# Aluminium - Cobalt - Gadolinium

Oksana Bodak

# Literature Data

Experimental studies in this system are mostly motivated by the search for magnetic properties. Solid solutions extending over significant ranges of compositions are confirmed in the literature. These phases are based on the binary compounds  $GdCo_2$ ,  $GdCo_5$  and  $GdAl_2$  and on the ternary compounds  $GdCo_{2-x}Al_x$  (0.98  $\leq x \leq 1.46$ ) and  $Gd_2Co_6Al_{11}$ , discovered by [1978Pop].

Since then there are numerous new publications on this system concerning phase equilibria, crystal structures or properties of phases. The CoAl-Gd isopleth was established by [1993Wan, 1994Wan]. They also confirmed the existence of the ternary phase GdCoAl ( $\tau_4$ ) and presence of a new ternary phase of stoichiometry Gd(Co,Al)<sub>1.5</sub>. [1994Liu, 2001Gu] prepared a series of alloys in the Gd<sub>2</sub>Co<sub>17-x</sub>Al<sub>x</sub> (x = 0-5) solid solution region to examine structures and properties. [1999She] investigated the structure and magnetic anisotropy of the alloy Gd<sub>2</sub>Co<sub>15</sub>Al<sub>2</sub>. Crystal structure and magnetic properties of several alloys, for example GdCo<sub>4</sub>Al, were studied by [1996Tha, 1997Gal. [2001Rou] reported the existence of the ternary phase Gd<sub>2</sub>Co<sub>3</sub>Al<sub>9</sub> including its structure and magnetic properties.

All samples were prepared by arc-melting from high-purity metals [1967Oes, 1970Shi, 1971Oes, 1973Zar, 1976Oes, 1978Pop, 1985Chu1, 1985Chu2, 1993Wan, 1994Liu, 1994Wan, 1997Che, 1997Gal, 1999She, 2000Jar, 2001Gu, 2001Rou]. They were investigated both in annealed and as cast state. For crystal structure determination the X-ray powder method was used. Single crystal of  $GdCo_4Al$  composition was grown by tri-arc Czochralski apparatus [1996Tha]. In most cases magnetic properties were studied, such as Curie temperature, magnetization, magneto-crystalline anisotropy [1978Pop, 1996Tha, 1997Che, 1999She, 2000Jar, 2001Gu, 2001Rou]. For these purpose different type of magnetometers were used to measure in magnetic fields up to 5.5T and in a temperature range of 2-300 K. In [1997Gal] the magnetic measurements were performed at 27-527°C and the temperature dependence of the electric resistivity was explored in the range of 4.2-500 K. The XPS measurements were performed in [2001Jar].

The present evaluation builds on a critical review of the literature data made in the MSIT Ternary Evaluation Program by [1991Gri]. It was based on published information pertaining to investigation of samples within the composition  $GdAl_2$ - $GdCo_2$  [1967Oes, 1969Tes, 1971Oes] and  $GdCo_{5-x}Al_x$  (x = 0-1.75) [1970Shi, 1976Oes, 1985Chu1, 1985Chu2]. Combing the earlier data with the isopleth established by [1993Wan, 1994Wan] now allows to draw an isothermal section at  $600^{\circ}$ C.

## **Binary Systems**

For phase relations in the binary Co-Gd the description given by [Mas2] still applies. The other edge binary data are accepted as evaluated in the MSIT Binary Evaluation Program: Al-Co by [2003Gru] and Al-Gd by [2002Bod].

#### **Solid Phases**

Four ternary phases were found in the system. Crystal structure was studied for three of them. Data about composition and structure of phases of the Al-Co-Gd system are shown in Table 1. Crystal structure and electronic structure of GdCoAl compound as well as its magnetic properties were subjected to investigation by [2000Jar, 2001Jar].

## Invariant Equilibria

The invariant ternary reactions given in Table 2 are mainly based on data from [1993Wan, 1994Wan].

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#### **Isothermal Sections**

A possible scheme of phase equilibria at  $600^{\circ}$ C shown in Fig. 1. It is obtained by combing (a) the data on  $GdCo_2$ - $GdAl_2$  reported by [1967Oes, 1971Oes] (b) CoAl-Gd vertical section by [1993Wan, 1994Wan] and (c) homogeneity ranges for the ternary as well as binary phases. According to the binary phase diagram  $GdCo_5$  decomposes at ~850°C [Mas2], however in ternary alloys a phase with the same  $CaCu_5$  type (3) structure was found in both as cast [1970Shi] and in alloys annealed at 900°C [1977Gal]. Figure 1 shows how this phase with the  $CaCu_5$  structure possibly extends into ternary compositions.

# **Temperature – Composition Sections**

The CoAl-Gd vertical section (Fig. 2) was determined by [1993Wan, 1994Wan]. At first sight this section seems to describe a pseudobinary system but the abstract given by [1994Wan] points out that presence of a three-phase field is possible on this section. According to [1993Wan, 1994Wan] solubility of Gd in CoAl is about 0.5 at.% at 1040°C.

#### Miscellaneous

It is reported that the Curie temperature of solid solution phases decrease with increasing Al content [1997Che, 2001Gu]. Gd<sub>2</sub>Co<sub>3</sub>Al<sub>9</sub> presents two characteristic magnetic anomalies around 100 and 20 K [2001Rou].

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 Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References  [Mas2, V-C2]		
(βGd) 1313-1200	<i>cF4 Fm</i> 3 <i>m</i> Cu	a = 540.5			
(αGd) < 1200	hP2 P6 <sub>3</sub> /mmc Mg	a = 363.3 c = 577.3	[Mas2, V-C2]		
(αCo) 422-1495	<i>cF4 Fm3m</i> Cu	a = 354.46	[Mas2]		
(εCo) < 422	hP2 P6 <sub>3</sub> /mmc Mg	a = 250.71 c = 406.95	[Mas2]		
(Al) < 660.452	<i>cF</i> 4 <i>Fm</i> 3̄ <i>m</i> Cu	a = 404.88	[Mas2]		
Co <sub>2</sub> Al <sub>9</sub> < 970	mP22 P2 <sub>1</sub> /a	a = 855.6 b = 629.0 c = 621.3 $\beta = 94.76^{\circ}$	[2003Gru]		
O-Co <sub>4</sub> Al <sub>13</sub> < 1080	oP102 Pmn2 <sub>1</sub> O-Co <sub>4</sub> Al <sub>13</sub>	a = 815.8 b = 1234.7 c = 1445.2	[2003Gru]		
M-Co <sub>4</sub> Al <sub>13</sub> 1093-?	mC102 C2/m Fe <sub>4</sub> Al <sub>13</sub>	a = 1517.3 b = 810.9 c = 1234.9 $\beta = 107.84^{\circ}$	[2003Gru]		
Y 1127-?	oI* Immm mC34 C2/m Os <sub>4</sub> Al <sub>13</sub>	a = 1531.0 b = 1235.0 c = 758.0 a = 1704.0 b = 409.0 c = 758.0 $\beta = 116.0^{\circ}$	[2003Gru]		
Z < 1158	C-centr.monocl.	a = 3984.0 b = 814.8 c = 3223.0 $\beta = 107.97^{\circ}$	[2003Gru]		
Co <sub>2</sub> Al <sub>5</sub> < 1188	hP28 P6 <sub>3</sub> /mmc Co <sub>2</sub> Al <sub>5</sub>	a = 767.2 c = 760.5	[2003Gru]		
$\frac{\text{Co}_{1-x}\text{Al}_x}{<1640}$	cP2 Pm3m CsCl	a = 285.7 a = 286.2 a = 285.9	x = 0.52 [2003Gru] x = 0.5 x = 0.43		

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Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
GdAl <sub>3</sub> < 1125	hP8 P6 <sub>3</sub> /mmc Ni <sub>3</sub> Sn	a = 633.2 c = 460.0	[2002Bod]
GdCo <sub>x</sub> Al <sub>2-x</sub> < 1520	cF24 Fd3m MgCu <sub>2</sub>	a = 790.3 a = 782.8 a = 775.9	x < 0.54 x = 0 [1967Oes] x = 0.3 [1967Oes] x = 0.45 [1967Oes]
Gd <sub>2</sub> Co <sub>17-x</sub> Al <sub>x</sub> < 1370	hR57 R3m Th <sub>2</sub> Zn <sub>17</sub>	a = 838.5 c = 1220.8 a = 838.6 c = 1219.5	x = 0 [2001Gu] x = 0 [1997Che]
		a = 840.0 $c = 1223.2$ $a = 841.6$	x = 1 [2001Gu] x = 1 [1997Che]
		a = 841.0 c = 1223.9 a = 841.8 c = 1227.2	x = 1 [1997Che] x = 2 [2001Gu]
		a = 844.4 c = 1228.0	x = 2 [1997Che]
		a = 844.4 $c = 1228.0$ $a = 845.0$	x = 2 [1999She] x = 3 [2001Gu]
		c = 1229.5 a = 847.6 c = 1231.3	x = 3 [1997Che]
		a = 846.9 $c = 1231.6$ $a = 851.0$	$x = 4 [2001 \text{Gu}] \text{ at } 1000^{\circ}\text{C}$ x = 4 [1997 Che]
		c = 1237.2 a = 854.4 c = 1239.7	x = 5 [1997Che]
GdCo <sub>5</sub> 1350-850	<i>hP</i> 6 P6/mmm CaCu <sub>5</sub>	a = 496.0 c = 398.9 a = 498 c = 398	[Mas2, V-C2] [1970Shi]
Gd <sub>2</sub> Co <sub>7</sub> < 1295	<i>hR</i> 54 <i>R</i> 3 <i>m</i> Er <sub>2</sub> Co <sub>7</sub>	a = 502.4 c = 3632	[Mas2, V-C2]
GdCo <sub>3</sub> < 1277	<i>hR</i> 36 <i>R</i> 3 <i>m</i> NbBe <sub>3</sub>	a = 502.6 c = 2445.6	[Mas2, V-C2]
GdCo <sub>2-x</sub> Al <sub>x</sub> < 1116	cF24 Fd3m MgCu <sub>2</sub>	a = 724.9 a = 729.3 a = 732	x = 0 [1967Oes] x = 0.2 [1967Oes] x = 0.35 [1967Oes]

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Phase/ Temperature Range [°C]	emperature Range Space Group/ [pm]		s Comments/References			
$*\tau_1$ , $Gd_2Co_6Al_{11}$	hP38 P6 <sub>3</sub> /mmc Th <sub>2</sub> Ni <sub>17</sub>	a = 872.3 c = 893.1	[1978Pop]			
*τ <sub>2</sub> , Gd <sub>2</sub> Co <sub>3</sub> Al <sub>9</sub>	$oS56$ $a = 1275.7 \pm 2$ $oS6$ $b = 757.0 \pm 5$ $oS6$ $c = 945.0 \pm 2$		[2001Rou]			
* $\tau_3$ , GdCo <sub>5-x</sub> Al <sub>x</sub>	hP6 P6/mmm CaCu <sub>5</sub>	a = 500 $c = 399$	$\sim 0.05 \le x \le 1.8$ x = 0.25 [1970Shi]			
		a = 501 c = 404 a = 505.095	x = 1 [1970Shi] x = 1 [1997Gal]			
		c = 403.958 a = 504	x = 1.5 [1970 Shi]			
		c = 406 $a = 505$ $c = 407$	x = 1.75 [1970Shi]			
*τ <sub>4</sub> , GdCo <sub>2-x</sub> Al <sub>x</sub> < 1170	hP12 P6 <sub>3</sub> /mmc		0.98 ≤ <i>x</i> ≤ 1.46; [1967Oes, 1971Oes, 1993Wan, 1994Wan]			
	$MgZn_2$	a = 537.0 c = 857.1	x = 1 [1971Oes]			
		a = 539.1 c = 853.2	x = 1 [1993Wan]			
		a = 544.5 c = 861.7	x = 1 [2000Jar]			
		a = 545.2 c = 861.2	x = 1.4 [1967 Oes]			
*τ <sub>5</sub> , Gd(Co,Al) <sub>1.5</sub> < 860			[1994Wan]			

 Table 2: Invariant Equilibria

Reaction	<i>T</i> [°C]	Type	Phase	Composition (at.%)		
				Al	Co	Gd
$L \rightleftharpoons CoAl + \tau_4$	1040	e	L	37.25	37.25	25.5
			CoAl	~49.2	~50.3	~0.5
			$\tau_4$	33.3	33.3	33.3
$L \rightleftharpoons \tau_4$	1170	congruent	L, τ <sub>4</sub>	33.3	33.3	33.3
$L + \tau_4 \rightleftharpoons \tau_5$	860	p	L	24	24	52
			$\tau_4$	33.3	33.3	33.3
			$\tau_5$	30	30	40
$L \rightleftharpoons \tau_5 + (Gd)$	707	e	L	18.25	18.25	63.5
			$\tau_5$	30	30	40
			(Gd)	-	-	100

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ΑI Data / Grid: at.% Fig. 1: Al-Co-Gd. Axes: at.% Scheme of presumable phase equilibria at 600°C. Co<sub>2</sub>Al<sub>9</sub> Section GdCo<sub>2</sub> - GdAl<sub>2</sub> 20 GdAl<sub>3</sub> according to [1967Oes]. O-Co<sub>4</sub>Al<sub>13</sub> Z -Co<sub>2</sub>Al<sub>5</sub> Section CoAl - Gd  $GdAl_2$ according to [1993Wan, 1994Wan] 40 60 -Co<sub>1-x</sub>Al<sub>x</sub> 60 80 20 -(aCo) 20 40 80 Gd Co GdĆo<sub>2</sub> GdĆo<sub>3</sub> Gd<sub>2</sub>Co<sub>7</sub>

