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Electron microscopy and magnetic properties of Fe–Cr–Co–Si permanent magnet alloys manufactured by rolling–ageing technique

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Four Fe–30/33Cr–11.5/12.5Co–0/1Si alloys (weight fraction) melted in air and treated by alternatively ageing and rolling have been studied by magnetic measurements and electron microscopy. The optimum treatment procedures have been determined and the best obtained magnetic properties are $Hc = 54.0\,\mathrm{kA\,m^{-1}}$, $Br = 1.19$ T and $(BH)\mathrm{m} = 29.6\,\mathrm{kJ\,m^{-3}}$. Transmission electron microscopy proves that rolling after spinodal ageing is effective in elongating and aligning the original isotropic spinodal structures. The extent of elongation is quantitatively related to the amount of area reduction in rolling. Magnetic properties are found to be not very sensitive to slight variations in composition, cooling rates and the temperature of intermediate rolling, and to be tailorable by the exact control of the rolling operation. The rolling-ageing technique as a manufacturing process for Fe–Cr–Co magnets is thought to be promising. Finally, ways of further improvement are discussed.

1. Introduction

Fe–Cr–Co permanent magnet alloys have been well-known for their ductility, low Co content and competitable magnetic properties with conventional Alnico alloys since the pioneer work of Kaneko *et al.* in 1971 [1].

The magnetic hardness of this alloy system has been found to arise from the fine dispersion of α_1 (Fe, Co-rich, ferromagnetic) and α_2 (Cr-rich, weakly ferromagnetic or paramagnetic) particles of approximately 30 nm in size due to spinodal decomposition [2, 3]. In order to attain superior magnetic properties, shape anisotropy was introduced by magnetic ageing to elongate α_1 particles resembling in every respect those of Alnico alloys [1]. As a result, the maximum energy product, (BH)m, up to $61.3\,\mathrm{kJ\,m^{-3}}$ (7.7 MGOe) for an Fe–25Cr–12Co alloy (in weight fraction, same hereafter) was reported [4], and was comparable to that of columnar Alnico 5 at the 24Co level. Jin, making use of the ductility of this alloy, developed deformation-ageing which by wire-drawing the spinodally decomposed isotropic alloy is able to elongate and align the α_1- and α_2-phases in a way even more effective than magnetic ageing [5, 6]. The (BH)m value of an Fe–35Cr–11.5Co alloy thus treated was 44 kJ $\mathrm{m^{-3}}$ (5.5 MGOe) comparable to Alnico 5 alloy [5].

However, wire-drawing is not suitable for producing 'wires' with diameters of up to a centimetre. In other respects, the microstructural features of deformation-aged structures have not been studied in detail elsewhere so far. Hence, there is a two-fold purpose of this study: (1) to evaluate the rolling-ageing as a method of manu-

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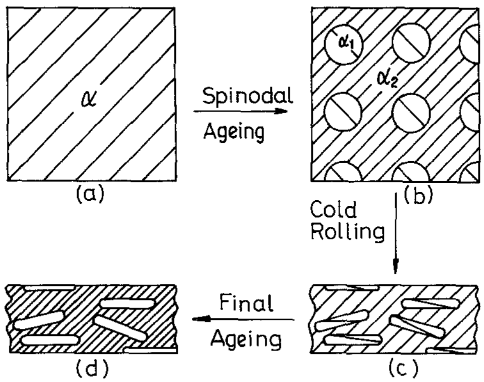

Figure 1 Schematic diagrams showing the theory of rolling-ageing to fabricate Fe–Cr–Co permanent magnets.

facturing rod magnets, and (2) to relate the deformed microstructures with magnetic properties.

2. Theory of rolling-ageing to manufacture Fe—Cr—Co permanent magnets

As shown in Fig. 1, the rolling-ageing is composed of: (a) attainment of homogeneous α-phase; (b) spinodal ageing to grow the oversize two-phase structure; (c) cold rolling to elongate and align the particles, and (d) final ageing to enhance concentration (thus the magnetization) difference between α_1- and α_2-phases.

There are also γ- and σ-phases in addition to α present in Fe-rich Fe–Cr–Co alloys. The former two are extremely detrimental to magnetic properties of these alloys [7, 8]. Thus the elimination of γ and σ is most essential. Usually a high temperature solution treatment at 1000 to 1300° C, according to the composition, is needed for this purpose.

Spinodal ageing at temperatures below spinodal temperature serves to obtain isotropic spinodal structure. For spinodal decomposition, please refer to the comprehensive review by Cahn [9]. The spinodal ageing can be carried out by isothermal ageing or continuous cooling ageing.

Cold rolling after spinodal ageing is used to impose the shape anisotropy needed in such permanent magnet alloys [10]. The extent of elongation which determines the anisotropy is expected to be controllable by the amount of area reduction (AR for short). However, the deformation mode in cold rolling is different from that of wire-drawing, the aligning efficacy of the elongated particles would be inferior in the former, and deviation from perfect alignment as shown in Fig. 1c and d may occur.

In final ageing, the concentrations of Fe, Co in α_1 and Cr in α_2 can be increased due to diffusion. The magnetization difference as a result of concentration variation is the most important factor in determining coercivity of shape-anisotropic permanent magnet alloys [10]. The final ageing may be carried out by either step tempering at successively lower temperatures or continuously cooling at controlled rates.

3. Experimental procedures

3.1. Materials fabrication

Four alloys designated K, L, M and N, with compositions shown in Table I, were studied. Alloy K is essentially the composition studied by Jin [5], 0.2% Si was used as deoxidizer. The L, M and N alloys are modifications of K composition. 4000 g of each of the alloys was prepared by melting together Fe, Cr and Co, all of the electrolytic grade, and Si of over 99.5% purity in a 5 kg Brown-Boveri induction furnace in the open air, and cast into a shell mould of 30 mm i.d. After homogenization at 1200° C for 1.5 h, the 30 mm diameter rods were hot rolled to 20 mm diameter then cold rolled to 15 mm diameter.

TABLE I The alloys under study and the resultant magnetic properties

Alloy	Composition* (wt %)			Magnetic properties		
	Cr	Co	Si	Hc, kA m^{-1} (Oe)	Br, T (kG)	(BH)m, kJ m^{-3} (MGOe)
K	33.0	11.5	0.2	47.6 (600)	1.22 (12.2)	27/2 (3.4)
L	33.0	11.5	1.0	49.2 (620)	1.25 (12.5)	28.0 (3.5)
M	33.0	12.5	1.0	50.8 (640)	1.26 (12.6)	27.2 (3.4)
N	30.0	12.5	1.0	54.0 (680)	1.19 (11.9)	29.6 (3.7)

*Balance Fe.

3.2. Rolling-ageing treatment and experiments

The treatments in rolling ageing, as shown in Fig. 2, comprise: (1) solution treatment at 1100° C for 1 h, water-quenching; (2) spinodal ageing by controlled-cooling from 680° C which is above the spinodal temperatures, after holding at 680° C for 1 h, at a rate of 20 to 50° C h^{-1} to 600° C; (3) cold rolling to 40 to 85% area reduction; (4) final ageing by controlled-cooling from 610° C x 1 h to 500° C x 5 h at constant rates varied from 4.2 to 20° C h^{-1}. The rate of cooling was controlled by a temperature programmer. The rolling was carried out by a small laboratory rolling mill with grooved rollers each 100 mm in diameter.

After the completion of treatments, the magnetic properties of each specimen were measured in an automatic d.c. hysteresisgraph which traces out and records the entire *B–H* loop. Points of interest were *H*c, the coercive force, *B*r, the remanence and (*BH*)m, the maximum energy product which represents the overall merit of a permanent magnet.

A thin foil of a treated specimen was prepared by an automatic electrolytic jet polisher using 20 parts perchloric acid to 80 parts acetic acid as electrolyte and examined with a Hitachi H700-H STEM. Since a rolled rod tends to be deformed more at the outer portion, foils for TEM study were taken from the central portion of the rod to reduce errors in comparison.

4. Results and discussion

The compositions of the alloys were determined by wet chemical methods and nitrogen/oxygen analyser. The Fe, Cr, Co contents were accurate to within 0.6% of the expected composition, the 1% Si added alloys contained 0.7 to 0.8% Si. The alloys typically contained 300 to 400 ppm oxygen and 500 to 1000 ppm nitrogen. The carbon contents were between 0.04 and 0.06% as determined by a Leco WR-12 Carbon Analyser. X-ray diffractometry showed that the phase after 1100° C x 1 h solution treatment is completely α-phase.

The effect of treatment parameters including (1) initial cooling rate, R_1, during spinodal ageing, (2) amount of cold rolling, (3) final cooling rate, R_2, and (4) composition on magnetic properties, especially the (*BH*)m, were each studied separately with other parameters being kept constant.

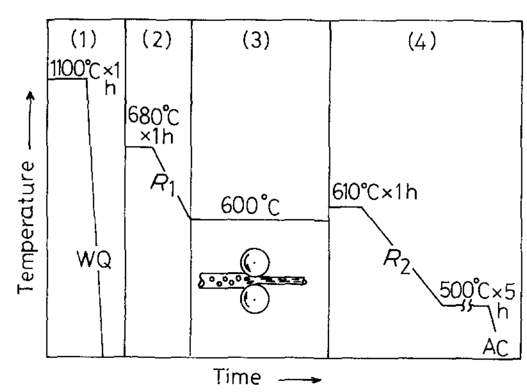

Figure 2 Heat treatment procedures and intermediate cold rolling.

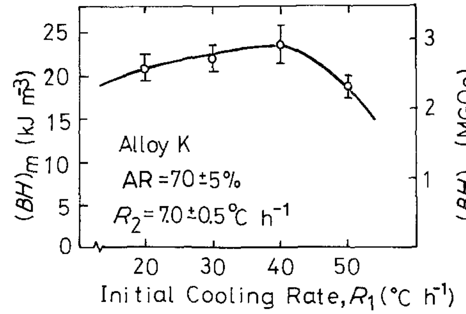

Figure 3 Effect of initial cooling rate, R_1, on (*BH*)m value of the alloy K.

4.1. Effect of treatment parameters

The effect of the initial cooling rate, R_1, on (*BH*)m value of alloy K is shown in Fig. 3. The optimum R_1 values are between 30 and 40° C h^{-1}. The shape of the curve reveals an important fact: slight over-ageing (slower cooling rate) has less effect than does underageing (higher cooling rates). This is due to the fact that slightly oversize resulting from overageing has a larger allowance for size reduction during cold rolling, and hence is preferred [5]. The variation of particle size with R_1 is to be demonstrated in Section 4.2.

The effect of the amount of cold working is

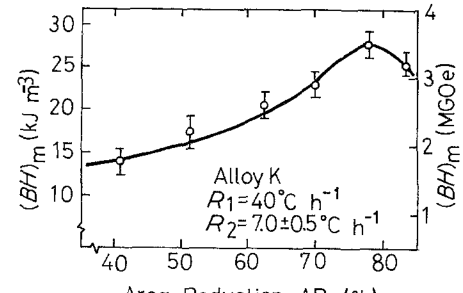

Figure 4 Effect of area reduction (AR) percentage on (*BH*)m value of the alloy K.

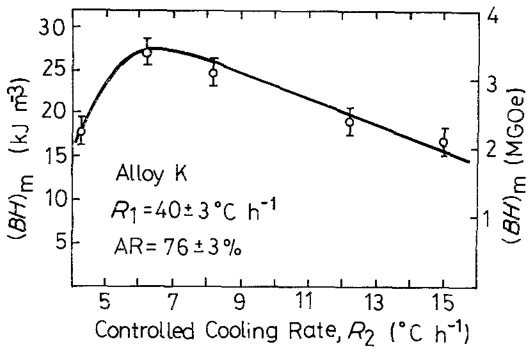

Figure 5 Effect of final cooling rate, R_2, on (BH)m value of the alloy K.

expressed in terms of area reduction (AR) percentage and shown in Fig. 4. In general, (BH)m increases with AR, very slowly at first and very fast at 60 to 78% then decreases again. The AR corresponding to the maximum (BH)m value is 78%. This behaviour is quite the same as that reported by Jin [5]. However, Jin reported that magnetic properties increased twice as AR reached 40%, while in our experiments 40% AR imposed a subtle increment only. The reason might be attributed to the cold rolling being not an ideal unidirectional deformation while wire-drawing is.

The effect of final cooling rate, R_2, on magnetic property is shown in Fig. 5. The optimum cooling rate is around 6 to 7° C h^{-1}. Outside this range, magnetic property decreases steeply. Usually, a faster R_2 results in underageing typical of lower Hc values, a slower R_2 results in overageing typical of bad B–H loop shaping in the second quadrant of the loop.

The alloys K, L, M, and N treated according to the optimum conditions described above resulted in magnetic properties shown in Table I. In spite of compositional variation, Cr from 30 to 33%, Co from 11.5 to 12.5%, Si from 0 to 1.0%, the magnetic properties remain practically unchanged: Hc = 51 ± 3 kA m^{-1}, Br = 1.20 ± 0.40 T and (BH)m = 28.5 ± 0.5 kJ m^{-3}. However, addition of Si and/or reducing the Cr content render easier cold rolling and result in a slightly higher (BH)m value of alloys K and M compared with alloys L and N, respectively. This inertness of magnetic properties on composition is especially significant in industry. The rolling temperatures below 600° C are found to have a negligible effect on magnetic properties in experiments.

4.2. Microstructure and magnetic properties

Fig. 6 shows the microstructure of alloy K after spinodal ageing by cooling at 20, 30 and 50° C h^{-1}, respectively, and final ageing without intermediate cold rolling. These micrographs are characteristic of isotropic spinodal structure, the white particles belong to the α_1-phase [2], with particle sizes varying from 20 to 50 nm according to the initial cooling rate. The optimum particle size for this process is around 35 nm as estimated from Fig. 6b.

Figs. 7 to 11 are typical transmission electron micrographs demonstrating the effect of cold rolling on the microstructure of alloy K: in each figure both microstructures taken at directions parallel and perpendicular to the rolling direction are shown. It is important to note that the elongating effect of cold rolling is not manifest until AR

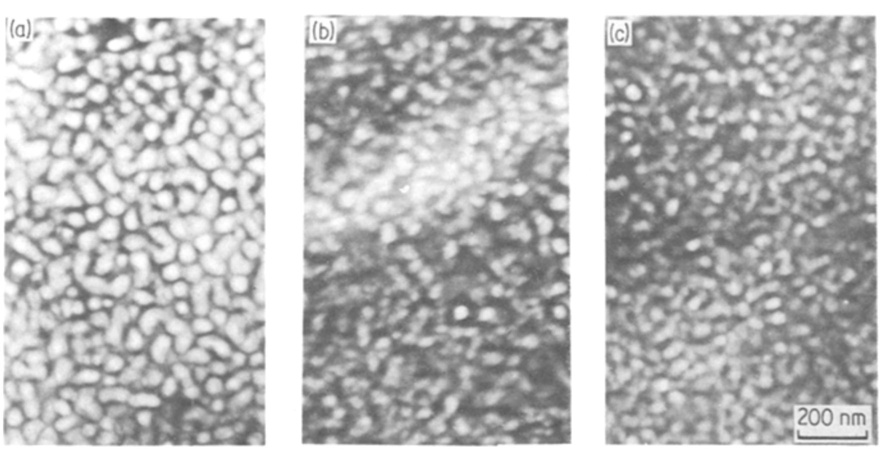

Figure 6 Transmission electron micrographs of the alloy K initially cooled at 20° C h^{-1} (a), 30° C h^{-1} (b) and 50° C h^{-1} (c) from 680 to 600° C, then finally cooled at 6.25° C h^{-1} from 610 to 500° C without intermediate cold rolling.

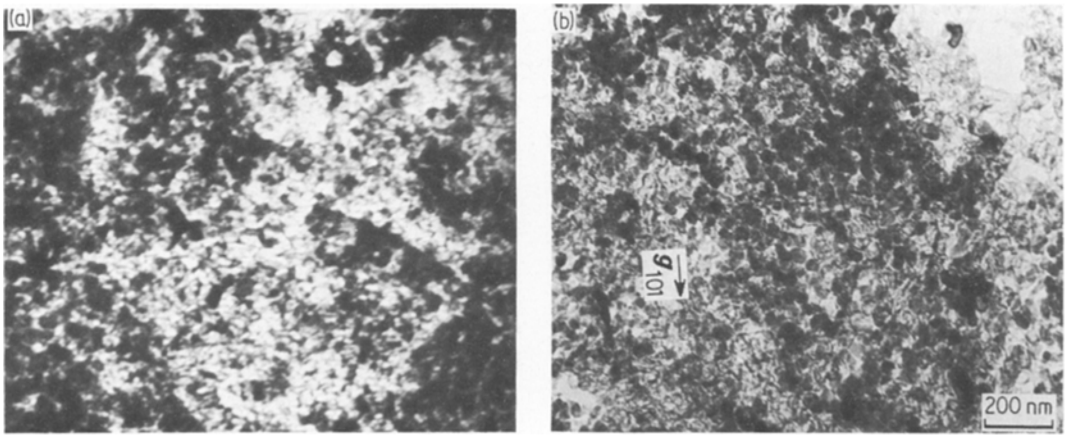

Figure 7 Transmission electron micrographs of the alloy K treated according to the optimum conditions (see text) except cold rolling to 41% AR, taken (a) perpendicular, and (b) parallel to the rolling direction.

is greater than 50% (Fig. 8). The cold rolling with AR smaller than 40% serves to rearrange the isotropic structure rather than elongate the particles, when comparing the morphologies in Fig. 7 with those of Fig. 6. As AR increases the measured mean aspect ratio (length over diameter of the particles, taken as a measure of the elongation of them) increases as well, from 1.8 ± 0.6 for 53% AR to 3.0 ± 0.8 for 63% AR, 6 ± 1 for 74% AR and 12 ± 2 for 83% AR.

Fig. 12 depicts the measured apsect ratio and the magnetic properties as a function of AR for alloy K. It is interesting that the increase in Hc, and hence the (BH)m value can be attributed to the sharp increase in aspect ratio from 1.8 to 6.0, which, by theory, is a requisite for shape anisotropic permanent magnets [10]. The decrease in Hc and (BH)m for AR greater than 80% is most likely due to a breaking up of some particles into fragments which are so small as to become superparamagnetic, resembling that found by Okada *et al.* [2] for secondary decomposition in magnetic-aged Fe–Cr–Co alloys.

One very important fact also shown in Fig. 12, is that the measured aspect ratio is always smaller than that theoretically calculated by a simple deformation model in which the dispersed particles are coherently and unidirectionally deformed together with the matrix, as shown by a dotted curve. Jin, however, claimed that in wire-drawing ageing the aspect ratios are near to those theoretically calculated [5]. This fact proves that unidirectional deformation of cold rolling as mentioned above is less perfect, at least for our experimental facilities.

However, it is quite obvious that microstructural

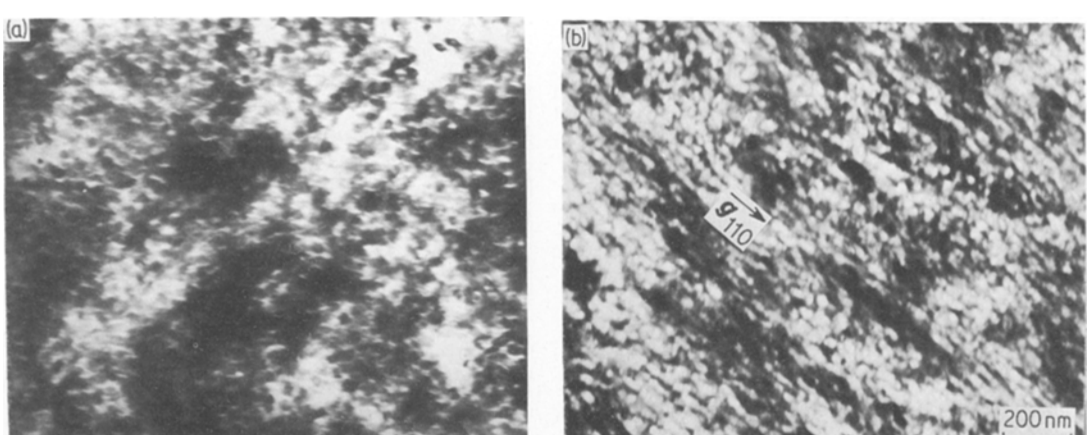

Figure 8 Transmission electron micrographs of the alloy K treated according to the optimum conditions (see text) except cold rolling to 52% AR, taken (a) perpendicular, and (b) parallel to the rolling direction.

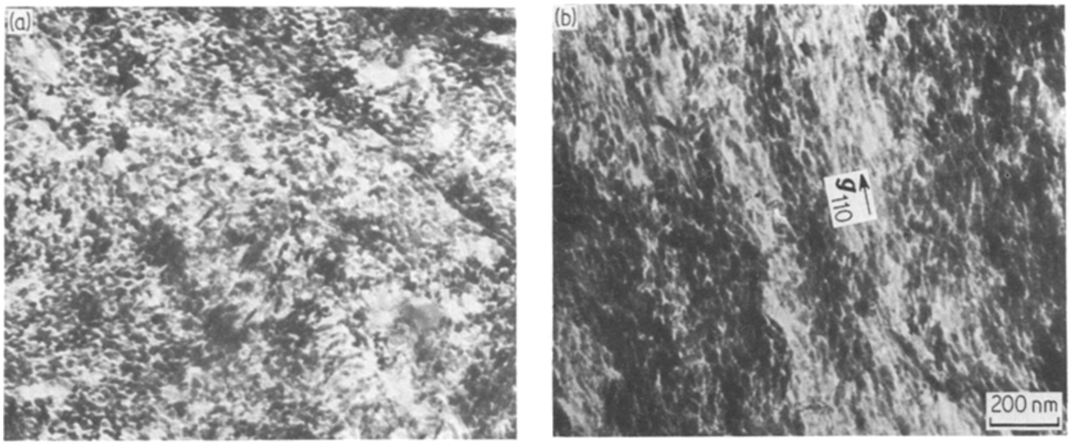

Figure 9 Transmission electron micrographs of the alloy K treated according to the optimum conditions (see text) except cold rolling to 64% AR, taken (a) perpendicular, and (b) parallel to the rolling direction.

features can be easily controlled by the amount of cold rolling, hence magnetic properties can be readily tailored by controlling this particular parameter.

4.3. Evaluation of rolling-ageing technique

Although magnetic ageing has been successful in producing twice the (*BH*)m value at the same Co content as in this study [4], there are several advantages of rolling-ageing as compared to magnetic ageing: (1) The magnetic properties are quite inert to cooling rates, composition and temperature of intermediate cold-rolling, and when considering industrial processes this is extremely beneficial. (2) The microstructure and hence magnetic properties can be readily controlled by AR in cold rolling. (3) Anisotropic magnetic properties can be obtained without a magnetic field which is extremely energy consuming in magnetic ageing treatment. (4) The rolling operation is a well-developed mass-production technique which is readily available in most steel works. (5) *H*c values greater than 49 kA m^{-1} are easily obtainable compared with typical values of 46 to 49 kA m^{-1} for magnetic-aged alloys at the same Co content [1–4]. (6) In comparison with wire-drawing ageing, rod products with diameters up to several centimeters are possible by cold rolling. These advantages make rolling-ageing a promising manufacturing process.

In this study the magnetic properties are inferior to those of Jin for wire drawing-aged alloys of the same composition melted under helium protection [5]. Apart from the less perfect unidirectional deformation of the cold rolling, another important fact can be deduced from the analysed com-

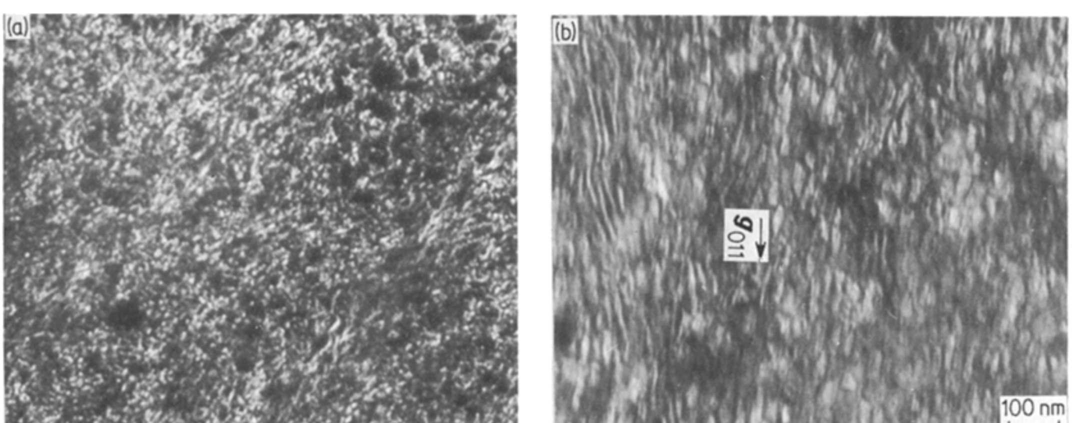

Figure 10 Transmission electron micrographs of the alloy K treated according to the optimum conditions (see text) except cold rolling to 74% AR, taken (a) perpendicular, and (b) parallel to the rolling direction.

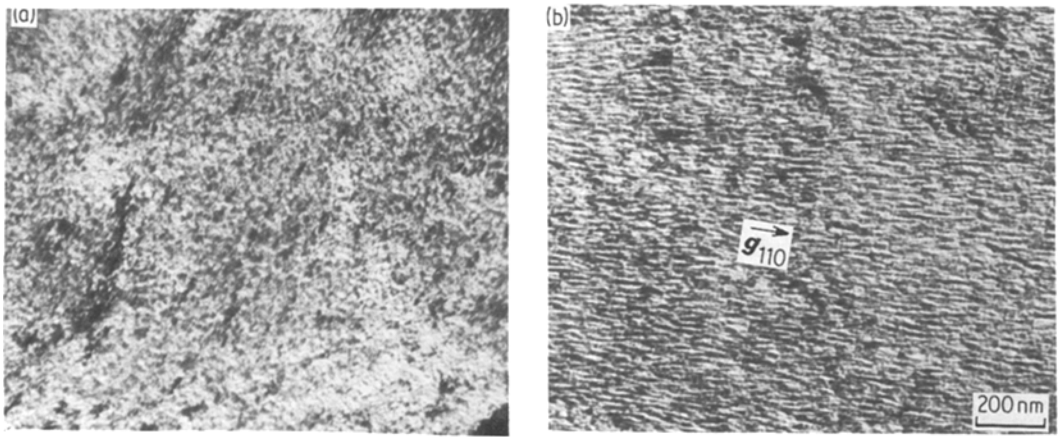

Figure 11 Transmission electron micrographs of the alloy K treated according to the optimum conditions (see text) except cold rolling to 83% AR, taken (a) perpendicular, and (b) parallel to the rolling direction.

position. The nitrogen content, which is extremely harmful to Fe–Cr–Co magnets [11], of the alloys is too high due to melting in the open air. One might expect an enhancement of magnetic properties by reducing the nitrogen content. In fact, the magnetic properties of an air-melted Fe–30Cr–12CO–1Si alloy modified by adding Ti and Cu, have been successfully raised to $(BH)\mathrm{m} = 40.8\,\mathrm{kJ\,m^{-3}}$ (5.1 MGOe), $Hc = 55\,\mathrm{kA\,m^{-1}}$ (690 Oe) and $Br = 1.26\,\mathrm{T}$ (12.6 kG) by the optimum treatment conditions mentioned above.

5. Conclusions

Four Fe–30/33Cr–11.5/12.5Co–0/1Si alloys melted in the open air and treated by alternatively rolling and ageing have been studied. The results show that rolling-ageing is able to produce good permanent magnetic properties: $Hc = 49$ to $54\,\mathrm{kA\,m^{-1}}$, $Br = 1.19$ to $1.26\,\mathrm{T}$, $(BH)\mathrm{m} = 28$ to $30\,\mathrm{kJ\,m^{-3}}$. The experimental optimum treatment procedures are solution treatment at $1100^\circ\,\mathrm{C} \times 1\,\mathrm{h}$, spinodal ageing from $680^\circ\,\mathrm{C} \times 1.0\,\mathrm{h}$ at 30 to $40^\circ\,\mathrm{C\,h^{-1}}$, cold rolling at temperatures below 600° C to 78% area reduction, then final ageing from $610^\circ\,\mathrm{C} \times 1\,\mathrm{h}$ to $500^\circ\,\mathrm{C} \times 5\,\mathrm{h^{-1}}$ at 6 to $7^\circ\,\mathrm{C\,h^{-1}}$. TEM proves that cold rolling is effective in elongating and aligning the original isotropic spinodal structure, the extent of which is closely related to the area reduction, and hence magnetic properties can be tailored by exact control of area reduction in cold rolling. Finally the rolling-ageing as a manufacturing process of Fe–Cr–Co magnets is estimated to be promising.

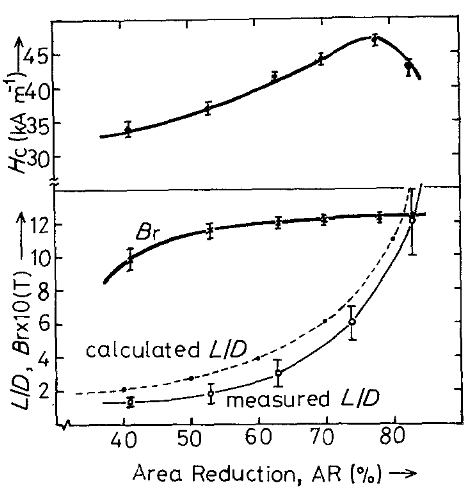

Figure 12 Hc, Br, the measured and calculated aspect ratio of the alloy K treated to the magnetically optimum states as a function of AR (%) in intermediate cold rolling.

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