On the Ternary B 2-Phase in the Al-Co-Ga System

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Summary. Lattice parameter values were determined for the ternary B 2-phase in the Al-Co-Ga system, and it was found that a continuous solid solution exists between β'-AlCo and β'-CoGa. Phase boundaries of the ternary phase at 1 100 K were derived from the variation of the lattice parameter with composition.

Keywords. Aluminum-cobalt-gallium; Phase diagram: Al-Co-Ga; Lattice parameter: Al-Co-Ga; B 2-phase: Al-Co-Ga.

Über die ternäre B 2-Phase im System Al-Co-Ga

Zusammenfassung. Im Bereich der ternären B 2-Phase im System Al-Co-Ga wurden die Werte des Gitterparameters bestimmt; es stellte sich heraus, daß eine durchgehende feste Lösung zwischen β'-AlCo und β'-CoGa besteht. Die Phasengrenzen der ternären Phase bei 1 100 K wurden aus der Änderung des Gitterparameters mit der Zusammensetzung abgeleitet.

Introduction

Both the Al-Co and the Co-Ga binary systems are characterized by the existence of a phase with the cubic triple-defect B 2-structure exhibiting a considerable range of homogeneity [1, 2]. Deviation from stoichiometry is accomplished by anti-structure atoms (on the cobalt-rich side) or by vacancies on the transition metal sublattice (on the aluminum- or gallium-rich side) [3, 4]. Although the phase diagrams of the two binary systems are well established [1], and the lattice parameters of the corresponding B 2-phases β'-AlCo and β'-CoGa have been measured repeatedly [3 – 8], nothing seems to be known about the ternary Al-Co-Ga system. Thus it was the object of the present study to determine the composition dependence of the lattice parameter of the ternary B 2-phase within the anticipated homogeneity range, and to derive therefrom its extension in the ternary diagram at a temperature of 1 100 K.

Experimental Part

All samples were prepared from cobalt foil (0.5 mm; >99.99%, Sherritt Gordon Mines Ltd., Canada), aluminum wire (2 mm ∅; 99.998%, Johnson-Matthey, Vienna, Austria), and gallium (99.99%; Koch-Light, U.K.). Co was cut into small pieces and cleaned by p. a. acetone, and Ga was cleaned by

melting in vacuum and filtering through quartz wool under a purified Ar-atmosphere, whereas the Al was used without any further purification. Calculated amounts of the pure elements (approx. 1 g total) were weighed on a semi-microbalance to within 0.05 mg. They were filled into small alumina crucibles contained in silica capsules which were then evacuated to 10^{-1} Pa, flushed several times with Ti-gettered Ar, and finally sealed under vacuum.

The samples were slowly (within two days) heated to about 1 100 K, and after furnace cooling they were melted in a high-frequency furnace and water quenched. Then the quartz capsules were broken, and the samples were pulverized. The powders were filled into silica ampules which were once again sealed under vacuum. They were homogenized at 1 100 K for time periods of at least three weeks and quenched in ice water.

X-ray measurements were carried out at room temperature with a Kristalloflex 2 (Siemens, Karlsruhe, F. R. G.) in Debye-Scherrer cameras with a diameter of 57.3 mm using unfiltered Co-radiation. Lattice constant values were obtained by linear regression and extrapolation to zero using the function $(\cos^2 \Theta / \sin \Theta + \cos^2 \Theta / \Theta)/2$.

Results and Discussion

The compositions of the investigated samples are shown in Fig. 1; they are also listed in Table 1 together with the corresponding lattice parameter values which are thought to be accurate within at least ± 0.2 pm. Figure 2 shows the variation of the parameter a with changing Co content for three different ratios x_{Ga}/x_{Al} (3/ 1; 1/1; 1/3); experimental data for the two limiting binary systems, taken from the literature [3 – 6, 8], are also included. All data for ternary samples refer to a quenching temperature of 1 100 K, whereas the a-values for the binary B 2-phases refer to different temperatures between 823 and 1 373 K. A plot of the lattice parameter as a function of the Ga content for a constant Co concentration of 50 at% is shown in Fig. 3.

Phase boundaries of the ternary B 2-phase were derived from breaks in the composition dependence of the lattice parameter (cf. Fig. 2) and from the appearance of additional diffraction lines in the powder diagrams of some of the samples (cf. Fig. 1). Samples No. 19, 21, 22, and 25 showed clearly the additional lines of a face centered cubic phase (with a_{fcc} between about 357.0 and 358.5 pm) which
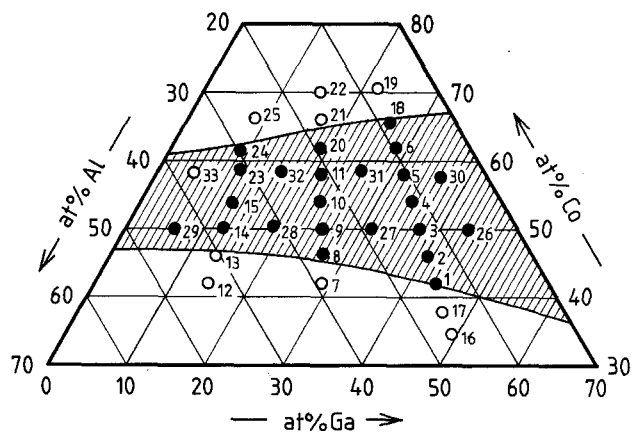

Fig. 1. Homogeneity range of the ternary B 2-phase in the Al-Co-Ga system at 1 100 K with the compositions of the investigated samples: ● single phase B 2; ○ additional phases present in samples quenched from 1 100 K

Table 1. Composition of samples and lattice parameter values

Sample No.	at% Co	at% Al	at% Ga	a pm	Remarks
1	42.0	14.6	43.4	2.846	
2	46.1	13.4	40.5	2.864	
3	50.0	12.6	37.4	2.876	
4	54.0	11.6	34.4	2.876	
5	58.0	10.5	31.5	2.874	
6	62.0	9.5	28.5	2.871	
7	42.0	29.0	29.0	2.855	$+ Co_2Al_5$?
8	46.1	26.9	27.0	2.857	
9	50.0	25.0	25.0	2.876	
10	54.0	23.1	22.9	2.872	
11	58.0	21.0	21.0	2.869	
12	42.0	43.5	14.5	2.861	$+ Co_2Al_5$?
13	46.0	40.4	13.6	2.859	$+ Co_2Al_5$?
14	50.0	37.6	12.4	2.867	
15	53.9	34.4	11.7	2.866	
16	34.6	16.1	49.3	2.857	$+ CoGa_3$
17	37.7	15.8	46.5	2.853	$+ CoGa_3$
18	65.5	8.5	26.0	2.868	
19	70.6	7.6	21.8	2.867	$+ (\alpha\text{-Co})$
20	61.9	19.1	19.0	2.865	
21	66.0	17.0	17.0	2.864	$+ (\alpha\text{-Co})$
22	69.9	15.1	15.0	2.863	$+ (\alpha\text{-Co})$
23	58.8	31.0	10.2	2.863	
24	61,4	29.7	8.9	2.863	
25	66.2	25.5	8.3	2.862	$+ (\alpha\text{-Co})$
26	50.0	6.2	43.8	2.879	
27	50.0	18.7	31.3	2.876	
28	50.3	31.0	18.7	2.868	
29	50.0	43.8	6.2	2.863	
30	57.6	6.0	36.4	2.876	
31	58.5	15.7	25.8	2.872	
32	58.4	26.0	15.6	2.861	
33	58.3	37.1	4.6	2.861	$+ (\alpha\text{-Co})$

was obviously (α-Co), i. e. the solid solution of Al and/or Ga in fcc Co. The strongest lines of this phase were also detected in the powder pattern of sample No. 33, although its composition was expected to lie within the single-phase region. It must be concluded that (α-Co) precipitated from the B2-phase in this sample during quenching. Considering the drastic decrease of the Co solubility with decreasing temperature for binary β'-AlCo [1], a similar effect may be responsible for the presence of (α-Co) in sample No. 33 after quenching.

Samples No. 16 and 17 were also two-phase, with the additional diffraction lines due to the phase $CoGa_3$. In this respect it is striking that for $x_{Ga}/x_{Al} = 3/1$ the lattice parameter varies markedly below 42.5 at% Co, i. e. below the presumed phase boundary (cf. Fig. 2); this seems to indicate that the tie-lines in the twophase
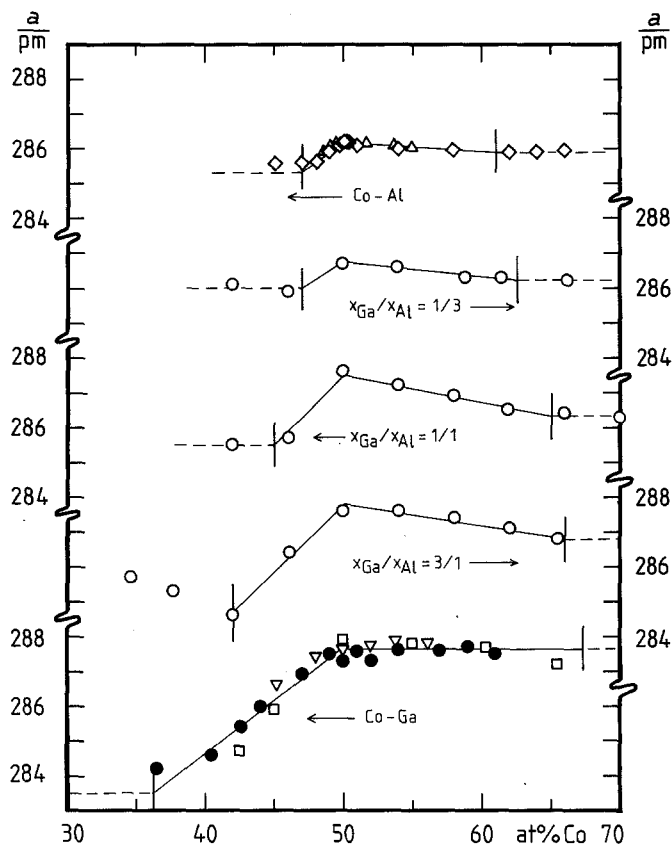
Fig. 2. Variation of the lattice parameter at 1 100 K for different x_{Ga}/x_{Al}-ratios with experimental data points (O); the data for the limiting binary systems are from the literature (with quenching temperatures in parentheses): ∇ Berner et al. [3]; ● Ipser et al. (1 173 K) [8]; □ Schubert et al. (823 K) [6]; △ Meyer et al. (1 273 K) [4]; ◇ Bashkatov et al. (1 373 K, furnace cooled) [5]. All phase boundaries are indicated for 1 100 K
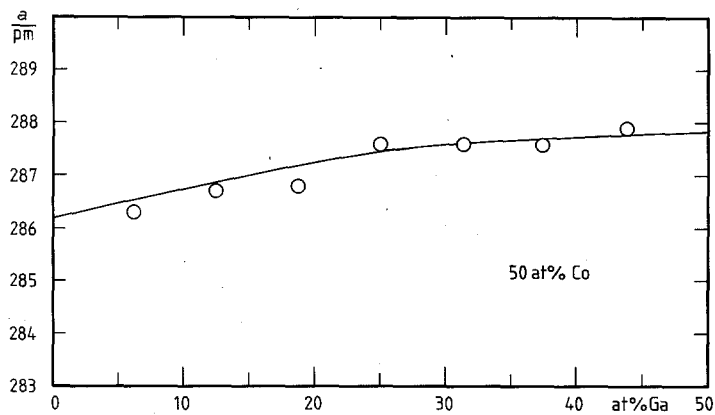

Fig. 3. Variation of the lattice parameter at 1 100 K with the Ga content at a constant Co concentration of 50 at% with experimental data (O)

field (B 2-phase + CoGa$_3$) are tilted with respect to the section with constant x_{Ga}/x_{Al}-ratio.

Additional lines were also found in the powder patterns of samples No. 7, 12, and 13, but they were more difficult to interpret. It is thought that they can be attributed to the presence of the phase Co$_2$Al$_5$ in the samples, since the d-values of these additional lines are in rough agreement with those of the most intensive lines of Co$_2$Al$_5$. However, nothing is known about the solubility of Ga in Co$_2$Al$_5$ and that of Al in CoGa$_3$.

The variation of the lattice parameter with the Co content in Fig. 2 reflects clearly the triple-defect mechanism responsible for the non-stoichiometry in the ternary B 2-phase. The marked increase of the values up to 50 at% Co is certainly caused by the gradual filling of the constitutional vacancies on the Co sublattice. It is followed by a slight decrease on the Co-rich side of stoichiometry which may be due to the substitution of Al and/or Ga atoms by the smaller Co anti-structure atoms.

Similarly, the increase of the lattice parameter with increasing Ga content at 50 at% Co (Fig. 3) is caused by the exchange of Al atoms by the larger Ga atoms on the corresponding sublattice.

The extension of the ternary B 2-phase at 1 100 K is shown in Fig. 1. The boundaries for the corresponding binary phases at the same temperature (which are also marked in Fig. 2) were taken from the literature: β'-AlCo extends from about 47 to 61 at% Co according to Massalski et al. [1], and β'-CoGa extends from about 36 to 67.5 at% Co according to Wunsch and Wachtel [7]. (However, it should be noted that some disagreement exists about the Co-rich boundary of β'-CoGa which is placed at about 72.5 at% Co by Feschotte and Eggimann [9].) It can be seen that the ternary phase constitutes a continuous solid solution between β'-AlCo and β'-CoGa, and that the homogeneity range becomes progressively wider with increasing Ga content.

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