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THERMOANALYTICAL STUDIES ON LIQUIDUS-SOLIDUS GAPS AND PHASE TRANSFORMATIONS OF MAGNETICALLY HARD $Fe_{48-x}Cr_{28}Co_{24}Si_x$ ALLOY

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Thermal analysis, measurements of saturation magnetization and microstructure observations were used to determine the effects of silicon content ($0 < x \leqslant 4.33$ wt.%) on the liquidus-solidus temperatures, phase transformations and critical cooling rate during solutioning of $Fe_{48-x}Cr_{28}Co_{2x}Si_x$ magnets. It was found that the addition of silicon on the investigated alloy (i) decreased the liquidus-solidus temperatures, the temperature changes for the solidus being greater than for the liquidus, and (ii) distinctly influenced the phase transition temperatures: The lower temperature of the range of γ-phase existence and the Curie temperature decreased, the γ-phase region became narrower and the σ-phase region became slightly broader.

FeCrCo alloys with compositions 20–35 wt% Cr, 5–30 wt% Co, Fe-balance and suitable Cr/Co proportions are ductile permanent magnetic alloys [1]. The magnetic energies $(BH)_{max}$ of these alloys exceed 32 kJ/m³ (Fig. 1 [2]).

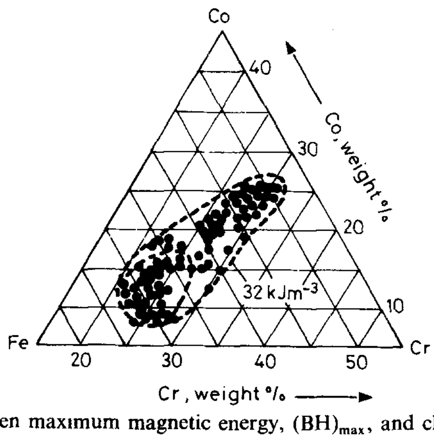

Fig. 1 Relationship between maximum magnetic energy, $(BH)_{max}$, and chemical composition in the Fe–Cr–Co ternary system [2]

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In order to achieve the magnetic properties of these alloys, it has been found necessary to incorporate the following three stages of heat treatment:

(i) homogenization to a single-phase b.c.c. condition and retention of the α-phase by rapid quenching,

(ii) isothermal heat treatment at 620–660° in the presence of strong (>160 kA/m) unidirectional magnetic field,

(iii) multi-stage tempering, in which the temperature is progeessively reduced from ca. 600° to ca. 540° in the absence of a magnetic field.

As a result of such heat treatment, the alloys attain the optimum magnetic properties and consist of two coherent b.c.c. phases, i.e. an iron-rich phase (α_1) and a chromium-rich phase (α_2) [3–5]. It is then necessary to designate the composition and the treatment mentioned to ensure avoidance of the f.c.c. γ-phase, which deteriorates the magnetic performance, or the tetragonal σ-phase, which markedly reduces the workability and the magnetic performance [1, 6]. It was also expected that the α-phase region would be extended by the addition of α-forming elements of iron-base alloy (e.g. Nb, Al, Ti, Si, Mo, Zr, V, Ge, Hf and W) [1]. However, it is known that, from among these α-forming elements, the addition of 1 wt% Si is effective in improving the magnetic properties [5, 7–9] and in upgrading the workability of these alloys [8, 10]. It should also be noted that the recent studies [5, 7–10] concern mainly the effects of these elements on the conditions of stages (ii) and (iii) of Fe–Cr–Co alloy heat treatment. At present there is a lack of systematic studies concerning the effects of silicon on the liquidus-solidus temperatures and phase transformation temqeratures as well as on the critical cooling rate for preventing decomposition of the α-phase. Such studies are therefore the main aim of this work. Their results, besides their cognitive value also have practical meaning because they should make it possible to determine, among others, the appropriate conditions for stage (i) of the heat treatment of magnetically hard Fe–Cr–Co alloy.

Experimental

$Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys with $0<\mathrm{Si}\leqslant 4.33$ wt% were induction melted in vacuum. The preparation of the alloys tested in described elsewhere [8].

The liquidus-solidus temperatures were determined with a Crystaldigraf apparatus produced by the Industrial Automatic Devices Works in Sosnowiec (Poland). This apparatus allows determination of the cooling curve $T = f(T)$ and the metal crystallization curve $T' = \frac{\mathrm{d}T}{\mathrm{d}t}$. These curves were obtained for metals cast in argon atmosphere into the measuring crucible (manufactured with the use of the croning method) of 35 cm^3 capacity with the PtRh–Pt thermocouple attached.

The phase transformation temperatures of the $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys in the solid state were determined with a Mettler thermoanalyser TA1. The furnace temperature and the temperature difference between the test and standard (Al_2O_3) samples were measured with a PtRh–Pt thermocouple. The test were carried out in an atmosphere of purified argon at a cooling rate of 25 deg/min. The accuracy of temperature determination was 4 deg.

Simultaneously with the above investigation, $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys homogenized at 1300, 1250, 1200 and 1150° and cooled at a raue of 3.5 deg/s $\leqslant v \leqslant$ 120 deg/s were measured.

The saturation magnetization of each alloys was determined at room temperature in a permanent magnetic field of 1000 kA/m, using the method describing by Klitzing [11].

The microstructure was observed in an optical and a scanning electron microscope.

Results and discussion

The cooling curves, their first derivatives and the DTA curves for the $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys (0.10 wt% $\leqslant x \leqslant$ 4.33 wt%) are exemplified in Figs 2–9. The characteristic points of these curves corresponding to the liquidus and solidus temperatures, high-temperature phase transformation (Figs 2–5) and phase transformation temperatures (Figs 6–9), were determined and are shown in Fig. 10. From the results obtained, the following conclusions may be drawn:

1. The liquidus and solidus temperatures fall with increase of the silicon content of the alloy, but the temperature changes are greater for the solidus than for the liquidus. This fact indicates that in the alloy examined silicon acts as an agent which widens the temperature difference between the solidus and the liquidus. The results coincide with those described in our earlier work [12].

2. Silicon does not affect the type of phase present in the alloy, but it affects the phase transformation temperatures considerably:

— the lower temperature of the range of α-phase occurrence decreases on Si addition, e.g. for silicon contents of 0.10, 1.04 and 4.30 wt% it is 1295°, 1240° and 1175°, respectively; this fact is of great advantage in the process of alloy production, because it allows homogenization treatment at lower temperature;

— it reduces the region of γ-phase existence;

— it'widens the region of σ-phase existence insignificantly;

— it decreases the Curie temperature.

By way of example, Fig. 10 depicts characteristic microstructures of

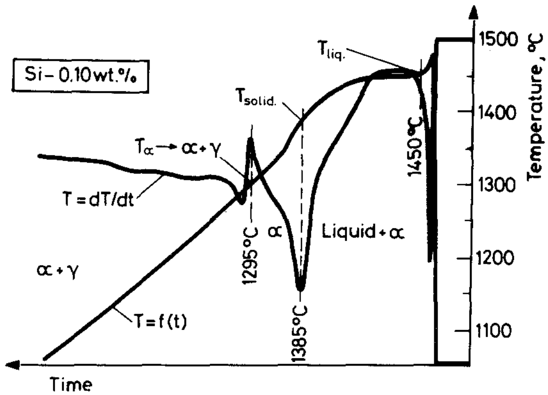


Fig. 2

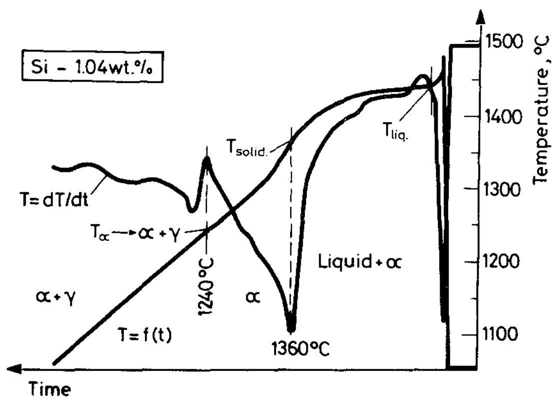


Fig. 3

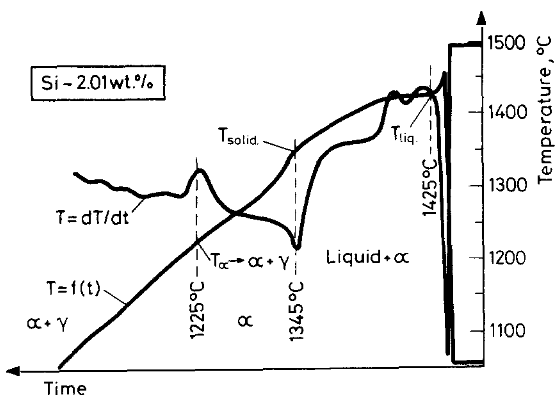


Fig. 4

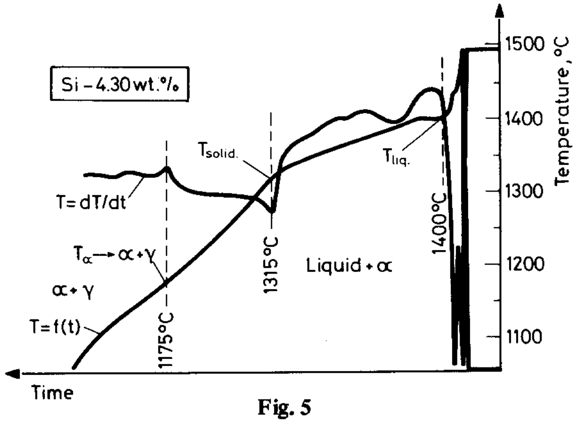


Fig. 5

Figs 2–5 Cooling curves and their first derivates for $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys (0.10 wt% $\leqslant x \leqslant$ 4.30 wt%)

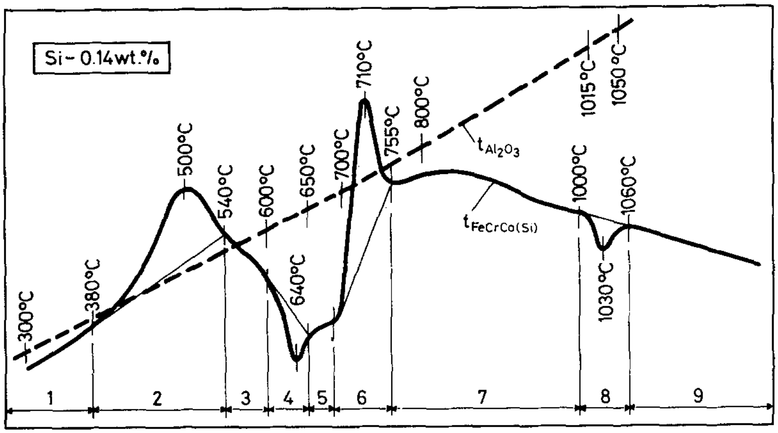
$Fe_{46.96}Cr_{28}Co_{24}Si_{1.04}$ alloy in various temperature ranges in which particular phases occur; Fig. 10a shows the α-phase, Fig. 10b the $\alpha+\gamma$-phases, and Fig. 10c the $\alpha+\gamma+\sigma$-phases.

The saturation magnetization I_s, of the $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys depends on the phase structure. The existence of non-magnetic γ- and σ-phases besides the ferromagnetic α-phase in the alloy structure causes a decrease in the saturation magnetization of the alloy: this is the higher, the larger the fraction of non-magnetic phases in the structure. Therefore, the value of I_s provides information on the phase structure of the alloy. In Fig. 11, the values of I_s for alloys homogenized at different temperatures reach the maximum at various silicon contents. On the assumption that the I_s maximum in these curves corresponds to the single-phase α alloy, the minimum homogenization temperature of the $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys was determined versus silicon content (Fig. 12). From the relationship presented in Fig. 12, the homogenization temperature of $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys decrease linearly with increase of the Si content of the alloy and may satisfactorily be described by the equation:

$$T = 1308.725 - 54.191 \cdot X\text{wt\% Si } (^\circ\text{C}) \qquad (1)$$

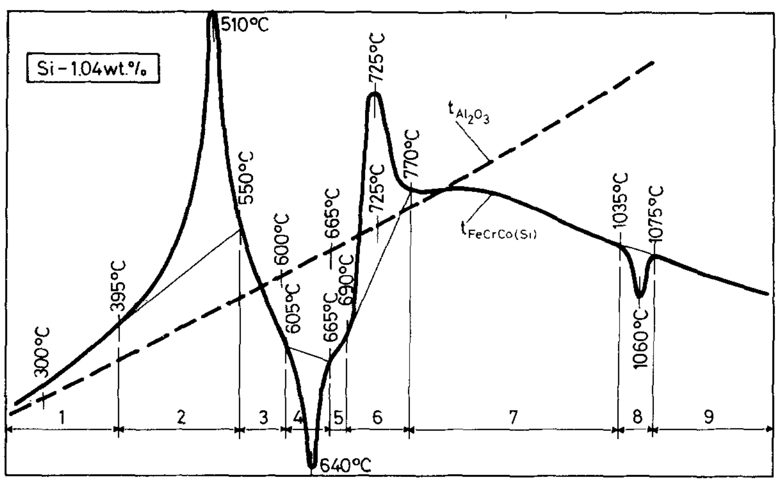
where the error is 0.5%.

Observations on the microstructure of alloys with different Si content, cooled at a rate of 120 deg/s from the homogenization temperatures determined via Eq. (1), confirmed the single-phase (α) structure of these alloys (see microstructure in Fig. 12); the inconsiderable amount of γ-phase occurring along the grain boundaries in $Fe_{47.86}Cr_{28}Co_{24}Si_x$ alloy (Fig. 12a) are connected with the deviation from the critical rate of cooling of the alloy from the homogenizing temperature. It should also be noted that the lower temperature limits of α-phase occurrence determined from the DTA curves and I_s measurements are in good agreement for the alloys tested.



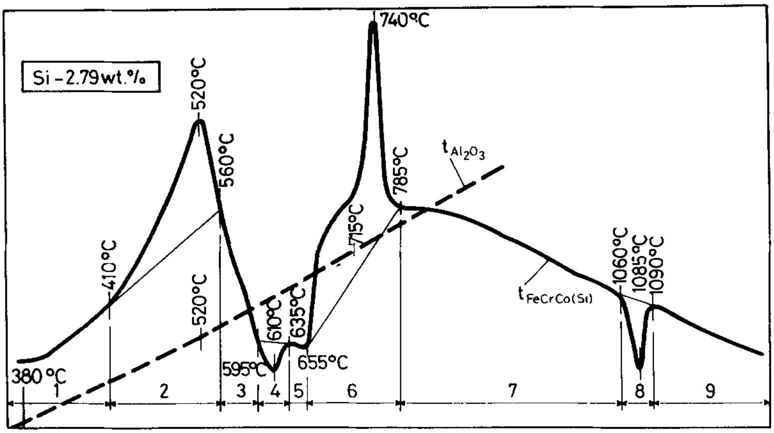
1 - α, 2 - $\alpha \rightarrow \alpha_1+\alpha_2$, 3 - $(\alpha_1+\alpha_2)_{ferromag}$, 4 - $(\alpha_1+\alpha)_{ferromag} \rightarrow \alpha_1+\alpha_{2\,paramag}$
5 - $\alpha_1+\alpha_{2\,paramag}$, 6 - $\alpha_1+\alpha_2 \rightarrow \alpha+\gamma+\sigma$, 7 - $\alpha+\gamma+\sigma$, 8 $\rightarrow \alpha+\gamma+\sigma \rightarrow \alpha+\gamma$
9 - $\alpha+\gamma$

Fig. 6



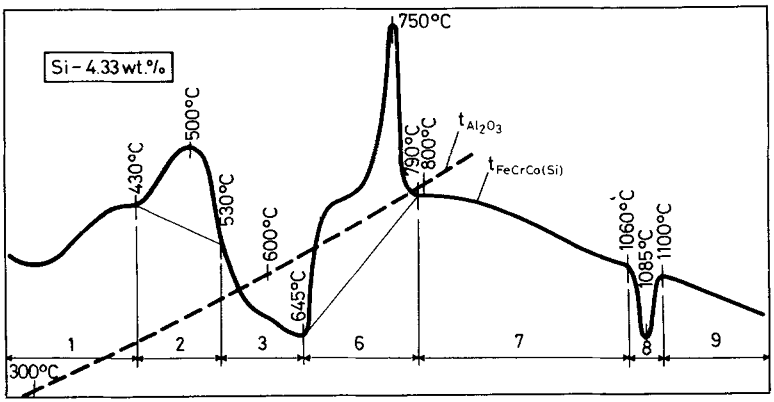
1 - α, 2 - $\alpha \rightarrow \alpha_1+\alpha_2$, 3 - $(\alpha_1+\alpha_2)_{ferromag}$, 4 - $(\alpha_1+\alpha)_{ferromag} \rightarrow \alpha_1+\alpha_{2\,paramag}$
5 - $\alpha_1+\alpha_{2\,paramag}$, 6 - $\alpha_1+\alpha_2 \rightarrow \alpha+\gamma+\sigma$, 7 - $\alpha+\gamma+\sigma$, 8 $\rightarrow \alpha+\gamma+\sigma \rightarrow \alpha+\gamma$
9 - $\alpha+\gamma$

Fig. 7



$1-\alpha$, $2-\alpha \rightarrow \alpha_1+\alpha_2$, $3-(\alpha_1+\alpha_2)_{ferromag}$, $4\ (\alpha_1+\alpha)_{ferromag.} \rightarrow \alpha_1+\alpha_{2\,paramag.}$
$5-\alpha_1+\alpha_{2\,paramag.}$, $6-\alpha_1+\alpha_2 \rightarrow \alpha+\gamma+\sigma$, $7-\alpha+\gamma+\sigma$, $8 \rightarrow \alpha+\gamma+\sigma \rightarrow \alpha+\gamma$
$9-\alpha+\gamma$

Fig. 8



$1-\alpha$, $2-\alpha \rightarrow \alpha_1+\alpha_2$, $3-(\alpha_1+\alpha_2)_{ferromag.}$, $4-(\alpha_1+\alpha)_{ferromag.} \rightarrow \alpha_1+\alpha_{2\,paramag}$
$5-\alpha_1+\alpha_{2\,paramag.}$, $6-\alpha_1+\alpha_2 \rightarrow \alpha+\gamma+\sigma$, $7-\alpha+\gamma+\sigma$, $8 \rightarrow \alpha+\gamma+\sigma \rightarrow \alpha+\gamma$
$9-\alpha+\gamma$

Fig. 9

Figs 6–9 DTA curves for $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys (0.14 wt% $\leqslant x \leqslant 4.33$ wt%)

In order to good magnetic properties, it is necessary to retain the α-phase after quenching. Systematic studies of the microstructures of $Fe_{48-x}Cr_{28}Co_{24}Si_x$ alloys ($0 < x \leqslant 4.33$ wt%) quenched at rates of 120 deg/s $\leqslant v \leqslant 9$ deg/s permit determination of the critical cooling rate required to prevent decomposition of the α-phase (Fig. 13). The relationship presented in Fig. 13 shows that the variations in

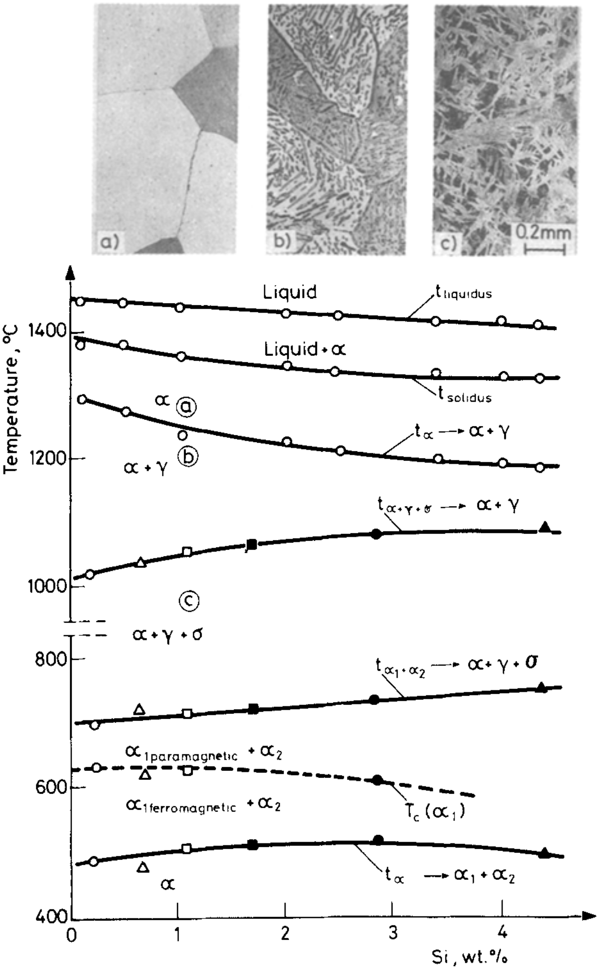


Fig. 10 Effects of silicon on solidus-liquidus temperatures and phase-transformation temperatures of $FeCr_{28}Co_{24}$ alloy (heating rate 25 deg/min) and microstructure of $Fe_{46.96}Cr_{28}Co_{24}Si_{1.04}$ alloy: a – α-phase (1250 °C/40 min), b – $(\alpha=\gamma)$-phases (1200 °C/40 min), $c-(\alpha+\gamma+\sigma)$-phases (900 °C/40 min)

the cooling rate, v, are distinctly dependent on the Si content of the alloy. Thus, within the range $0<\mathrm{Si}\leqslant 1.08$ wt% these changes are rapid and described by the equatoion:

$$v_1 = 127.953 - 103.254 \cdot X\text{wt\% Si (deg/s)} \tag{2}$$

while within the range 1.08 wt% $<\mathrm{Si}\leqslant$ 4.33 wt% the changes are considerably slower and may be represented by the equation:

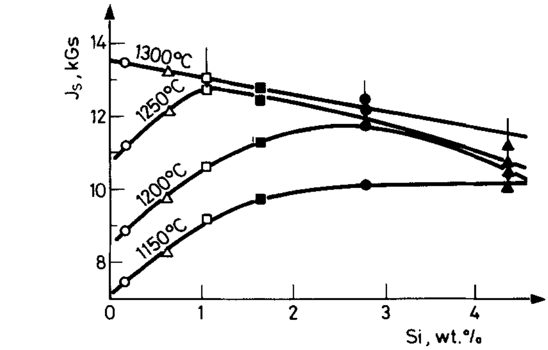


Fig. 11 Saturation magnetization of $FeCr_{28}Co_{24}$ alloy *vs.* silicon content at different homogenization temperatures

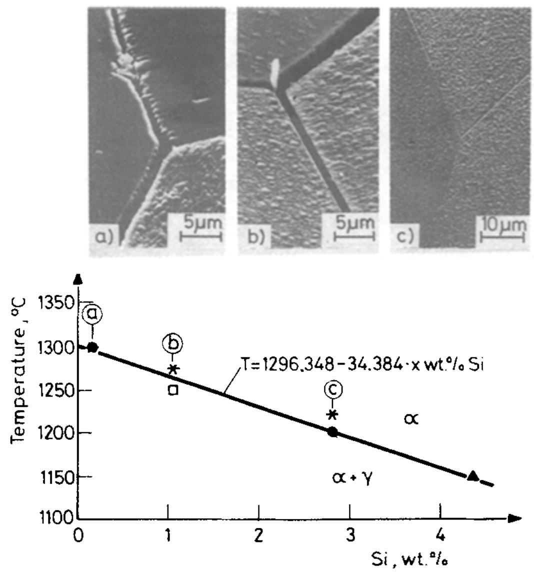


Fig. 12 Homogenization temperature and microstructure of $FeCr_{28}Co_{24}$ alloy *vs.* silicon content

$$v_2 = 18.087 - 1.06 - X\text{wt\% Si (deg/s)} \qquad .3)$$

where the mean error is 5%.

Additionally, Fig. 13 presents the microstructures of $Fe_{46.96}Cr_{28}Co_{24}Si_{1.04}$ alloy cooled from 1250° at rates of 35 deg/s (a), 27 deg/s (b), 20 deg/s (c), 15 deg/s (d) and 3.5 deg/s (e). These microstructures demonstrate that only cooling rate (a) led to an alloy with the α-phase structure (Fig. 13a). At cooling rates of 27 deg/s $\leq v \leq$ 15 deg/s, the alloy structure contains not only the α-phase, but also

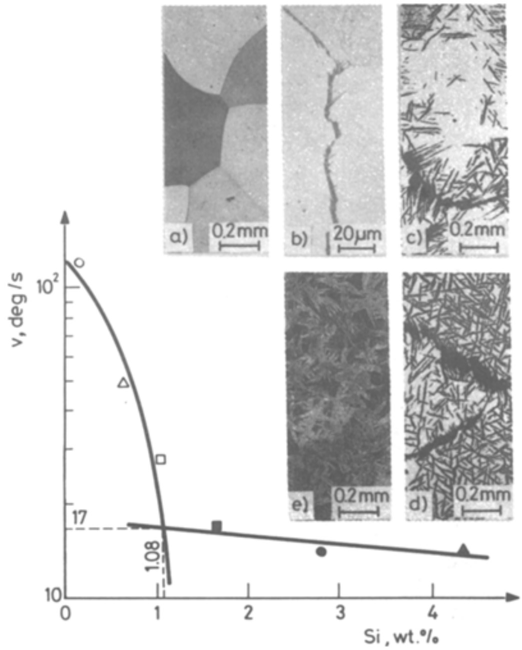


Fig. 13 Critical cooling rate of $FeCr_{28}Co_{24}$ alloy *vs.* silicon content and microstructure of $Fe_{46.96}Cr_{28}Co_{24}Si_{1.04}$ alloy *vs.* cooling rate (deg/s): a – 35, b – 27, c – 20, d – 15, e – 3.5

the γ-phase (Fig. 13b–d), whereas at $v = 3.5$ deg/s the σ-phase is generated (Fig. 13e).

Finally we wish to note the results obtained in this work show that the addition of 1 wt% Si to the $Fe_{48}Cr_{28}Co_{24}$ alloys favourably simplifies the manufacturing process and stabilizes the magnetic properties. The results of this study are complementary to those of earlier research [5, 8, 9] concerning the effects of silicon on the magnetic, mechanical and metallurgical properties of magnetically hard $Fe_{48}Cr_{28}Co_{24}$ alloys.

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Zusammenfassung — Mittels Thermoanalyse, magnetischen Sättigungsmessungen und Untersuchungen des Mikrogefüges wurde der Einfluss des Siliziumgehaltes ($0 < Si < 4.33\%$) von $Fe_{48-x}Cr_{28}Co_{24}Si_x$ auf Liquidus-Solidus Temperaturen, Phasenumwandlungstemperaturen und kritische Abkühlgeschwindigkeiten ermittelt. Es wurde festgestellt, dass Zusatz von Silizium zu der untersuchten Legierung eine Herabsetzung der Liquidus-Solidus Temperaturen (Herabsetzung der solidustemperaturen ist grösser als die der Liquidustemperaturen) bewirkt und die Phasenumwandlungstemperatur deutlich beeinflusst: Die untere Temperatur des α-Phasenbereiches und die Curie-Temperatur werden vermindert, der γ-Phasenbereich wird schmaler und der σ-Phasenbereich wird verbreitert.

Резюме — Термический анализ, измерения магнитного насыщения и микроструктурные исследования были использованы для определения влияния содержания кремния ($0 < x \leqslant 4{,}33$ вес.%) на температуру ликвидус-солидуса, фазовые превращения и критическую скорость охлаждения при пересыщении магнетиков $Fe_{48-x}Cr_{28}Co_{24}Si_x$. Найдено, что добавление кремния и изученному сплаву уменьшает температуры ликвидус-солидуса, причем температурные изменения для солидуса больше, чем для ликвидуса. Введение кремния различным образом сказывается на температуре фазовых переходов, вызывая понижение температурной области существования α-фазы и уменьшение температуры Кюри. Область γ-фазы становится узкой, а область σ-фазы становится слегка более широкой.