Magnetic and Mössbauer studies on ductile Fe-Cr-Co permanent magnet alloys

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Abstract. Iron–chromium–cobalt alloys possess attractive magnetic properties combined with good formability and hence are identified as technologically important magnetic materials. Alloys with compositions Fe-28.9 Cr-15.6 Co and Fe-28.4 Cr-20.1Co (weight percent) have been studied. Heat-treatment parameters during thermomagnetic treatment viz temperature, time and external magnetic field were optimized with reference to magnetic properties. The fully treated anisotropic alloys develop remanence = 11.5–12.0 kilo Gauss, coercivity = 600–650 Oersted and energy product = 4–4.5 million Gauss Oersted. Electron microscopic and Mössbauer spectroscopic techniques were used to identify the original and transformed phases. During the various stages of the development of the alloy, the changes in mechanical hardness were correlated with magnetic hardness.

Keywords. Magnetic properties; heat treatments; phase identification; development of ductile permanent magnet; Mössbauer studies; iron–chromium–cobalt alloys.

1. Introduction

Iron–chromium–cobalt magnetic alloys, first reported by Kaneko *et al* (1971) combine excellent permanent magnetic properties with good ductility. The magnetic properties such as remanence (B_r), coercivity (H_c) and energy product $(BH)_{\max}$ obtained in these alloys are comparable (Chin 1980) to those of Alnico V, a conventional magnetic material widely used for many applications. The Fe-Cr-Co alloy, completely free from nickel, needs less cobalt than the brittle Alnico V and hence has been identified as technologically important magnetic material (Chin 1978). Due to these superior features, considerable effort has been made for the development and better understanding of these alloys (Belli *et al* 1978; Chin 1978; 1980; Chin *et al* 1978, 1983 a, b; Cremer and Pfeiffer 1975; Gin and Gayle 1980; Green *et al* 1980; Homma 1977; Houghton *et al* 1978; Kaneko *et al* 1972, 1975 a, b, 1976, 1977; Livingston 1981; Mahajan *et al* 1978; Minowa *et al* 1980; Okada *et al* 1978; Sherwood *et al* 1979; Tin 1979; Tin *et al* 1980 a, b; Wang Run *et al* 1984; Zijlstra 1978). Studies carried out in the course of development of two alloys, namely Fe-28.9Cr-15.6Co and Fe-28.4Cr-20.1Co, are presented and discussed in this paper.

2. Experimental

Armco iron, electrolytic cobalt and chromium in appropriate quantities were melted in magnesia crucibles under a dynamic vacuum of 10^{-3} torr in a 15 kW, 8000 Hz Stokes vacuum induction furnace. The alloy in each case was poured at 1650°C into preheated

Figure 1. Heat treatment schedule for Fe-Cr-Co magnetic alloys.

25 mm round cast iron moulds. The ingots were processed by hot forging and hot rolling at 1250°C to 12.7 mm dia rods and test samples of the size 10 mm dia × 15 mm long were prepared. The chemical composition of the two alloys by wt % was as follows: Fe-28.9Cr-15.6Co (alloy-1) and Fe-28.4Cr-20.1Co (alloy-2). The heat-treatment procedure adopted in the present study is schematically given in figure 1. The samples were solution-treated at 1300°C for one hour and quenched in brine water to retain the high temperature single phase (bcc phase) at room temperature. Optical metallography and x-ray diffraction techniques were used to confirm the presence of this single phase. To carry out the critical thermomagnetic treatment (TMT), an isothermal treatment in a magnetic field, a small Kanthal-wire-wound furnace was fabricated and housed between the poles of a heavy duty electromagnet capable of generating a uniform magnetic field of 3750 Oersted. The important parameters controlled during TMT were: (i) the temperature, (ii) soaking time and (iii) the strength of the external magnetic field.

Experiments were carried out to optimize these parameters keeping two of the variables constant at a time and varying the third. The samples were subsequently step-tempered at 600°C/2 hr, 580°C/4 hr and 560°C/6 hr as given in figure 1. After every stage of the heat-treatment, the magnetic properties of the samples were measured using a double yoke ferrotester and the hardness of the alloys was also measured. Electron microscope was used to note the morphology of the phases formed during the treatment. For Mössbauer studies, solution-treated samples of alloy-1, electrochemically thinned to 50 µm thickness, were encapsulated in evacuated quartz tube and subjected to all the treatments as shown in figure 1. However, since the samples were thin foils, the duration of the treatments was suitably reduced to avoid overaging and the following schedule was used: 635°C/20'/2000 Oe, 600°C/1 hr, 580°C/2 hr, 560°C/3 hr was followed. The Mössbauer transmission spectrum after each stage of treatment was recorded at room temperature using ECIL Mössbauer spectrometer.

(MBS 35) with 10 milli Curie strength ^{57}Co radioactive source in palladium matrix in the constant acceleration mode.

3. Results and discussion

The magnetic properties (B_r , H_c and $[BH]_{\max}$) of the two alloys after complete step tempering treatments have been plotted in figures 2 a, b, c for the experimental conditions indicated therein. It can be seen from figure 2a that the magnetic properties, especially coercivity and energy product are sensitive to the changes in the temperature of TMT and the variation is parabolic. In alloy 1, B_r remains constant throughout the treatment while in alloy 2 a slight decrease in B_r at high temperature has been observed. The maximum H_c is obtained at the spinodal decomposition (Homma 1977) temperature 635°C and 645°C for alloys 1 and 2 respectively. The observed increase in the decomposition temperature for alloy 2 is due to the increase in cobalt content (Chin 1978).

The spinodal decomposition in Fe-Cr-Co alloy, at temperatures below 700°C , leading to the high temperature single phase α decomposing into two isomorphous phases α_1 (rich in Fe and Co) and α_2 (rich in Cr) has been investigated by earlier workers (Homma 1977; Okada *et al* 1978; Wang Run *et al* 1984). Due to the difference in their chemical composition, the two phases possess different values of saturation magnetisation and curie temperature. During the step-tempering treatment, diffusion of Fe and

Figure 2. Magnetic properties of fully treated Fe-Cr-Co alloys vs TMT parameters.

Co from α_1 to α_2 occurs (Okada *et al* 1978) thus making α_1 strongly ferromagnetic and α_2 paramagnetic. The presence of magnetic and non-magnetic phases and the complex domain wall interactions account for the high coercivity in these alloys (Mahajan *et al* 1978; Livingston 1981). For a group of oriented ellipsoidal single domain particles in a less magnetic matrix, Stoner and Wohlfarth (1948) derived the following relationship for coercivity:

$$H_c = p(1 - p)(N_2 - N_1)(I_1 - I_2)^2/I_s$$

where N_1 and N_2 are demagnetization factors along major and minor axes respectively; I_1 and I_2 , saturation magnetization of the ellipsoid and the matrix respectively; I_s , the average saturation magnetization and p , the volume fraction of the particles.

The demagnetization factors explain the magnetic anisotropy whereas the volume fractions and the saturation magnetization values account for the mechanism of domain wall motion for coercivity. This theory has been widely accepted (Mason *et al* 1970) for Alnico alloys. Since Fe-Cr-Co alloys are akin to Alnicos in achieving high magnetic hardness, the present experimental observations on the coercivity could be understood on the basis of the Stoner and Wohlfarth theory. Due to the asymmetric shape of the miscibility gap in Fe-Cr-Co system (Kaneko *et al* 1977; Minowa *et al* 1980) the volume fractions of the α_1 and α_2 change with TMT temperature. It has been reported (Okada *et al* 1978) that during the step-tempering treatments, the morphology and volume fractions of the phases essentially remain unchanged. Hence the ultimate volume fractions of the phases which control the coercivity through Stoner and Wohlfarth relationship mainly depend on the temperature of TMT, thus explaining the parabolic variation of H_c and $(BH)_{\max}$.

Figure 2b shows that H_c of the alloys increases with soaking time when treated at optimized temperatures. A minimum period of 60' and 30' are needed for the alloys 1 and 2 respectively to maximize coercivity by imparting magnetic anisotropy and completing the decomposition of α phase to the required level. The decreasing trend in H_c due to prolonged treatment can be noted from the curve for alloy 2. The need for more soaking time for the low cobalt alloy is due to slower kinetics at lower temperature. During the initial stages, this alloy exhibits lower values of remanence which may be due to the isotropic nature (Okada *et al* 1978) of products of the decomposition. The improvement in magnetic anisotropy and completion of the decomposition reaction which alter the demagnetization factors and saturation magnetization values of the phases increase the coercivity as expected from the Stoner and Wohlfarth relation.

Figure 2c shows the strong dependence of B_r on the external magnetic field applied during the treatment. A significant increase from 8000 G to 12000 G in B_r is observed due to the presence of the field. The purpose of the application of an external field during TMT is to align the phases and elongate them in its direction and this effect can be observed from the electron micrographs (carbon replica) for the alloy 1 presented in figures 3a, b. The coalescence of the spherical phases in the form of ellipsoids elongated in the direction of the field not only improves B_r but also enhances magnetic anisotropy. A minimum field of 1500–2000 Oe is essential to maximize B_r . Though from figure 2c no apparent effect of magnetic field on coercivity is seen, figure 4 (Curves 4 and 5) however shows that the magnetic field affects the shape of the demagnetization curves. The 'knee of the demagnetization curve' is absent in samples treated without the

Figure 3. Carbon replica micrograph of alloy-1. (a) Spherical morphology of the decomposed phase aligned along the direction of the applied field. (b) Coalescence of the phases to ellipsoid shape.

magnetic field which indicates the absence of strong magnetic anisotropy in these samples.

The gradual improvement in coercivity with step tempering treatments is shown in figure 4. The observed increase in H_c is associated with the increase in the difference in the saturation magnetization values of α_1 and α_2 phases upon step-tempering through diffusion-controlled composition variations in the phases. Thus thermomagnetic treatment plays the important role of fixing the volume fractions and magnetic anisotropy while the step-tempering treatments help in widening the difference in saturation magnetization values between the phases. Hence the Stoner-Wohlfarth relation for coercivity has been found to fittingly explain the experimental observations in achieving magnetic properties of Fe-Cr-Co alloys. The isotropic and anisotropic magnetic properties of the fully treated alloys are listed in table 1.

The close relationship between mechanical and magnetic hardness is established through figure 5 in which the values are plotted stagewise. In the solution-treated condition, the alloys are mechanically soft and machining operations are possible in

Figure 4. Second quadrant demagnetization curves for Fe-Cr-Co alloys. The gradual improvement in coercivity, shape of the curve upon heat treatment (curves 1 to 4) and the absence of 'knee of the demagnetization curve' in isotropic magnets (curve 5) can be observed.

Table 1. Permanent magnetic properties of Fe-Cr-Co alloys

Alloy	Remanence B_r (gauss)	Coercivity H_c (Oersted)	Energy product (BH) _{max} (MGOe)
Fe-28.9Cr-15.6Co			
(a) Anisotropic	11750 ± 250	600 ± 25	4.0 ± 0.2
(b) Isotropic	8250 ± 250	500 ± 25	1.5 ± 0.2
Fe-28.4Cr-20.1Co			
(a) Anisotropic	11750 ± 250	650 ± 25	4.5 ± 0.2
(b) Isotropic	8250 ± 250	625 ± 25	2.0 ± 0.2

this condition. As a result of the heat treatments, due to the decomposition of α -phase and enrichment of chromium in α_2 the values of mechanical as well as magnetic hardness increase simultaneously.

3.1 Mössbauer studies

In the Fe-Cr-Co system, due to the magnetic phases available after TMT and the constant changes in the magnetic nature of the phases during step-tempering treatments, Mössbauer spectroscopy has been effectively utilised (Houghton *et al* 1978; Chen Ming-Yan *et al* 1982) to understand the decomposition mechanisms.

In figure 6 are presented the Mössbauer spectra of alloy 1 along with the spectrum of α -Fe for reference and to serve as a calibration standard for the estimation of hyperfine

Figure 5. Improvement in mechanical (a) and magnetic (b) hardness in Fe-Cr-Co alloys upon heat treatment.

fields. The spectrum at 6-B of the solution-treated sample shows single phase structure (α) of the alloy. Broad distribution of hyperfine fields and the small isomer shift indicate randomized atomic distribution within the single phase. The hyperfine field has been found to be centred near about 250 KOe. From the spectrum at 6-C which pertains to TMT, there is evidence for two hyperfine fields of 355 KOe and 202 KOe corresponding to the two phases α_1 and α_2 respectively both being ferromagnetic with different magnitudes of intensity of magnetization. The corresponding two six-line spectra could not be resolved because of overlapping (Houghton *et al* 1978) of outer lines of smaller field with the second and fifth lines of larger field. The existence of α_2 in paramagnetic state is indicated by the presence of a small peak at the centre of the spectrum. The spectra from 6-D to F correspond to those for step-tempering treatments. The gradual increase in the spectral area of the central paramagnetic peak and the narrowing of the other lines indicate that the volume fraction of paramagnetic α_2 increases with step-tempering. This is due to the progressive conversion of α_2 from weakly ferromagnetic to paramagnetic state.

Under the present experimental conditions, (with thickness of sample being around 50 μm) it will be difficult to quantitatively correlate the spectral areas to the volume fractions of the phases. However, an attempt has been made to derive qualitative correlations. The relative area of central line of α_2 to the total area of the spectrum has been found to be 0.03, 0.06 and 0.10 for the three step-tempering treatments at 600°, 580° and 560°C respectively indicating the increase in the amount of paramagnetic α_2 . The observed increase in coercivity with these treatments (figure 4) can be explained on this basis.

Figure 6. Mössbauer spectra of α -Fe (for calibration) and alloy 1 at various stages of heat treatment.

The conversion of weakly ferromagnetic α_2 to paramagnetic state occurs by the diffusion of Fe-rich phase from α_2 to α_1 . The migrating Fe-rich phase forms a third intermediate phase whose presence is evidenced by the occurrence of small peaks in the spectrum 6-D to F. The hyperfine field corresponding to this phase has been found to be 320 KOe. During the step-tempering treatments, it can be seen that the spectral area of this phase decreases, which may be attributed to the migration from α_2 to α_1 . However, no corresponding change in the hyperfine field of α_1 due to this addition has been noticed.

4. Conclusions

The following conclusions are drawn from the present studies.

- (i) Fe-28.9Cr-15.6Co and Fe-28.4Cr-20.1Co alloys develop attractive permanent magnetic properties $B_r = 11.5\text{--}12.0$ K Gauss, $H_c = 600\text{--}650$ Oe and $(BH)_{\max} = 4.0\text{--}4.5$ MGOe.
- (ii) The coercivity of the alloys is sensitive to thermomagnetic treatment and improves gradually upon step-tempering treatment. The remanence of the alloys depends on the strength of the external magnetic field applied during TMT and is not altered during step-tempering.
- (iii) TMT parameters such as 635°C , 60 minutes time and 2000 Oe field are characteristic for alloy 1 while 645°C , 30 minutes time and 2000 Oe field are so for alloy 2.
- (iv) The widely accepted Stoner and Wohlfarth theory for coercivity in Alnico alloys has been applied to explain qualitatively the experimental observations in Fe-Cr-Co alloys.
- (v) From Mössbauer studies, it has been confirmed that soon after TMT, the alloy develops a strongly ferromagnetic phase α_1 and a second phase α_2 existing in weakly ferromagnetic and paramagnetic states. On step-tempering, ferromagnetic α_2 becomes paramagnetic with the presence of a third intermediate Fe-rich phase.

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