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Fe–Cr–Co Permanent Magnet Alloys Heat-Treated in the Ridge Region of the Miscibility Gap

MOTOFUMI HOMMA, MASUO OKADA, TAKEHISA MINOWA, AND EIJI HORIKOSHI

Abstract—**By heat-treating in the ridge region of the miscibility gap, the magnetic properties of the Fe–Cr–Co permanent magnet alloys have been remarkably enhanced. The optimum procedure of the heat treatments, such as thermomagnetic treatment and step-aging sequence for the "ridge" alloys, is examined. Such heat treatments are discussed in conjunction with their microstructures. It is found that thermomagnetic treatment in the ridge region is effective in aligning and elongating the FeCo-rich particles parallel to the applied magnetic field direction. An Fe-22Cr-15Co alloy achieves the magnetic properties as Br = 1.56 T (15.6 kG), bHc = 51.6 kA/m (645 Oe) and (BH)max = 66.4 kJ/m^3 (8.3 MGOe), which are almost comparable to those of the columnar Alnico family.**

INTRODUCTION

Fe–Cr–Co permanent magnet alloys have received much interest in replacing available ductile magnets and some of the Alnico alloys in the present permanent magnet market because of their good ductility and excellent magnetic properties [1]-[9]. These alloys were designed by following the miscibility gap in the Fe–Cr system into the Fe–Cr–Co ternary system [1]. The magnetic hardening of the alloys is associated with decomposition within the miscibility gap, producing modulated structures consisting of two phases, an iron-rich phase (α_1) and a chromium-rich phase (α_2) [10]-[12].

Nishizawa *et al.* [13], based on their thermodynamic computations, suggested that the shape of the miscibility gap is not parabolic but of a peculiar shape, protruding to the Fe side along the Curie temperature. The part of the protrusion of the miscibility gap is called the "ridge" because of its shape resemblance. Kaneko *et al.* [14] determined the miscibility gap in an Fe–Cr–Co system using mechanical hardness and Curie temperature measurements. However, the precise shape of the ridge region of the miscibility gap could not definitely be detected by the techniques because of the small difference in the composition of the two phases formed in the ridge region. Recently Minowa, Okada, and Homma [15] further studied the shape of the miscibility gap by monitoring the microstructures and the magnetic properties of the alloys, and identified the existence of the ridge of the miscibility gap, which is shown in Fig. 1. We have also suggested the possibility of the improvement of the alloys situated in the ridge.

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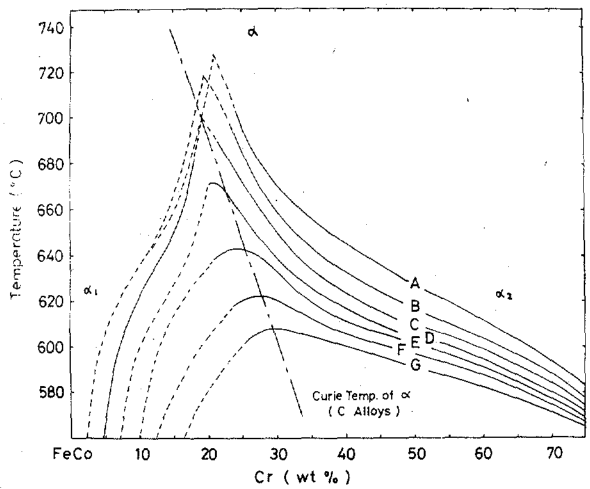

Fig. 1. Vertical sections of the miscibility gap of Fe–Cr–Co system along conjugated lines. Curie temperatures of α phase of alloys C are extrapolated from those measured in high Cr (>45 percent Cr) alloys (after [15]).

The purposes of this work are the following: 1) to develop the suitable heat treatments for improving the magnetic properties of the alloys utilizing the ridge region of the miscibility gap; and 2) to establish some of the microstructure-property relationship in Fe–Cr–Co ridge alloys, resulting from such suitable heat treatments.

APPROACH

There are two relevant theories on the elongation and alignment of the ferromagnetic particles by means of thermomagnetic treatment (TMT) [16], [17]. Cahn [16] takes into account the magnetostatic and elastic energies in his theoretical model on the effect of magnetic aging on spinodal decomposition. According to his theory, the effectiveness of the applied magnetic field on a polycrystalline alloy will be increased, since the elastic energy which favors {100} waves and the degree of undercooling are small, and since the magnetostatic energy, which favors the wave parallel to the field, dominates. Zijlstra [17], [18] proposed a model in which fine spheres change to spheroids in minimizing the magnetostatic energy. In his model the effectiveness of the applied magnetic field will be increased, as the interfacial energy is small and the magnetostatic energy is large. Referring to the ridge region of the miscibility gap in an Fe–Cr–Co system shown in Fig. 1, the desirable characteristics of the "ridge" are speculated on the basis of these two TMT models as follows: 1) the small difference in the composition of the two phases formed within the

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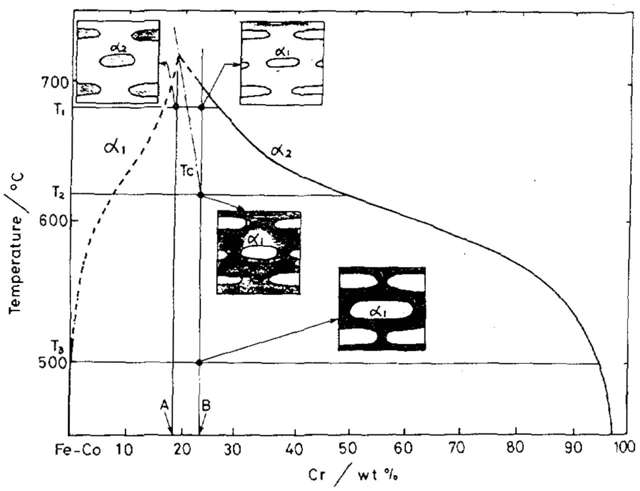

Fig. 2. Schematic illustration of anticipated microstructure formed in ridge region with vertical section of miscibility gap.

ridge region leads to a decrease in the elastic energy indicated by Cahn and the interfacial energy in Zijlstra's model; and 2) in the ridge region, the Curie temperature of an α phase of the alloy is located so closely to the miscibility gap that the efficiency of the applied magnetic field becomes enhanced.

Utilizing the desirable characteristics of the ridge suggested above, suitable ridge alloys and their TMT temperatures must be selected for these studies. They are chosen based on the following two criteria: 1) the alloys require having the phase region where the ferromagnetic α_1 particle can be formed as an isolated particle in the α_2 matrix phase; and 2) the alloys require having the TMT temperature at which the two conditions for the effective TMT are satisfied. For an example, in Fig. 2, aging the alloy A at any temperature will produce the undesirable microstructure [10] in which the α_2 phase is embedded in a ferromagnetic α_1 phase, namely, unsatisfying criterion 1). On the other hand, the alloy B fulfills criterion 2), but also 1), as the aging temperatures are above T_2, below which the α_2 phase is formed as an isolated minor phase. The alloy B is therefore suitable for this approach. Thus in the present investigation, the chromium content of the Fe-Cr-(12-15) wt% Co ridge alloys varies from 21 wt% to 30 wt%, and their TMT temperatures are between 630°C and 700°C.

Experimental Procedure

The Fe-(21-30) wt% Cr-(12-15) wt% Co alloys were chosen for this investigation. The preparation procedure of the ingots was described in [15]. In order to find the optimum condition of the heat treatment for the ridge alloys, the optimum thermomagnetic treatment was first determined by the procedure schematically shown in Fig. 3. It should be noted that the alloys are not continuously slow-cooled to the thermomagnetic treatment temperature because of the formation of the γ or σ phase during the cooling. After the solution treatment at 1200°C-1300°C, the alloys were aged in a magnetic field of 2 kOe (160 kA/m) at 630-700°C for 10 min-3 h and were held at 620°C for 5-60 min. They were then control-cooled at a rate of 20°C/h to 500°C and was subsequently aged at 500°C for 10 h. After finding the optimum condition of TMT, the optimum step-aging procedure was selected by aging the alloys at the temperature of every 20°C interval below 620°C. A transmission electron microscopy is employed for establishing some of the microstructure-property relationship in Fe-Cr-Co ridge alloys.

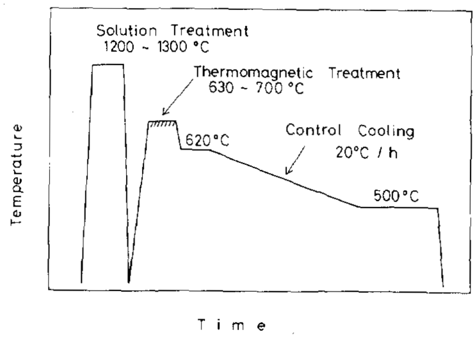

Fig. 3. Schematic diagram of heat treatment.

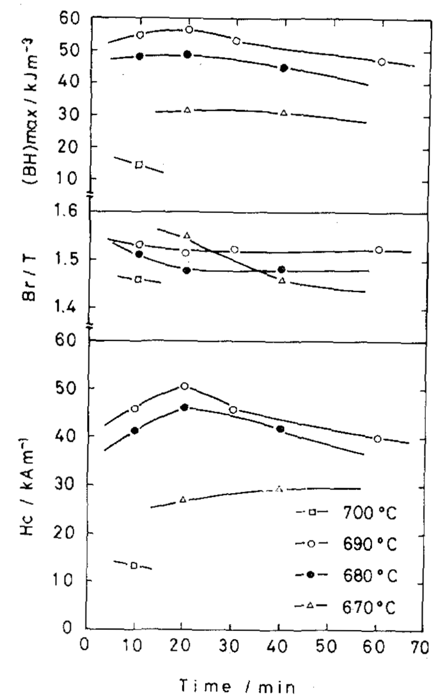

Fig. 4. Variation of magnetic properties of Fe-22Cr-15Co alloy versus TMT time with varying TMT temperature.

Results

A. Magnetic Properties

1) Thermomagnetic Treatment (TMT): Fig. 4 shows the example of the variation of the magnetic properties of an Fe-22Cr-15Co alloy that underwent various TMT with varying aging temperature and time, followed by the heat treatment shown in Fig. 3. It indicates that the optimum condition of TMT for the alloy is aging at 690°C for 20 min. This temperature, 690°C, is located at almost 10°C below the miscibility gap, referring to the shape of the miscibility gap shown in Fig. 1. The performance of the TMT at such a high temperature has not been noticed so far. Fig. 5 shows the magnetic properties of the Fe-25Cr-12Co alloy versus magnetic aging time with varying the temperature. It is found that the optimum TMT condition of the alloy is aging at 655°C for 80 min.

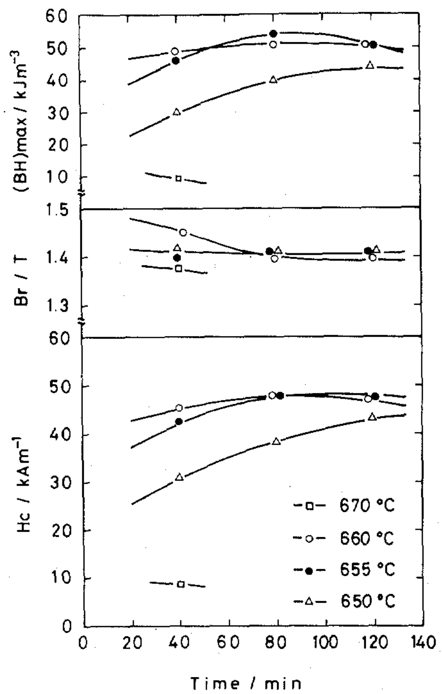

Fig. 5. Variation of magnetic properties of Fe-25Cr-12Co alloy versus TMT time with varying TMT temperature.

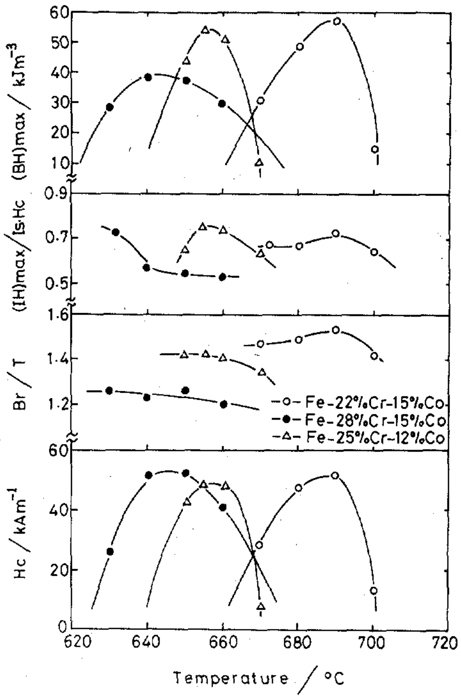

Fig. 6. Magnetic properties versus TMT temperature in Fe-22Cr-15Co, Fe-28Cr-15Co, and Fe-25Cr-12Co alloys.

As the cobalt content is decreased, the TMT temperature and time become respectively lower and longer. This stems from the fact that the miscibility gap temperature of the 12 percent Co alloys exists lower than that of 15 percent Co alloys. The optimum magnetic properties obtained with these alloys are summarized as a function of their TMT temperatures in Fig. 6, which exhibits that the magnetic properties such as Hc and (*BH*)max are sensitive to the TMT temperature. The optimum TMT temperature of the various Cr alloys achieved in this

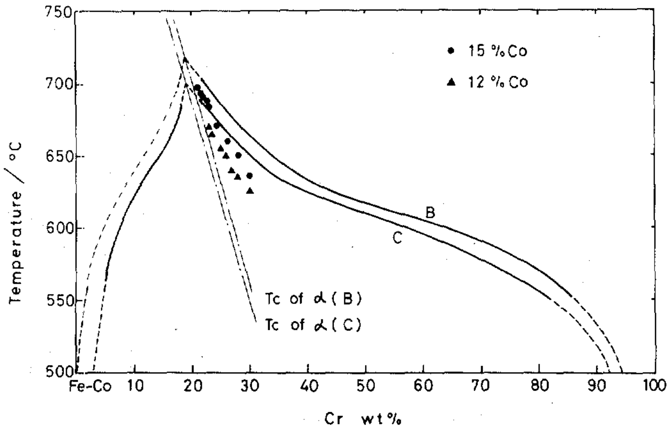

Fig. 7. Schematic plot of optimum TMT temperature of Fe-Cr-(12-15)Co alloys in vertical section of miscibility gap.

study is plotted in the vertical section of the miscibility gap, as shown in Fig. 7. It is illustrated that the optimum TMT temperature is located at 15°C ± 5°C below the miscibility gap. At the lower Cr content of the alloys, the closer their optimum TMT temperatures are to their Curie temperatures, but at the higher Cr content, the farther apart are their temperatures. This implies that the shape of the miscibility gap, as well as the Curie temperatures of the alloys, are important factors in determining the optimum TMT temperature, as anticipated in the approach section.

2) Step-Aging: The optimum TMT temperature is settled by the heat treatment procedure shown in Fig. 3. This section further develops the optimum step-aging sequence by means of step-aging the alloys at the temperature of every 20°C interval below 620°C. Fig. 8(a) shows the increment of the coercive force of the alloys versus step-aging time. The coercive forces of an Fe-22Cr-15Co alloy and an Fe-25Cr-12Co alloy increase by 1.6 kA/m and 2.4 kA/m, respectively, in comparison with those obtained by the cooling rate of 20°C/h. The optimum step-aging sequence of each alloy is approximated partially by the controlled cooling, 5°C/h for an Fe-25Cr-12Co alloy and 8°C/h for an Fe-22Cr-15Co alloy, as schematically illustrated with a dashed line in Fig. 8(b). Thus the optimum step-aging procedure of the 15 percent Co alloys after TMT is that the alloys are aged at 620°C for 1 h and at 600°C for 40 min, followed by the controlled-cooling at a rate of 8°C/h to 500°C, and then held at 500°C for 7 h. The optimum procedure of the 12 percent Co alloys is that the alloys are aged at 620°C for 1 h and at 600°C for 2 h, followed by the controlled-cooling at a rate of 5°C/h to 500°C and then held at 500°C for 10 h.

The magnetic properties of the alloys that underwent such an optimum heat-treatment procedure are summarized with varying the Cr content in Fig. 9. The energy products of the 12 percent Co and 15 percent Co alloys are at their maximum with the 25 percent Cr and 22 percent Cr alloys, respectively. The magnetic properties of an Fe-25Cr-12Co alloy are given as bHc = 50.4 kA/m (630 Oe), Br = 1.45 T (14.5 kG) and (BH)max = 61.6 kJ/m^3 (7.7 MGOe). Those of Fe-22Cr-15Co alloys are bHc = 51.6 kA/m (645 Oe), Br = 1.56 T (15.6 kG) and (BH)max = 66.4 kJ/m^3 (8.3 MGOe). The corresponding demagnetization curves of the alloys are shown in Fig. 10 in

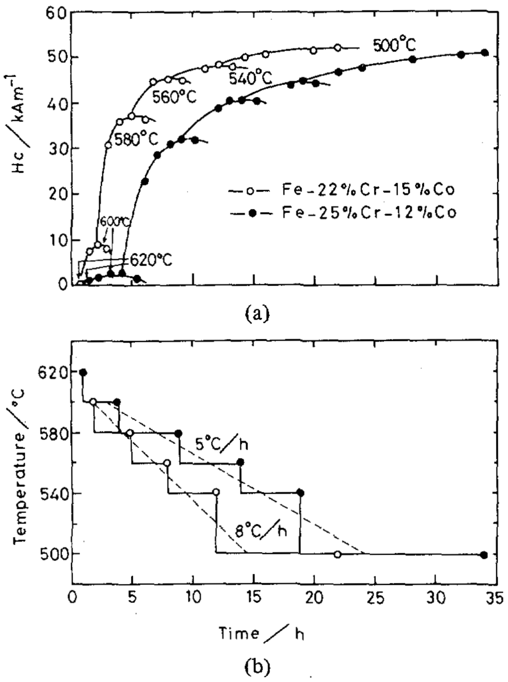

Fig. 8. (a) Increment of coercive force of Fe–22Cr–15Co and Fe–25Cr–15Co alloys during step-aging process, (b) approximation of step-aging process with controlled cooling.

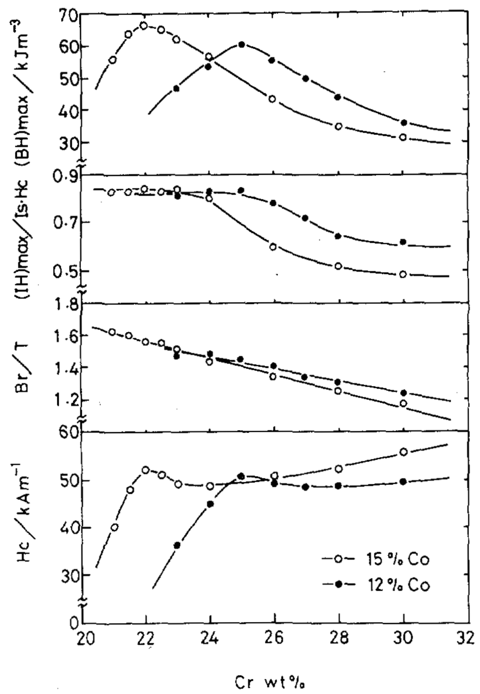

Fig. 9. Magnetic properties versus Cr content in Fe–Cr–(12–15)Co alloys.

comparison with that of Columax [19]. It should be noted that the characteristics of the properties of the ridge alloys are high remanent magnetization up to 1.56 T, and excellent squareness (96 percent) of the demagnetized curve defined by Br/4π Is.

B. Microstructures

The magnetic properties of the alloys are highly affected by a fine two-phase microstructure [10], [11]. The desirable

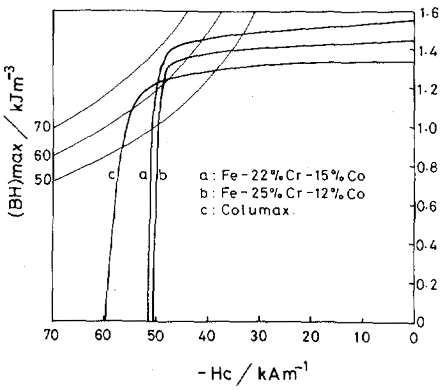

Fig. 10. Demagnetization curves of the alloys: (a) Fe–22Cr–15Co, (b) Fe–25Cr–12Co, (c) Columax.

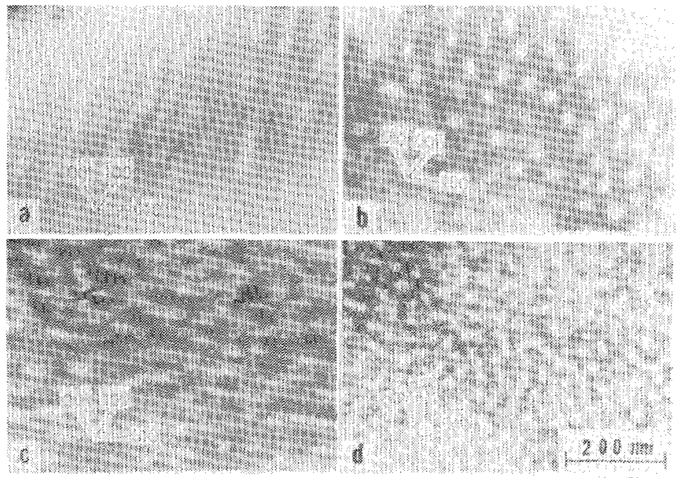

Fig. 11. Bright field micrographs of Fe–22Cr–15Co alloy thermomagnetically aged (a), (c) parallel and (b), (d) perpendicular to applied field direction, for 20 min (a), (b) at 690°C and (c), (d) at 670°C.

features of the ridge alloys stated in the approach must be reflected to the microstructure. Fig. 11 shows the microstructures taken from the Fe–22Cr–15Co alloy thermomagnetically aged for 20 min at 690°C (Fig. 11(a), (b)) and at 670°C (Fig. 11(c), (d)). The contrast between the two phases in the micrograph is weak because of the small difference in the composition of the two phases formed in the ridge region. The α_1 particles with bright contrast in Fig. 11(b), which is taken perpendicular to the applied field, are spherical, indicating that they are well-aligned along the field direction. However, the α_1 particles thermomagnetically aged at 670°C in Fig. 11(d) have a rod shape with a tendency to decompose along ⟨100⟩, not exactly elongated along the field direction. These pictures are seen in corresponding microstructures parallel to the field in Fig. 11(a) and (c). At the lower TMT temperatures, dispersion is finer, the volume fraction of the α_1 particle increases, and the two phases more interconnected with the rod-like shapes. In view of the morphology of the microstructures, the TMT at 690°C for an Fe–22Cr–15Co alloy is most effective on the alignment of the particles.

Fig. 12 shows the microstructures parallel and perpendicular to the magnetic field of the Fe–22Cr–15Co alloy given the TMT at 690°C for 20 min, followed by the optimum step-aging sequence shown in Fig. 8. Referring to Fig. 11(a), (b) and Fig. 12, it can be said that a high degree of alignment of

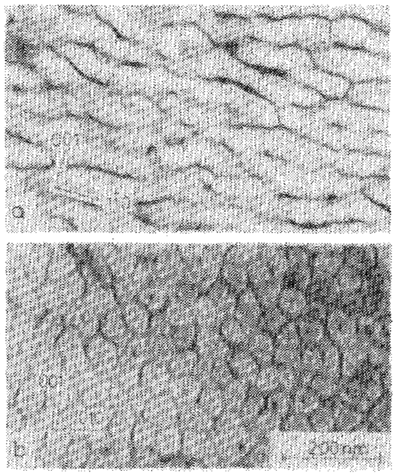

Fig. 12. Bright field micrographs of step-aged Fe-22Cr-15Co alloy.

TABLE I
CHANGES OF FeCo-RICH PARTICLES IN AN Fe-22Cr-15Co ALLOY DURING THE HEAT TREATMENT

	d(nm) (diameter)	m (aspect ratio)	$\frac{V_{\alpha 1}}{V_{\alpha 1}+V_{\alpha 2}}$ (%) (volume fraction)	n/μm² (number of particle)
T_1 (TMT) 690°C 20min	24	4.8	24	530
T_2 → 620°C	33	4.9	50	480
T_3 → 500°C	36	5.0	72	400

the particles induced by TMT remains unchanged throughout the step-aging sequence. The changes in the α_1 phase that occurred during the step-aging sequence are summarized in Table I. The diameter and the volume fraction of the α_1 phase increase almost from 240 Å to 360 Å and from 24 percent to 72 percent, respectively, while the ratio of length to diameter of the α_1 phase remains unchanged. The final product microstructure is such that the high volume fraction (72 percent) FeCo-rich phase with a diameter of 360 Å and an aspect ratio of nearly five is embedded in a Cr-rich α_2 phase.

DISCUSSION

These investigations verified that the ridge alloys produce the excellent magnetic properties up to $(BH)\max \simeq 66.4$ kJ/m^3 (8.3 MGOe) with an Fe-22Cr-15Co alloy. It should be emphasized that the alloys contain only 15 wt% Co, and the properties are almost comparable to those of the columnar Alnico family [19]. The energy product reported with the Fe-Cr-15Co alloys had been up to 5.5 MGOe [3], [4], since the existence of the ridge had not been noticed and the Cr content of the investigated alloys varied from 25 percent to 30 percent. The characteristics of the ridge alloys are to produce the high remanent magnetization up to 1.56 T (15.6 kG) as well as the excellent squareness of the demagnetized curve. This is attributed to the fact that the volume fraction of the FeCo-rich phase is high (nearly 70 percent), and the TMT in the ridge region is effective on the alignment of the FeCo particles.

The optimum TMT temperature of the ridge alloys appears

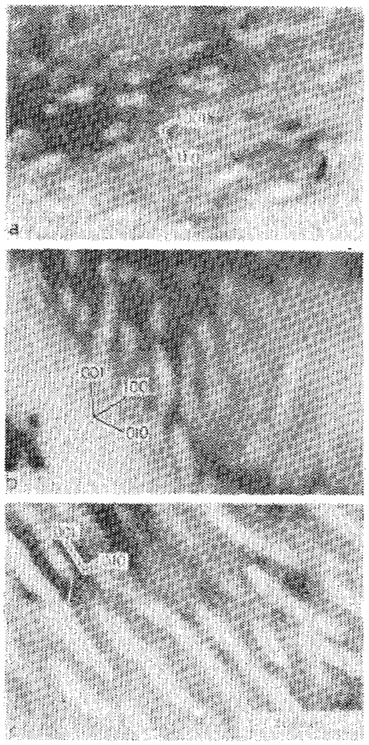

Fig. 13. Bright field micrographs of the Fe-22Cr-15Co alloy thermomagnetically aged at 690°C for (1) 10 min, (b) 20 min, and (c) 60 min.

to be located at 15°C ± 5°C below the miscibility gap temperature. The corresponding microstructures indicate that the FeCo rich phase has a rod-like shape, highly elongated and aligned parallel to the field. The aspect ratio of the FeCo particle is nearly five, which is larger than that (nearly three) of the Fe-31Cr-23Co alloy [10]. The good effect of the TMT in the ridge region would be explained with a combination of Cahn's and Zijlstra's models as described in the Approach Section. In the early stage of thermomagnetic aging, until the spinodal decomposition is completed, Cahn's model would be suitable, and Zijlstra's model would be applicable to the growth stage of the decomposed phases. Mössbauer's experiments suggested that the spinodal decomposition was completed within about 10 s for 560°C aging of an Fe-33 at% Cr-21.5 at% Co alloy [20]. Thus it would be expected for the ridge alloys that Cahn's model might be appropriated for the very short time of magnetic aging. However, it is experimentally difficult to verify this model. On the other hand, the series of the micrographs of the Fe-22Cr-15Co alloy magnetically aged at 690°C for 10 min, 20 min, and 60 min, as shown in Fig. 13 indicate that the prolonged aging causes the α_1 phase to be more elongated parallel to the field direction, and that the aspect ratio of the α_1 particles increases with increasing aging time up to 1 h. This implies that most of the elongation process of the α_1 particle would be subject to Zijlstra's model.

The high alignment of the FeCo-rich particles induced by TMT was held during step-aging sequence. It is stressed that the step-aging at 620°C and 600°C is important in growth of the FeCo-rich phase because the equilibrium volume fraction of FeCo-rich particles is expected to be nearly 50 percent, and enough diffusion time to grow the particle is required. The number of the FeCo-rich particles during the step-aging sequence is kept almost constant, as shown in Table I, implying that the FeCo-rich particles formed during TMT are grown not by the Ostwald ripening-type coarsening [21], but grown simply to reach its equilibrium volume fraction. The final microstructures consist of a high volume fraction (72 percent) of the FeCo-rich phases, which could have not been resulted unless the ridge region had existed in the relatively low Cr side (20 percent < Cr < 25 percent).

A heat treatment in the ridge region of the miscibility gap is applied to the 12-15 percent Co containing Fe-Cr-Co alloys in this investigation, but is also applicable to the low cobalt Fe-Cr-Co alloys. It is reported that low Co (4-9 percent) containing Fe-Cr-Co alloys is required to be continuousally cooled for a long time (about 100-250 h) within the miscibility gap to produce good magnetic properties [7], [8]. Our preliminary investigations in low Co alloys designate that the aging time can be shortened to within approximately 50 h by the suitable heat treatment in the ridge region [22].

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