Further Studies of the Miscibility Gap in an Fe-Cr-Co Permanent Magnet System

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SUMMARY

The effect of magnetic field aging on the permanent magnet properties of low-cobalt Cr-Co-Fe alloys containing 5-9% Co was studied. Square loop and high energy products of \( (BH)_{\text{max}} \approx 4-6 \text{ MG} \cdot \text{Oe} \) were obtained by slow continuous cooling under an applied magnetic field. The slow cooling rates required for these alloys could be beneficial in industrial field heat treatments of heavy section magnets or a large quantity of magnets in a relatively small batch furnace.

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Abstract—The miscibility gap of an Fe-Cr-Co system is further examined by monitoring the microstructures and the magnetic properties of the alloys. It is shown 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. It is demonstrated that the alloys in the ridge region can exhibit very good magnetic properties. An Fe-25%Cr-12%Co alloy gives the magnetic properties as \( B_r = 1.45 \text{ T}(14.5 \text{ kG}), B_{ir} = 50.1 \text{ kA/m}(630 \text{ Oe}) \) and \( (BH)_{\text{max}} = 61.3 \text{ kJ/m}^3 \), which are almost comparable to those of the columnar Alnico 5 magnets.

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INTRODUCTION

NEWLY DEVELOPED Fe-Cr-Co alloys have the technological potential to replace available ductile magnets and some of the Alnico alloys in the present permanent magnet market [1]-[5]. Because of their good ductility, Fe-Cr-Co alloys can provide expanded applications for high-performance small-magnet circuits, which are difficult to make with Alnico or ferrite magnets [6], [7].

The magnetic hardening of the alloys is associated with their modulated structures, consisting of two phases: an iron-rich phase \( (a_1) \) and a chromium-rich phase \( (a_2) \) [1], [8], [9]. The features of the decomposition are consistent with those expected from spinodal decomposition of the high-temperature
phase (α) during aging. Kaneko et al. [10] determined the miscibility gap in an Fe-Cr-Co ternary system using mechanical hardness and Curie temperature measurements. Their results are illustrated in Fig. 1, showing the asymmetry of the miscibility gap of the system. The asymmetry of the miscibility gap yields various modulated microstructures as discussed by Okada et al. [9].

Very recently Nishizawa et al. [11] computed the miscibility gap of αFe-X systems by thermodynamic treatments, taking into account their magnetic effects, and found that the miscibility gap is not a simple parabolic but is of abnormal shape expanding toward the Fe side, and it has a sharp horn at the Curie temperature. The part of the protrusion of the miscibility gap is hereafter called a “ridge” because of its shape resemblance. The anomalies in the miscibility gap due to the magnetic effect could be enlarged by the addition of Co to an αFe-X system. Their results also suggest the existence of the peculiar “ridge” of the miscibility gap in the Fe-Cr-Co system, which could not be detected in the previous experimental studies [10].

Thus the purpose of the present investigation is to further study the shape of the miscibility gap in Fe-Cr-Co alloys by experimental methods different from the previous ones, such as the direct microstructural observations by a transmission electron microscope and monitoring the change of the magnetic properties. The direct microstructure observations were made with the alloys aged inside the miscibility gap and the magnetic properties of the alloys aged outside. The heat-treatment procedure adopted for method 2) is schematically shown in Fig. 2. After the solution treatment, the alloys were at first aged at various temperatures for 1 h in a magnetic field of 2 kOe, then held at certain other temperatures and control cooled to 500°C at a cooling rate of 15°C/h, and then quenched in water.

**RESULTS**

The series of bright field micrographs shown in Fig. 3 were taken from the Fe-26%Cr-12%Co alloy aged in a magnetic field of 2 kOe for 1 h at 670°C, 660°C, 650°C, and 640°C, respectively.
respectively. The observed plane is perpendicular to the field direction. The phase with bright contrast is identified as the FeCo-rich ($\alpha_1$) phase, and the phase with dark contrast is identified as the Cr-rich ($\alpha_2$) phase. In these micrographs the $\alpha_1$ phase is a minor phase. The micrographs reveal that the miscibility gap of the alloy is around 665°C, and they also show that the volume fraction of the $\alpha_1$ phase is very small (around 12 percent) after aging at 650°C just below the miscibility gap temperature, and it rapidly increases upon lowering the aging temperature. Another example of the determination of the miscibility gap by microstructure observations is shown in Fig. 4. Microstructures in Fig. 4 are taken from the Fe-23%Cr-12.5%Co alloy thermomagnetically aged for 1 h at 685°C, 680°C, and 670°C, respectively, and indicate that the miscibility gap of the alloy is located around 683°C. The occurrence of the decomposition at such high temperature in the alloy containing low Cr (23%Cr), which has not been noticed so far, indicates that the miscibility gap shifts in the FeCo side.

The temperature of the miscibility gap could be also determined by monitoring the change of the magnetic properties. The coercive force is the most sensitive parameter for the determination of the miscibility gap. Fig. 5 shows the variation of the coercive force of the Fe-26%Cr-12%Co alloy heat treated as shown in Fig. 2 with varying the temperature of the thermomagnetic treatment. The coercive force varies after heating up above 400°C [9], [10]. Thus the Curie temperatures of the "ridge" alloys must be deduced from those measured in high-Cr alloys. The Curie temperatures of the alloys located along the conjugate line C are extrapolated from the reported data [10] of the high-Cr alloys (>45%Cr) which are below 400°C, as shown in Fig. 7.

It is concluded that the miscibility gap of the Fe-Cr-Co system has a knife-like "ridge" shape protruding toward the FeCo side. The "ridge" region persists to exist at high temperature with increasing Co content. These characteristics of the "ridge" shape of the miscibility gap agree with the ones thermodynamically predicted by Nishizawa et al. [11].

**DISCUSSION**

The present investigation substantiates that the miscibility gap of the Fe-Cr-Co system has the "ridge" shape protruding the FeCo side along the Curie temperature. However, the top part and low-Cr side (<21%Cr) of the miscibility gap denoted by the dashed lines in Figs. 6 and 7 were not definitely determined since the solution treatment to obtain a single $\alpha$ phase was not successful for these alloys. Fig. 7 also suggests that the "ridge" could not be identified by the hardness test adopted in the previous studies [10] because of the small difference in the composition of the two phases formed in the "ridge" region.

Preliminary study indicates the possibility of the improvement of the magnetic properties of the alloys in the "ridge." For the example, an Fe-25%Cr-12%Co alloy can achieve the magnetic properties: $B_r = 1.45$ T (14.5 kG), $b/hc = 50.1$ kA/m (630 Oe), and $(BH)_{max} = 61.3$ kJ/m$^3$ (7.7 MG·Oe), when the alloy was thermomagnetically aged at 655°C for 80 min and was held at 620°C and 600°C for 1 h each, respectively, followed by controlled cooling at a rate of 5°C/h to 500°C and quenched in water. It should be emphasized that this alloy contains only 12% Co, and the magnetic properties obtained here are almost comparable to those of the columnar Alnico 5 magnet [12]. The corresponding magnetic hysteresis loop of
Fig. 6. Miscibility gap of an α phase in Fe-Cr-Co system. Investigated alloys are marked by solid circle.

Fig. 7. Vertical sections of the miscibility gap along the conjugate lines A-G shown in Fig. 6. The Curie temperatures of the α phase of the alloys C are extrapolated from those measured in the high-Cr (>45% Cr) alloys.

The alloy as shown in Fig. 8 shows the excellent squareness (96 percent) of the demagnetized curve defined by $B_r/4\pi I_s$ in spite of the alloy being polycrystalline. Fig. 9 shows the micrographs of the alloy corresponding to Fig. 8, where (a) is parallel and (b) is perpendicular to the applied magnetic field direction, and suggests that the FeCo-rich phase has nearly a rod shape well aligned parallel to the applied field direction. The excellent squareness of the hysteresis loop with suitable coercive force would arise from the microstructure in which the well-aligned FeCo-rich phase is imbedded within the Cr-rich phase. The degree of the alignment of the FeCo-rich phase is mainly determined by the thermomagnetic treatment [8], [9] so that effective thermomagnetic treatment must have been done within the “ridge” region. Nishizawa et al. [11] suggested by the computer calculation that the chemical spinodal line in the ferromagnetic alloy system is located within the “ridge” region. It is reasonable that the spinodal line within the “ridge” region is approximated by the chemical one because of the small elastic energy expected within the “ridge.” According to the Cahn’s theory on the magnetic aging of spinodal alloys [13], mainly three factors have an influence on the perfection of the morphology of the microstructures: 1) elastic energy which favors {100} waves in cubic crystals; 2) the degree of undercooling, the increment of which makes the waves other than the waves parallel to the field possible; and 3) magneto-static energy which favors the wave parallel to the field. The effectiveness of the applied magnetic field on polycrystalline
alloy will be increased when factors 1) and 2) are small and factor 3) dominates. In referring to Figs. 6 and 7, it is speculated that 1) a small difference in the composition of the two phases formed within the “ridge” region leads to a decrease in the elastic energy, and 2) in the “ridge” region, 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. A detailed analysis of the conditions of the thermomagnetic treatment, microstructures formed within the “ridge” region, and their correlation with the magnetic properties will appear in a future publication.

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