DOI 10.1007/s11041-017-0100-6
*Metal Science and Heat Treatment*, Vol. 59, Nos. 1 – 2, May, 2017 (Russian Original Nos. 1 – 2, January – February, 2017)

UDC 620.18:669.018.58:669.12'26'25'781

# CONCERTATION-INHOMOGENEOUS HARD MAGNETIC ALLOYS OF THE Fe – Cr – Co SYSTEM WITH ELEVATED CONTENT OF COBALT AND BORON

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Translated from *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 1, pp. 43 – 47, January, 2017.

The structure and magnetic properties of a powder alloy based on the Fe – Cr – Co system with elevated content of cobalt and boron are studied. The dependences of the magnetic induction and of the coercivity on the aging temperature are determined experimentally. It is shown that the introduction of boron into the alloy hinders precipitation of σ-phase and makes it possible to raise the cobalt content by 4% as compared to standard alloy 30Kh23K.

***Key words:*** hard magnetic alloys of the Fe – Cr – Co system, structure, powder metallurgy, highly coercive alloy.

## INTRODUCTION

Creation of special equipment in aviation, shipbuilding and other high-end technologies requires materials combining high mechanical, magnetic and process properties. Magnetic alloys based on the Fe – Cr – Co (KhK) system meet all these requirements [1].

These alloys have been developed in the 1930s by W. Koester [2]. However, the necessity for special facilities for thermomagnetic treatment (TMT) and the intense research of Fe – Al – Ni – Co (alnico) alloys have delayed the studies of Fe – Cr – Co-base magnetic materials to the middle the 1970s, and their commercial production started in Russia in the early 1980s [1].

Alloys of the Fe – Cr – Co system (GOST 24897–81) possess a high level and stability of magnetic properties and corrosion resistance and are substantially superior to other hard magnetic materials with respect to the adaptability to manufacture [1, 3]. The magnetic properties of the alloys of this class are provided by a structure containing a strongly magnetic cobalt-rich $\alpha_1$-phase and a weakly magnetic $\alpha_2$-matrix [4].

As compared to the materials of type YuNDK (for example, YuNDK24AA) obtained by directed crystallization, the alloys of the KhK system possess a lower magnetic induction $B_r$ and a lower maximum magnetic product $(BH)_{max}$. Therefore, their magnetic properties should be raised in order to widen the range of their application.

A substantial disadvantage of hard magnetic materials with high magnetic properties obtained by directed crystallization of melt, casting, etc. is their unsatisfactory processibility in a highly coercive condition. Powder metallurgy makes it possible to raise the adaptability to mechanical treatment and to produce billets with shape and size close to those of a ready part. However, the inevitable porosity and concentration inhomogeneity of billets from hard magnetic powder materials lower substantially the level of their magnetic characteristics as compared to directionally crystallized alloys [5].

Competitive powder hard magnetic alloys based on the Fe – Cr – Co system can be obtained by liquid-phase sintering with "disappearance of liquid phase in the heating process." Contact fusion is implementable due to additions of ferroalloys (ferrosilicon, ferrotitanium, ferroboron) [6, 2]. Additions of vanadium to high-cobalt alloys lower the magnetic and mechanical properties due to the appearance or growth of the content of σ-phase [8]. The kinetics of formation of σ-phase can be represented by a *C*-curve the form and the position of which depend on the composition of the alloy [9].

The level of magnetic properties of alloys of the Fe – Cr – Co system can be elevated by increasing the concentration of cobalt. However, cobalt is a strong σ-forming element. It enters the σ-phase and widens the concentration

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range of its existence [10]. Increase of the content of cobalt requires other regimes of sintering, TMT and IHT than the known ones. By the data of [10] the highest rate of formation of σ-phase in alloys with different cobalt contents corresponds to a temperature of about 750°C.

To compensate increase in the cobalt concentration, the alloy is enriched with alloying elements arranged over grain boundaries and promoting creation of thermodynamically unfavorable conditions for formation of σ-phase. We used boron as a horophilic element hindering precipitation of σ-phase over grain boundaries. The introduction of boron widens the temperature range of formation and increases the volume of liquid phase in the stage of sintering, which intensifies shrinkage and improves the homogeneity of the alloy. The content of silicon was limited to 1 wt.%, because its elevated concentrations lower noticeably the magnetic induction $B_r$ and the maximum product $(BH)_{max}$ [7].

The aim of the present work was to study the structure and the set of mechanical and magnetic properties of powder alloys with elevated content of cobalt and boron.

## METHODS OF STUDY

We studied powder alloy 30Kh27KSR containing (in wt.%) 30 Cr, 27 Co, 1 Si, 0.07 B and 41 Fe and, for comparison, alloy 30Kh23K (GOST 24897–81) in isotropic and anisotropic conditions as well as the powder alloys of system KhK with the best properties. Boron was introduced to lower the rate of formation of σ-phase due to blocking of grain boundaries. This approach may be called a kinetic one, because it provides a thermodynamically nonequilibrium state with elevated magnetic properties which vary stepwise with further growth of the temperature and/or duration of the hold.

The initial components were iron powder of grade OSCh 6-2, chromium powder of grade PKh-1S and cobalt powder of grade PK-1. Liquid-phase sintering was implemented by adding powders of ferrosilicon and ferroboron. All the powders were sieved through a sieve with 63-μm cells (GOST R 51568–99). The blend was prepared in a mixer with shifted rotation axis for 24 h. The billets were cold pressed at a pressure of 600 MPa and sintered at 1350°C in vacuum with residual pressure $10^{-2}$ Pa for 2 h. To obtain an α-solid solution, the sintered billets were quenched from 1300 – 1400°C in water. The stage of aging for determining the temperature of TMT and obtaining an isotropic state was conducted for the first group of specimens at 600 – 700°C with a 20-min hold without magnetic field. The optimum magnetic properties corresponded to the temperature range of 670 – 680°C (20 min), which differs substantially from the TMT temperature of the known alloys with high cobalt content. Thermomagnetic treatment was applied to the second group of specimens at 670°C with a hold for 20 min. The second stage of aging was conducted for all the specimens in succession at 600°C for 1.5 h, 580°C for 2 h, 560°C for 3 h, 540°C for 3 h, and 520°C for 2 h without magnetic field.

The microstructure of the specimens was studied by optical microscopy at magnifications × 100, × 500 and × 1000 using a Neophot 32 microscope. The magnetic properties were measured according to GOST 24897–81. The density of the billets after pressing and sintering was determined by hydrostatic weighing according to GOST 25281–82.

The phase transformations were studied under continuous heating by the method of differential scanning calorimetry (DSC) using a STA 449 C Jupiter device. Small (up to 3 g) weighted pieces were studied in an argon environment. The rates of the heating and of the cooling were 10 K/min.

The x-ray phase analysis of the heat treated specimens was conducted using cobalt and copper $K_\alpha$-radiation at an accelerating voltage of 30 kV and a force of current of 5 mA. The phase composition was determined for the range of angles 2θ typical for local intensity maximums of the reflections from the α-, σ- and γ-phases and borides. The content of the σ-phase was evaluated by comparing the x-ray diffraction patterns [11] and the results of the metallographic analysis of specimens with different proportions of σ- and α-phases.

## RESULTS AND DISCUSSION

The mean value of the density of the specimens of alloy 30Kh27KSR after sintering was 7.9 ± 0.1 g/cm$^3$; the density of the sintered specimens of alloy 30Kh23KA was lower and amounted to 7.7 ± 0.1 g/cm$^3$ on the average. The cooling after the sintering was conducted at a rate of at most 500 K/h. The structure of alloy 30Kh27KSR (Fig. 1*a* and *b*) contained precipitates of σ-phase with a lamellar morphology (light gray) and layers of α-phase (dark gray). The σ-phase grew the most intensely over grain boundaries [7]. The mean diameter of the grains determined by optical microscopy was 0.3 ± 0.1 mm; the content of the pores did not exceed 1 – 2%.

The dependence of the phase composition of the powder alloy 30Kh27KSR on the temperature of heating for quenching (1300, 1350 and 1400°C) was studied by the methods of x-ray diffraction analysis[2] and is presented in Fig. 2.

Heating to 130°C yields a σ-phase, which is proved by the manifested peak of reflection intensity corresponding to angle 2θ = 59°58′. When the heating temperature is raised to 1400°C (Fig. 2*c* ), the γ-phase stabilizes and its post-quenching content is increased; the extremum in the diffraction pattern corresponds to angle 2θ = 55°53′. The lowest content of undesirable phases is obtained after quenching the specimens from 1350°C (Fig. 2*b* ). The interplanar spacing of the peak with maximum intensity is 2.02 Å and corresponds to a solid solution of a Fe – Cr – Co composition [11]. The presence of

[2] The authors are grateful to Prof. A. S. Ivanov for the help with the x-ray diffraction study.

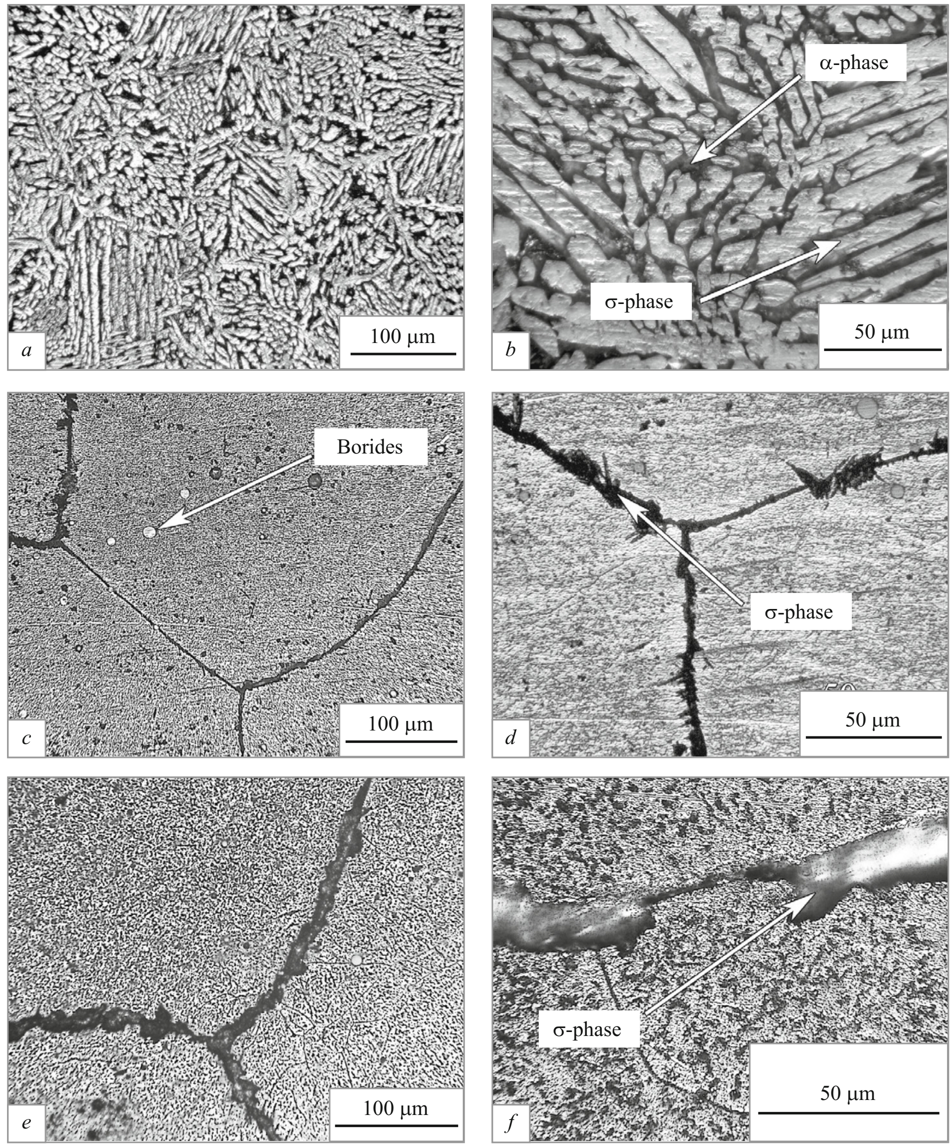


**Fig. 1.** Microstructure of alloy 30Kh27KSR after sintering (*a*, *b* ), after quenching (*c*, *d* ), and after aging at 670°C (*e*, *f* ): *a*, *c*, *e*) × 100; *b*, *d*, *f* ) × 500.

borides is confirmed by the results of the x-ray diffraction analysis (Fig. 2*b* ). The interplanar spacing of the borides is 2.82 Å ($2\theta = 40°23'$, plane [020] of FeB] and 2.55 Å ($2\theta = 44°50'$, plane [200] of $Fe_2B$) [11].

The microstructure of the specimens of alloy 30Kh27KSR after quenching from 1350°C (Fig. 1*c* and *d* ) consists of an α-solid solution (light gray) and some precipitates of an σ-phase (dark gray) arranged chiefly over grain

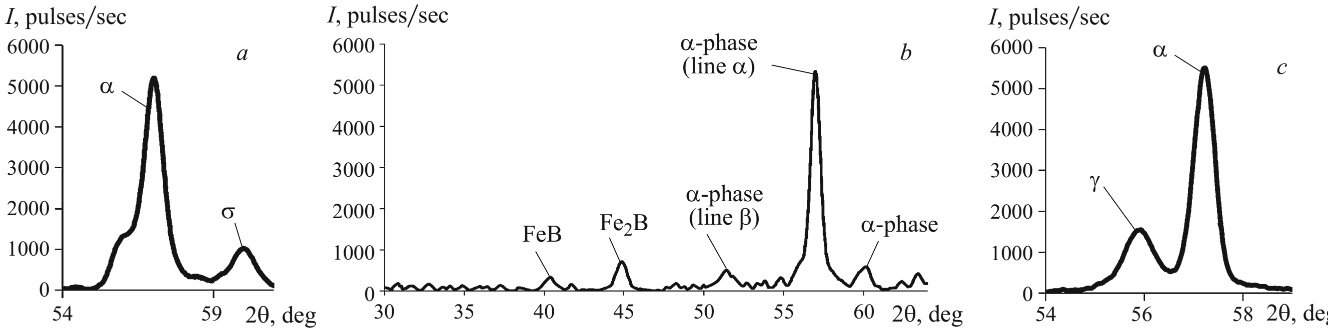


**Fig. 2.** X-ray diffraction patterns of alloy 30Kh27KSR after quenching from 1300 (*a*), 1350 (*b* ), and 1400°C (*c*).

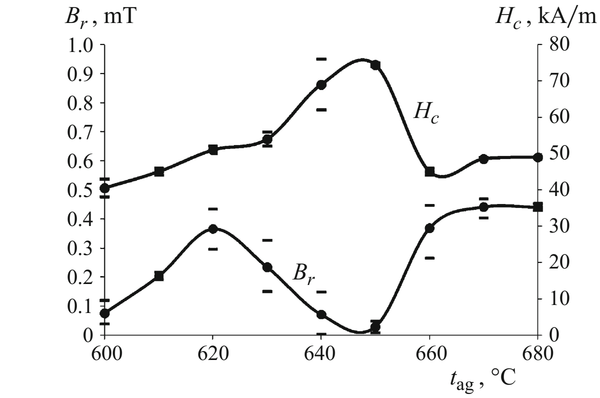


**Fig. 3.** Coercivity $H_c$ and magnetic induction $B_r$ as a function of the aging temperature of alloy 30Kh27KSR.

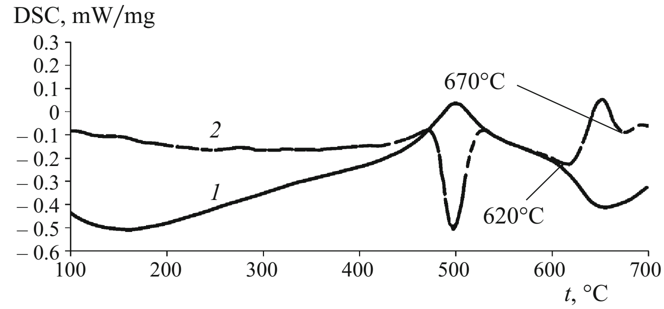


**Fig. 4.** DSC curve for alloy 30Kh27KSR (*1*) and its derivative (*2*) under heating at a rate of 40 K/min.

boundaries. By the data of the optical microscopy the proportion of the σ-phase is 1 – 3%. The $\alpha \to \sigma$ transformation develops by a shear mechanism, which is proved by the lamellar pattern of the precipitates (Fig. 1*d*) and confirmed by the published data on invariability of the chemical composition of grain boundaries during the transformation [12]. The structure of the quenched alloy 30Kh27KSR contains borides of an elliptical shape with semiaxes little differing in size with diameters from 10 to 20 μm.

The temperature and time parameters of the aging of alloy 30Kh27KSR have been chosen experimentally for the first group of specimens. The dependence of the coercivity $H_c$ and of the magnetic induction $B_r$ on the aging temperature was a function with local extremums (Fig. 3). Maximum magnetic induction was observed after aging at 620 and 670°C, which is confirmed by the presence of local extremums at these temperatures on the DSC curves (Fig. 4).

The highest magnetic product $(BH)_{max}$ corresponds to the aging temperature of 670°C (Table 1).

The structure of alloy 30Kh27KSR in a highly coercive condition is represented by an α-solid solution with small inclusions of σ-phase over grain boundaries and borides (Fig. 1*e* and *f*); the α-phase has a relatively homogeneous structure.

The mode of the TMT ($t = 670$°C, $\tau = 20$ min) was chosen after studying the DSC curves (Fig. 4) and the dependences of the magnetic properties on the aging temperature (Fig. 3). Subsequent multistage aging was conducted in the range of 620 – 540°C. The magnetic properties obtained after the MT and the second aging stage and the properties of alloy 30Kh23KA matching GOST 24897–81 are presented in Table 2. For comparison, we also give in Table 2 the properties of one of the best powder alloys of the system studied (30Kh20K2M2B) [13]. The ridge powder alloys of the KhK system have somewhat higher $B_r$ at close values of $(BH)_{max}$, but their $H_c$ is substantially lower [14, 15].

Thus, the powder alloy 30Kh27KSR after the TMT at 670°C and subsequent multistage aging in the temperature range 620 – 540°C has substantially higher properties than the deformable alloy 30Kh23KA (GOST 24897–81).

## CONCLUSIONS

1. Introduction of ferroboron into powder alloys promotes formation of liquid phase under sintering, which improves the density and the homogeneity of the alloys.

2. With increase of the cobalt content in the Fe – Cr – Co system the recommended temperature for TMT is increased, and the concentration of cobalt in the $\alpha_1$-solid solution (prior to the start of formation of σ-phase) is increased too, which promotes growth of the magnetic induction and of the residual magnetization.

3. The inevitable formation of σ-phase with growth of the concentration of cobalt can be hindered by introduction of horophilic elements. For example, the addition of up to 0.07 wt.% ferroboron to the alloy has made it possible to raise the cobalt content by 4%.

4. In the alloys with elevated concentration of cobalt and a structure of $\alpha_1 + \alpha_2$ phases the residual induction and the maximum product $(BH)_{max}$ are elevated and the coercivity exceeds 60 kA/m.

**TABLE 1.** Magnetic Properties of the Alloys in Isotropic Condition

| Alloy | $H_c$, kA/m | $B_r$, T | $(BH)_{max}$, kJ/m$^3$ |
|---|---|---|---|
| 30Kh27KSR, powder | 60 | 0.84 | 17 |
| 30Kh23KA, deformable | 50 | 0.75 | 12 |

* Aging without magnetic field.

**TABLE 2.** Magnetic Properties of the Alloys in Anisotropic Condition

| Alloy | $H_c$, kA/m | $B_r$, T | $(BH)_{max}$, kJ/m$^3$ |
|---|---|---|---|
| 30Kh27KSR, powder | 63 | 1.1 | 38.6 |
| 30Kh23KA, deformable | 55 | 1.0 | 30 |
| 30Kh20K2M2B, powder | 60 | 1.0 | 32.8 |

* Aging in magnetic field.

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