pieces, and was etched deeply in aqua-regia prior to installation in the diffractometer. Changes of the relative volume fractions of fcc and bcc phases present were estimated from the relative changes of the integrated intensities of the fcc (111) and bcc (110) lines, which were adjacent to each other.

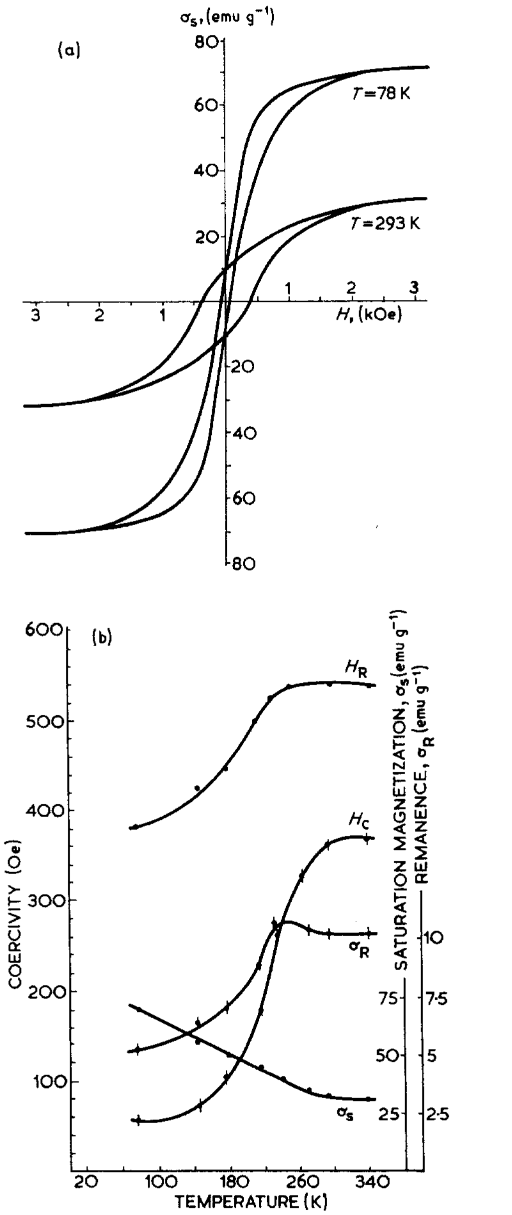

Figure 1 Magnetic behaviour of Vicalloy after ageing for 50 min at 634°C. (a) Magnetization loops at 78 and 293K. (b) Magnetic properties as a function of temperature.

3. Observations

In the temperature range 80K $\leqslant T \leqslant$ 300K, the magnetic properties of the alloy studied proved to behave anomalously in that large decreases of H_C, H_R and σ_R occurred on cooling, while σ_S increased almost linearly. These changes were associated with the development of "wasp-waisted" hysteresis loops. Typical behaviour of the parameters is shown in Fig. 1a and b, which corresponds to the state of optimum H_C at room temperature.

For temperatures greater than about 320K, the anomalous behaviour disappeared, and variations of the parameters shown in Fig. 1 became normal. It was found that specimens aged at 634° C for periods greater than about 20 min exhibited reversible behaviour of the type shown in Fig. 1b, while for ageing times less than this, reversibility could be established by traversing the cooling cycle a few times. Thus, a connection exists between the magnetic behaviour and the state of metallurgical equilibrium.

The results presented below are of great complexity, and in the interest of clarity, general inferences will be drawn in the following subsection, a working hypothesis will be made in Section 3.2, and subsequent observations will be discussed in terms of this.

3.1. Saturation magnetization (σ_s) and X-ray observations

The $\sigma_S - T$ curve shown in Fig. 1 was similar in form to those found for all ageing times. The time development of σ_S at various measurement temperatures is shown in Fig. 2 from which it

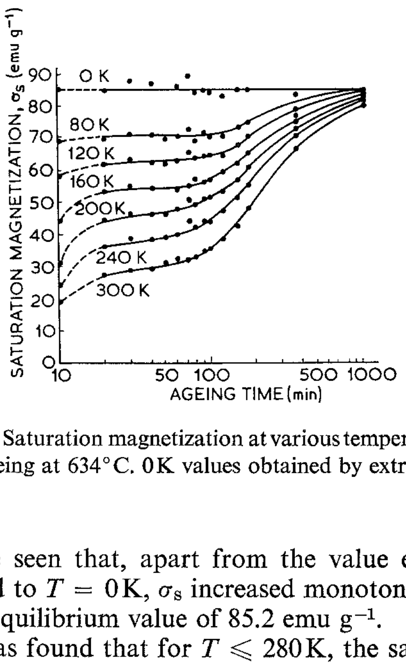

Figure 2 Saturation magnetization at various temperatures after ageing at 634° C. 0 K values obtained by extrapolation.

will be seen that, apart from the value extrapolated to $T = 0$ K, σ_S increased monotonically to an equilibrium value of 85.2 emu g^{-1}.

It was found that for $T \leqslant 280$ K, the saturation magnetization for any one ageing time varied linearly with the temperature. In general, for ageing times less than about 20 min, the curve of Fig. 2 could be represented fairly accurately by

$$\sigma_S(T, t) = 85.2 - a(t)T. \text{ emu g}^{-1} \qquad (1)$$

where t is the ageing time in minutes. Here $a(t)$ is a positive monotonically decreasing function given by

$$a(t) = 0.205 \exp\{-(t/\tau)^{3/2}\} \text{ emu g}^{-1} \text{ K}^{-1} \qquad (2)$$

where the time constant $\tau \approx 310$ min. For temperatures greater than 280 K, σ_S began to flatten off, and at 320 K variations in σ_S were small in accordance with a material having a Curie temperature (T_C) in the neighbourhood of 1000 K. Experimental points for short ageing times (10 min) carry large relative errors because metallurgical stability is not yet established (cf. below). Consequently, these points deviate from the given expressions.

Following Baran *et al* [5], it is assumed that the room temperature magnetization originates in the ordered α' phase. This is confirmed by the Mössbauer work done by Gorodetsky and Shtrikman [6]. σ_S (300 K, t) is, therefore, proportional to the α' volume fraction and it is found that

$$\sigma_S(300, t) = a + b[1 - \exp\{-(t/\tau)^{3/2}\}] \qquad (3)$$

with $a = 27.1$ emu g^{-1}, $b = 58.1$ emu g^{-1} and $\tau \approx 310$ min. The values of a and b do not follow from Equations 1 and 2 since 300 K lies outside their range of validity. Equation 3 is similar to an expression derived by Ham [7] for the growth by diffusion-limited processes of spheroidal and ellipsoidal particles whose axial ratios are not too different from unity. It is to be concluded, therefore, that on ageing at 634° C, diffusion-limited growth of the ordered bcc phase (α') takes place.

The existence of large reversible temperature-dependent variations of σ_S which vanish when measuring above a threshold temperature to reveal stable ferromagnetic behaviour indicates the presence of two distinct ferromagnetic structures in this material. The flat, higher temperature region of the σ_S-curve must be due to a phase (α') having $T_c \approx 1000$ K, in accordance with the observations of Baran *et al* [5], while the varying lower temperature region must originate in an inhomogeneous metallurgical phase containing a continuous range of Curie temperatures with an upper limit of about 320 K. As will be seen below, strong evidence exists for the disordered α-phase to be the phase containing this range of Curie temperatures.

X-ray diffraction measurements showed that all specimens quenched to room temperature from 1050° C contained the high temperature fcc phase (γ) together with varying amounts of bcc material. Intensity measurements showed that the volume ratio of bcc to fcc material could be increased almost irreversibly by more than 200% either by cooling the quenched specimen to liquid nitrogen temperature or by cold-working it. Such rapid large scale transformations at low temperatures can only take place by means of diffusionless processes, and this confirms the existence of the $\gamma \rightarrow \alpha$ martensitic transformation reported by Henkel [4].

It was also found that the room temperature saturation magnetization was markedly increased either by cooling an as-quenched specimen to liquid nitrogen temperature or by cold-working it. In view of the above comments, and since the bcc phase forms at the expense of the fcc, it is concluded that the bcc phase is the ferromagnetic phase in this alloy.

X-ray and magnetic measurements showed that the $\gamma \rightarrow \alpha$ phase transformation was strongly inhibited by ageing at 634°C. For example, after cooling an as-quenched sample to 77K for the first time, an irreversible increase of about 235% was observed in the bcc volume fraction; ageing an as-quenched sample for 15 min at 634°C prior to first cooling to 77K caused this increase to be reduced to less than 10%, and specimens aged for longer periods exhibited negligible changes in the bcc volume fraction when cooled to 77K for the first time. It would appear, therefore, that ageing at 634°C had the effect of "locking-in" the martensitically formed bcc distribution, thus preventing further growth of this phase but allowing an ordering reaction to proceed within it. That is, α' grows at the expense of α. Furthermore, from Equations 1 and 2, it will be seen that

$$\sigma_S(0, t) = \sigma_S(T, t \rightarrow \infty)\,, \tag{4}$$

implying that the total amount of ferromagnetic material having all possible Curie temperatures is constant as ageing proceeds. The evidence, therefore, points strongly towards the disordered α-phase containing a range of Curie temperatures, presumably due to variations in the degree of order or fluctuations of composition induced by the internal ordering reaction which takes place at intermediate ($\approx$ 650°C) temperatures.

From X-ray line-width measurements of quenched samples, it was concluded that the bcc phase was present at room temperature as particles of diameter about 400Å. It was found that a rapid quench from 1050°C to room temperature produced a distribution consisting of a high density of such small particles, while lower quench rates produced larger magnetic particles. This is not surprising in view of the manner of formation of the magnetic particles and it is to be expected, therefore, that the initial quench rate plays a primary role in determining the ultimate performance of a Vicalloy magnetic material.

3.2. A proposed model

In the sections to follow, the observations will be interpreted in terms of a model based primarily upon the results of the preceding section and various aspects of this model will be amplified as the need arises.

The hypothesis is that, because of the practical impossibility of an infinite quench rate (which would produce martensitic particles of uniform disordered composition), a limited ordering reaction occurs so that the martensitically formed bcc particles consist of small ellipsoidal cores of ordered α'-material with $T_C \approx$ 1000K, surrounded by a shell of disordered α-phase. This shell contains order or composition variations such that T_C decreases continuously outwards from a value of about 320K at the $\alpha - \alpha'$ interface, to effectively 0K at the particle surface. This is shown diagrammatically in Fig. 3. Since

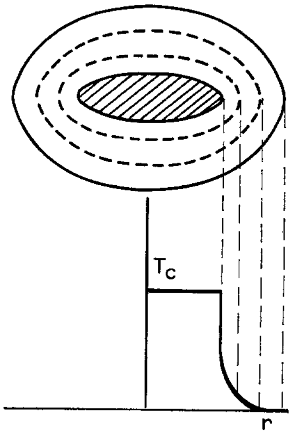

Figure 3 Schematic diagram of variation of Curie temperature within a bcc particle. Shaded area is ordered phase.

the composite particles have diameters $\approx$ 400Å, it is reasonable to assume that the α'-cores are of single domain or sub-domain size, and that much of the magnetic behaviour conforms to the theory of Stoner and Wohlfarth [8].

For the purposes of this model, it will be further assumed that in the disordered shell, while T_C might be strongly dependent upon the degree of order or composition, the spontaneous magnetization of any region for which $T < T_C$ is not very different from that of the α'-core. In terms of this, cooling below room temperature leads to an increase in the size of the magnetic regions of the particles and this produces a rapid decrease of the magnetic hysteresis. The mechanisms by which this might occur will be discussed in the following section.

3.3. The coercivity, H_c

On cooling below room temperature, a very marked decrease of H_c was observed, typified by the behaviour shown in Fig. 1. The variations of H_c at seven measurement temperatures in the range $80\,K \leqslant T \leqslant 300\,K$ is shown in Fig. 4 as a

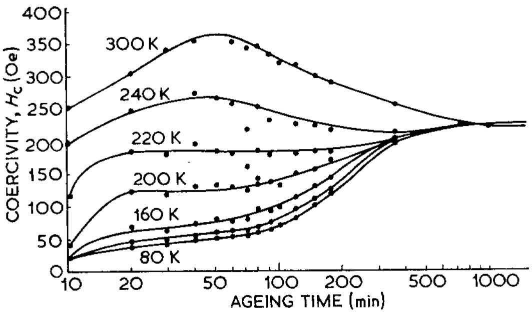

Figure 4 Coercivity at various temperatures after ageing at 634° C.

function of the ageing time. It will be seen that above 220K, normal magnetic hardening curves were obtained in that H_c increased from an initially low value to a maximum (368 Oe at 300K) after ageing for about 50 min, and subsequently decreased to an equilibrium value corresponding to the state of over-ageing. Below 220K, no intermediate maximum of H_c was found and H_c increased monotonically to an equilibrium value of about 220 Oe. It will also be seen from Fig. 4 that the extent of the anomalous behaviour of H_c, represented by the differences of the value at 300K and at 80K, decreased as the ageing time increased, eventually vanishing after about 800 min. For even longer ageing times, normal behaviour set in, as is evidenced by the fact that at 80K, H_c was greater than the room temperature value. In this over-aged state, the coercivity varied linearly with temperature in the temperature range considered.

The observations are consistent with the model proposed in Section 3.2 if one realizes that, in the as-quenched state, many of the α'-cores may be small enough to behave in a super-paramagnetic manner at room temperature. Growth of these regions due to the bcc ordering reaction leads to the establishment of a magnetically hard array of single domain particles, and still further ageing causes these regions to grow to sizes permitting easier magnetization reversal.

The mechanisms by which the increase in the sizes of the magnetic regions leads to an easing of the magnetization reversal is rather obscure. It could be that the sizes become large enough to allow domain walls to form in these regions, or magnetization curling might occur (Frei *et al* [9]). Alternatively, magnetization rotation in unison might take place for the entire range of particle sizes, but associated with the increase in the volume of the magnetic regions is a decrease in the uniaxial anisotropy. This possibility will be discussed further in Section 4.

That an increase of the size of a magnetic core produces magnetization reversal at lower fields is shown by the very large drop of the ensemble coercivity (H_c) on cooling. Since it is the larger particles which are assumed to reverse for small applied fields, the ensemble magnetic moment would be reduced to zero quite rapidly, thus depressing H_c severely.

3.4. The remanent coercivity, H_R

The behaviour of H_R at 80K and 300K is shown as a function of ageing time in Fig. 5, from which

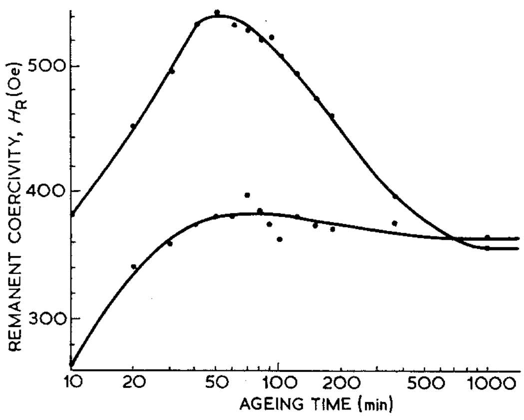

Figure 5 Remanent coercivity for ageing at 634° C.

it will be seen that H_R (300K) exhibited a maximum of 548 Oe after ageing for 50 min at 634° C. This ageing time corresponds to that required for optimum H_c at room temperature.

It will also be seen from Fig. 5 that the low temperature value of H_R rose sharply initially on ageing and was reasonably constant thereafter. In the state corresponding to optimum room temperature magnetic hardness, the coercivity ratio (H_R/H_c) had values 1.49 at 300K, and rose to 7.3 at 80K. These values are appreciably greater than 1.094, predicted by Stoner and Wohlfarth [8], and strongly suggest the presence of large magnetically soft particles in addition to the hard single domain array. These soft particles become more predominant as the temperature decreases. This is supported by the observed behaviour of the relative remanence which, in the optimum state, had a value 0.34 at 300K and decreased to 0.07 at 80K. On ageing to equilibrium, these two ratios converged on 0.28.

4. Discussion

From the observations and comments presented in the preceding sections, it would appear as if the magnetic hardening and anomalous temperature dependence of the magnetic properties of this Fe-Co-V alloy can be explained, qualitatively at least, in terms of a model possessing the following features:

(a) particles of the bcc phase form martensitically in the fcc matrix on quenching from 1050°C;

(b) the quench rate determines the distribution of the bcc particles, rapid quenching favouring the formation of a high density of small particles;

(c) these particles consist of an ordered core surrounded by a shell of disordered material;

(d) at room temperature and above, only the ordered cores of these particles are ferromagnetic, but the disordered shells contain a continuous range of Curie temperature so that, on cooling below room temperature, the magnetic volume of the bcc particles increases;

(e) associated with the temperature induced increase of magnetic region size is a rapid decrease of the individual coercivities of the particles;

(f) ageing at 634°C has the effect of inhibiting further martensitic transformation, and causes the ordering reaction to proceed in the bcc particles.

It remains for this model to be placed on a quantitative basis, and this can be done in terms of a phenomenological approach. It would seem reasonable to regard the bcc particle system as comprising an array of magnetic particles distributed in the γ-phase matrix with random orientations and having sizes distributed about some mean value dependent upon the temperature.

We assume that the magnetic ensemble consists of two distinct classes of magnetic particles: those which are magnetically hard and those which are magnetically soft. Membership of these classes is determined by the magnetic particle size so that a given particle might change its class of behaviour on altering its size. In terms of the suggested model, such size changes could be produced either by altering the temperature ($T <$ room temperature) or by growth of the ordered cores ($T >$ room temperature).

Let the magnetic volume fraction of the hard sub-assembly be α, and that of the magnetically soft sub-assembly, β. If the spontaneous magnetization of the ferromagnetic material is σ_0, we have

$$\sigma_S = (\alpha + \beta)\sigma_0 \,. \tag{5}$$

We assume that the hard sub-assembly behaves in accordance with Stoner-Wohlfarth theory [8] and that the soft sub-assembly exhibits constant relative susceptibility (χ) for applied fields less than about 400 Oe, and contributes nothing to the remanence of the assembly.

In terms of the above, the remanence at zero internal field (σ_R') originates only in the hard sub-assembly and is given by

$$\sigma_R' = \tfrac{1}{2}\,\alpha\,\sigma_0 \,. \tag{6}$$

Similarly, the remanent coercivity results from the hard sub-assembly only. In the Stoner-Wohlfarth theory, the reduced fields (h) are proportional to the applied fields (H), the constant of proportionality depending upon the anisotropy present. In this theory, the (reduced) remanent coercivity is $h_R = 0.524$; thus for the present mode, the proportionality constant is $0.524/H_R'$ and the reduced fields may be expressed as

$$h = 0.524\,(H/H_R') \,. \tag{7}$$

H_R' is the remanent coercivity corrected for demagnetization effects.

For small reverse fields, the Stoner-Wohlfarth demagnetizing curve is approximately linear and may be written as

$$i(h) = 0.5 + 0.8\,h \,. \tag{8}$$

The range of validity of this approximation is $0 \geqslant h \geqslant -0.28$, which may be expresssd in terms of the applied field as $|H| \leqslant 0.534\,H_R'$ by substituting in Equation 7.

Thus, from Equations 7 and 8, the contribution to the assemble magnetization arising purely from the hard sub-assembly, for $|H| \leqslant 0.534\, H_R'$, is

$$\sigma_\alpha(H) = \alpha[0.5 + 0.419\, H/H_R']\sigma_0 \tag{9}$$

while the soft sub-assembly contributes

$$\sigma_\beta(H) = \beta H \sigma_0 \chi\,. \tag{10}$$

The volume fractions α and β are obtained from Equations 5 and 6, and the ensemble magnetization is given by

$$\sigma(H) = \sigma_\alpha(H) + \sigma_\beta(H)\,. \tag{11}$$

The coercivity is the field $H = -H_c$ satisfying $\sigma(H) = 0$. This yields

$$\left(\frac{1}{H_c} - \frac{0.838}{H_R'}\right) = \chi\left(\frac{\sigma_s}{\sigma_R'} - 2\right), \tag{12}$$

which relates the four parameters without taking account of the effect of demagnetizing fields. To a first order approximation, these may be introduced by approximating the observed magnetization loops to straight lines of slope (σ_R/H_c) in the region of low fields ($|H| \langle \approx H_c$). Then, if D is the specimen demagnetizing factor and ρ the specimen density,

$$\sigma_R' = \sigma_R H_c/(H_c - \rho D \sigma_R) \tag{13}$$

and

$$H_R' = \rho D \sigma_R + H_R(H_c - \rho D \sigma_R)/H_c \tag{14}$$

where σ_R and H_R are the uncorrected measured values.

Setting $\rho = 8$ g cm^{-3} and $D = 0.7$, experimental data were inserted into Equation 12 with the appropriate substitutions from Equations 13 and 14. Fig. 6 shows the resulting fit for a specimen aged for 60 min at 634°C; this was typical of the fit obtained for all ageing times. Thus, apart from a small ($\approx 1.4 \times 10^{-3}$ Oe^{-1}) reasonably constant offset (presumably due to thermal effects), the relationship predicted by Equation 12 is verified and it is to be concluded that the complex behaviour of the magnetic properties of this alloy may be represented reasonably well by suitable superpositions of Stoner-Wohlfarth single domain behaviour and linear, very soft magnetization loops.

By fitting the magnetic data to Equation 12, it was found that the relative susceptibility (χ) of the soft sub-assembly was constant to within 5% over the entire range of ageing times examined. The mean value of χ was 4.38×10^{-3} Oe^{-1}. A particle having demagnetizing factor, N, and density, ρ, has a relative susceptibility

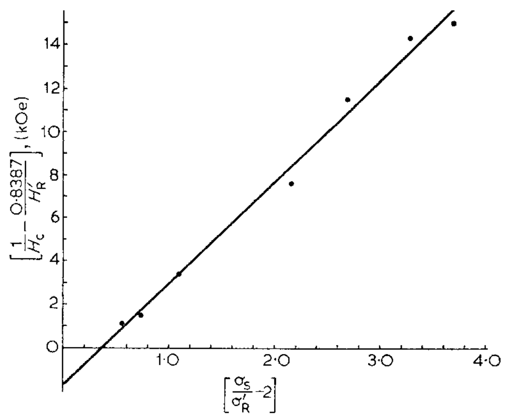

Figure 6 The function $\left[\frac{1}{H_c} - \frac{0.838}{H_R'}\right]$ versus $\left[\frac{\sigma_s}{\sigma_R'} - 2\right]$, after ageing at 634°C for 60 min. H_R' and σ_R' defined in Equations 13 and 14.

(defined by Equation 10) of $\chi = 1/N\rho\sigma_0$ if it is composed of a truly soft material. Using the above value of χ and putting $\rho = 8$ g cm^{-3}, $\sigma_0 \approx 200$ emu g^{-1}, one obtains $N \approx 0.14$. Thus, assuming the magnetic particles to be present in the form of prolate spheroids, this value indicates an axial ratio of approximately 15/1, which places the model within the bounds of physical possibility and agrees with the observed needle-like precipitates reported by Tufton and Nicholson [11].

It seems, therefore, that the proposed model for the structure of the magnetic precipitates in this ternary alloy accounts for the observed behaviour in a reasonably satisfactory manner, and that the treatment given above, while crude in its over-simplification of what is obviously a complicated problem, does contain some grains of truth. Of the assumptions made, the most difficult to justify is the reason why an increase in volume associated with cooling should lead to a softening of the magnetic behaviour. As mentioned in Section 3.3, this could be due either to a transition from single domain behaviour to processes involving domain walls, or to a reduction of the magnetic anisotropy on cooling the system of single domain particles. Baran *et al* [5] have shown that magneto-crystalline anisotropy plays no significant part in these alloys, while Müller and Schmidt [10] ruled out strain anisotropy because of the absence in these alloys of strains due to the formation of precipitates.

If, on cooling below room temperature, the magnetic particles remain as single domains, the present results can best be understood in terms of a uniaxial shape anisotropy in these particles. From the observed behaviour of the room temperature coercivity, and the fact that ageing at 634°C produces only a growth of the ordered bcc cores in their disordered surrounding shells, this assumption implies the formation of ordered cores having prolate ellipsoidal shapes inside ellipsoidal shells which are less prolate. This situation is shown schematically in Fig. 3, and it will be seen that growth of the ordered cores, or increasing the sizes of the magnetic regions by cooling would both decrease the anisotropy. Obviously, an examination of the microstructure of these materials by transmission electron microscopy would be a valuable aid in understanding the observed behaviour, particularly since the ordering reaction might then be studied in greater detail. In the present work, great difficulty was experienced in the preparation of thin films and no satisfactory micrographs of this material were obtained. However, the formation of small needle-like precipitates in Vicalloy has been observed by Tufton and Nicholson [11], and Fahlenbrach [12] reports the presence of more spherical particles. At present, the nature of the anisotropy and its behaviour in the processes described can only be inferred in a most indirect manner.

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