EFFECTS OF MOLYBDENUM CONTENT AND ISOTHERMAL THERMOMAGNETIC TREATMENT ON COERCIVITY AND MICROSTRUCTURE OF Fe-Cr-Co-Mo ALLOYS

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Abstract
The effects of molybdenum content and isothermal thermomagnetic treatment temperature on the microstructure and magnetic properties of Fe-30Cr-15Co-(1-5)Mo-0.5Ti alloys were investigated by transmission electron microscopy and magnetostatic methods. An optimal duration and temperature ITMT were defined and the specific high coercivity microstructure formation was established.

1. INTRODUCTION
Hard magnetic Fe-Cr-Co alloys are known as permanent magnet materials with relatively high coercive force ($H_C \approx 65$ kA/m) and high mechanical properties. The alloys of Fe-Cr-Co system belong to a group of alloys with a miscibility gap on the phase diagram (Fig. 1). It can be seen in Fig. 1 that the alloys consist of one single phase ($\alpha$ solid solution) at high temperature. The presence of miscibility gap causes the $\alpha$ phase to decompose into two phases $\alpha \rightarrow \alpha_1+\alpha_2$ when an alloy is kept at temperatures confined within the gap for some time [1].

![Fig. 1 Miscibility gap of the Fe-Cr-Co phase diagram [1]](image)

Both the Fe-Co particles ($\alpha_1$ phase) and Cr-rich matrix ($\alpha_2$ phase) have the isomorphic bcc structure. It was supposed that the phase separation $\alpha \rightarrow \alpha_1+\alpha_2$ upon annealing at a temperature within the gap proceeds by spinodal decomposition [2]. The highest magnetic properties of Fe-Cr-Co alloys correspond to a microstructure that consists of the nanocrystalline particles of ferromagnetic $\alpha_1$ phase surrounded weakly magnetic $\alpha_2$ matrix. The $\alpha_1$ particles have the single-domain size and rod-like shape. The thermomagnetic treatment leads to anisotropic magnets in which the elongated $\alpha_1$ particles are mainly parallel to the direction of the magnetic field applied during treatment.

One of the ways to increase the magnetic properties of Fe-Cr-Co alloys is the addition of elements with large atom radius, such as Mo or W. The main effect of molybdenum addition is to increase the difference between the lattice parameters of $\alpha_1$ and $\alpha_2$ phases. During heat treatment, a continuous change in the composition
takes place due to the diffusion of Mo atoms to $\alpha_2$ phase. The increase of the interfacial energy leads to growth of $\alpha_1$ phase mainly parallel to $<100>$ directions of the cubic structure and produces the large shape anisotropy of ferromagnetic $\alpha_1$ particles [3].

In the case of Fe-Cr-Co-Mo alloys the forming of magnetic anisotropy during thermomagnetic treatment and followed tempering treatment is due to competition influence of the elastic energy and magnetic energy of the elongated particles in the applied field. Despite the fact that much attention has been paid to the Fe-Cr-Co-Mo alloys the data of optimum content of molybdenum in Fe-Cr-Co alloys and its influence on microstructure and magnetic properties is very contradictory [3-5]. In order to understand this problem further, we investigated some Fe-Cr-Co-Mo alloys with different Mo content (from 1 to 4 wt %). The aim of this paper is to present a brief overview of the coercivity and microstructure changes in Fe-Cr-Co-Mo alloys with different content of Mo in dependence of the duration and temperature of isothermal thermomagnetic treatment (ITMT).

2. EXPERIMENTAL PROCEDURES

The samples Fe-30Cr-15Co-(1-5)Mo-0.5Ti (wt %), alloys № 1–5 respectively, were prepared by induction melting in Ar atmosphere followed by casting in a copper mould. All samples were aged at 1200°C for 20 min and then quenched in water. The treatment of as cast samples includes the isothermal thermonagnetic treatment and followed full tempering treatment (TT) consisted of the annealing at 605 °C 5 h + 580 °C 1 h + 560 °C 3 h + 540 °C 5 h. The temperature of ITMT was varied from 650 to 605 °C. The time of ITMT was 20 minutes.

Phase identification was carried out by X-ray diffraction using Co-Kα radiation. Simplified Rietveld method was used for quantitative phase analysis. Microstructural observations were performed by transmission electron microscopy (TEM) using a Tecnai G²20Twin instrument on thin foils prepared by jet electrolitical polishing TenuPol-5 in standard electrolit А8 (solution Cr₂O₃ in orthophosphorus acid). Magnetic measurements were carried out on cylindrical magnets of 10 mm diameter, using hysteresisgraph.

3. RESULTS AND DISCUSSION

The data characterizing influence of time ITMT on magnetic properties of alloys № 1-5 are presented in Table 1. The maximum level of magnetic properties is reached on alloys with 2-3 % Mo. It has been established that the optimum duration of isothermal TMT was 20-25 minutes for all alloys with different content of Mo. Decrease of magnetic properties at more shorter or longer influence of magnetic field means that formation of nanocrystalline microstructure with shape anisotropy of $\alpha_1$ particles occurs during all time of ITMT. Short treatment is not enough to form elongated particles. The increase of time ITMT more than 10 min, apparently, causes the new precipitations of $\alpha_1$ phase to grow across the elongated axis of particles and that coalescence of the ferromagnetic $\alpha_1$ particles decrease of coercivity.
Table 1. Dependence of magnetic properties of alloys 1-5 on duration of ITMT

| $T_{ITMT}$, min | Alloy № 1 | | | Alloy № 2 | | | Alloy № 3 | | | Alloy № 4 | | | Alloy № 5 |
|----------------|-----------|---|---|-----------|---|---|-----------|---|---|-----------|---|---|-----------|---|---|
|                | $H_c$, kA/m | $\mu_0\mu_r$ | T  | $H_c$, kA/m | $\mu_0\mu_r$ | T  | $H_c$, kA/m | $\mu_0\mu_r$ | T  | $H_c$, kA/m | $\mu_0\mu_r$ | T  | $H_c$, kA/m | $\mu_0\mu_r$ | T  |
| 5              | 9,6        | 0,90 |     | 20,0       | 0,94 |     | 29,6       | 1,07 |     | 52,0       | 0,93 |     | 54,4       | 0,90 |     |
| 10             | 43,2       | 1,20 |     | 49,6       | 1,15 |     | 56,0       | 1,10 |     | 60,0       | 0,93 |     | 61,6       | 0,90 |     |
| 15             | 52,0       | 1,22 |     | 58,4       | 1,15 |     | 65,6       | 1,10 |     | 64,0       | 0,93 |     | 56,8       | 0,90 |     |
| 20             | 56,8       | 1,22 |     | 68,0       | 1,15 |     | 68,0       | 1,10 |     | 61,6       | 0,95 |     | 56,8       | 0,95 |     |
| 25             | 54,4       | 1,25 |     | 68,0       | 1,15 |     | 65,6       | 1,12 |     | 59,2       | 0,95 |     | 52,0       | 0,95 |     |
| 30             | 53,6       | 1,25 |     | 64,8       | 1,15 |     | 64,8       | 1,15 |     | 56,0       | 0,95 |     | 49,6       | 0,98 |     |
| 35             | 52,8       | 1,25 |     | 64,0       | 1,15 |     | 64,0       | 1,15 |     | 54,4       | 0,95 |     | 49,6       | 1,00 |     |
| 40             | 51,2       | 1,25 |     | 63,2       | 1,15 |     | 58,4       | 1,15 |     | 51,2       | 0,95 |     | 47,2       | 0,98 |     |
| 45             | 44,8       | 1,25 |     | 56,0       | 1,15 |     | 58,4       | 1,15 |     | 48,0       | 0,95 |     | 46,4       | 0,98 |     |
| 60             | 44,8       | 1,25 |     | 52,8       | 1,00 |     | 56,8       | 1,15 |     | 48,0       | 0,95 |     | 46,4       | 0,98 |     |

Fig. 2 reveals the effect of temperature $ITMT$ on coercive force of Fe-30Cr-15Co-2Mo-0.5Ti alloys (alloy № 2) after full $TT$ (annealing at 605 °C 5 h + 580 °C 1 h + 560 °C 3 h + 540 °C 5 h). Two maxima of $H_c$ are distinctly observed at temperatures 635 and 620°C. The dependences $H_c (T_{ITMT})$ for all investigated alloys have similar character. For alloys № 1-3 (1-3 wt % Mo) the maxima of $H_c$ are appeared at 635 and 620°C. For Mo-rich alloys № 4, 5 (4 and 5 wt % Mo) these maxima are observed at 625 and 615°C, accordingly (Fig. 2b).

TEM bright field images of the sample № 2 after $ITMT$ at different temperatures are presented in Fig. 3 a-e. It reveals two-phase nanostructure constituting of fine particles of size 50÷200 nm inside matrix phase. Microdiffraction pattern of (b) area is shown in Fig. 3f. Calculations of microdiffraction patterns show that elongated particles of $\alpha_1$ phases are mainly directed along directions <100>.

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**Fig. 2** Dependences of $H_c$ on temperature $ITMT$ for alloy № 2 (a) and alloy № 4 (b) after full tempering treatment

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TEM bright field images of the sample № 2 after $ITMT$ at different temperatures are presented in Fig. 3 a-e. It reveals two-phase nanostructure constituting of fine particles of size 50÷200 nm inside matrix phase. Microdiffraction pattern of (b) area is shown in Fig. 3f. Calculations of microdiffraction patterns show that elongated particles of $\alpha_1$ phases are mainly directed along directions <100>. 
The comparison of microstructures in Fig. 3 a-e shows that the middle size of $\alpha_1$ particles decreases with reducing the temperature ITMT from 640 to 615°C. At the same time the maximum of anisotropy form of ferromagnetic $\alpha_1$ particles distinctly corresponds to maxima of coercivity at 635°C (Fig. 3b) and 620°C (Fig. 3d).

Competing influence of a magnetic field and elastic energy on microstructure formation during isothermal thermomagnetic treatment and the subsequent tempering treatment is visible at comparison of microstructure alloys № 2 with low Mo content and Mo-rich alloys № 4, accordingly.

TEM bright field images of the sample № 4 after ITMT at different temperatures are presented in Fig. 4 a-c. Microdiffraction pattern of (a) area is shown in Fig. 4d. It reveals two-phase cellular nanostructure constituting of the fine $\alpha_1$ particles perpendicular each other and $\alpha_2$ phase inside cellular. This microstructure testifies to a prevailing role of elastic energy through the high coercivity decomposition.
The increase of Mo content in alloys apparently is accompanied not only with increase of elastic energy between neighbouring phases and their influence on microstructure formation, but also change the volume parity of \( \alpha_1 \) and \( \alpha_2 \) phases, that defines extreme dependence of magnetic properties on the molybdenum content (Fig. 5). The image of the alloy № 2 (Fig. 3) reveals that in microstructure prevail the light \( \alpha_1 \) phase particles. On the contrary, in Mo-rich alloy № 4 (Fig. 4) prevail dark \( \alpha_2 \) phase and the \( \alpha_1 \)-phase forms a thin layer of the matrix phase.

Fig. 4 TEM images of the sample № 4 after \( ITMT \) at different temperatures after full followed full tempering treatment: \( T_{ITMT} = 625^\circ C \) (a), \( 620^\circ C \) (b), \( 615^\circ C \) (c), d) microdiffraction pattern of (a) area

Fig. 5 shows the effect of molybdenum content on coercive force of alloys № 1-5 (Fe-30Cr-15Co-(1-5)Mo-0.5Ti) after optimal \( ITMT \) and followed full tempering treatment.

Fig. 5 Dependence of \( H_c \) on Mo content for alloy № 1-5 after full \( TT \)
The maximum of magnetic properties is obtained at the molybdenum content 2-3 %. Similar nonmonotonic
dependence was observed earlier in Fe-Ni-Al alloys [6] where depending on the nickel content reveals a
change of the mechanism of microstructure formation. On the base of these data one can assume that the
increase of molybdenum content from 1 to 5 % also leads to change the morphology of microstructure of
considered Fe-Cr-Co alloys and to change the mechanism of remagnetization.

4. CONCLUSIONS
1. For alloys Fe-30Cr-15Co-(1-5)Mo-Ti with different molybdenum content the optimum duration and
optimum temperature of isothermal thermomagnetic treatment are defined which to produce the
maximum magnetic properties.
2. Increase of molybdenum content in Fe-30Cr-15Co-(1-5)Mo-Ti alloys from 1 to 5 % leads to increase
an elastic energy and to growth the α₁ particles along directions <100> perpendicularly each other,
irrespective of a direction of the applied magnetic field.
3. Increase of molybdenum content from 1 to 5 % causes to change the volume parity of α₁ and α₂
phases and to change the morphology of nanocrystalline microstructure of alloys.

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LITERATURE


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