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Heat treatment and magnetic properties of Fe–23Cr–16Co–X alloys

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Fe–23Cr–16Co alloys containing titanium and titanium and niobium simultaneously were investigated. A dependence was noted between the parameters of TMA and low-temperature ageing influencing the level of B_r, H_c and $(BH)_{max}$ and alleviating the action of niobium on alloy sensibility on fluctuations of these parameters was noticed. TEM investigations revealed the existence of the phase connected with the presence of niobium in the alloy. The results confirm α-creative action of niobium and titanium and point to a substantial influence of the temperature of annealing, preceeding solutioning on the final magnetic properties.

1. Introduction

Fe–Cr–Co permanent magnet alloys belong to the group of materials in which the mechanism of magnetic hardening is associated with an effect of spinodal decomposition of the iron-rich bbc α-phase. Solid-state transformations in the Fe–Cr–Co alloys lead to the formation of an extreme fine-scale modulated microstructure consisting of ferromagnetic FeCo-rich regions (α_1-phase) and magnetically weak or non-magnetic chromium-rich regions (α_2-phase) [1–3]. The changes in microstructure during magnetic hardening heat treatment are referred to in the literature as either changes of the amplitude and wavelength of chemical composition [4–6] or as the amplitude changes only, for fixed wavelength during spinodal decomposition [7–9].

The macro- and microstructure of the magnets is determined by chemical composition of the alloy and the conditions of the formation of this structure. The values of the parameters describing the magnetic properties of Fe–Cr–Co alloys are a function of the geometrical features of the microstructure, being described by (1) size of the α_1 and α_2 regions, (2) their volume ratio, (3) their mutual distribution and, in the case of anisotropic magnets by (4) the degree of anisotropy of microstructure.

Modification of the chemical composition of Fe–Cr–Co alloys introducing some micro-additions can lead to the following effects.

(i) A change of the conditions of phase transformations leading to either widening or narrowing of the range of occurrence of the phases typical of Fe–Cr–Co system;

(ii) Intensification and dynamization of structural transformation leading to an increase in the values of the B_r, H_c and $(BH)_{max}$;

(iii) Optimization of the technological conditions determining the course of the magnetic hardening;

(iv) An influence on the economics of the production process of Fe–Cr–Co type alloy magnets, involving the relationship between the magnetic properties, the price of raw materials and the energy expenditure associated with the production of magnets.

The aim of the investigations was to determine the influence of titanium additions as well as the additions of both titanium and niobium on the microstructure and the values B_r, H_c and $(BH)_{max}$ of the Fe–23Cr–16Co alloy.

2. Experimental procedure

The alloys were prepared from technically pure materials in the vacuum induction furnace and were cast into the ingot mould. The chemical composition of the alloys is given in Table I.

The ingots obtained underwent hot-plastic deformation and rods of diameter 15 mm were obtained. The magnets were cut out from the rods. Samples were heat-treated according to the scheme presented in Fig. 1.

Heat treatment was performed in the arrangement with automatic temperature control, with an accuracy of ± 1 K in the case of isothermal annealing and

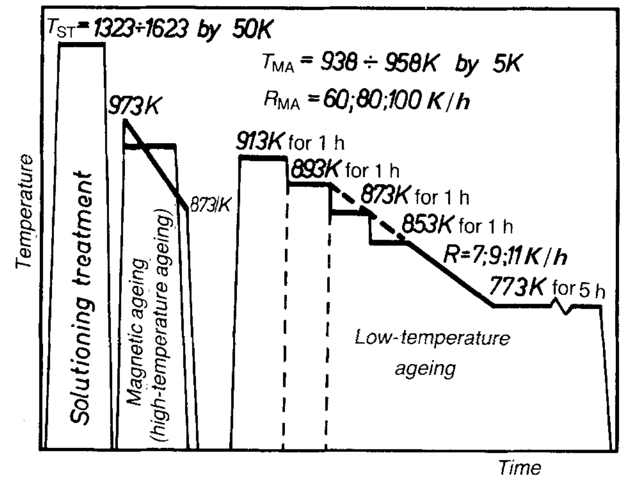
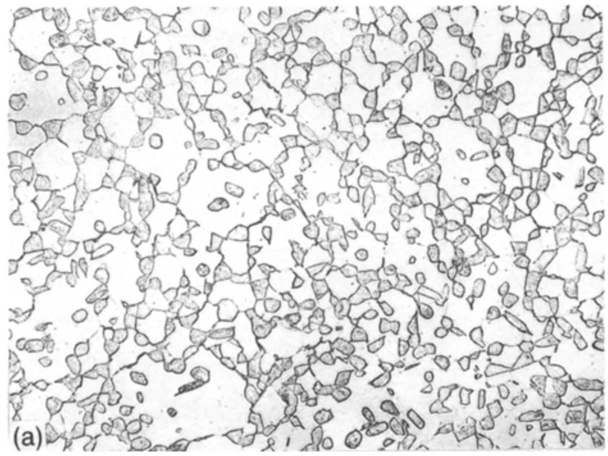
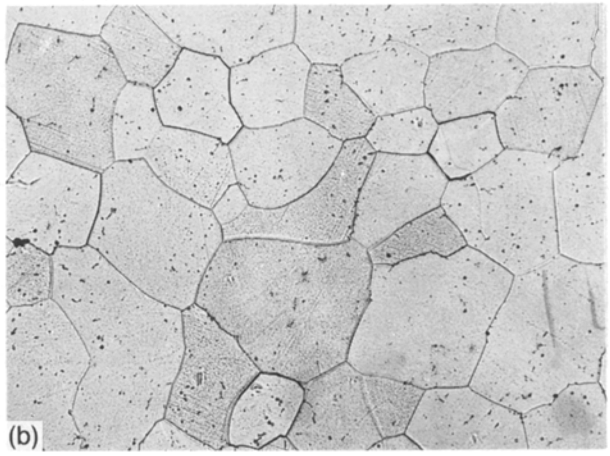


Figure 1 Scheme of heat treatments of the Fe–23Cr–16Co–X alloys.





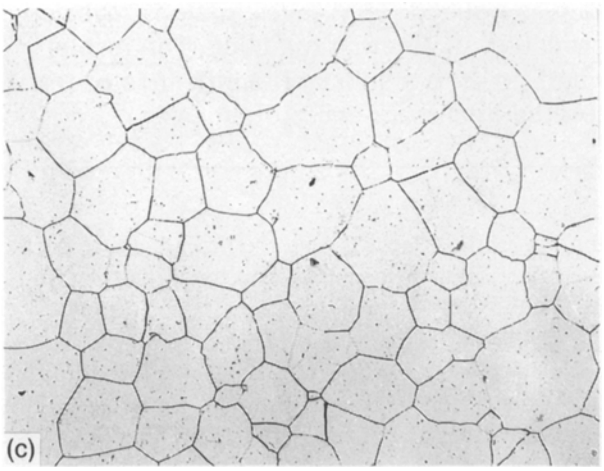


Figure 2 Structures of the Fe–23Cr–16Co–X alloys after solutioning from the temperature of 1423 K (cooling in oil). Magnification ×88; (a) Fe–23Cr–16Co alloy, (b) Fe–23Cr–16Co–1Ti alloy, (c) Fe–23Cr–16Co–1Ti–1Nb alloy.

±0.5 K/h for the non-isothermal case. The measurements of magnetic properties were performed using a Yokogawa histograph, with an error not exceeding 2%. TEM microstructures were observed using the Jeol 100B microscope; the specimens were thinned electrolytically by the two-sides method, in the electrolyte of composition: 20 parts of $HClO_4$, 80 parts of CH_3COOH.

3. Results and discussion

3.1. Optimization of the conditions of heat treatment

3.1.1. Solutioning

The first stage of heat treatment of Fe–Cr–Co alloys consists of solutioning in order to obtain a single-phase α structure. An alloy is annealed at the temperature at which the α phase is an equilibrium phase; the annealing time should provide homogenization of an alloy and cooling should be performed in such a way as to preserve its single-phase structure. In order to determine the optimum annealing conditions the samples were annealed at the following temperatures: 1473, 1523, 1573 and 1623 K for 1 h, and cooling was performed in water, oil and compressed air. The structural state was estimated on the grounds of observations of the microstructure using an optical microscope.

A single-phase structure was obtained only in the alloys containing titanium as well as in those containing both titanium and niobium after solutioning from the temperature of 1473 K; to the contrary, the alloys without titanium or titanium and niobium addition maintained their two-phase structure ($\alpha + \gamma$) over the full range of the applied annealing temperatures (Fig. 2).

Structural examinations of Fe–23Cr–16Co–X alloys after solutioning from temperatures in the range 1473 to 1673 K allowed a comparison with the controversial information in the literature concerning the range of occurrence of the α phase in this alloy [9]. In the alloys with addition of titanium as well as titanium and niobium it has been found that the range of occurrence of the single-phase α region was extended (which is in agreement with the literature [10]).

Fe–23Cr–16Co was excluded from further investigations since the formation of a single-phase α structure was not achieved in this case. The influence of cooling conditions during solutioning on the magnetic

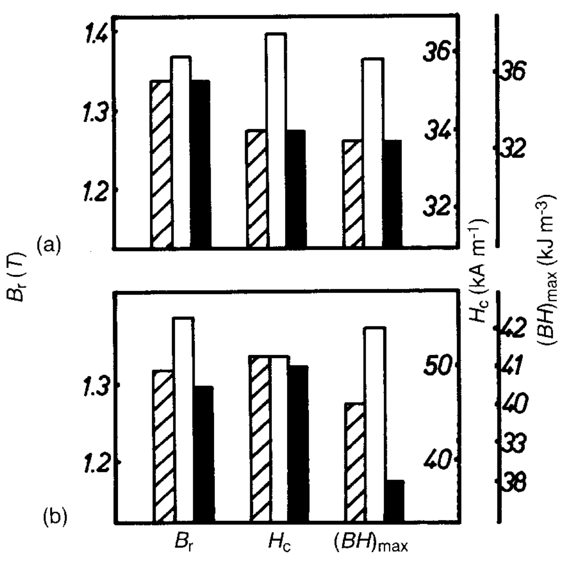


Figure 3 Influence of the cooling medium during solutioning on the level of values of B_r, H_c, $(BH)_{max}$; (a) Fe–23Cr–16Co–1Ti alloy, high-temperature ageing 953 K for 1 h, (b) Fe–23Cr–16Co–1Ti–1Nb alloy, high-temperature ageing 948 K for 1 h, low-temperature ageing: 913 K for 1 h + 893 K for 1 h + 11 K/h + 773 K for 5 h. (▨ water, □ oil, ■ compressed air).

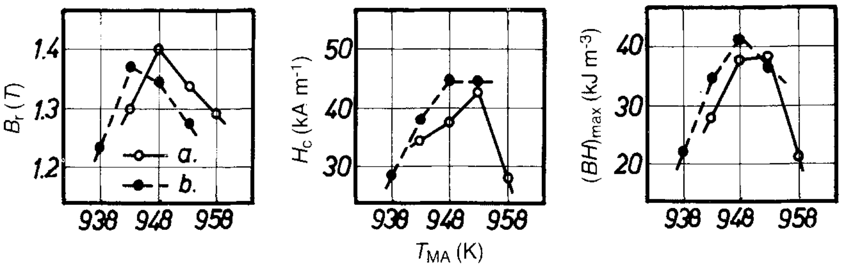


Figure 4 Influence of the temperature of isothermal high-temperature ageing in the external magnetic field (TMA) on the magnetic properties of the alloys; (a) Fe–23Cr–16Co–1Ti, (b) Fe–23Cr–16Co–1Ti–1Nb; low-temperature ageing 913 K for 1 h + 893 K for 1 h – 11 K/h – 773 K for 5 h.

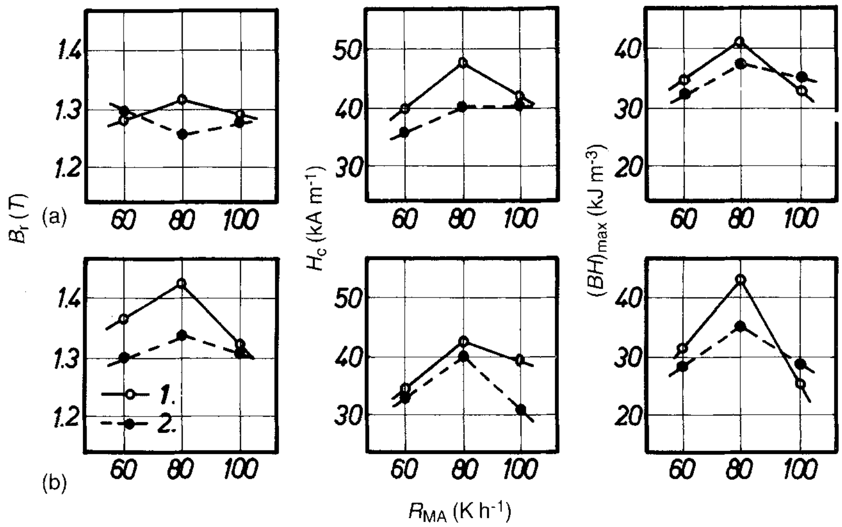


Figure 5 Influence of cooling rate (R_{MA}) during high-temperature ageing in external magnetic field (temperature range 973 to 873 K) on the magnetic properties of the alloys: (a) Fe–23Cr–16Co–1Ti–1Nb, (b) Fe–23Cr–16Co–1Ti; low-temperature ageing: (1) 913 K for 1 h + 893 K for 1 h + 11 K/h + 773 K for 5 h, (2) 893 K for 1 h + 11 K/h + 773 K for 5 h. (○ 1, ● 2).

properties of an alloy was estimated by comparing the values of B_r, H_c and $(BH)_{max}$ after complete heat treatment (Fig. 3).

Comparison of magnetic properties of samples after solutioning from the same temperature showed an evident influence of the cooling medium on both alloys examined. In the titanium-containing alloy as well as in that containing both titanium and niobium, the highest values B_r, H_c and $(BH)_{max}$ were obtained after solutioning involving cooling in oil. This is most likely to be associated with the state of stresses occurring in the solutioned material, which, in the case of cooling in oil, is the beneficial from the viewpoint of structural transformation during high- and low-temperature ageing.

3.1.2. High-temperature ageing in the external magnetic field (TMA)

Studies of the influence of the conditions of high-temperature ageing in an external magnetic field were focused on the temperature of isothermal annealing for 1 h (Fig. 4) and on the conditions of cooling rate in the temperature range from 973 to 873 K (Fig. 5). In all cases the external magnetic field intensity was 320 kA m^{-1}.

In both alloys examined a similarity in the changes in the values of B_r, H_c, $(BH)_{max}$ was observed as a function of temperature of isothermal annealing in the external magnetic field. Addition of niobium, besides the titanium content, influences favourably the values of H_c and $(BH)_{max}$ and reduces the temperature of thermomagnetic treatment to an optimum as regards the magnetic properties of an alloy, thus also reducing the energy expenditure of the process.

The changes in the values of B_r, H_c and $(BH)_{max}$ for the alloys examined as a function of cooling rate during high-temperature ageing in an external magnetic field is presented for two different variants of low-temperature ageing (Fig 5). The character of changes in B_r, H_c and $(BH)_{max}$ and their maximum level is similar to the case of isothermal treatment.

It has been observed that in the case of the TMA with continuous cooling deviations of an order of 5 K/h from the conditions determined as the optimum ones do not cause significant changes in B_r, H_c and $(BH)_{max}$. However, in the case of isothermal treatment it is necessary to maintain the TMA value with an accuracy of ± 2 K. Moreover, it has been noticed that a lower sensitivity to the deviations in the parameters of high-temperature ageing in the external magnetic field is observed for an alloy containing both titanium and niobium, which is in agreement with the results previously reported [11].

TABLE I Chemical composition of the Fe–Cr–Co–X alloys (wt %)

Alloy	Cr	Co	Ti	Nb	Mn	C	Al	Fe
Fe–23Cr–16Co	22.6	15.8	–	–	0.06	0.01	0.2	rest
Fe–23Cr–16Co–1Ti	22.5	15.9	1.3	0.08	0.06	0.01	0.16	rest
Fe–23Cr–16Co–1Ti–1Nb	22.4	15.7	1.02	1.01	0.06	0.02	0.1	rest

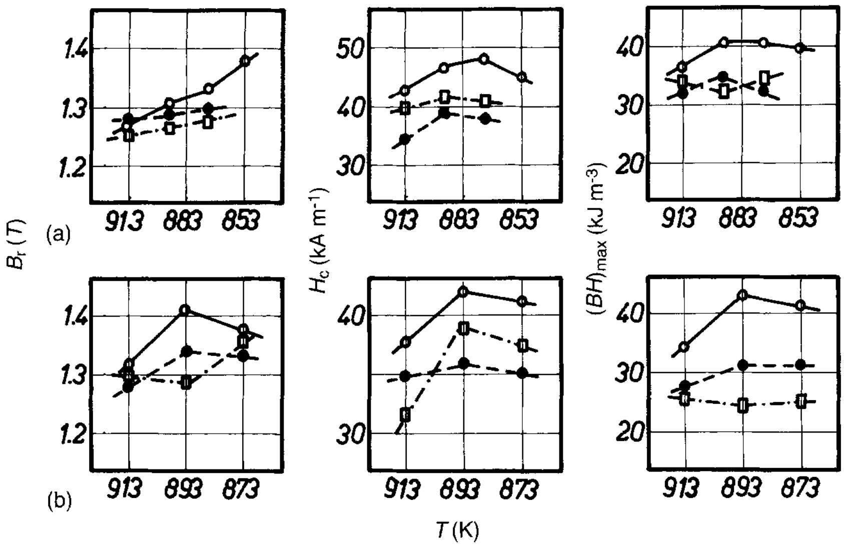


Figure 6 Influence of the temperature of the first stage of low-temperature ageing on the magnetic properties of alloys; (a) Fe–23Cr–16Co–1Ti–1Nb, (b) Fe–23Cr–16Co–1Ti–1Nb; high-temperature ageing in external magnetic field in the temperature range 973 to 873 K; low-temperature ageing 873 K for 1 h + 11 K/h + 773 K for 5 h. (● R_{MA} = 60 K/h, ○ R_{MA} = 80 K/h, □ R_{MA} = 100 K/h).

3.1.3. Low-temperature ageing

Studies of the dependence of magnetic properties on the parameters of low-temperature ageing comprised an influence of temperature of the first stage of low-temperature ageing as well as the rate of continuous cooling on the values of B_r, H_c and $(BH)_{max}$ (Figs 6 and 7). The temperature and time of the last stage of low-temperature ageing were kept constant, i.e. 773 K for 5 h.

Comparison of the magnetic properties presented in Fig. 6 confirms earlier observations concerning the lower sensitivity of an alloy with niobium addition to the conditions of heat treatment. Differences in the nature of the dependence of the magnetic properties of the investigated alloys on the parameters of low-temperature ageing may suggest dissimilar dynamics of transformation leading to magnetic hardening at this stage of ageing. The examinations performed also indicate the close relationship between the temperature of the first stage of low-temperature ageing (being an optimum as regards the magnetic properties) as well as the cooling rate during this treatment and the conditions of high-temperature ageing in the external magnetic field.

3.4. Structural examinations

Structural examinations were aimed at the determination of an influence of the differences in chemical composition of the Fe–23Cr–16Co–1Ti and Fe–23Cr–16Co–1Ti–1Nb alloys on their microstructure formed as a result of spinodal decomposition. The microstructures of the examined alloys for cross-sections parallel and perpendicular to the external magnetic field lines are presented in Fig. 8.

In both cases (Figs 8b and d) the elongated and evidently aligned α_1 particles (bright regions in the photographs) and the α_2 particles (dark regions in the photographs) can be seen while the morphology and dispersion of α_1 and α_2 phases are comparable.

The main difference in the microstructure between the examined alloys consists in the occurrence of fine non-identified precipitations (dark in the photographs) in titanium and niobium containing alloys, not observed in the alloy containing only the titanium addition.

This observation is in agreement with previous results [15–17], where there is occurrence of the phase referred to as the Laves' phase of $MgZn_2$ or $MgNi_2$ type of structure.

The images of microstructures presented in Fig. 8 were obtained for the magnets characterized with the highest values of B_r, H_c, $(BH)_{max}$ obtained for the examined alloys. The demagnetization curves for these experimental points are presented in Fig. 9.

On the grounds of the examination presented it is

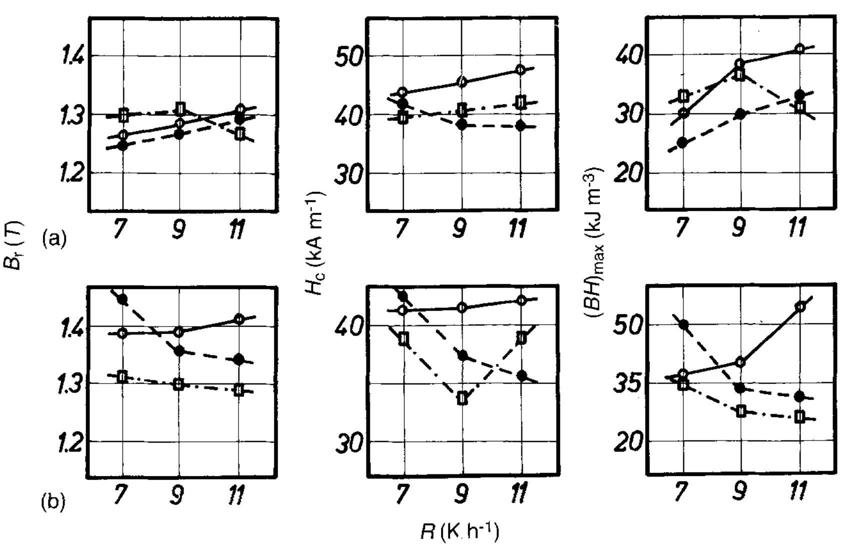


Figure 7 Influence of the cooling rate during low-temperature ageing 893 K for 1 h + *R* + 773 *K* for 5 h on the magnetic properties of the alloys; (a) Fe–23Cr–16Co–1Ti–1Nb, (b) Fe–23Cr–16Co–1Ti–1Nb; high temperature ageing in external magnetic field in the temperature range 993 to 873 K. (● R_{MA} = 60 K/h, ○ R_{MA} = 80 K/h, □ R_{MA} = 100 K/h).

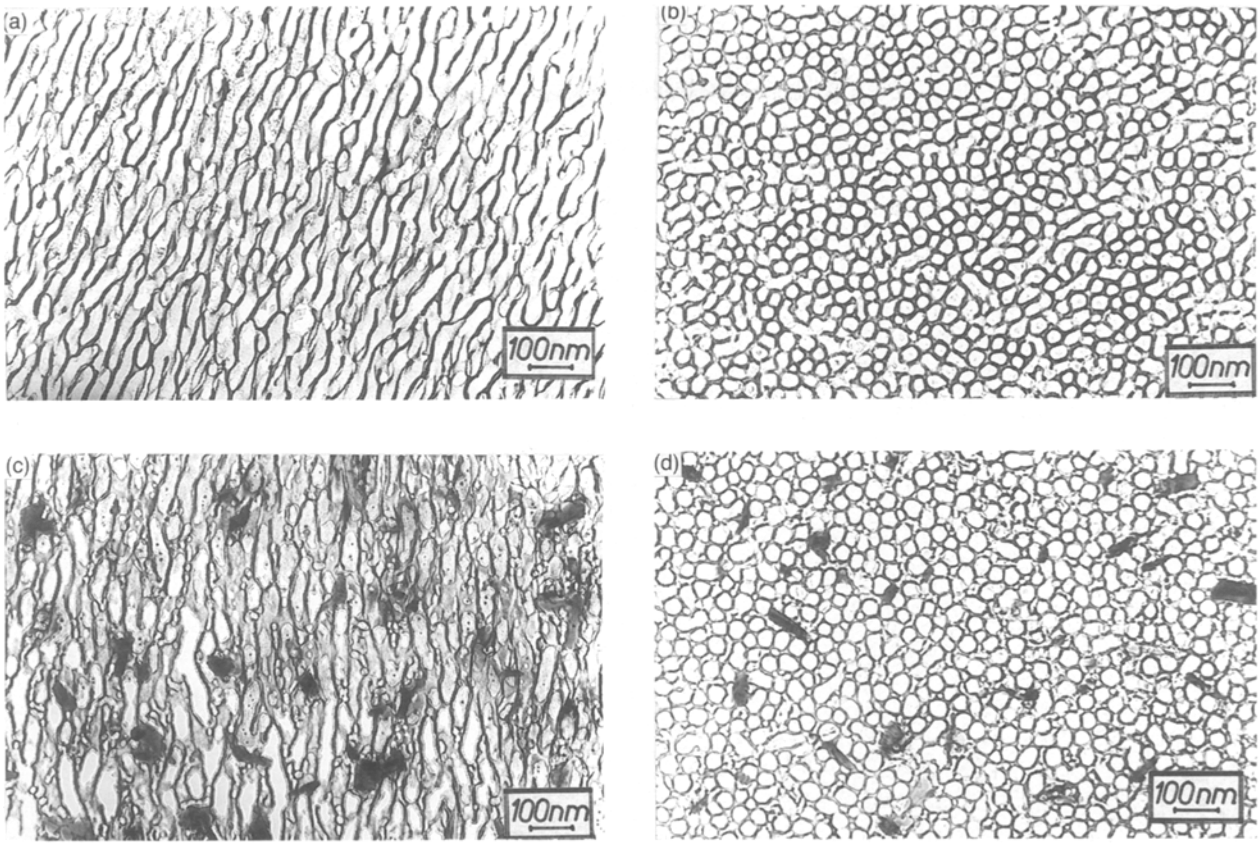


Figure 8 Microstructures of the alloys; (a), (b) Fe–23Cr–16Co–1Ti and (c), (d) Fe–23Cr–16Co–1Ti–1Nb; cross-sections perpendicular (a), (c) and parallel (b), (d) to the external magnetic field lines. High-temperature ageing 973 K/h + 80 K/h + 873 K/h; low-temperature ageing 893 K/h + 11 K for 1 h + 773 K for 5 h.

difficult to definitely estimate the affect of niobium content on the structure and the level of values of the parameters describing magnetic properties. It can only be expected that the increased value of B_r and the lower value of H_c for the niobium-containing alloy, as compared with the respective values for the alloys not containing niobium can result from the occurrence of the additional phase in this alloy.

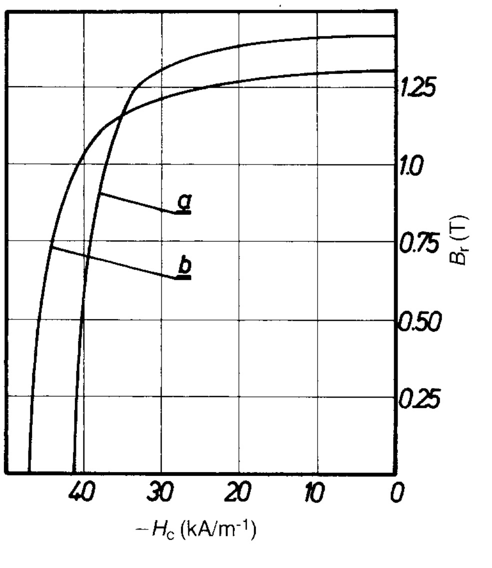


Figure 9 Demagnetization curves for the alloys (a) Fe–23Cr–16Co–1Ti, (b) Fe–23Cr–16Co–1Ti–1Nb; high-temperature ageing in external magnetic field 973 K for 1 h, 80 K for 1 h + 873 K for 1 h; low-temperature ageing 893 K for 1 h + 11 K for 1 h + 773 K for 5 h.

Investigations on the demagnetization in Fe–Cr–Co alloys [12–14] may allow for formulation of the thesis that the precipitations of the non-identified phase observed in the alloy are the points of the domain walls pinning which makes their rotation difficult, thus resulting in the higher level of the values in the alloy in which such precipitations occur. However, the lowering of the B_r values in the Fe–23Cr–16Co–1Ti–1Nb alloy can be explained by structural discontinuity (most likely of paramagnetic character, thus being the isolator for the induction stream in the material), which can be one of the reasons for the differences in the values of B_r in the examined alloys.

4. Discussion and conclusions

The examinations performed allowed the affect of the addition of titanium as well as of titanium and niobium on the dependence of the magnetic properties of Fe–23Cr–16Co alloy on the parameters of heat treatment to be determined.

Observations of microstructures permitted the qualitative determination of the differences between the investigated alloys on the structural level of the α_1 and α_2 regions. On the grounds of the presented results of investigations the following conclusions can be formulated.

(1) Addition of titanium or titanium and niobium to the Fe–23Cr–16Co alloy extends the range of occurrence of the solid solution α,

(2) The cooling rate after solutioning influences considerably the obtained level of values of the magnetic properties;

(3) The alloy containing titanium and niobium reveals considerably lower sensitivity to the changes in the parameters of heat treatment than the alloy containing only titanium addition,

(4) There is a close relationship between the affect of thermomagnetic treatment and the influence of low-temperature ageing on the magnetic properties of the Fe–23Cr–16Co–1Ti and Fe–23Cr–16Co–1T–1Nb alloys.

Niobium content in the investigated alloys causes fine-dispersive precipitations of the non-identified phase in the microstructure which can be one of the reasons for differences in the shape of the demagnetization curves for the alloys under investigation.

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