Evolution Process of $\langle 100 \rangle$ Texture in Fe–Cr–Co–Mo Permanent Magnets

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The present work describes the process of grain growth during secondary recrystallization, which develops the $\langle 100 \rangle$ texture in Fe–Cr–Co–Mo hard magnets. The secondary recrystallization was caused by heat-treating the alloys in the sequence of $\alpha$, $\alpha + \gamma$, $\alpha + \gamma + \sigma$, $\alpha$ phase regions of Fe–Cr–Co–Mo alloys (HTSR). This heat treatment results in the development of $\langle 110 \rangle\langle 110 \rangle$ textures with $\langle 100 \rangle$ directions aligned along the transverse direction (TD) of cold-rolled strips. The process of grain growth during secondary recrystallization can be considered as follows: (1) $\gamma$ and $\sigma$ phases precipitate along grain boundaries and within grains by the heat treatment in $\alpha + \gamma$ and $\alpha + \gamma + \sigma$ region in HTSR. It results in refining the $\alpha$ grains and increasing the interfacial energy of $\alpha$ grains. (2) The precipitated $\gamma$ phase inhibits the normal grain growth of $\alpha$ phase and thus maintains the driving energy for secondary recrystallization. But the volume fraction of $\gamma$ phase decreases with increasing temperature during the last heat treatment of HTSR in $\alpha$ phase region. It results that the pinning effect of $\gamma$ phase decreases and secondary recrystallization occurs.

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I. Introduction

Fe–Cr–Co permanent magnets exhibit excellent magnetic properties comparable to those of Alnico family, with good ductility. The magnetic hardening of the alloys is performed by heat-treating within the miscibility gap, in producing a modulated structure consisting of two phases, an Fe–Co rich phase ($\alpha_1$) and a Cr rich phase ($\alpha_2$). A uniaxial magnetic anisotropy is usually induced by magnetic aging in elongating the $\alpha_1$ phase parallel to the applied field direction. In order to expand their applications, the enhancement of coercivity is strongly demanded.

It is to be noted that the addition of Mo to this alloys increases the coercive force because of the anisotropic decomposition along the $\langle 100 \rangle$ directions. Good magnetic properties can be expected by utilizing the anisotropic decomposition more efficiently and align the $\alpha_1$ phase along the applied field direction in $\langle 100 \rangle$ texture samples.

This was done in an Fe–30%Cr–15%Co–3%Mo (in mass%) alloy by developing the $\langle 100 \rangle$ recrystallization texture, as reported in our previous papers. The $\langle 100 \rangle$ texture is developed by the mixture of cold-rolling and annealing. The alloys are annealed within the phase regions in the sequences of $\alpha$, $\alpha + \gamma$, $\alpha + \gamma + \sigma$, $\alpha$ in Fe–Cr–Co–Mo alloys. The secondary recrystallization occurs and $\langle 110 \rangle\langle 110 \rangle$ grains grow by heat treatment. Hereafter, this heat treatment for secondary recrystallization is abbreviated to HTSR. The best magnetic properties as $H_c = 82$ kA/m (1025 Oe), $(BH)_{max} = 60.8$ kJ/m$^3$ can be obtained in the transverse direction (TD) of cold-rolled strips.

But the mechanism of $\langle 100 \rangle$ texture development in Fe–Cr–Co–Mo alloys by this method, which is a mixture of cold-rolling and HTSR, is not clear yet. Especially, the grain growth during secondary recrystallization is not clear. In our previous paper, the secondary recrystallization is not occurred by the annealing only in $\alpha$ phase region such as the heat treatment at 1200°C for 40 h. By the HTSR, the grain growth is occurred and it results in the fact that the average grain size increases from 120 μm to 3 mm. The total heat treatment time of HTSR is very short as compared with that of conventional heat treatment only in $\alpha$ phase region. Thus the purpose of this work is to clarify the process of grain growth during secondary recrystallization occurred by HTSR. This is studied by observing the morphological changes of the microstructure in every stage of HTSR and by specifying what is the inhibitor for the normal grain growth of $\alpha$ phase.

II. Experimental Procedures

The experimental procedure is shown in Fig. 1. Fe–30%Cr–15%Co–3%Mo (in mass%) alloys were chosen for this investigation. The alloys were induction-melted in Ar atmosphere and cast into a cylindrical specimen in a mold with an inside diameter of 25 mm. The chemical composition of this alloys was verified as Fe–29.7%Cr–15.0%Co–3.05%Mn–0.053%Mn–0.0660%S–0.0747%O–0.019%N–0.0660%C. The ingots were hot-forged to a bar of approximately 18×18 mm$^2$ in cross section. The bars were solution-treated at 1300°C (1573 K) for 30 min
The microstructure was observed by optical microscopy, transmission electron microscopy (TEM) and X-ray energy dispersion analysis (EDX). The texture was at first judged by the relative intensity \(I/I_0\) of the each X-ray peak diffracted by the surface of the cold-rolled and annealed strips, where \(I_0\) exhibits the X-ray intensity of each diffracted peaks from equiaxed alloys. If the \(I/I_0\) value of the certain peak is over one, it means that the crystallographic plane corresponded the peak is the one of the main crystallographic components for the strips. But when the grain size of the strips is large, this method cannot determine the texture. Then in order to determine the orientation of grains, the shape of etching pits formed on the surface of the strips was observed\(^{3(9)}\). In this study electrolytic and chemical etchings were used in order to produce distributed micropits uniformly. The reagent for these etching are oxalic acid and aqua regia, respectively\(^{37}\).

### III. Results and Discussion

Figure 2 shows the schematic diagram of the annealing method for secondary recrystallization (HTSR) and the optical microstructures (a, b, c, and d) taken from the rolling plane of the alloys at every stage of HTSR (A, B, C, and D). Figure 2(a) exhibits that the primary recrystallization has already finished and the microstructure is composed of \(\alpha\) phase grains whose average grain size is 150 \(\mu m\) after the first heat treatment in the \(\alpha\) phase region. The second heat treatment in the \(\alpha + \gamma\) region, gave the \(\gamma\) phase precipitated along grain boundary (Fig. 2(b)). The third heat treatment in the \(\alpha + \gamma + \sigma\) phase region results in \(\gamma\) and \(\sigma\) phases precipitated not only along grain boundaries but within grains (Fig. 2(c)). From Fig. 2(a)–(c), remarkable grain growth does not occur in these stages of HTSR. But the last heat treatment in the \(\alpha\) phase region accelerates the grain growth and results in the average grain size of over 3 \(mm\) as shown in Fig. 2(d). It can be said that the secondary recrystallization occurs at the last heat treatment of HTSR in the \(\alpha\) phase region.

Figure 3 shows the etching pits taken from the rolling plane of the alloys after the (a) first and (b) last heat treatment of HTSR, which correspond to Fig. 2-A and Fig. 2-D, respectively. From the shape of etching pits shown in Fig. 3(a), the grains of the alloys annealed in the first stage of HTSR have the \(\{111\}\) and \(\{100\}\) components. But the grains after the last stage of HTSR have the \(\{110\}\) components with \(\{110\}\) directions along RD shown in Fig. 3(b). It can be considered that the texture mainly composed of \(\{110\}\)\((\{110\) is obtained after the last stage of HTSR.

In order to investigate how the grain growth takes place during the last heat treatment, the observation of optical microstructure taken from the alloys heat-treated at 1150°C (1423 K) for 15 min (0.9 \(\times\) 10\(\text{s}\)) was carried out. The results are shown in Fig. 4. Figure 4(b) is a high magnification photograph at the same place exhibited by an arrow in Fig. 4(a). The grain size of the secondary recrystallized grain shown in right side of Fig. 4(a) is
Fig. 2 The schematic diagram of the annealing method for secondary recrystallization (HTSR) and the optical microstructure taken from the alloys at every stage of HTSR.

over 2 mm. It can be considered that the secondary recrystallization has occurred. The sub-grains cannot be seen in the secondary recrystallized large grain but are observed in the smaller grains which undergo only primary recrystallization. The secondary recrystallized grain, which component can be estimated as \{110\}<110>, from the etching pits, grows at the expense of other small grains.

The further observation of optical microstructure taken from the alloys heat-treated for a short time of 5 min (0.3 ks) was carried out. But the results reveal that the secondary recrystallization has already been occurred. It is necessary to investigate the morphological changes of the grain evolution within 5 min (0.3 ks). Considering the heat treatment temperature of the third and last stages of HTSR, the phase transformation from the \(\alpha + \gamma + \sigma\) phase to the \(\alpha\) phase is caused with increasing temperature when the specimens are inserted into the furnace heated at 1150°C (1423 K). It can be considered that this phase transformation influences the grain evolution at this stage. Then the morphological change of microstructure was investigated after the insertion of specimens into the furnace. The result is shown in Fig. 5. The optical microstructures shown in Fig. 5(a)–(d) are taken from the alloys quenched into water from the temperatures of 1000–1150° C, respectively. The precipitated \(\gamma\) and \(\sigma\) phases decrease and disappear with increasing quenching temperatures. In stead of \(\gamma\) and \(\sigma\) phases, the sub-grains can be seen within grains at 1150°C (1423 K) (Fig. 5(d)). Figure 6 shows the optical microstructure taken at higher magnification from the specimen corre-
Fig. 4  The optical microstructure and etching pits taken from the alloys heat-treated at 1150°C for 15 min at the last stage of HTSR.

Fig. 5  The optical microstructure taken from the alloys quenched into water when the furnace temperature reached at 1000-1150°C (1273-1423 K).

d-responding to Fig. 5(c). The sub-boundary exhibited by arrows exists near the γ precipitates. It is apparent that the formation of sub-boundary is closely related to disappearance of γ phases on heating. The sub-boundary may be formed at the sites where the γ phases disappeared. The formation of subgrains results in refining α phase grains and in increasing the interfacial energy of α grains.

The process of grain growth in secondary recrystallization caused by HTSR can be schematically illustrated in Fig. 7. After the heat treatment at 1250°C (1523 K) for 30 min (1.8 ks) (Fig. 7(A)), the grains are composed of only α phases. Primary recrystallization has been finished in this stage. Annealing of the alloys at 970°C (1243 K) gives rise to the precipitation of γ phases along grain boundary (Fig. 6(B)), and one at 900°C (1173 K) results in the precipitation of γ and σ phases within grains. Microstructure observations shown in Fig. 6 suggest that annealing at 1150°C (1423 K) shows the morphological changes of microstructures as shown in Figs. 7(D-1) to (D-4). The γ and σ phases disappear with increasing temperatures and subgrains are formed within grains. Some of these subgrains combine each other and become larger. These larger grains grow at the expense of other subgrains and become huge α phase grains, which are free from sub-structure.

It is well known that small precipitates or inclusions, which inhibit normal grain growth, are necessary for the development of ⟨100⟩ textures in Si-Fe steels[10]. In order to find what are the inhibitors for the development of ⟨100⟩ textures in Fe-Cr-Co-Mo alloys, the microstructure was analyzed by EDX. Figure 8 shows the TEM micrographs taken from the alloys quenched into water from (a) 1100°C (1373 K) and (b) 1150°C (1423 K),
which is the last heat treatment of HTSR in the α phase region. The compositions of some phases, which are exhibited by H–J, were analyzed by EDX and the results are shown in Fig. 8. The small second phase exhibited by H exists at sub-boundary at 1100°C (1373 K). This phase is estimated as the γ phase by considering the composition of this phase. But at 1150°C (1423 K) as shown in Fig. 8(b), the γ phase disappears and the sub-boundary exhibited by an arrow curves and protrudes. It can be considered that the precipitated γ phase inhibits the normal grain growth of α phase. But the volume fraction of the γ phase decreases with increasing temperature, and the pinning effect of the γ phase decreases and secondary recrystallization proceeds.

**Fig. 6** The relationship between γ phases and subgrains.

**Fig. 7** The schematic view of grain growth process in secondary recrystallization caused by HTSR.

![Image of Fe-30Cr-15Co-3Mo](image)

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**Fig. 8** The TEM micrographs and the results of EDX analysis taken from the alloys quenched into water at (a) 1100°C (1373 K) and (b) 1150°C (1423 K) at the last heat treatment of HTSR.

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**REFERENCES**