

## **THERMAL ANALYSIS AND LONGTIME STABILITY OF AMORPHOUS $\text{Co}_{100-x}\text{B}_x$ ALLOYS**

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Crystallization behaviour of amorphous  $\text{Co}_{100-x}\text{B}_x$  alloys ( $17 < x \leq 40$ ) has been investigated by differential thermal analysis (DTA) and dynamic temperature X-ray diffraction (DTXD) methods in the freshly prepared state and at a period of about eight years after preparation. The crystallization temperatures lie in the range 670 K–760 K. An average decrease of about 1.25 K/year over a period of eight years has been observed to take place in the crystallization temperatures of these materials. The value of heat of crystallization ( $\Delta H_{cr}$ ) and activation energy lie in the range 2.3 kJ/g-at – 5.9 kJ/g-at and 2.1 eV – 2.4 eV, respectively. The phases obtained at crystallization temperatures during DTXD analysis have been discussed.

**Keywords:** amorphous magnetic materials, Co-B alloys

### **Introduction**

Amorphous magnetic materials based on the Co–B system are of great technological importance because of their superior magnetic properties.  $\text{Co}_{100-x}\text{B}_x$  alloys can easily be obtained in the amorphous state (by rapidly quenching their melts) over a wide composition range  $17 \leq x \leq 40$  [1–7 and res. given therein]. A comprehensive study of the crystallization behaviour of amorphous Co–B alloys (crystallization temperature, heat of crystallization, activation energy) is lacking and to our knowledge, no investigations (regarding the longtime stability of melt-quenched amorphous Co–B alloys) have been reported yet. In the present work, results of thermal investigations of Co–B alloys over the whole amorphous range are reported.

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## Experimental

$\text{Co}_{100-x}\text{B}_x$  alloys, each of mass about 10 g, were prepared in the composition range  $17 \leq x \leq 40$  by high-frequency (263 kHz) induction melting of the constituents in water-cooled quartz tubes under an atmosphere of purified argon at a pressure of 400 mbar. The purities of the starting elements were 99.98 wt% and 99.8 wt% for Co and B, respectively. The final compositions of the alloys were assumed to be that of the weighed components.

Amorphous Co–B alloys were prepared in the form of thin ribbons (about 1 to 2 mm in width and 30 to 50  $\mu\text{m}$  in thickness) by free jet melt-spinning under purified helium atmosphere at a pressure of 250 mbar, using the outer surface of a rapidly rotating copper wheel as a substrate and quartz-tubes with a melt ejection orifice of 0.4 mm. The details are given elsewhere [9]. Room temperature X-ray diffraction was carried out by a Guinier-de Wolf camera. For dynamic temperature X-ray diffraction (DTXD) analysis (i.e. continuous recording of X-ray diffraction patterns during continuous heating of samples), a modified Guinier-Lenné high temperature camera [8] was used.

Crystallization temperatures,  $T_{\text{cr}}^{\text{OLD}}$ , were measured with a modified Linseis differential thermal analysis (DTA) equipment at a heating rate of 10 deg/min at a pressure of 500 mbar of purified argon gas for all samples. This work was done already in 1983 by one of the authors [5].

Crystallization temperatures,  $T_{\text{cr}}^{\text{NEW}}$ , and the heats of crystallization were remeasured by DTA for the present work using the samples prepared in 1983.

Activation energies have been calculated using the single heating rate as described by Kneller *et al.* [11]. This method provides reasonable activation energies for thermal processes taking place during crystallization of amorphous metallic materials.

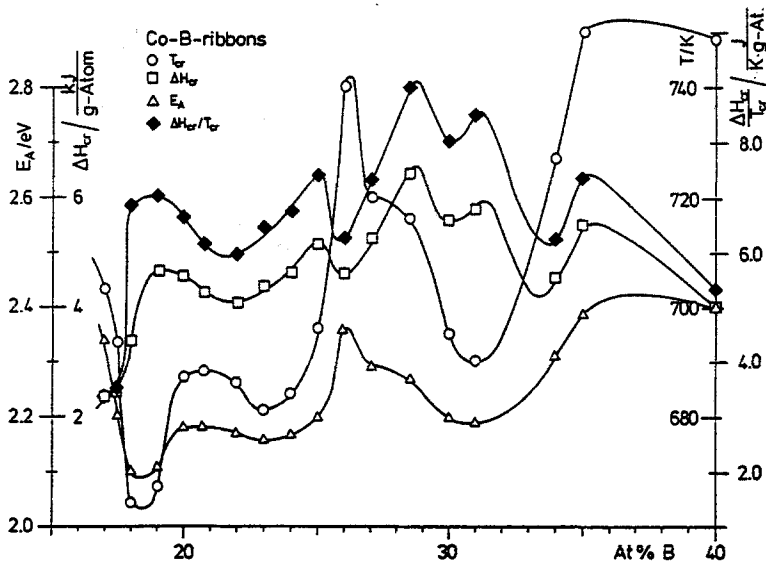
## Results and discussion

The results of DTA investigations of the crystallization behaviour of  $\text{Co}_{100-x}\text{B}_x$  amorphous alloys are given in Table 1 and Fig. 1. It is seen, that, in general, in the composition range  $17 < x \leq 40$ , crystallization temperatures increase with increasing B content from 664 K ( $x = 18$ ) to 750 K ( $x = 40$ ). In spite of this general behaviour we found four narrow composition ranges,  $x = 17, 21, 26$  and  $35$ , giving rise to maxima of crystallization temperatures, whose origin is not yet understood.

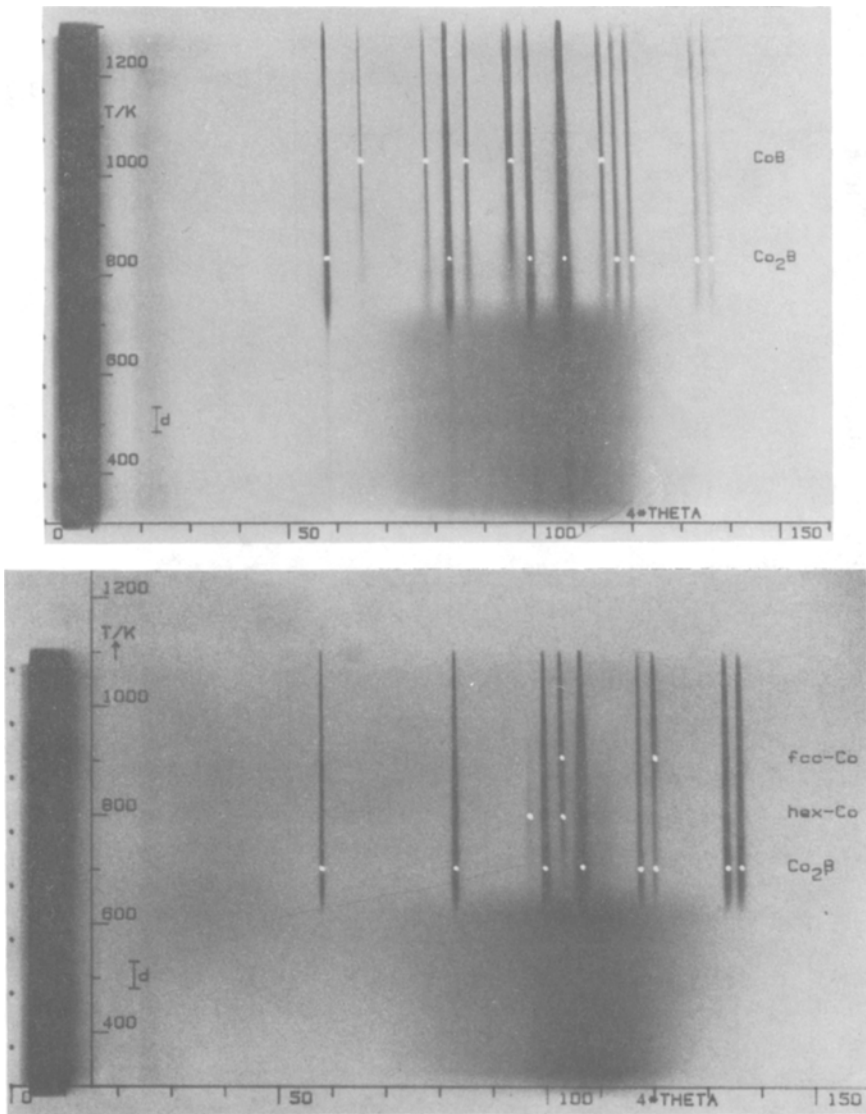
DTXD analysis in the temperature range 300 K–1200 K has revealed that a 'polymorphic' type crystallization takes place for the composition range  $20 \leq x \leq 40$ . The phase of first crystallization was found to be bct  $\text{Co}_2\text{B}$  for  $27 \leq x \leq 40$ , see Fig. 2a and b. Along with this phase a second phase crystallizes at a slightly

**Table 1** Crystallization data of the amorphous  $\text{Co}_{100-x}\text{B}_x$  alloys

	$T_{\text{cr}}^{\text{NEW}} /$ K	$T_{\text{cr}}^{\text{OLD}} /$ K	$\Delta H_{\text{cr}} /$ $\text{kJ} \cdot (\text{g-at})^{-1}$	$E_A /$ eV	$\Delta H_{\text{cr}} / T_{\text{cr}} /$ $\text{J}(\text{K} \cdot \text{g-at})^{-1}$
$\text{Co}_{60}\text{B}_{40}$	752	—	4.00	2.40	5.33
$\text{Co}_{65}\text{B}_{35}$	750	760	5.53	2.39	7.37
$\text{Co}_{66}\text{B}_{34}$	727	—	4.55	2.31	6.26
$\text{Co}_{69}\text{B}_{31}$	690	700	5.87	2.19	8.51
$\text{Co}_{70}\text{B}_{30}$	695	703	5.60	2.20	8.05
$\text{Co}_{71.5}\text{B}_{28.5}$	716	724	6.45	2.27	9.01
$\text{Co}_{73}\text{B}_{27}$	720	725	5.27	2.29	7.32
$\text{Co}_{74}\text{B}_{26}$	740	750	4.63	2.36	6.26
$\text{Co}_{75}\text{B}_{25}$	696	706	5.18	2.20	7.44
$\text{Co}_{76}\text{B}_{24}$	684	693	4.65	2.17	6.79
$\text{Co}_{77}\text{B}_{23}$	681	698	4.41	2.16	6.47
$\text{Co}_{78}\text{B}_{22}$	686	—	4.10	2.17	5.97
$\text{Co}_{79.25}\text{B}_{20.75}$	688	694	4.29	2.18	6.15
$\text{Co}_{80}\text{B}_{20}$	687	695	4.56	2.18	6.63
$\text{Co}_{81}\text{B}_{19}$	667	675	4.69	2.11	7.03
$\text{Co}_{82}\text{B}_{18}$	664	673	3.39	2.10	6.86
$\text{Co}_{82.5}\text{B}_{17.5}$	693	700	2.43	2.20	3.51
$\text{Co}_{83}\text{B}_{17}$	703	709	2.39	2.23	3.40

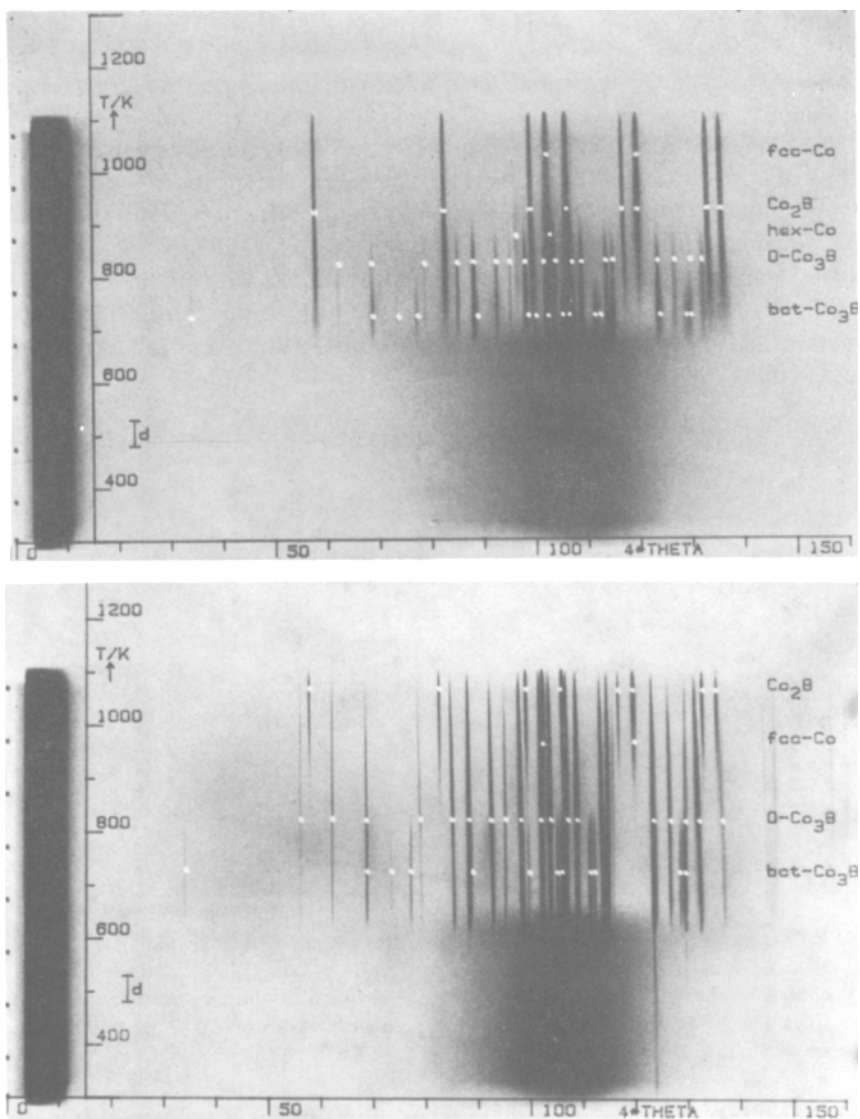


**Fig. 1** Crystallization-temperatures,  $T_{\text{cr}}^{\text{OLD}}$ ,  $T_{\text{cr}}^{\text{NEW}}$ , heat of crystallization,  $\Delta H_{\text{cr}}$ , activation energy,  $E_A$ , and entropy of crystallization,  $\Delta H_{\text{cr}} / T_{\text{cr}}$ , of amorphous  $\text{Co}_{100-x}\text{B}_x$  alloys



**Fig. 2a, b** DTXD-pattern of the amorphous  $\text{Co}_{100-x}\text{B}_x$  alloys taken with  $\text{CoK}\alpha$  radiation (30 kV, 30 mA, 5 mm slit width [8]) in the temperature range 300 K-1200 K at a heating rate of 50 K/h. The black dots on the left along the ordinate are primary beam marks 100°C apart. The X-ray diffraction reflections marked with white dots on a horizontal line are due to the phase printed on the right. a)  $x = 37$ , b)  $x = 30$

higher temperature, identified as CoB for  $x > 35$  and fcc Co for  $26 \leq x \leq 35$ . For  $20 \leq x < 26$  the crystallizing phases are however bct  $\text{Co}_3\text{B}$ /orthorhombic  $\text{Co}_3\text{B}$ , see Fig. 2c and d. For  $x < 20$  a 'eutectic' type crystallization takes place with hexagonal Co (saturated with B) and orthorhombic  $\text{Co}_3\text{B}$ , see Fig. 2e. These find-



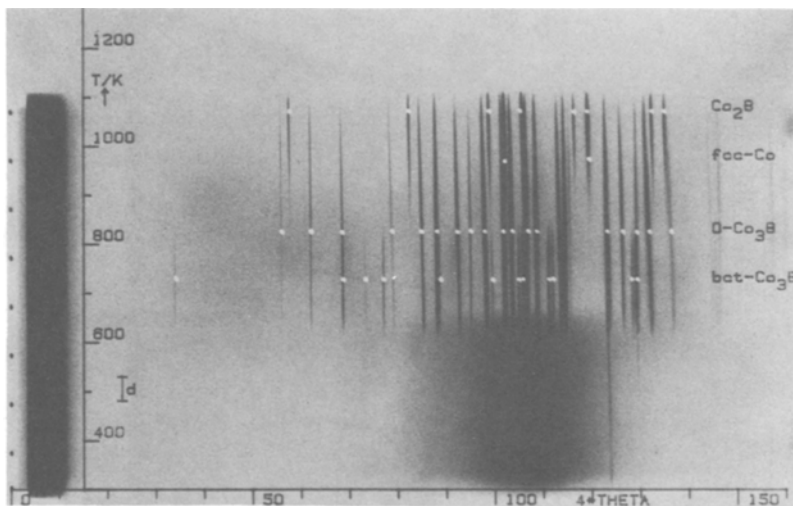
**Fig. 2c, d** DTXD-pattern of the amorphous  $\text{Co}_{100-x}\text{B}_x$  alloys taken with  $\text{CoK}\alpha$  radiation (30 kV, 30 mA, 5 mm slit width [8]) in the temperature range 300 K–1200 K at a heating rate of 50 K/h. The black dots on the left along the ordinate are primary beam marks 100°C apart. The X-ray diffraction reflections marked with white dots on a horizontal line are due to the phase printed on the right. c)  $x = 26$ , d)  $x = 24$

ings are in agreement with thermomagnetic analysis of the same samples described elsewhere [7].

Activation energies involved in the crystallization process were calculated with single heating rate,  $\Phi$  (deg/s), using the following equation,

$$E_A = k_B T_p [\ln [(T_p - T_{300}) / \Phi] + 29.1],$$

[11], where  $T_{300}$  and  $T_p$  are room temperature ( $\approx 300$  K) and peak maximum temperatures, respectively;  $k_B$  is the Boltzmann constant. The results are given in Table 1 and Fig. 1. It is seen that activation energies show the same behaviour (as a function of composition of these alloys) as crystallization temperatures. The opposite behaviour is found for heat of crystallization,  $\Delta H_{cr}$  released at crystallization temperatures and for entropy of crystallization,  $\Delta H_{cr} / T_{cr}$  (if at all valid). As can be seen from Fig. 1, with increasing crystallization temperatures,  $\Delta H_{cr}$  and  $\Delta H_{cr} / T_{cr}$ , both decrease. A correlation between  $\Delta H_{cr} / T_{cr}$  and the ordering of crystal structures, as observed in the quasi-binary  $\text{Fe}_3\text{B-Ni}_3\text{B}$  system [12], could not be found in this Co-B system.



**Fig. 2e** DTXD-pattern of the amorphous  $\text{Co}_{100-x}\text{B}_x$  alloys taken with  $\text{CoK}\alpha$  radiation (30 kV, 30 mA, 5 mm slit width [8]) in the temperature range 300 K-1200 K at a heating rate of 50 K/h. The black dots on the left along the ordinate are primary beam marks 100°C apart. The X-ray diffraction reflections marked with white dots on a horizontal line are due to the phase printed on the right. e)  $x = 17.5$

As Co-B alloys are of great technological interest, because of their remarkable magnetic properties, a long-time-stability investigation of the amorphous state of  $\text{Co}_{100-x}\text{B}_x$  glassy alloys is of great importance. Therefore we took eight years old amorphous ribbons (i.e. stored in air for 8 years) and reinvestigated their crystallization behaviour,  $T_{cr}^{\text{NEW}}$ , and compared our results to those taken eight years ago,  $T_{cr}^{\text{OLD}}$  (Table 1). It is seen, that crystallization temperatures have decreased by about approximately 10 K in 8 years. A linear extrapolation (which although not correct, however pertain to the lowest limit) reveals that it would

take more than about 600 years till the crystallization temperatures of these materials decrease to the room temperature value.

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**Zusammenfassung** — Mittels DTA und temperaturabhängiger Röntgendiffraktion (DTXD) wurde das Kristallisationsverhalten von amorphen  $\text{Co}_{100-x}\text{B}_x$  Legierungen (17 x 40) im frisch präparierten Zustand und etwa acht Jahren nach der Herstellung untersucht. Die Kristallisationstemperatur liegt im Bereich 670-760 K. Für die Kristallisationstemperatur dieser Materialien konnte über die Periode von acht Jahren hinweg eine mittlere Abnahme von etwa 1.25 K/Jahr beobachtet werden. Die Werte für Kristallisationswärme ( $H_{cr}$ ) und Aktivierungsenergie liegen im Bereich 2,3-5,9 kJ/g-At beziehungsweise 2,1-2,4 eV. Die während der DTXD bei den Kristallisationstemperaturen erhaltenen Phasen wurden eingehend besprochen.