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Lattice Parameters and Melting Behavior of the B 2-Phase in the Ternary Gold—Cadmium—Zinc System

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Lattice parameter and DTA-measurements were performed in the range of the ternary B 2-phase in the gold—cadmium—zinc system. It could be shown that a continuous range of homogeneity exists between β′-AuCd and β′-AuZn. Lattice parameter values are reported for a number of compositions. The ternary liquidus projection is given between about 40 and 60 at % Au. The congruent melting point of the binary β′-AuZn phase was found to be at 51.5 ± 0.5 at % Au and 758 ± 3 °C.

(Keywords: Gold—cadmium—zinc; Phase diagram: Au—Cd—Zn*; Phase diagram:* Au—Zn*; Lattice parameters:* Au—Cd—Zn*; B 2-phase:* Au—Cd—Zn*)*

Gitterparameter und Schmelzverhalten der B 2-Phase im ternären System Gold—Cadmium—Zink

Im Bereich der ternären B 2-Phase im System Gold—Cadmium—Zink wurden Gitterparameter bestimmt und Differenz-Thermo-Analysen durchgeführt. Es konnte gezeigt werden, daß zwischen β′-AuCd und β′-AuZn ein durchgehender Homogenitätsbereich existiert. Es werden Werte für den Gitterparameter bei einer Anzahl von Zusammensetzungen angegeben. Weiters wird die Projektion der ternären Liquidusoberfläche zwischen etwa 40 und 60 At% Au gezeigt. Der kongruente Schmelzpunkt der binären Phase β′-AuZn wurde bei 51,5 ± 0,5 At% Au und 758 ± 3 °C gefunden.

Introduction

In both the gold—cadmium and in the gold—zinc binary system phases with the ordered CsCl (B 2) structure are formed around the equiatomic composition exhibiting a wide range of homogeneity[1–4]. Their degree of disorder has been derived by applying to the experimentally determined partial molar thermodynamic properties a theoretical model based on substitutional defects[5–7]. By very careful DTA-

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measurements *Komarek* et al.[8] confirmed the findings of earlier investigations[9,10] that the congruent melting point of β′-AuCd is not exactly at the stoichiometric composition but is shifted to higher gold contents by about 3 at%.

It was the purpose of the present study to investigate the extension of the B 2-phase in the ternary gold—cadmium—zinc system and to determine the variation of the corresponding lattice parameter with composition. Furthermore, it was attempted to establish the liquidus surface in the region of this phase by differential thermal analysis (DTA). Based on the experience from the β′-AuCd phase it was also thought worthwhile to check the accurate position and temperature of the congruent melting point of β′-AuZn which is shown at exactly 50 at% in the literature[1,4].

Experimental Method

Starting materials were gold sheet (99.99%, Ögussa, Austria), cadmium rod and zinc shot (both 99.999%, ASARCO, U.S.A.); cadmium and zinc were cleaned prior to use from any surface oxide by melting in vacuum and filtering through quartz wool under a purified argon atmosphere.

Calculated amounts of the pure elements (approx. 0.6 g total) were weighed on a semi-micro balance to within ± 0.05 mg. They were filled into quartz capsules which were then evacuated to 10^{-1} Pa, flushed several times with Ti-gettered argon, and finally sealed under vacuum. In order to avoid evaporation of cadmium or zinc during the sealing process, the capsules were cooled with ice. The two series of samples with 46.9 and 53.4 at% Au were obtained by mixing appropriate amounts of alloys with 50 at% Au with either those containing 44.0 or 57.0 at % Au, respectively.

The samples were heated for about one day at 400 °C, then the temperature was raised slowly (within one or two days) to 800 °C where they were kept for another two days. After cooling in the furnace the capsules were broken and a small part of each sample (~ 0.1 g) was ground or filed (depending on the ductility). These powders were combined again with the corresponding remaining ingots and annealed at 500 °C for at least one week. This heat treatment was finished by quenching in ice water.

Two of the binary gold—zinc alloys for DTA-measurements (No. 35 and 36) were obtained by heating a weighed amount of thin gold wire (99.99%, Ögussa, Austria) contained in a little graphite crucible inside a quartz capsule with a zinc reservoir at about 650 °C for one week. After that the alloys which had been formed by reaction via the gas phase were reweighed and their composition was computed from the weight gain.

DTA-measurements were performed with a commercial thermal analyzer (DTA 404 S/3, Netzsch, Selb, F.R.G.) using samples of about 0.5 g sealed under vacuum in special quartz containers. The Pt/Pt-10% Rh thermocouples were calibrated at the melting points of high-purity Zn, Sb, and Au. Generally, a heating rate of 2 K/min was selected; however, lower heating rates (down to 0.1 K/min) were employed in some instances, expecially for the determination of accurate solidus and liquidus temperatures in the binary gold—zinc system.

Table 1. *Composition of the samples, lattice parameters, and liquidus temperatures*

Sample No.	Composition (at%) Au	Cd	Zn	Lattice Parameter (A°)	Liquidus Temperature (°C) Heating	Cooling
1	64.5	15.5	20.0	[a]	633	628
2	60.0	29.7	10.3	3.271	625	619
3	61.1	20.0	18.9	3.244	632	628
4	60.0	10.2	29.8	3.206	671	667
5	57.0	43.0	—	[a]	637	629
6	57.0	32.3	10.7	3.277	632	626
7	57.0	21.5	21.5	3.240	647	637
8	57.0	10.8	32.2	3.198	689	684
9	57.0	—	43.0	3.163	747	740
10	53.4	46.6	—	[a]	632	628[b]
11	53.4	35.0	11.6	3.277	635	622
12	53.4	23.3	23.3	3.237	651	647
13	53.4	11.7	34.9	3.196	696	693
14	53.4	—	46.6	3.152	758	756[b]
15	50.0	50.0	—	3.324[c]	630	626
16	50.0	37.5	12.5	3.283	632	622
17	50.0	25.0	25.0	3.235	651	647
18	50.0	12.5	37.5	3.186	698	693
19	50.0	—	50.0	3.145	758	751
20	46.9	53.1	—	[a]	622	617
21	46.9	39.8	13.3	3.277	619	—
22	46.9	26.6	26.5	3.230	642	639
23	46.9	13.3	39.8	3.181	691	686
24	46.9	—	53.1	3.142	746	744[b]
25	44.0	56.0	—	[a]	603	599
26	44.0	42.0	14.0	3.272	603	592
27	44.0	28.0	28.0	3.224	630	626
28	44.0	14.0	42.0	[a]	675	669
29	44.0	—	56.0	[a]	724	718
30	39.5	45.2	15.3	[a]	548	543
31	39.7	30.0	30.3	[a]	572	570
32	39.9	14.8	45.3	[a]	616	614
33	36.8	31.6	31.6	[a]	522	522
34	55.0	—	45.0	3.158	751	749[b]
35	51.7	—	48.3	3.153	758	752[b]
36	49.5	—	50.5	3.147	757	753[b]
37	48.5	—	51.5	3.147	751	749[b]

[a] Not single-phase β′.
[b] Measured with 0.1 K/min.
[c] Quenched from 300 °C.

X-ray measurements were made with a Kristalloflex 4 (Siemens, Karlsruhe, F.R.G.) in *Debye-Scherrer* cameras with a diameter of 57.29 mm using filtered CoK_α-radiation. The lattice constants were obtained by linear regression and extrapolation to zero using the function $1/2\ (\cos^2\Theta/\sin\Theta + \cos^2\Theta/\Theta)$.

Results and Discussion

The compositions of the investigated samples are listed in Table 1 together with the corresponding lattice parameter values (for single-phase β′-alloys) and the liquidus temperatures. In Fig. 1 the positions of

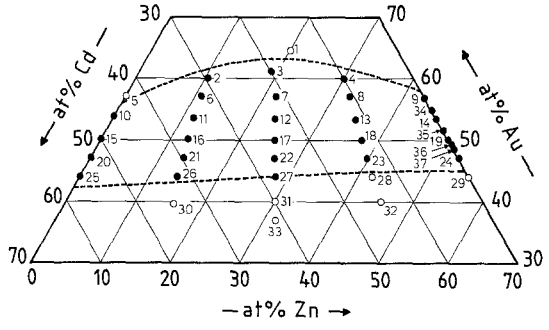

Fig. 1. Compositions of the investigated samples and homogeneity range of the ternary B 2-phase at 500 °C; ● = single-phase; ○ = not single-phase

the samples in the ternary diagram are shown graphically. The results of the X-ray investigation demonstrate clearly that there exists a continuous solid solution between β′-AuCd and β′-AuZn. The estimated homogeneity range of the ternary B 2-phase at 500 °C is given by dashed lines. The variation of the lattice parameter with composition is shown in Fig. 2 for four sections with constant gold contents of 57.0, 53.4, 50.0, and 46.9 at%; a linear decrease can be observed on substitution of cadmium by zinc. No lattice parameter values are given for the binary β′-AuCd phase except at the stoichiometric composition (No. 15), since for all samples quenched from 500 °C no cubic diffraction pattern was obtained due to the occurrence of complicated transformations at lower temperatures as already observed by other investigators (see for example Refs.[11,12]). Nevertheless, samples No. 10, 15, 20, and 25 are marked single-phase in Fig. 1 considering the homogeneity range of the binary phase at 500 °C according to literature data[1,4,7,8]. It has been shown by *Matsuo* et al.[13] that the transformation temperatures decrease drastically with the addition of zinc reaching values far below room temperature within a few at%.

The results of the lattice parameter measurements can be compared with previously reported values: For binary β′-AuCd (50.0 at% Cd) $a = 3.324$ Å was obtained from the powder pattern of a sample quenched from 300 °C (where no additional lines were detectable); this is in fair agreement with the value of 3.312 Å reported by *Byström* and *Almin*[11] for an alloy with 50.1 at% Cd quenched from 400 °C. For β′-AuZn (50 at% Zn) a value of $a = 3.145$ Å was derived which is very close

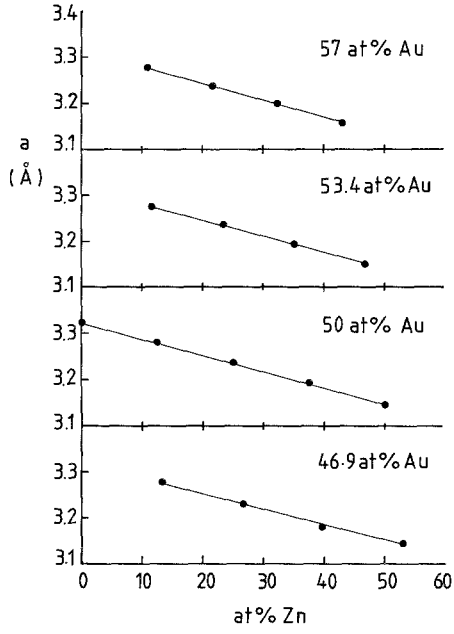

Fig. 2. Variation of the lattice parameter at constant gold contents

to the one reported by *Carpenter* et al.[14] (3.1482 Å). Recently *Matsuo* et al.[13] determined the composition dependence of the lattice parameter of $Au_{50}Cd_{50-x}Zn_x$; their results (taken from their Fig. 3) show a linear decrease from 3.325 Å for β′-AuCd to 3.150 Å for β′-AuZn, which is nearly identical with the curve given in Fig. 2 for the same section.

Fig. 3 shows solidus and liquidus curves for four different isopleths with constant gold contents obtained from the thermal analyses. The solidus temperatures were evaluated from heating curves whereas for the liquidus both values—obtained on heating or cooling, resp.—are given. Generally, the heating values are thought to be somewhat more reliable since in some cases supercooling was observed. The phase relationships on the cadmium-rich side in Fig. 3 a are shown schemati-

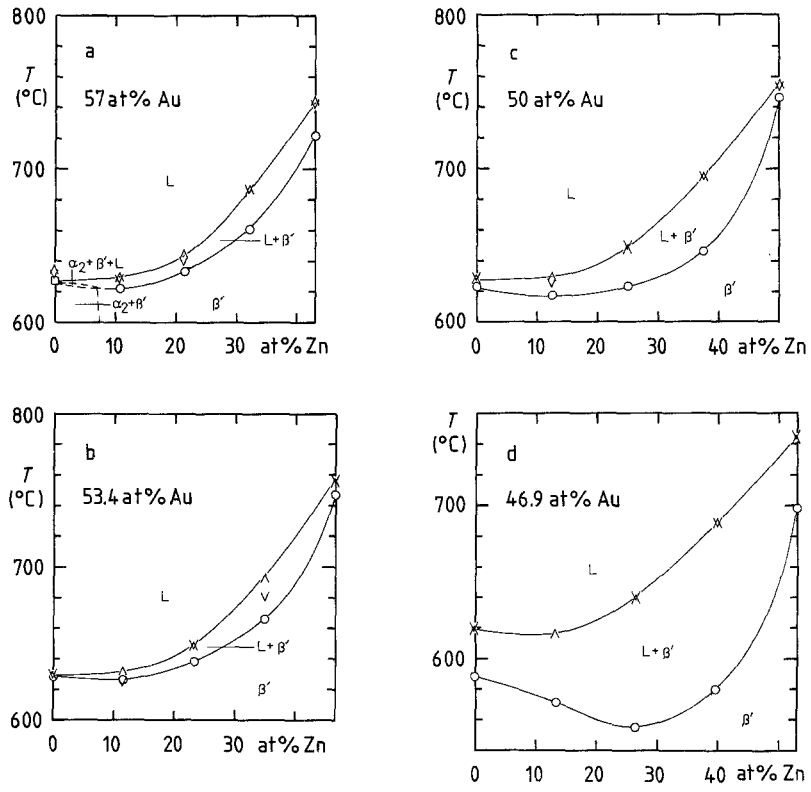

Fig. 3. Four isopleths at constant gold contents of the ternary gold—cadmium—zinc phase diagram; Λ, V = liquidus on heating or cooling, resp. (the point of the symbol marks the temperature), ○ = solidus, □ = invariant thermal arrest

cally by dashed lines; this part was constructed in such a way to be consistent with the very precise measurements of *Komarek* et al.[8].

From the liquidus temperatures which were determined for all samples (cf. Table 1) the ternary liquidus surface was constructed for the composition range from about 40 to 60 at% Au (Fig. 4 a). Since the slope of this surface is very flat on the cadmium-rich side, this region is shown in Fig. 4 b on a larger scale. It is suspected that the two troughs originating from the points e and p which mark the positions of a eutectic and a peritectic point, resp., in the Au—Cd binary system meet a similar one originating from the eutectic between α and β′-phase in the binary Au—Zn system to form a class I four-phase equilibrium.

The melting behavior of the binary β′-AuZn phase obtained from

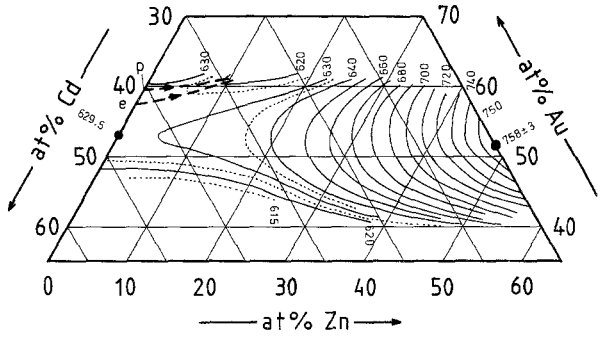

Fig. 4 a. Ternary liquidus projection in the range of the B 2-phase in the gold—cadmium—zinc system; e = binary eutectic point, p = binary peritectic point, ● = congruent melting point

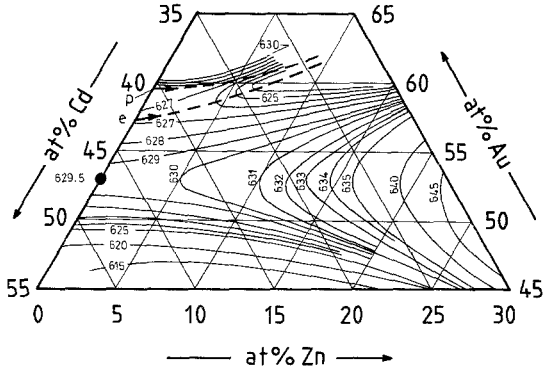

Fig. 4 b. Cadmium-rich part of Fig. 4 a in more detail

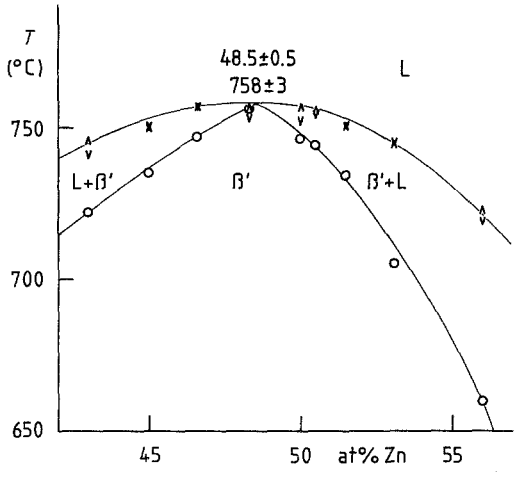

Fig. 5. Melting behavior of the binary β'-AuZn phase; Λ, V = liquidus on heating or cooling, resp. (the point of the symbol marks the temperature), ○ = solidus

the DTA-measurements is shown in Fig. 5. Contrary to the literature data[1,4] which report the congruent melting point to be at 725 °C and at exactly the equiatomic composition, the maximum was found in the present study not only at considerably higher temperatures (758 ± 3 °C), but also shifted to higher gold contents (51.5 ± 0.5 at% Au). Thus it is shown that the deviation of the melting point maximum from the stoichiometric composition—as observed previously in the case of β′-AuCd—is by no means an exception; it is rather suspected to be a common feature of congruently melting phases with appreciable ranges of homogeneity.

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