Magnetic properties of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti hard magnetic alloy in anisotropic and isotropic states

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Abstract. The magnetic properties of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti (in wt. %) hard magnetic alloy in anisotropic and isotropic states after various heat treatments were studied. The alloy was prepared by the methods of powder metallurgy. The relative density was 98 %. The coefficient of thermal expansion of the alloy during heating and cooling was 17.4*10^{-6} K^{-1} and 19.0 *10^{-6} K^{-1} in the temperature range of 100 °C – 1300 °C. The kinetics of σ-phase formation caused by an isothermal annealing at T = 750 °C was investigated by means of the hardness measurements. The best magnetic properties of the alloy in anisotropic state were obtained after thermomagnetic treatment with cooling rate 200 °C/h as B_r = 1.22 T, H_c = 42.2 kAm^{-1} and (BH)_{max} = 31.2 kJm^{-3} and on the alloy in isotropic state with cooling rate 40 °C/h.

1. Introduction
Fe-Cr-Co alloys are well-known for their magnetic and high mechanical properties, ductility and corrosion resistance [1-2].

The addition of Mo and Ti to the ternary Fe-Cr-Co alloys as α-forming elements improves the magnetic properties [3-6]. They extend the α-phase region and prevent the σ-phase formation in the alloy, because σ-phase presence deteriorates properties of the alloy. It was found that the maximum σ-phase formation rate in Fe-Cr-Co alloys was at the temperature of 750 °C [7-8].

The magnetic properties of Fe-Cr-Co alloys are formed by the spinodal decomposition of high temperature α-phase into iron-rich phase α_1 and chromium-rich phase α_2. The magnetic properties are very sensitive to the condition of decomposition within the miscibility gap. It is important to study the phase transformation temperatures during various heat treatments to find the optimum conditions.

The typical heat treatment of the Fe-Cr-Co alloy includes solution treatment from α-phase region, high-temperature aging during spinodal decomposition and low temperature aging after it.

Isotropic and anisotropic magnets can be produced from Fe-Cr-Co alloys depending on heat treatment [9-14]. Thermomagnetic treatment (TMT) allows to receive optimal magnetic properties of Fe-Cr-Co alloy. An anisotropic microstructure containing elongated α_1-phase particles is attained by the application of the magnetic field during the annealing process [15-17]. These particles are parallel to the applied field. Due to this heat treatment the residual induction B_r and coercive force H_c of the alloy. TMT also reduces time of receiving of the needed magnetic properties.
In this paper the magnetic properties of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti (in wt. %) hard magnetic alloy in anisotropic and isotropic states after various heat treatments have been studied.

2. Materials and methods

2.1. Preparation

The alloy Fe-24%Cr-15%Co-3%Mo-1.5%Ti (in wt. %) was prepared by the methods of powder metallurgy. Metallic powders of iron, chrome, cobalt, molybdenum and titan of 99.9 wt. % purity have been used.

 Powders were mixed in C 2.0 “Turbula” mixer (Russia) for 320 min. Single-ended dry pressing at 600 MPa in a zinc stearate lubricated hardened steel pressing die with internal diameter of 13.6 mm on a manual press KNUTH-130042 (Germany) was used to compact the samples.

The density of the samples was measured by hydrostatic weighing. Then compacted samples were sintered at the temperature of 1350 °C during 2.5 hours in a shaft furnace SshV-1,25/24-I (Russia) in 10^{-2} Pa vacuum. The relative density of sintered samples was 98 %.

2.2. Chemical composition

The chemical composition of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy was estimated by two different methods. The mean values are shown in Table 1.

|                | Fe     | Cr     | Co     | Mo     | Ti     |
|----------------|--------|--------|--------|--------|--------|
| Initial        | Bal.   | 24.0   | 15.0   | 3.0    | 1.5    |
| XRF            | Bal.   | 24.8   | 14.2   | 3.2    | 1.6    |
| EDS            | Bal.   | 22.5   | 14.0   | 3.5    | 1.1    |

Rigaku Ultima IV diffractometer (Japan) was taken to obtain the X-ray fluorescence (XRF) patterns. The scanning electron microscopy (SEM) TESCAN VEGA II SBU (Czech Republic) equipped with the energy dispersive X-ray spectroscopy (EDS) on large areas was also used. The oxidation of the alloy was detected by EDS method.

The results are in a good agreement with initial alloy composition due to the fact, that powder metallurgy process was successfully performed.

2.3. Characterization

The heat treatment of the samples of Ø 12 x 20 mm in size was carried out in the standard laboratory furnace equipped with armored electromagnet and laboratory muffle furnace (Russia). The temperature was kept and monitored by proportional–integral–derivative controller.

Magnetic properties (residual induction $B_r$, coercive force $H_c$, and maximum energy product $(BH)_{max}$) were measured by hysteresisgraph Permagraph L EP-3 (Germany) at room temperature. The measurement error for coercive force $H_c$ and residual induction $B_r$ was 3 %, and it was 6 % for maximum energy product $(BH)_{max}$. The surface of sample was cleaned from slag using abrasive disk before measurements of the magnetic properties.

In order to study phase transformation temperature, the dilatometry experiments on dilatometer NETZCH DIL 402 C72G (Germany) was carried out in high purity argon atmosphere with the rate of the gaz 75 ml/min to prevent oxidation. The samples were heated to the temperature 1300 °C and cooled to room temperature with the rate of 10 °C/sec. The coefficient of thermal expansion (CTE) of the alloy was determined.
The X-ray diffraction (XRD) analyses were carried out using diffractometer Rigaku Ultima IV (Japan) with an x-ray tube with Cu Kα radiation. The XRD patterns were recorded in the 2θ range of 30–100° (step size of 0.05° and the time per step of 1 s).

The microstructure of the alloy was studied by optical metallography methods.

3. Results and discussions

3.1. Phase transformations and microstructures

The dilatometry curves for Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy sample are shown at the Figure 1.

The average CTE during heating and cooling of the alloy in the temperature range 100 °C – 1300 °C was between 17.4*10⁻⁶ K⁻¹ and 19.0 *10⁻⁶ K⁻¹.

![Dilatometry curves for the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy during heating (a) and cooling (b).](image)

According to the Fe-Cr and Fe-Co phase diagrams and obtained experimental data the phase transformation of α→α₁+α₂ would be expected at the temperature range 614 – 625 °C. There is the destabilization process of high-temperature α-phase because of the σ-phase presence before spinodal decomposition.

The microstructure of the solution treated sample for 15 min at 1300 °C followed by rapid quenching in water is shown at the Figure 2. The single α-phase can be observed.

![Microstructure of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy after quenching at 1300 °C during 15 minutes.](image)

The kinetics of the σ-phase formation caused by an isothermal annealing at T = 750 °C was investigated by means of the hardness measurements. The hardness of the alloy increases from 32.3 to
49.3 HRC during 20 hours of annealing at 750°C (Figure 3). The microstructure of the Fe-24% Cr-15%Co-3%Mo-1.5%Ti alloy is shown at the Figure 4. The σ-phase occurs at grain boundaries.

**Figure 3.** Hardness HRC of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy versus time of annealing at 750°C.

**Figure 4.** Microstructure of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy after annealing at 750°C during 20 hours.

In accordance with XRD data the quantity of the σ-phase was about 5 vol. % after 20 hours of annealing (figure 6). The following lattice parameters have been calculated: α-phase – a = 0.2877 nm, σ-phase – a = 0.8835 nm, c = 0.4596 nm.

3.2. Magnetic properties

The heat treatment temperatures were chosen according to the phase transformation temperatures based on dilatometry curves and study of the σ-phase formation.

The samples were quenched in water from the temperature 1300 °C for 15 minutes, then heated to the temperature 710 °C which exceeded the temperature of spinodal decomposition of the α-solid solution, and cooled with a critical rate to the T = 680 °C. Then the samples were cooled with the cooling rate of \( v_1 \) from 40 to 250 °C/h to the temperature 600 °C under a magnetic field of 4 kOe or without it. From the temperature 600 °C to 500 °C the samples were cooled with a constant rate of 8 °C/h.

The coercive force of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy versus cooling rate \( v_1 \) during first step aging is shown at the Figure 5.

**Figure 5.** Variation of coercive force \( H_c \) of the Fe-24%Cr-15%Co-3%Mo-1.5%Ti alloy versus cooling rate \( v_1 \) during first step aging.

The coercive force increases after TMT (anisotropic state of the alloy) and decreases during heat treatment without magnetic field (isotropic state). The best magnetic properties were received after TMT with cooling rate \( v_1 = 200 \) °C/h.
Experimental data in table 2 show the best magnetic properties that were received on samples in different states.

| State   | Heat treatment condition | $B_r$, T | $H_c$, kAm$^{-1}$ | $(BH)_{max}$, kJm$^{-3}$ | $\eta = (BH)_{max}/(B_r*H_c)$ |
|---------|--------------------------|----------|-------------------|--------------------------|-------------------------------|
| anisotropic | 680 → 600 ºC, 200 ºC/h with magnetic field | 600 → 500 ºC, 8 ºC/h | 1.22 | 42.2 | 31.2 | 0.61 |
| isotropic  | 680 → 600 ºC, 40 ºC/h no magnetic field | 600 → 500 ºC, 8 ºC/h | 0.56 | 22.2 | 3.5 | 0.28 |

The slower cooling rate, the better coercive force on the alloy in isotropic state is.

4. Conclusion
The hard magnetic alloy Fe-24%Cr-15%Co-3%Mo-1.5%Ti (wt. %) was prepared by the methods of powder metallurgy. The relative density was 98 %.

The coefficient of thermal expansion during heating and cooling of the alloy was $17,4*10^{-6}$ K$^{-1}$ and $19,0 *10^{-6}$ K$^{-1}$ in the temperature range of 100 ºC – 1300 ºC.

The kinetics of the $\sigma$-phase formation caused by an isothermal annealing at $T = 750$ ºC was investigated in the alloy by means of the hardness measurements. The quantity of $\sigma$-phase in hard magnetic alloy Fe-24%Cr-15%Co-3%Mo-1.5%Ti (wt. %) was about 5 vol. %.

The best magnetic properties of the alloy in anisotropic state were obtained after thermomagnetic treatment with cooling rate 200 ºC/h as $B_r = 1.22$ T, $H_c = 42.2$ kAm$^{-1}$ and $(BH)_{max} = 31.2$ kJm$^{-3}$ and on the alloy in isotropic state with cooling rate 40 ºC/h as $B_r = 0.56$ T, $H_c = 22.2$ kAm$^{-1}$ and $(BH)_{max} = 3.5$ kJm$^{-3}$.

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