Phase transformation in rapidly quenched Fe-Cr-Co-Mo-Ti-Si-B alloys

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Abstract. The research results of phase transformations in Fe-24Cr-16Co-3Mo-0.2Ti-1Si-B alloys (with a boron content of 1 to 3% by mass) obtained by rapid quenching are presented. The structure formation regularities during the melt spinning and during the subsequent crystallization annealing in rapidly quenched bands of the Fe-Cr-Co-Mo-Ti-Si-B system alloys were studied. The changes in the phase composition of the rapidly quenched Fe-Cr-Co-Mo-Ti-Si-B system alloys after quenching at various quench rates and at different boron concentrations in the alloys are studied. It is shown that during crystallization from an amorphous state, at temperatures above 570 °C, in addition to the α-phase, the σ-phase appears first, followed by the γ-phase. Heat treatment of rapidly quenched bands to high-coercive state was carried out. A qualitative assessment of magnetic properties in a high-coercivity state was carried out. An evaluation of the level of magnetic properties in a high-coercivity state allows us to conclude that the application of a magnetic field during crystallization from an amorphous state leads to anisotropy of the magnetic properties, that is, an anisotropic effect of thermo-magnetic treatment is detected.

1. Introduction
Traditionally fabricated deformable high-coercive alloys based on the Fe-Co-Cr system provide magnetic properties at the levels: \( H_c \) - at least 500 Oe, \( B_r \) - at least 10-12 kG and \( (BH)_{max} \) - at least 4-5 MGOe [1–3]. When the magnetic and crystalline textures are combined in the investigated alloys, they can be obtained in a high-coercivity state. Despite the relatively low level of magnetic properties in the high-coercive state (especially relative to permanent magnets with rare earth elements), alloys do not lose their relevance due to a fine combination of high mechanical properties, high Curie temperature and good temperature stability of magnetic properties.

High-coercive state in Fe-Cr-Co alloys is formed as a result of isothermal thermomagnetic treatment, during which the α-phase (solid solution) decomposes into 2 isomorphic phases by the spinodal decomposition: into a high magnetic \( \alpha_1 \) phase (enriched by Fe and Co) and a weakly magnetic \( \alpha_2 \) phase (enriched by Cr) [4]. As a result, an ensemble of high magnetic isolated single-domain elongated particles is formed in a weakly magnetic matrix. Long axes of the particle are oriented along the magnetic field. The coercive force will then depend on the angle between the long axis of the particle and the crystallographic direction <100>, which for the bcc alloys is the “easy magnetization” axis. When the Fe-Cr-Co based alloys is alloyed with molybdenum, the latter, being located during the spinodal decomposition mainly in the \( \alpha_2 \)-phase, leads to an increase in the lattice...
period difference between $\alpha_1$ and $\alpha_2$-phases, and an increase in the modulus of elasticity difference in the $<100>$ and $<111>$ directions, in connection with which the allocation of the $\alpha_1$ phase is "tied" to the crystallographic direction $<100>$. Using thermomagnetic treatment for the Fe-Cr-Co-Mo system alloy with a crystalline texture will result in all the $\alpha_1$-phase particles in the sample being oriented along the magnetic field [5–7]. The magnetic texture (preferential orientation of the magnetic moments of all $\alpha_1$-phase particles) thus obtained will lead to a significant increase in magnetic properties.

Thereby, one of the ways for further development of these materials is the use in their production of the spinning process of the melt and the production of a thin ribbon with a crystalline texture $<100>$, which can later be used to make permanent magnets.

The results of studying the effect of multi-stage annealing on the magnetic properties of the Fe-12Co-24Cr-1.5Si ribbon magnets obtained by melt spinning were published in [8]. Xu-hao Han et al succeeded in obtaining $H_c = 742$ Oe. In a study by Ushakova et al [9], it was possible to obtain $H_c = 1160$ kOe (at $B_r = 0.85$ kG) by optimizing the thermomagnetic treatment of a cold-rolled Fe-30Cr-15Co(2-5) Mo alloy. Z. Ahmad et al [10], while studying the relationship between texture, microstructure and magnetic properties of the Fe-28Cr-15Co-3.5Mo alloy, obtained $H_c = 867$ Oe at $B_r = 11.2$ kG. A number of researches were devoted to the study of the formation regularities of a high-coercive state in alloys doped with Si [11–13]. Despite the low level of the obtained magnetic properties ($H_c$ up to 550 Oe, $B_r$ up to 9.2 kG), silicon, being an $\alpha$-stabilizer, leads to a decrease in the critical cooling rates during thermomagnetic treatment.

These and many other researchers note the fact that the most significant changes in the microstructure of Fe-Cr-Co-based alloys, resulting in the formation of a high-coercive state, occur during thermomagnetic treatment and the first annealing steps. In accordance with it, in this work, studies were carried out to obtain a rapidly quenched ribbon of Fe-Co-Cr-Mo alloys and to study the structural transformations that occur in them during thermal processing to a high-coercive state.

### 2. Materials and methods

X-ray phase and structural analysis techniques were used to study the phase and structural transformations that took place during rapid quenching and subsequent crystallization annealing in Fe-Cr-Co alloys doped with boron.

Magnetic properties were determined using a multifunctional complex PPMS (Physical Properties Measurement System, Quantum Design) with a VSM attachment (vibration magnetometer measurement) in a superconducting solenoid in fields up to 5 T.

The charge materials used were pure charge components and homogenized ferroboron containing 9.0% boron by weight.

### 3. Experimental procedures and discussion

The study of the structure of the modified lead-tin-base bronze

The receipt of a rapidly quenched band was carried out in two stages. At the first stage, mixing of the charge components, smelting of the billet in a quartz crucible in an induction melting furnace and casting into a copper ingot were performed. The obtained pre-sample was cleaned of slags and oxides crystallizing on the surface, and re-melted in a crucible-feeder with a diameter of 10 mm, followed by pouring on a rotating wheel. After melting (stage 1), the chemical composition of the alloy was monitored by X-ray energy-dispersive spectrometry, the structure of the alloy was determined by X-ray diffractometry.

The chemical analysis results of cast alloys are given in Table 1. The microstructure of cast alloys has not been investigated.
Table 1. The results of the chemical (EDS) analysis (± 0.3% by weight) of the smelted alloys

| Alloy ID | Co | Cr | Si | Ti | Mo | B |
|---------|----|----|----|----|----|---|
| B       | 15 | 24 | 0.8| 0.2| 3  | 1 |
| C       | 15 | 24 | 0.8| 0.2| 3  | 2 |
| D       | 15 | 24 | 0.8| 0.2| 3  | 3 |

At the second stage, a rapid quenching of the previously prepared alloys was carried out according to the regimes indicated in Table 2.

Table 2. Regimes of rapid quenching of B-D alloys and marking of samples

| Quench rate | Sample ID | rpm | 3000 | 3400 | 3800 | 4500 | 5000 | 5500 |
|-------------|-----------|-----|------|------|------|------|------|------|
| m/s         |           | 31.6| 35.8 | 40.0 | 47.4 | 52.6 | 58.0 |
| B           | B1        | -   | -    | B4   | B5   | B6   |
| Alloy ID    | C         | C1  | -    | C3   | C4   | C5   |
|             | D         | D1  | D2   | D3   | D4   | -    |

Alloy melting was carried out in atmosphere in the working chamber under a pressure of 18-22 kPa; casting on a wheel was performed at a pressure of 68-72 kPa above the crucible. The weight of the cast alloy is from 16 to 19 g. The linear rotational speed of the wheel varied from 30 to 60 m/s.

Effect of rapidly quenched alloys annealing on crystallization from an amorphous state

The effect of the crystallization annealing temperature on the phase transformation of rapidly quenched B-D alloys was studied by differential thermal analysis (DTA) using the differential scanning calorimeter NETZSCH DSC 204 F1 in a protective atmosphere of argon at a heating rate of 10 °C/min.

To determine the reversibility of the transformations, each sample was heated twice: once directly from the rapidly quenched state and immediately after the first cooling to a temperature of 40-50 °C. DTA curves for alloy D, quenched on a wheel with a linear velocity of 47 m/s (sample D4) are shown in Figure 1.

Figure 1. Differential thermal analysis curves of sample D4 (the blue line is the first heating after rapid quenching; the red line is the second heating after fast quenching; the heating rate is 10 K/min; the effects temperature is 502 °C, 574 °C, 602 °C; all effects are exothermic)
At the initial time, sample D4 was a mixed amorphous-nanocrystalline state with a crystalline phase content of less than 10% by volume. During the first heating, three exothermic effects were detected on the DTA curve: at temperatures of 502 °C, 574 °C and 602 °C, respectively. The accuracy of determining the temperature of the effects was ± 5 °C.

On DTA of the reheat curve, no effects were detected. This fact indicates that all three thermal effects are associated with irreversible processes - the processes of phase crystallization from an amorphous state.

To determine the transformations occurring during crystallization from an amorphous state, annealing of rapidly quenched bands was carried out at temperatures of 20 K and above, determined during DTA, namely at 520 °C, 595 °C and at 620 °C for 40 minutes. The annealing was carried out in a vacuum oven of electrical resistance under vacuum no less than 2 \cdot 10^{-3} \text{ mm Hg}, the heating rate was at least 150 °C/min, the cooling rate of 300 °C was less than 80 °C/min. Phase state monitoring was carried out using X-ray phase analysis on a Rigaku Ultima IV diffractometer. The diffraction spectra of the annealed bands are shown in Fig. 2.

![Diffractogram](image)

**Figure 2.** Diffractogram of B-D alloys after rapid quenching (sample D4) and subsequent crystallization annealing at temperatures of 520 °C, 595 °C and 620 °C for 40 minutes

Since all the phase transformations during crystallization in the B-D alloys are identical, only the curves for alloy D are given. Comparing the data obtained during differential thermal analysis and X-ray phase analysis of bands annealed at intermediate temperatures, one can determine the sequence of reactions that take place during crystallization annealing:

\[
\text{amorphous phase} \rightarrow \alpha \rightarrow \alpha + \sigma \rightarrow \alpha + \sigma + \gamma
\]  

(1)

When the temperature is raised to 502 °C, the crystallization reaction begins: an \( \alpha \)-phase is released from the amorphous phase, the particle size of the \( \alpha \)-phase determined by X-ray structural analysis is 10 to 30 nm. When the annealing temperature is raised to 574 °C, the \( \sigma \)-phase begins to be emitted from the \( \alpha \)-phase, and the \( \gamma \)-phase when the annealing temperature is raised to 602 °C.

Annealing was performed at a temperature of 620 °C for 5, 10, 20 and 30 minutes in the same previous series of annealing conditions to determine the phase appearance kinetics (including the
Diffraction spectra of annealed rapidly quenched bands under different temperature-time conditions are shown in Fig. 3.

**Figure 3.** Diffractogram of B-D alloys after rapid quenching (sample D4) and subsequent crystallization annealing at 620 °C for 10, 20 and 30 minutes, respectively.

X-ray phase analysis showed that after annealing for 10 minutes, the volume of the nanocrystalline α-phase increases to 50% by volume (see Figure 3). 20 minutes after the start of annealing, the volume of the α-phase reaches 60%, the σ-phase begins to be released (up to 20% by volume), the remaining 20% by volume is the remaining amorphous phase. 30 minutes after the start of annealing, the amorphous phase disappears completely and there are 3 phases in the tape: α-phase (20%), σ-phase (60%) and γ-phase (20%).

It follows from the data that reaction (1) proceeds precisely in this sequence, irrespective of whether the sample is heated at a constant rate or isothermal annealing is carried out at a constant temperature.

**Magnetic properties of annealed rapidly quenched alloys**

To determine the level of magnetic properties attainable on rapidly quenched bands, samples D4, C5 and B6 (i.e., samples containing not less than 90% of the amorphous phase) were subjected to a full cycle of heat treatment to obtain a high coercivity state using follow steps: isothermal treatment with magnetic field 240 kOe, 635 °C × 30 min; 605 °C × 5 h; 580 °C × 1 h; 560 °C × 1 h; 540 °C × 5 h. Since the alloy in the initial state was a two-phase system (amorphous phase + α-phase), conventional annealing for such alloys did not require preliminary annealing to obtain a single-phase state.

The results of X-ray phase analysis, as in the case of thermal treatments described above, show that the alloy is in a three-phase state: α + γ + σ.

The results of measuring the magnetic properties (typical hysteresis loop shown in Fig. 4) on a vibration magnetometer show that samples D4, C5 and B6 are in a high-coercive state with a coercive force of 500 to 600 Oe. In addition, although there is no explicit splitting of the α-phase lines on the lines from the α1 and α2 phases on the diffractograms, but only broadening, the level of the magnetic properties clearly indicates that the high-coercive decay has passed to the end and reaction (1) can be written in the form:
amorphous phase $\rightarrow \alpha \rightarrow \alpha + \sigma \rightarrow \alpha + \sigma + \gamma \rightarrow \alpha_1 + \alpha_2 + \sigma + \gamma$  \hspace{1cm} (2)

Fig. 4. The shape of the hysteresis loop for alloy D (sample D4) after carrying out a complete heat treatment cycle to reach a high coercive state.

4. Conclusion
(1) Rapid quenching regimes are established for Fe-Co-Cr-Mo-Si-Ti-(1-3)B alloys during which the maximum amount of amorphous phase is formed.
(2) It is established that during the crystallization from the amorphous state, 3 processes proceed: the separation of the $\alpha$ phase from the amorphous phase; the separation of the $\sigma$ phase and, then, the separation of the $\gamma$ phase. The absence of thermal effects during cooling and reheating indicates that these processes are irreversible.
(3) In the course of the conducted studies, it was found that in the temperature range of 650-500 °C, the decay of a single-phase $\alpha$-solution in a rapidly quenched strip of the Fe-15Co-24Cr-3Mo-0.8Si-0.2Ti-3B alloy occurs more intensively than in samples of cast alloys, and, in addition, is accompanied by the separation of the $\sigma$ and $\gamma$ phases.

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