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Crystal structure of orthorhombic Co_4Al_{13}

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Abstract

The crystal structure of Co_4Al_{13} has been investigated using metallography, X-ray single crystal and powder diffraction methods. A sample with the composition $Co_{24}Al_{76}$ has been synthesized in a high frequency furnace and heat treated at 850 °C to achieve homogenization. The crystal structure of Co_4Al_{13} belongs to a new structure type: Pearson's symbol, oP102; space group, *Pmn*2_1; $a = 8.158(1)$ Å, $b = 12.342(1)$ Å, $c = 14.452(2)$ Å; $V = 1455.1(5)$ Å^3; $Z = 6$. The final value of the reliability factor is 0.0618 for 839 symmetry-independent reflections ($|F| > 4\sigma(F)$) with isotropic extinction and anisotropic thermal displacement coefficients. The shortest interatomic distances are those of Co–Co (2.86 Å), Co–Al (2.24 Å) and Al–Al (2.24 Å). The coordination numbers of the atoms are 8–11 for Co and 9–13 for Al. The structure of Co_4Al_{13} is built from the same structure segments as Fe_4Al_{13} but differs from that of Fe_4Al_{13} by the stacking sequence (numeric symbol 1_2 for Co_4Al_{13} and ∞ for Fe_4Al_{13}). In both structures, pentagonal "channels" occur. The atoms with pentagonal-prismatic or icosahedral environment are located on the axes of these channels.

1. Introduction

In the concentration area from 50 to 100 at.% Al, the phase diagram of the binary system Co–Al [1–3] shows the following intermetallic phases: CoAl (CsCl type) [4], Co_2Al_5 (Co_2Al_5 type) [5, 6], $CoAl_3$, Co_4Al_{13} and Co_2Al_9 (Co_2Al_9 type) [7]. Except CoAl, these phases are formed by peritectic reactions [1–3]. For $CoAl_3$ and Co_4Al_{13}, there is some uncertainty in the description of the phase equilibria, as well as in the determination of the crystal structure. This arises from the fact that both intermetallic compounds are situated in the narrow range of compositions from $Co_{25}Al_{75}$ to $Co_{23.5}Al_{76.5}$.

$CoAl_3$ and Co_4Al_{13} were first observed by Bradley and Seager during powder diffraction investigations [8]. On the basis of metallographical as well as differential thermal analysis (DTA) investigations, the following phase equilibria were proposed by Gödecke [1]: $CoAl_3$ forms by a peritectic reaction from Co_2Al_5 and the melt at 1135 °C; Co_4Al_{13} forms peritectically from $CoAl_3$ and the melt at 1093 °C.

Hudd and Taylor investigated the structure of the alloy $Co_{26.34}Al_{73.66}$ annealed at 600 °C for two weeks, using a single-crystal X-ray method [9]. Because no truly single crystals were found, a twinned crystallite cubic in a form with edges 0.15 mm long was used for the structural investigation. The structure of this phase is related to that of Fe_4Al_{13} [10], Pearson's symbol mC102.0-7.2, space group *Cm*, $a = 15.183$ Å, $b = 8.122$ Å, $c = 12.340$ Å, and $\beta = 107.90°$. Following the homeotypism of Black's structure Fe_4Al_{13}, the stoichiometry of this phase was described by the formula Co_4Al_{13} [9], although the composition of the alloy investigated (73.66 at.% Al) and that of the structure proposed (74.7 at.% Al) differ from the exact stoichiometry of 4:13.

The monoclinic structure can be stabilized at a cobalt content of 23.65 at.% by the addition of a third component [11]. For example, structural investigation of the ternary alloys $Co_4Al_{13-x}Cu_x$ showed that the monoclinic structure with the space group *Cm* was found only in alloys with the copper amount higher than 2 at.% [12].

Using X-ray powder diffraction and high resolution electron microscopy, an orthorhombic unit cell was recently proposed by Li *et al.* [13]: $CoAl_3$; space group, *Pnmn*; $a = 14.44$ Å, $b = 8.12$ Å, $c = 12.25$ Å.

The present study follows X-ray investigations made on the binary system Co–Al [14], as well as morphological [15] and structural investigations made on structures showing pentagonal channels [16].

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2. Experimental details

Samples with compositions between $Co_{23}Al_{77}$ and $Co_{25}Al_{75}$ were prepared by melting 99.9% Co (Ventron) and 99.999% Al (Heraeus) in an induction furnace under an argon atmosphere (5.0 Messer-Griesheim). For the following heat treatment, the samples were sealed in an evacuated silica tube.

To determine the homogeneity and grain size, the samples were investigated using metallographical methods. Powder diffraction investigations of the annealed alloy were carried out using an Enraf-Nonius FR552 Guinier camera with Fe $K\alpha_1$ and Co $K\alpha_1$ radiation. Silicon (M"9N", Ventron) was used as the reference material. The Guinier photographs were densitometrically analysed on an LS-20 line-scanner.

For the single-crystal investigation, crystals were selected from the crushed, annealed $Co_{24}Al_{76}$ alloy. Rotation and Weissenberg photographs were taken using Mo $K\alpha$ and Co $K\alpha$ radiation. The single-crystal X-ray diffraction measurements were made on a Siemens R3m/V four-circle diffractometer (Mo $K\alpha$ radiation; graphite monochromator).

Crystallographic calculations were performed using the CSD software package [17].

TABLE 1. Atomic parameters for Co_4Al_{13}

Atom	*x/a*	*y/b*	*z/c*	B_{eq} [a]
Co1	0	0.8978(6)	0.00000	0.93(13)
Co2	0	0.0901(6)	0.5114(4)	0.51(10)
Co3	0	0.1977(5)	0.8250(5)	0.94(13)
Co4	0	0.7720(5)	0.3167(5)	0.86(13)
Co5	0	0.5986(6)	0.8248(4)	0.81(11)
Co6	0	0.4119(6)	0.3137(4)	0.95(11)
Co7	0	0.7309(5)	0.5180(4)	0.42(12)
Co8	0	0.2877(5)	0.0076(5)	0.96(14)
Co9	0.2257(5)	0.9099(4)	0.7346(3)	1.23(9)
Co10	0.2181(5)	0.5969(4)	0.0984(3)	0.86(8)
Al1	0	0.9945(13)	0.8151(11)	1.7(3)
Al2	0	0.0914(14)	0.9569(10)	1.5(3)
Al3	0	0.9053(14)	0.6226(9)	0.8(3)
Al4	0	0.9085(12)	0.4431(8)	0.4(2)
Al5	0	0.1394(11)	0.6728(10)	1.1(3)
Al6	0	0.8113(14)	0.1564(10)	1.4(3)
Al7	0	0.8092(13)	0.8360(12)	2.0(4)
Al8	0	0.252(2)	0.414(2)	1.0(2)
Al9	0	0.407(2)	0.8520(9)	1.3(3)
Al10	0	0.401(2)	0.1491(11)	2.1(3)
Al11	0	0.6837(13)	0.6749(11)	1.7(4)
Al12	0	0.590(2)	0.3960(8)	1.2(3)
Al13	0	0.5271(13)	0.0054(12)	1.6(4)
Al14	0	0.5986(14)	0.2149(11)	2.1(3)
Al15	0.2135(12)	0.2138(7)	0.0996(6)	0.7(2)
Al16	0.2138(11)	0.9020(8)	0.2831(6)	0.7(2)
Al17	0.2401(10)	0.0829(9)	0.4088(6)	1.0(2)
Al18	0.2534(10)	0.2550(12)	0.9172(13)	1.1(2)
Al19	0.2251(12)	0.9810(7)	0.0935(7)	0.9(2)
Al20	0.2214(14)	0.2229(8)	0.5500(7)	1.7(2)
Al21	0.2259(11)	0.5885(9)	0.5422(6)	0.9(2)
Al22	0.2244(12)	0.2946(7)	0.7352(6)	0.7(2)
Al23	0.2291(12)	0.4220(8)	0.4252(6)	1.1(2)
Al24	0.2133(11)	0.5174(7)	0.7338(7)	1.0(2)
Al25	0.2319(13)	0.2763(8)	0.2849(7)	1.2(2)
Al26	0	0.7111(13)	0.9668(13)	2.6(4)
Al27	0	0.1047(14)	0.2380(11)	1.9(3)
Al28	0	0.4179(12)	0.5881(10)	1.1(3)

[a] $B_{eq}=1/3\{B11\times(a^*)^2\times a^2+\ldots\ 2B23\times(b^*)\times(c^*)\times b\times c\times\cos(\alpha)\}$.

3. Results

Bulk alloys $Co_{23.5}Al_{76.5}$ and $Co_{24}Al_{76}$ were heat treated at 850 °C for 3 days, after which the samples were powdered and the powders annealed at 600 °C (50 days), 700 °C (35 days), 850 °C (30 min) and 1000 °C (5 min) respectively. The diffraction patterns (Guinier photographs) of all these samples did not conform to the monoclinic structure Co_4Al_{13} [9]. Metallographical investigations of the $Co_{24}Al_{76}$ annealed at 850 °C for 3 days showed a microstructure with pleochroitic grains as a main phase (Fig. 1). The average grain size is 150 μm. The portion of minority phase was found to be less than 5%.

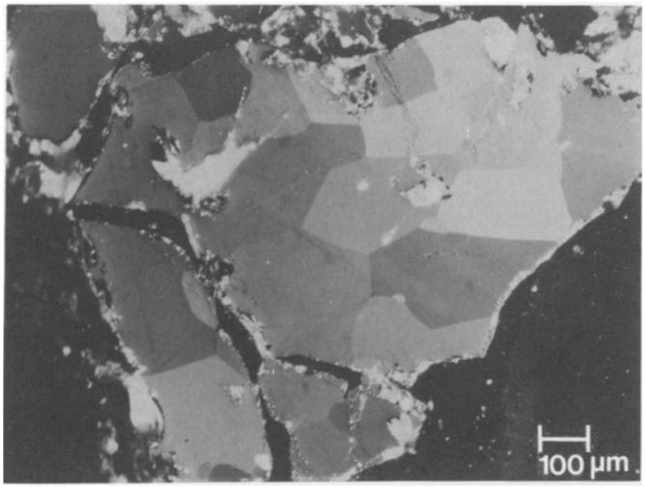

Fig. 1. Photomicrograph of the annealed $Co_{24}Al_{76}$ alloy (polarized light).

For the full structural investigation, a single-crystal fragment with an irregular shape (average size of 0.1 mm) was selected from the crushed $Co_{24}Al_{76}$ alloy annealed at 850 °C for 3 days. Weissenberg and rotation photographs show orthorhombic symmetry (Laue group, *mmm*). The unit cell parameters were distinguished from these photographs and refined by a least-squares method using the diffraction angles of 37 reflections from the Guinier photograph (Fe $K\alpha_1$ radiation; $27° < 2\theta < 65°$): $a=8.158(1)$ Å, $b=12.342(1)$ Å, $c=14.452(2)$ Å; $V=1455.1(5)$ Å^3.

A set of 1948 reflections corresponding to the primitive Bravais lattice was measured on the Siemens R3m/V four-circle diffractometer up to $2\theta_{max} = 55°$ ($0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 18$). Empirical absorption correction was performed using a psi-scan procedure. The usual angle-dependent corrections (Lorentz and polarization) were applied. After excluding weak peaks, the final set of 839 reflections ($|F| > 4\sigma(F)$) was used for the following structure solution and refinement.

The following special reflection conditions were observed in the experimental data set: $h0l$, with $h+l=2n$. According to ref. 18, two space groups are possible, *i.e.* $Pmn2_1$ and $Pmnm$ (standard setting, $Pmmn$).

The crystal structure was solved in the space group $Pmn2_1$ by means of direct methods (cobalt atoms), in combination with Fourier calculations (aluminum atoms). The structural refinement using the isotropic atomic displacement led to $R_F = 0.0735$ for all the reflections used (128 refined parameters). Anisotropic approximation of the thermal displacement (268 refined parameters) reduced R_F to 0.0618. The Becker–Coppens two-parameter isotropic extinction correction formalism was used. No essential effect of the extinction was found. The final atomic coordinate parameters and isotropic thermal displacement coefficients are shown in Table 1. No marked anisotropy of the atomic thermal displacement was obtained. (The table with the anisotropic thermal displacement coefficients can be requested from the authors.)

The interatomic distances are listed in Table 2. The short distances of 2.24 Å observed for some aluminum sites (Al7, Al27) are caused by unsuitable crystal quality. Similar effects were found on refinement of the Fe_4Al_{13} structure [16].

4. Discussion

Complete filling of the atomic positions of the orthorhombic phase Co_4Al_{13} at the chemical composition yielded by the structural refinement ($Co_{23.5}Al_{76.5}$) corresponds well to the phase diagram proposed by Gödecke [1]. Moreover, the composition of the refined orthorhombic structure does not significantly differ from that of the alloy used for the structural investigations ($Co_{24.2}Al_{75.8}$). Here, it can be presumed that the orthorhombic phase is situated at the stoichiometry 4:13, and the monoclinic phase investigated by Hudd and Taylor [9] is at the stoichiometry 1:3. The alloy used by Hudd and Taylor for structural investigation of the monoclinic phase in fact showed less aluminum in its composition ($Co_{26.34}Al_{73.66}$) [9]. Recently, it has been shown that the monoclinic structure can be stabilized mainly by the substitution of aluminum by copper [11].

TABLE 2. Interatomic distances for Co_4Al_{13}

Co1–10Al	2.34–2.81	Al12–12Al	2.62–3.57
Co2–10Al	2.41–2.80	Al12–3Co	2.47–2.52
Co3–10Al	2.31–2.72	Al13–7Al	2.35–2.71
Co4–10Al	2.36–2.66	Al13–3Co	2.39–2.75
Co5–11Al	2.40–2.75	Al14–7Al	2.62–2.76
Co6–10Al	2.38–2.75	Al14–4Co	2.45–2.71
Co7–10Al	2.34–2.71	Al15–8Al	2.63–2.98
Co8–9Al	2.38–2.76	Al15–3Co	2.38–2.71
Co9–9Al	2.24–2.66	Al16–8Al	2.57–2.90
Co10–8Al	2.31–2.56	Al16–3Co	2.42–2.72
		Al17–8Al	2.68–2.97
Al1–8Al	2.30–3.00	Al17–3Co	2.46–2.53
Al1–3Co	2.43–2.51	Al18–8Al	2.64–2.94
Al2–11Al	2.36–3.44	Al18–4Co	2.47–2.56
Al2–3Co	2.31–2.53	Al19–8Al	2.63–3.02
Al3–6Al	2.60–2.85	Al19–3Co	2.48–2.69
Al3–3Co	2.45–2.63	Al20–9Al	2.63–3.07
Al4–11Al	2.60–3.59	Al20–3Co	2.38–2.81
Al4–3Co	2.45–2.49	Al21–9Al	2.63–2.91
Al5–10Al	2.73–2.98	Al21–3Co	2.47–2.76
Al5–2Co	2.32–2.41	Al22–8Al	2.57–2.85
Al6–10Al	2.75–3.01	Al22–3Co	2.43–2.66
Al6–2Co	2.36–2.51	Al23–9Al	2.57–3.05
Al7–7Al	2.24–2.80	Al23–3Co	2.47–2.65
Al7–4Co	2.61–2.66	Al24–9Al	2.69–2.99
Al8–10Al	2.68–3.23	Al24–3Co	2.40–2.75
Al8–2Co	2.43–2.46	Al25–8Al	2.53–2.97
Al9–9Al	2.67–3.23	Al25–3Co	2.43–2.73
Al9–3Co	2.40–2.69	Al26–7Al	2.24–3.01
Al10–10Al	2.60–3.14	Al26–4Co	2.34–2.97
Al10–4Co	2.38–3.10	Al27–11Al	2.93–3.17
Al11–10Al	2.75–2.90	Al27–2Co	2.24
Al11–2Co	2.34–2.41	Al28–11Al	2.87–3.23
		Al28–2Co	2.31

For the values of the lattice parameters, the observed orthorhombic structure agrees with the observation of an orthorhombic phase $CoAl_3$ made by Li *et al.* [13]. The space group $Pmn2_1$ found in the present work is a subgroup of the space group $Pmnn$ found in ref. 13. In fact, if aluminum atoms (Al2, Al9, Al4 and Al12) were in pairs in identical positions on the channel axes mentioned below, the whole structure symmetry would be described by the space group $Pmnn$.

The crystal structure of orthorhombic Co_4Al_{13} is the first representative of the new structure type. A projection of the unit cell on the (0*yz*) plane and selected coordination polyhedrons of atoms are shown in Fig. 2. The coordination polyhedrons of cobalt atoms can be interpreted as trigonal prisms with 2–5 additional vertices in front of the side faces of the prism (coordination number CN = 9–11; see Co1, Co5, Co8, Co9 and Co10 in Fig. 2). In contrast, aluminum shows a more complicated environment. Some aluminum atoms have the trigonal prismatic coordination like that of cobalt atoms (CN = 9–11; see Al1 and Al3 in Fig. 2). The next group of polyhedrons is related to a pentagonal prism with additional vertices in front of the side and

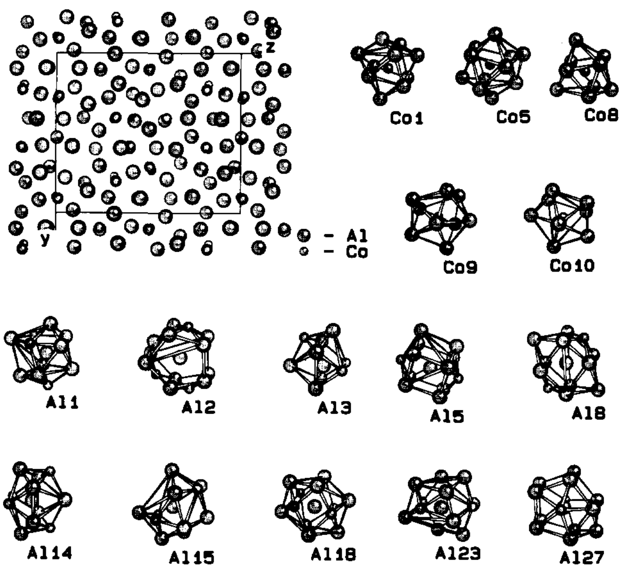

Fig. 2. Projection of the crystal structure of the orthorhombic Co_4Al_{13} on the (0yz) plane, and coordination polyhedrons of selected atoms.

base faces of the prism (CN = 12–15; see Al2, Al5 and Al27 in Fig. 2). Defect or normal icosahedrons also can be found as an aluminum atom environment in the Co_4Al_{13} structure (CN = 11, 12; see Al8, Al14, Al15, Al18 and Al23 in Fig. 2).

The pentagonal prisms around Al2, Al4, Al9 and Al12 build the channels along the [100] direction. The neighboring channels are pair connected. In general, pentagonal prismatic channels are special structure features of the aluminum-rich compounds of transition metals. Similar pair-connected channels have been observed in the monoclinic Fe_4Al_{13} structure [10]. The significant difference between the structures of the quasi-homologous compounds Fe_4Al_{13} (Pearson's symbol, mC102.0-0.3) and Co_4Al_{13} (oP102) is related to the various orientations of the neighboring channel pairs (Fig. 3).

The relationship between the Fe_4Al_{13} and Co_4Al_{13} structures also can be described in terms of homogeneous linear structure series [19]. According to this concept, both structures are built from two-dimensionally infinite structure segments (outlined in Fig. 3). These segments are identical in terms of their compositions, atomic environments and own symmetry. In the case of Fe_4Al_{13}, the segments are stacked in the same positional orientation according to the numeric symbol ∞ ("brick"-like packing of the paired channels in Fig. 3); in the case of the orthorhombic Co_4Al_{13} structure, the segments are in two different orientations and the packing corresponds to the numeric symbol 1_2 ("parquet"-like packing of the paired channels in Fig. 3). Therefore, both structures are the initial ("parent" [19]) structures of the new homogeneous series. Other members of this structure series can be built up by different stackings of the segments shown in Fig. 3.

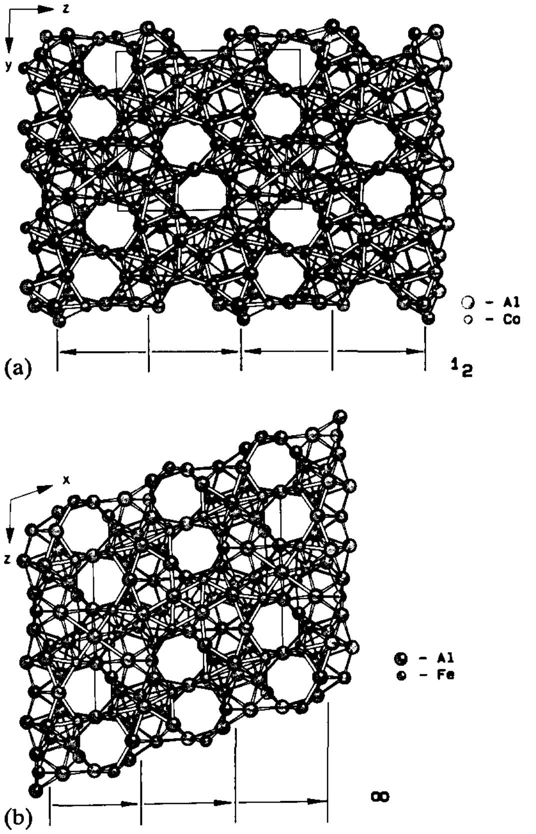

Fig. 3. Pair-connected pentagonal prismatic channels in the structures of (a) orthorhombic Co_4Al_{13} and (b) monoclinic Fe_4Al_{13}.

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