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Study of Co-Fe-V Permanent Magnet Alloys (Vicalloys)

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The historical development of Co–Fe–V permanent magnet alloys (vicalloys), their technological importance and scientific study, are reviewed. The basic, as yet unsolved, problem of the origin of their magnetic hardness is examined.

Results of recent work employing Mössbauer spectroscopy and magnetic measurements at different temperatures, as well as some X-ray and electron-optical analysis, are presented and discussed. Mössbauer spectroscopy established the fact that vicalloy in the permanent magnet state is composed of two phases: ordered ferromagnetic α' (bcc, ferrite) and paramagnetic γ (fcc, austenite). Samples quenched from the high temperature γ field consist almost entirely of retained austenite. However, on cooling to cryogenic temperatures (liquid and solid nitrogen, 60 to 80° K), or by cold work, some of it is transformed irreversibly into disordered ferromagnetic α. This is confirmed by magnetic measurements in the cryogenic range; the results were inconsistent with a previously postulated model based on a reversible paramagnetic γ to ferromagnetic γ transition or on some superparamagnetic process. The measurements, when correlated with Mössbauer data, confirm that the phase transition is not accompanied by any change in iron content of the phases.

An interesting change in magnetic anisotropy of flat, thin samples following cold-work and heat-treatment for optimum permanent magnet properties was confirmed by Mössbauer spectroscopy.

X-ray diffraction confirmed the above findings on the phase structure of vicalloy and no direct evidence was found for a third metastable phase, intermediate between α and γ, which was proposed by Henkel to account for the magnetic hardness of vicalloy. However, one unidentified diffraction line in the X-ray pattern of optimum heat-treated vicalloy calls for more attention to this postulate. Electron microscopic results did not remove the existing ambiguity as to the rôle of shape anisotropy in promoting magnetic hardness of vicalloy. On the other hand, a possible contribution by crystalline anisotropy is suggested by some electron diffraction patterns.

1. Historical Introduction

For more than fifty years, iron-cobalt alloys have been known to attain higher magnetic saturation than their pure constituents [1]. Their commercial application, however, was not pursued until the late 1920's.

In 1929 a USA patent was granted to Elmen [2] on the 50% iron – 50% cobalt composition which was intended for construction of small magnetic pole-pieces of sound recorders, loudspeakers and earphones of deaf-aid sets. However, fabrication problems were immediately encountered owing to the hardness and brittleness of this material.

An empirical research programme was soon started at the Bell Telephone Laboratories in an attempt to overcome this lack of workability. White and Wahl made systematic additions of high melting point metals, thus finding [3] that 2 to 4% vanadium improved the machineability without considerably affecting the magnetic remanence of these equiatomic Fe–Co alloys.

Kelsall and Nesbitt [4] continued this work, finally developing, in 1940, machineable permanent magnets composed of 30 to 52% iron, 36 to 62% cobalt and 6 to 16% vanadium. These were named *vicalloys* [5], and displayed typical values of 9000 Gauss for remanence, 300 Oersted for coercivity and 10^6 Gauss-Oersted (1 MGO) for maximum energy product $(BH)_{\max}$. The manufacturing process consisted of annealing at 800 to 1300° C, quenching to room temperature or below, heat-treating for several hours at about 600° C, and magnetising. In 1942 Nesbitt [6] introduced a cold-working stage before the final heat-treatment. This step raised the maximum energy product $(BH)_{\max}$ to about 3×10^6 Gauss-Oersteds in the case of alloys containing 12 to 16% vanadium, 52 ± 5% cobalt, balance iron.

Full results of the study which led to the above patents were not published until after World War II [7]. The equilibrium structure of vicalloy at room temperature was found to be body-centred cubic (α-phase or ferrite), and at high temperatures (above 800° C) face-centred cubic (γ-phase or austenite). The α-phase is ferromagnetic whereas γ is paramagnetic. Heat-treatment at about 600° C, which is in the two-phase $(\alpha + \gamma)$ region, results in precipitation of fine γ particles in the α matrix. This fine dispersion of the two phases was believed to cause the observed mechanical and magnetic hardness.

Additions of vanadium lower the $\alpha \rightleftharpoons \gamma$ equilibrium temperature. At higher vanadium concentrations (above about 12% V) some γ is even retained after quenching to room temperature. Cold-work transforms this γ into ferromagnetic α, thus raising the magnetisation of these vanadium-rich alloys, which were designated vicalloy II (as opposed to vicalloy I of lower vanadium content and smaller sensitivity to cold work).

In 1952 Martin and Geisler [8] of the GE Research Laboratory, questioned Nesbitt's interpretation of the hardening phenomena. They proposed ordering of α rather than precipitation of γ as a more probable explanation. The superlattice of ordered α was detected by filtered cobalt Kα X-ray diffraction, and the disordering temperature (about 700° C) was found by inverse rate thermal analysis.

Fountain and Libsch [9] of Lehigh University in 1953 published accurate lattice parameters of the two phases comprising vicalloy: $a_\alpha = 2.860$ Å, $a_\gamma = 3.575$ Å. Ordering was found to occur in the 600 to 700° C range. The lattice parameter of α increased with vanadium content until γ began to form; thereafter it started to decrease. This was interpreted to mean that vanadium dissolves more readily in the face-centred (γ) phase.

The use of vicalloy has spread to Europe, especially Germany, under the names Koerzit, Koerflex and Gaussit [10, 11]. Part of the vanadium was replaced by less expensive chromium. A series of papers describing results of magnetic and other studies of these materials has been published by Fahlenbrach's group at Krupp Widia-Fabrik (Essen) during the past decade [12-17]. Their main, though unsuccessful, effort was to discover the origin of the internal anisotropy responsible for the magnetic hardness of vicalloy.

The possibility of uniaxial strain anisotropy, which was believed at first [12, 13] to be a by-product of γ precipitation, had to be abandoned after East German workers had shown by X-ray measurements that γ formation did not cause residual strains in vicalloy [18, 19].

Shape anisotropy is difficult to accept (or discard) owing to contradictory electron microscopic results: Fahlenbrach *et al* [10, 17] reported equiaxed morphology which eliminates shape anisotropy, whereas Tufton and Nicholson [20] claimed a morphology of needle-like fine particles which could definitely lead to shape anisotropy.

Two other facts were difficult to explain: (*i*) The anisotropy energy was found to be quite high (about 10^5 erg/cm^3 in the optimum permanent magnet state) [13], whereas the coercive force was relatively low (around 300 Oersted). (*ii*) The direction of the easy magnetic axis in flat samples of vicalloy was found [14] to be perpendicular to the plane of the sample following cold-work, but became parallel to this plane after the subsequent heat-treatment.

The latest attempt of Fahlenbrach [15] to explain all the above facts was to suggest the possibility of some anisotropy due to internal demagnetisation effects in the $(\alpha + \gamma)$ morphology of the permanent magnet samples.

An entirely different view of the "vicalloy problem" was taken by Henkel [21, 22] of East Germany. According to him, martensitic α needles are formed in the first quenching treatment owing to a diffusionless (martensitic) $\gamma \rightarrow \alpha$ transformation. Cold-work can also cause this reaction transforming the retained austenite (γ-phase) into martensitic ferrite (α-phase).

As had previous workers, he also noticed the order-disorder transition ($\alpha_0 \rightarrow \alpha_D$) above 400° C, but he dismissed its relevance to the magnetic hardness. Hardening of vicalloy I, according to him, starts at about 550° C through partial decomposition of γ into an intermediate metastable structure, which transforms into stable austenite (fcc) above 675° C. In vicalloy II, martensite is formed by cold-work and the subsequent heat-treatment causes precipitation and dispersion of small ferromagnetic α single domain particles in a non-magnetic matrix.

The intermediate phase was detected by Cr Kα radiation but its structure was not determined. It does not appear to be hexagonal martensite, neither is it $Co_3V(\gamma')$ nor any other known phase in the Co–Fe–V diagram; yet vanadium is considered to play an important rôle in it. Henkel speculates that the intermediate phase must be composed of single domain particles which lead to shape anisotropy, but he does not report any real findings to support this thesis.

For the past twelve years vicalloy has also been studied by a group of Soviet workers headed by Shur and Luzhinskaya at the USSR Institute of Metal Physics [23-28]. They concentrated on the relation between elastic stress and magnetic properties of elongated samples, finding that tensile stress increased the coercivity and remanent induction several times. Torsion increased coercivity but reduced remanent induction [23]. A "thermomechanical" treatment based on this phenomenon [24] led to an increase of about 25% in coercivity and up to 50% in the energy product of wire samples subjected to tensile stresses during their ageing.

Nesbitt, Willens *et al* [29] have recently succeeded in obtaining splat-cooled vicalloy samples of higher than usual coercivities (about 600 Oe). They have noticed a considerable difference in the magnetic moments of untreated samples at cryogenic and room temperatures: about 6000 Gauss at 1.4° K and 1000 Gauss at 300° K. The difference practically disappeared after the usual heat treatment (1 h at 600° C). They explained this phenomenon by the existence of superparamagnetic particles (about 50 Å in diameter) in the untreated samples. They proposed that a similar process might also be responsible for the magnetic properties of regular (not splat-cooled) vicalloy samples.

A recent contribution to the study of phase transformations in 52% Co, 40% Fe and 8% V alloys was made by the French worker Josso [30]. Essentially he re-established the correctness of the phase diagram proposed by Martin and Geisler [8].

Mössbauer spectroscopy was first used to investigate vicalloy samples by Gorodetsky and Shtrikman [31] of this laboratory. Paramagnetic absorption peaks were noticed in heat-treated samples lending support to the description of vicalloys as fine-particle magnets.

The present study was undertaken in order to re-examine some of the points which, as shown above, are still disputed in the literature. We have also hoped to reveal new facts which might help clarify the as yet unsolved problem of the origin of magnetic hardness in vicalloy.

The investigated vicalloy samples were kindly provided by various manufacturers and researchers. Table I lists all of them together with other pertinent data.

2. Examination Procedures

2.1. Resonant γ-ray Spectroscopy

Resonant γ-ray spectroscopy, better known as the Mössbauer effect, is a relatively recent*, but already widely accepted, technique for studying magnetic materials. It is particularly useful for investigating substances which contain Fe^{57} nuclei. Only the most essential features of this method will be presented here; fuller descriptions are available in several review articles and monographs [e.g. G. K. Wertheim, "Mössbauer Effect: Principles and Applications" (Academic Press, London & New York, 1964)].

The fundamental asset of resonant γ-ray spectroscopy is the extremely narrow linewidth (in terms of energy: 10^{-11} to 10^{-6} eV) of the radiation used. This consists of some γ-ray lines, in the range 1 to 100 keV, recoillessly emitted by excited nuclei decaying into their ground state. The lines are so very sharp that small energy shifts or splittings of the ground state or of the excited state are readily detectable.

Consider for instance the case of magnetic hyperfine interactions. The interaction of a magnetic field with the magnetic moment of the nucleus will remove the spin degeneracy of a nuclear state. Magnetic fields at the nucleus (H_i) are produced by the electrons of a paramagnetic

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*Discovered in 1958

TABLE I List of vicalloy samples.

No.	Symbol	Origin	Form and size	Heat treatment	Composition wt. %
1	VIC–TEL–01	D. N. Griffith, Telcon Metals Ltd, Crawley, Sussex, UK	flat rolled from 0.025 to 0.0025 mm	quenched from 1050° C (before cold-rolling to 0.0025 mm)	51 to 52 % Co, 10 to 11.7 % V, 0.4 to 0.7 % Mn, 0.4 to 0.7 % Si, balance Fe
2	VIC–TEL–02	,,	,,	2 h at 600° C (after cold-rolling)	,,
3	VIC–TEL–03	D. R. Driver, Telcon Metals Ltd	,,	flash-heated for ½ min at 640° C	,,
4	VIC–TEL–04	,,	,,	flash-heated for ½ min at 650° C	,,
5	VIC–TEL–05	,,	,,	flash-heated for ½ min at 660° C	,,
6	VIC–TEL–06	,,	flat, 0.25 mm thick	quenched from 1050° C (not cold-rolled thereafter)	,,
7	VIC–TEL–07	,,	flat rolled from 0.025 to 0.0025 mm	quenched from 1050° C (after cold-rolling to 0.0025 mm)	,,
8	VIC–ARN–01	S. P. Wilbur, The Arnold Flat Engineering Company	0.0025 mm thick	quenched from 950° C (before cold-rolling to 0.0025 mm)	52 % Co, 10 % V, 38 % Fe
9	VIC–ARN–02	,,	,,	1 to 4 h at 600° C	,,
10	VIC–PMA–01	M. McCaig, Permanent Magnet Association, Sheffield, UK	rectangular 7 mm × 35 mm × 43 mm	unknown	vicalloy II
11	VIC–PMA–02	,,	rod 4 mm × 85 mm cold-drawn	quenched from about 1000° C prior to cold-drawing	52.2 % Co, 12.9 % V, 0.4 % Si, 0.35 % Al, balance Fe
12	VIC–GE–01	F. E. Luborsky, General Electric Co, Schenectady, NY, USA	cold-drawn rod ϕ 2 mm × 45 mm	unaged	unknown
13	VIC–GE–02	,,	Rod ϕ 2 mm × 40 mm	1 h at 1200° C, oil quenched and aged for 8 h at 600° C	,,

ion. In undiluted paramagnetic substances the spin lattice relaxation is fast, thus averaging the field to zero. Therefore, and especially at higher temperatures, one will observe only one "central" peak in a γ resonant spectrum of a paramagnetic material, as for example in fig. 3a of this article. Magnetic (or Zeeman) splitting will be detected only in crystals exhibiting ordered magnetism (e.g. ferro-, antiferro- and ferrimagnets). In Fe^{57} the ground state will split into two levels and the first excited state into four. The allowed transitions between these Zeeman levels produce typical six-line patterns as found, for example, in metallic iron. Fig. 1b of this article shows a spectrum of another ferromagnetic material exhibiting six similar, although less sharp, "lateral" peaks, three on each side of the centre.

Resonant absorption will be observed only if the energy difference required in order to match the absorbing nuclei with the actually emitted radiation is somehow provided by the experimental set-up. Such matching is possible by applying a Doppler shift to the γ line. Relative velocities of the order of 1 to 10 mm/sec between emitter and absorber are in most cases sufficient to shift the lines over several linewidths and thereby account for all possible shifts and splittings due to the hyperfine magnetic interactions.

In the case of iron, Co^{57} is used as the radioactive source (it has a conveniently long half-life of 270 days). It is converted into Fe^{57} following electron capture and emission of 14.4 keV γ-rays. The latter represents a transition from the first excited state ($I = 3/2$) to the ground state ($I = 1/2$) of stable Fe^{57}.

Thin samples of vicalloy were investigated at room temperature employing a Mössbauer spectrometer which was developed in this laboratory [32] and is now commercially manufactured [33]. It employs an electromagnetic drive for moving the source (emitter) relative to the sample, and a proportional counter for measuring the intensity of the transmitted radiation. The results are recorded either by an x–y recorder (x for velocity and y for intensity of transmitted radiation) or by a multichannel analyser. Direct feeding of data into a digital computer (via a paper tape) is also available.

Additional Mössbauer spectra of several samples in the range of liquid nitrogen to room temperature were obtained with the same spectrometer equipped with a specially developed cryostat [34]. This attachment is now also commercially manufactured [35].

2.2. Magnetic Measurements

All magnetic measurements were performed in a locally constructed motor driven vibrating sample magnetometer. This is a modified version of an instrument originally designed by Flanders and Doyle [36].

Essentially two types of data were obtained: (*i*) M–H hysteresis loops, and (*ii*) magnetisation (σ) versus temperature (T) plots. In the latter case a glass cryostat was employed which enabled the sample to be cooled down to about 50° K (by vacuum pumping on liquid nitrogen) and reheated to above 300° K.

The first set of data yielded numerical values for saturation magnetisation (M_S), remanence (M_R) and coercive force (H_C). The second resulted in values for the magnetic moment per gram of material (σ) at typical temperatures.

2.3. Structural Analysis

X-ray back-reflection photographs were taken in order to detect possible effects of rolling on the texture of flat samples. It was thought necessary to make this crude check on the existence of preferred orientation before deciding to use elaborate quantitative detection schemes.

Lattice constants were measured employing the Straumanis powder diffraction camera. A very thin needle of the sample was inserted in place of the usual powder-filled capillary. Filtered Cobalt Kα radiation was used and the data were corrected and analysed with the aid of a special computer program.

Metallographic examination was performed employing optical and electron microscopy. The JEM-7 electron microscope was used in the latter case. Replication and transmission techniques were utilised. A two stage plastic carbon replica technique was found suitable for replication. For transmission, the Teflon holder technique, originated by Briers *et al* [37], was employed to produce circular electropolished specimens 3 mm in diameter.

3. Results

3.1. Mössbauer Spectra

Fig. 1 presents resonant γ absorption spectra of cold-worked Telcon vicalloy before (sample VIC–TEL–01) and after (sample VIC–TEL–02) heat-treatment for optimum permanent magnetic properties. Spectra of the flash-heated samples are shown in fig. 2. Quenched Telcon vicalloy (sample VIC–TEL–07) was studied in the Mössbauer spectrometer at room temperature before (fig. 3a) and after immersion in liquid nitrogen (fig. 3b).

From the spectra of fig. 1, as from those of VIC–ARN–01 and VIC–ARN–02 published previously [31], it is possible to deduce that a paramagnetic phase is formed in vicalloy by heat-treatment. (A splitting of the "central" paramagnetic peak is observed in VIC–TEL–02, in contrast to VIC–ARN–01 and the flash-heated

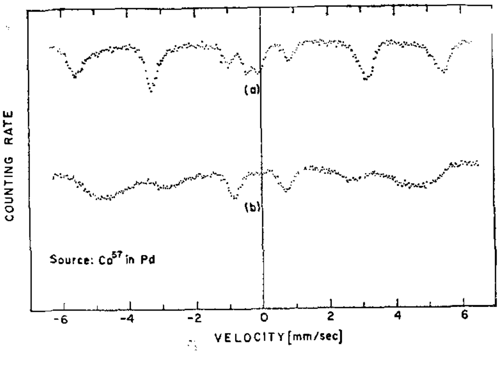


Figure 1 Mössbauer spectra of Telcon vicalloy: (a) in optimum permanent magnet state (VIC–TEL–02); (b) cold-rolled but not heat-treated (VIC–TEL–01).

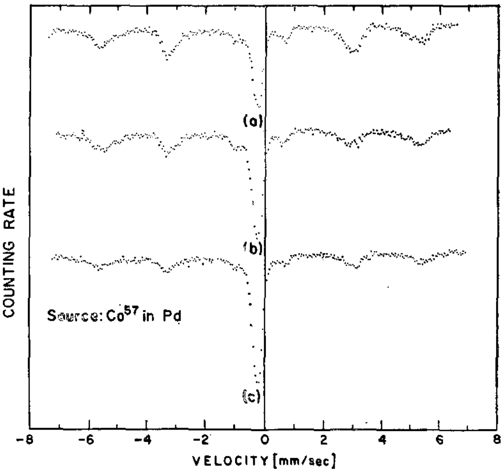


Figure 2 Mössbauer spectra of Telcon vicalloy samples flash-heated for $\frac{1}{2}$ min at: (a) 640° C (VIC–TEL–03); (b) 650° C (VIC–TEL–04); (c) 660° C (VIC–TEL–05).

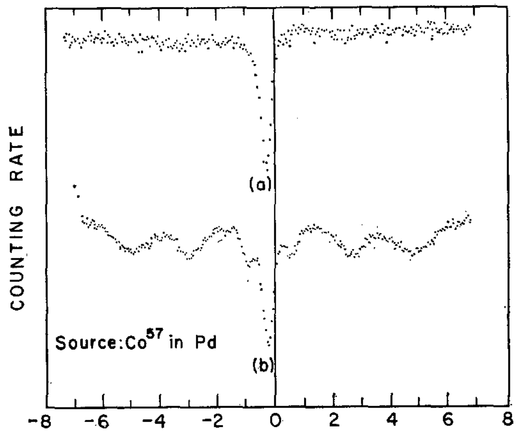


Figure 3 Mössbauer spectra of Telcon vicalloy sample quenched from 1050°C (VIC–TEL–07): (a) at room temperature; (b) after immersion in liquid nitrogen.

samples, but we are satisfied that it is irrelevant to the presently studied problems.)

Ferromagnetic, "lateral", peaks are almost non-existent in the spectrum of VIC–TEL–07 (fig. 3a) which was quenched from above 1000° C. However, following immersion in liquid nitrogen, the ferromagnetic "lateral" peaks become quite distinct and do not change on reheating to room temperature (fig. 3b).

This phenomenon implies *irreversible* formation of a ferromagnetic phase in the cryogenic range, rather than magnetic transition (e.g. cooling below Curie point) as suggested by Fahlenbrach *et al* [12] for the γ-phase, or superparamagnetic effects as proposed by Nesbitt *et al* [29].

In addition, it is evident that the relative intensity of the ferromagnetic "lateral" peaks, as expressed by their integrated areas, changes on heat-treatment. The ratios of the three conjugate peak areas may serve to determine the direction of the internal magnetic field H_i [38] and thus the axis of easy magnetisation. Table II lists the results for all Telcon samples. Averages of the conjugate peaks (I, outer peaks; II, intermediate peaks; III, inner peaks) were used to obtain the ratios presented in the table. Peak I was normalised to 3.0 in one case and peak III to 1.0 in the other.

TABLE II Relative intensity of ferromagnetic peaks and internal magnetic fields of α vicalloy phase obtained from Mössbauer spectra of Telcon samples.

Sample	Ratio I : II : III I = 3.0	 III = 1.0	H_i kOe
VIC–TEL–01	3.0 : 0.8 : 1.1	2.8 : 0.7 : 1.0	294
VIC–TEL–02	3.0 : 3.9 : 1.4	2.2 : 2.9 : 1.0	344
VIC–TEL–03	3.0 : 4.2 : 1.6	1.9 : 2.7 : 1.0	341
VIC–TEL–04	3.0 : 2.8 : 1.7	1.8 : 1.6 : 1.0	339
VIC–TEL–05	3.0 : 2.9 : 2.2	1.8 : 1.7 : 1.0	340
*VIC–TEL–07LN_2	3.0 : 2.2 : 1.4	2.1 : 1.5 : 1.0	301

*This is VIC–TEL–07 after immersion in liquid nitrogen

It should be noted that the obtained ratios of peak intensity lead only to qualitative conclusions, regarding the direction of the internal field (relative to the axis of γ-radiation, which was travelling normal to the plane of the alloy sheet). In the ideal case of a single crystalline ferromagnet the following ratios [38] are predicted by theory: (*i*) for radiation perpendicular to internal magnetic field ($H \perp \gamma$) I : II : III = 3 : 4 : 1; (*ii*) for radiation parallel to internal magnetic field ($H \parallel \gamma$) I : II : III = 3 : 0 : 1; (*iii*) In the case of a randomly oriented (isotropic) polycrystal (or powder) I : II : III = 3 : 2 : 1.

The numbers in table II do not completely correspond to these ideal ratios; however, a general correspondence can be noticed. Thus VIC–TEL–01 tends to fit the ratio I : II : III = 3 : 0 : 1 ($H \parallel \gamma$), VIC–TEL–02 to I : II : III = 3 : 4 : 1 ($H \perp \gamma$) and VIC–TEL–07LN_2 to I : II : III = 3 : 2 : 1 (isotropic). This finding is in general agreement with the data on easy magnetisation directions of vicalloy sheets obtained by Fahlenbrach's group [14, 15] employing a magnetometer.

It is also evident that the flash-heated samples differ in their anisotropy from the cold-rolled sample although they have not yet attained the orientation of either the fully heat-treated or the quenched samples. Yet some correspondence between the lower flash-temperature sample (VIC–TEL–03) and the heat-treated one can be observed, whereas the higher flash-temperature samples tend to fit the condition of the quenched sample.

Referring to the sharpness of the ferromagnetic peaks it can be observed that proper heat-treatment is associated with narrower lines; cold-rolling (VIC–TEL–01) and overheating (VIC–TEL–05) cause broadening. This phenomenon probably stems from ordering effects, as pointed out by Gorodetsky and Shtrikman [31]. An aiding factor may be the degree of plastic deformation (dislocation and stacking fault density) of the samples.

Additional data obtained from the spectra, namely values of the internal magnetic field H_{i}, are listed in table II. These show that non-heat-treated vicalloy (VIC–TEL–01, VIC–TEL–07LN$_2$) has a lower internal field (about 300 kOe) than the heat treated (about 340 kOe).

3.2. Magnetic Properties

All but the quenched samples (VIC–TEL–06 and VIC–TEL–07) displayed reversible magnetisation versus temperature curves in the liquid nitrogen to room temperature range, as shown in fig. 4. The curves are almost horizontal straight lines in the case of VIC–TEL–01 and VIC–TEL–02. The flash-heated samples possess somewhat higher magnetisations at low temperatures.

Fig. 5 presents results of two cycles of cooling and heating of vicalloy quenched from above 1000° C (VIC–TEL–07). It is observed that the magnetic moment per gram is irreversibly raised by cooling to almost twice the original room temperature value. This leads again to the conclusion that a new phase, magnetically stronger than the original, is formed in the cryogenic range.

Table III sums up all the results of the

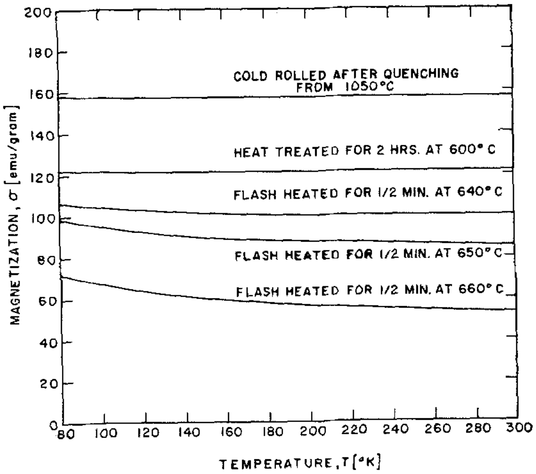


Figure 4 Magnetisation versus temperature curves of five different Telcon vicalloy samples (VIC–TEL–01 to VIC–TEL–05).

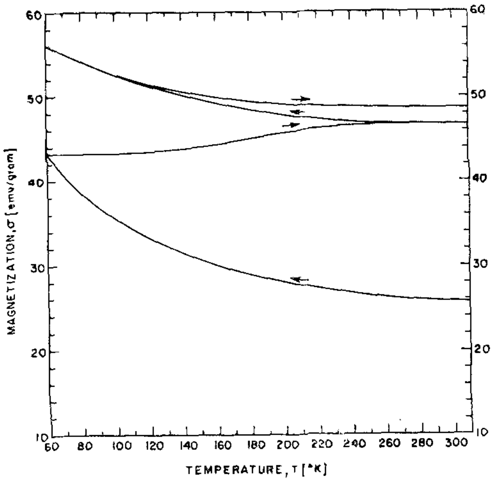


Figure 5 Magnetisation versus temperature curve of quenched (VIC–TEL–07) Telcon vicalloy sample.

TABLE III Results of magnetic measurements on Telcon samples.

Sample	σ emu/g R.T.	LN$_2$	H_c Oe	M_s Gauss	M_R Gauss
VIC–TEL–01	157	158	65	1300	250
VIC–TEL–02	121	122	250	1000	850
VIC–TEL–03	100	107	220	800	450
VIC–TEL–04	85	99	250	700	400
VIC–TEL–05	53	72	270	400	200
VIC–TEL–07LN$_2$	43	53	120	350	100

magnetic measurements, including coercivities (H_c), saturation magnetisation (M_S) and remanence (M_R) at room temperature (obtained from the hysteresis loops using 8.2 g/cm^3 [39] as the density of vicalloy and rounding off to the nearest 50 Gauss).

3.3. Structural Features

X-ray diffraction revealed that cold rolled vicalloy consists of only one phase, α. The lattice spacing was found to be $a_\alpha = 2.86$ Å, in accordance with previously published results [9]. Vicalloy heat-treated for optimum permanent magnet properties contained both α- and γ-phases. The lattice spacing of γ ($a_\gamma = 3.57$ Å) also corresponds to the known value. However, one weak reflection could not be identified with either the α- or γ-phases.

This weak reflection appeared only in the optimally heat-treated sample and could not be associated with any ordering phenomena. No clue was found to its identification; if it was due to some additional phase, for instance the one mentioned by Henkel, this phase would be impossible to characterise by a single diffraction line.

All other samples displayed only ($\alpha + \gamma$) reflections. No significant deviations from the quoted lattice parameters were detected.

The intensity of the α reflections relative to those of the γ-phase in the quenched samples (VIC-TEL-06 and VIC-TEL-07) was raised considerably by immersion in liquid nitrogen. A similar effect was observed whenever specimens were prepared by cutting rather than etching. This implies formation of α from retained γ (by cryogenic treatment in the first case, and cold-work in the second).

Results of electron microscopy and diffraction are presented in fig. 6 and fig. 7. Fig. 6 shows the morphology of a, vicalloy I (VIC-PMA 01) and b, vicalloy II (VIC-GE-02). Both were heat-treated for optimum permanent magnet properties. Vicalloy I displays a second phase of nearly equiaxed particles, about 500 Å in diameter, uniformly dispersed in the matrix. In vicalloy II similar particles seem to form a network rather than being uniformly dispersed. The micrographs are very similar to those published by Baran *et al* [12, 13] in the early 1960's. They lead to the conclusion that shape anisotropy is improbable in the first case but quite possible in the second.

Fig. 7a is a typical diffraction pattern of a 4 μm^2 area of cold-rolled vicalloy(VIC-TEL-01), and fig. 7b is a pattern of a similar area of a heat-treated sample (VIC-TEL-02). The first shows continuous rings of α-phase whereas the second displays diffraction spots of a nearly single crystalline α-phase particle oriented with its {111} planes perpendicular to the electron beam.

4. Discussion

All the experimental techniques used in this study confirmed the fact that magnetic hardness

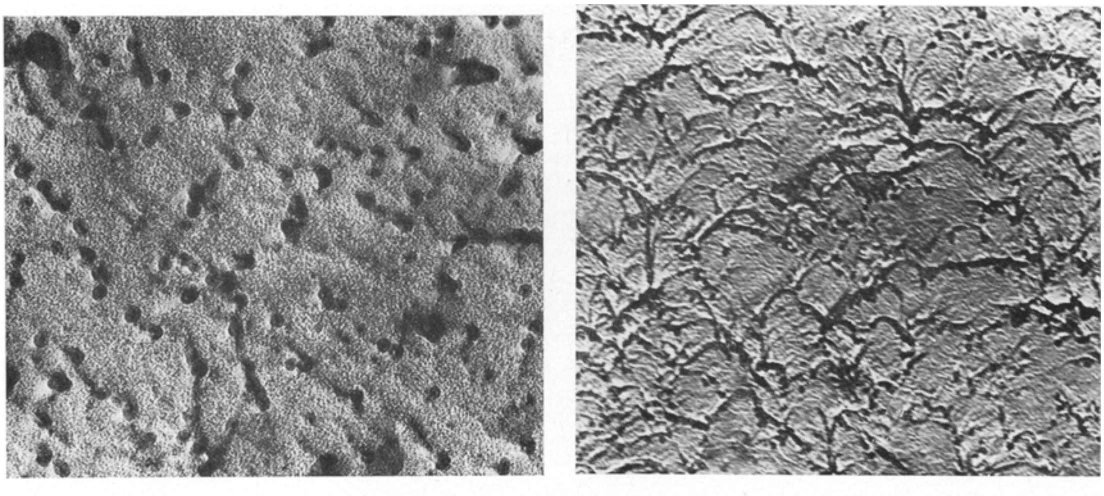
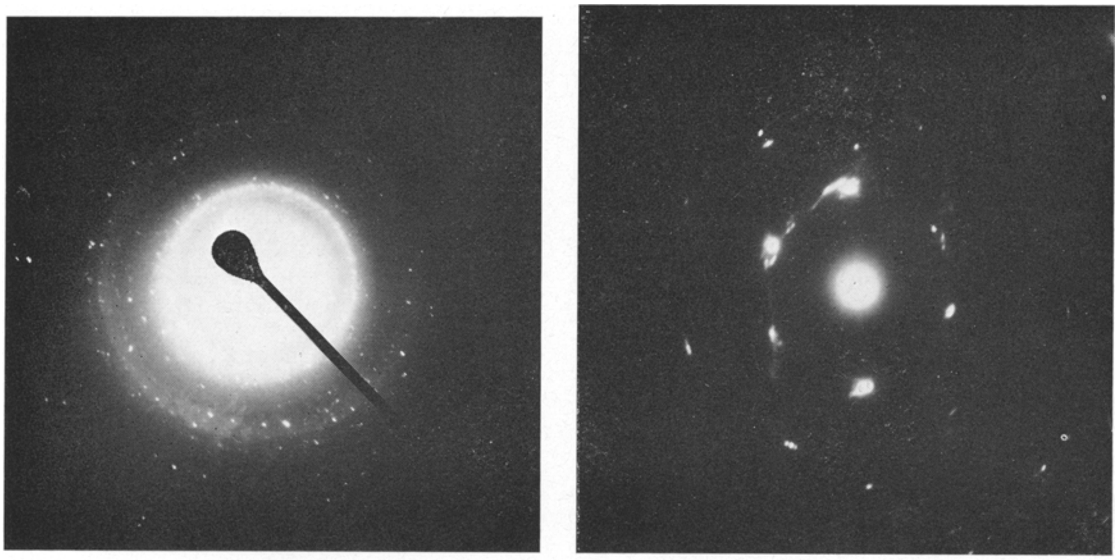

(a) (b)

Figure 6 Electron micrographs (plastic-carbon replica) of: (a) vicalloy I (VIC-PMA-01); (b) heat-treated vicalloy II (VIC-GE-02), both at × 30 000.



(a)

(b)

Figure 7 Selected area electron diffraction patterns of: (a) cold-worked (VIC–TEL–01); (b) heat-treated (VIC-TEL–02), Telcon vicalloy samples.

in vicalloy is associated with the coexistence of two phases; one ferromagnetic and the other paramagnetic. Some insight has been also gained into the nature of magnetic anisotropy in the various stages of alloy preparation.

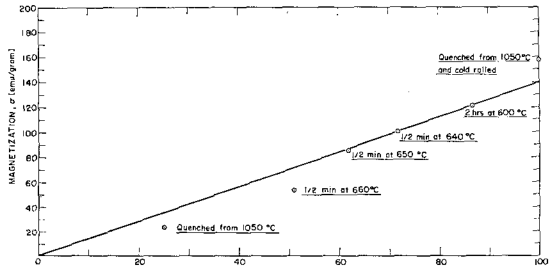


Figure 8 Magnetisation versus per cent of area occupied by ferromagnetic peaks in Mössbauer spectra.

A correlation between magnetometer measurements of magnetisation and the Mössbauer spectra can be obtained by calculating the ratio of ferromagnetic peaks area to total area of the spectra (including paramagnetic peaks). A plot of magnetisation versus per cent area occupied by ferromagnetic peaks is shown in fig. 8. It is evident that magnetisation increases roughly linearly with the ratio of ferromagnetic to total peak area. This can be interpreted to mean that: (*i*) the relative amount of the ferromagnetic phase in any sample is directly related to the magnetisation of that sample, and consequently (*ii*) that the amount of iron, which was the only constituent participating in the Mössbauer effect measurements, is the same in both phases.

Cold-rolled vicalloy consists entirely of the α-phase, a fact which was also confirmed by X-ray and electron diffraction. Proper heat-treatment causes formation of a limited amount of paramagnetic γ, which considerably raises the coercive force (from 65 to 250 Oe) without greatly lowering the magnetisation. Overheating, as in the case of the three flash-heated samples (VIC–TEL–03 to 05), leads to a larger proportion of the paramagnetic phase, lowering the magnetisation still further. Heating to the γ region (above 800° C) and quenching to room temperature results in mostly paramagnetic material. Cryogenic treatment (immersion in liquid nitrogen) as well as cold-work transforms part of the γ into α. Moreover, from the relative breadth of the Mössbauer peaks and the value of the internal magnetic field (H_i) we conclude that this transformed α is in the disordered state (see fig. 1 and table II). The same ferromagnetic α-phase appears to be ordered in the other samples which were subjected to some degree of heat-treatment.

No other evidence was found for the existence of a third phase as postulated by Henkel [22]. However, the unidentified line in the X-ray diffraction pattern of heat-treated vicalloy calls for more accurate diffraction analysis in search for such a phase.

The rôle of crystalline anisotropy, hardly considered previously, is implied by Mössbauer and electron diffraction results of this study. From the relative intensity of the ferromagnetic peaks it was deduced that the hard axis rotates from an orientation parallel to the plane of flat cold-rolled samples to one perpendicular to this plane following heat-treatment. This is in accordance with the orientation of the $\langle 111 \rangle$ axes of recrystallised relatively large α grains as found in the heat-treated sample by electron diffraction (fig. 7b). It has been known for many years [40] that the $\langle 111 \rangle$ axes of α iron are the hardest crystallographic axes of magnetisation.

The departure from isotropy following cold-work might be due to the residual stresses introduced by the rolling process. However, this has not hitherto been considered or measured. Residual strains in the plane of rolling would not be unexpected and could probably lead to a hard magnetic axis in this plane as indicated by the work of the Russians [23].

The otherwise puzzling effect of the amount of cold-work on permanent magnet properties of heat-treated vicalloy [15] also becomes easier to understand if one considers the crystalline anisotropy contribution. It is well known that a higher degree of cold-work will cause a more pronounced degree of preferred orientation following recrystallisation and, therefore, a higher anisotropy and better permanent magnet properties.

In reality the mechanisms involved in the onset of permanent magnetism in vicalloys are certainly more complex. For example, some electron micrographs, such as fig. 6b, show that shape anisotropy cannot be completely neglected.

More work is needed, especially in careful preparation of transmission electron microscopic specimens, before a better understanding can be gained of the processes inducing magnetic hardness in vicalloys. Even so it is hazardous to predict that a complete solution of this problem will ever be reached owing to the material and physical complexity of the system.

5. Conclusions

In summary it can be concluded that although no simple solution was found to the basic problem of the origin of magnetic hardness in vicalloys, it was definitely established that these alloys are fine-particle permanent magnets consisting of ferromagnetic and paramagnetic phases. Experimental evidence points to the fact that several kinds of magnetic anisotropy, such as shape, stress and magnetocrystalline, rather than just one of these, leads to the observed magnetic hardness.

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