

**( $\beta$ Zr) and ( $\alpha$ Zr) Terminal Solid Solutions**

The melting point of  $\beta$ Zr and the  $\beta$ Zr  $\leftrightarrow$   $\alpha$ Zr allotropic transformation temperature are 1855 and 863 °C, respectively [Massalski]. The maximum solubility of Bi in ( $\beta$ Zr) is about 15 at.% [64Ham]. The peritectoid transformation temperature of ( $\beta$ Zr) to ( $\alpha$ Zr) is about 900 °C [63Bad, 64Ham]. It is shown at 901 °C in Fig. 1 as in [Metals], because the  $\beta$ Zr  $\leftrightarrow$   $\alpha$ Zr transition temperature in [64Ham] was assumed to be 862 °C. The solubility of Bi in ( $\alpha$ Zr) at the peritectoid temperature is about 4 at.% [63Bad, 64Ham].

**Crystal Structures and Lattice Parameters**

Crystal structure and lattice parameter data for Bi-Zr phases are given in Tables 2 and 3, respectively.

**Thermodynamics**

According to emf measurements, the activity coefficient of infinitely dilute Zr solution can be expressed as:  $\ln \gamma_{Zr} = 5.190 - 7631/T$  for  $T = 750$  to  $1000$  K [79Leb].

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\* Indicates key paper.

# Indicates presence of a phase diagram.

Bi-Zr evaluation contributed by H. Okamoto, ASM INTERNATIONAL, Materials Park, OH 44073. This work was supported by ASM INTERNATIONAL. Literature searched through early 1987. Dr. Okamoto is the ASM/NIST Data Program Category Editor for miscellaneous binary alloys.

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# The Br-In (Bromine-Indium) System

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**Equilibrium Diagram**

In-Br phase diagrams were proposed by [61Wal] and [62Mor] for the composition range between 50 and 75 at.% Br. Although the assessed In-Br phase diagram (Fig. 1) is based on the data of [62Mor] because of the larger number of data points used to determine the diagram, the disagreement between [61Wal] and [62Mor] is minor. Five intermediate phases exist in the In-Br system—InBr, In<sub>5</sub>Br<sub>7</sub>, In<sub>4</sub>Br<sub>7</sub>, InBr<sub>2</sub>, and InBr<sub>3</sub>. Special points of

the assessed diagram are given in Table 1. The existence of InBr, InBr<sub>2</sub>, and InBr<sub>3</sub> was known early in this century [04Thi].

**(In) Terminal Solid Solution**

The melting point of In is 156.634 °C [Melt]. In(L) and InBr(L) are immiscible [62Mor].

**InBr**

The melting point is 280 [61Wal] or 285.2 °C [62Mor]. The latter value is accepted in this assessment.

# Br-In

## In<sub>5</sub>Br<sub>7</sub>

The congruent melting point of In<sub>5</sub>Br<sub>7</sub> is 234.6 °C [62Mor]. [65Bra] confirmed the existence of this compound by determining the crystal structure, and the "In<sub>2</sub>Br<sub>3</sub>" in [61Wal] corresponds to this phase.

## In<sub>4</sub>Br<sub>7</sub>

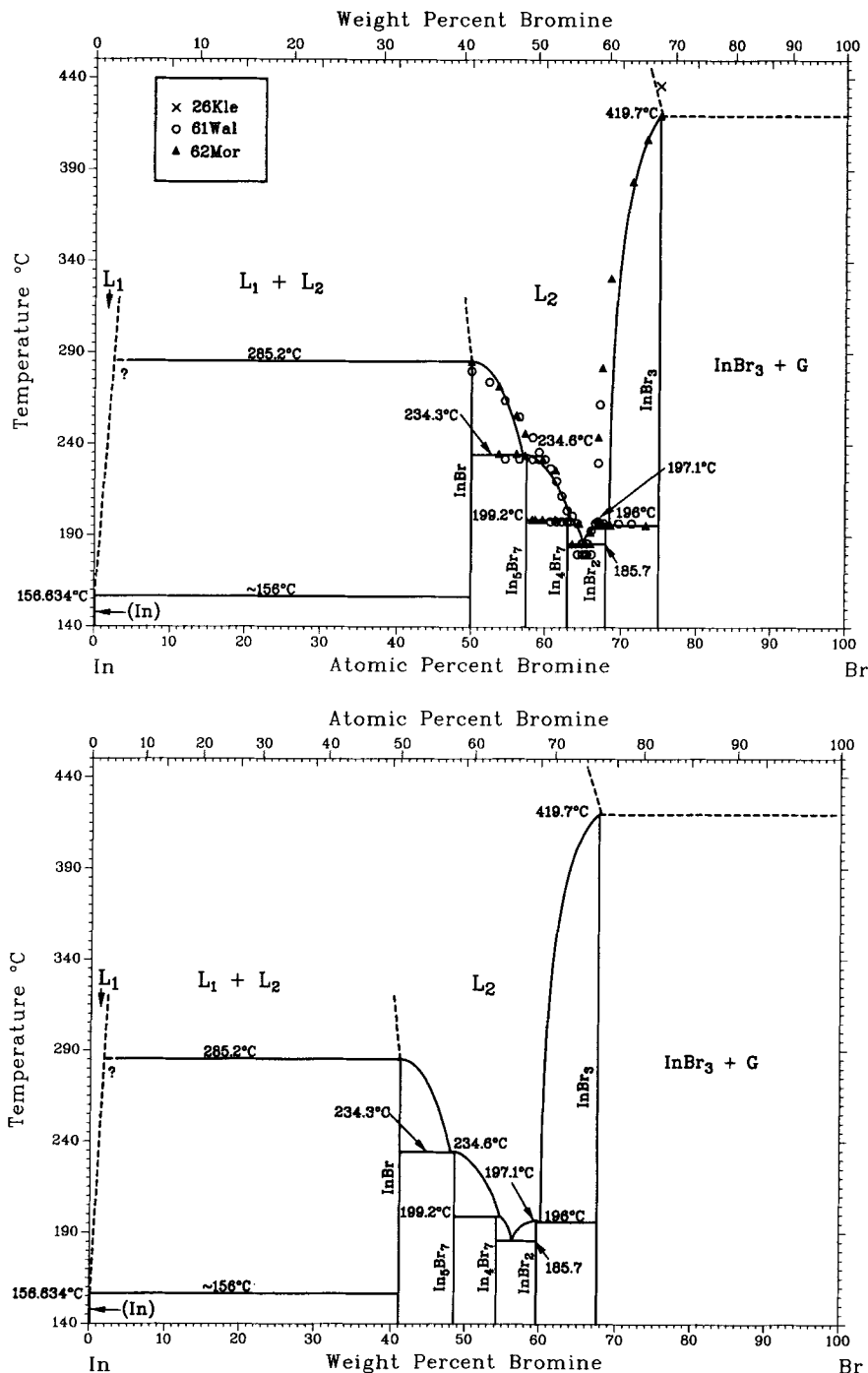
The peritectic melting temperature of In<sub>4</sub>Br<sub>7</sub> is 199.2 °C [62Mor]. The composition is displaced to 63.4 at.% Br

from the ideal position of 63.6 at.% Br, apparently due to vacancies at the In lattice sites. [61Wal] considered In<sub>4</sub>Br<sub>7</sub> to melt congruently at 201 °C.

## L ↔ In<sub>4</sub>Br<sub>7</sub> + InBr<sub>2</sub> Eutectic Reaction

The eutectic point was reported at 65.3 at.% Br and 180 °C [61Wal] or 65.4 at.% Br and 185.7 °C [62Mor]. The disagreement of 5.7 °C in the eutectic temperature is exceptionally large, comparing the data sets of [61Wal] and

**Fig. 1 Assessed In-Br Phase Diagram**



H. Okamoto, 1990.

Table 1 Special Points of the Assessed In-Br Phase Diagram

Reaction	Compositions of the respective phases, at.% Br		Temperature, °C	Reaction type
L ↔ In.....	0		156.634	Melting point
L ↔ (In) + InBr.....	~0	0 50	~156	Eutectic?
L ↔ InBr.....	50		285.2	Congruent
L ↔ InBr + In <sub>5</sub> Br <sub>7</sub> .....	58.2	50 58.3	234.3	Eutectic
L ↔ In <sub>5</sub> Br <sub>7</sub> .....	58.3		234.6	Congruent
L + In <sub>5</sub> Br <sub>7</sub> ↔ In <sub>4</sub> Br <sub>7</sub> .....	63.7	58.3 63.4	199.2	Peritectic
L ↔ In <sub>4</sub> Br <sub>7</sub> + InBr <sub>2</sub> .....	65.4	63.4 66.7	185.7	Eutectic
L ↔ InBr <sub>2</sub> .....	66.7		197.1	Congruent
L ↔ InBr <sub>2</sub> + InBr <sub>3</sub> .....	66.8	66.7 75	196.0	Eutectic
L ↔ InBr <sub>3</sub> .....	75		419.7	Congruent
Br <sub>2</sub> (g) ↔ L.....	100		59.10	Boiling point
L ↔ Br.....	100		-7.25	Triple point

Table 2 In-Br Crystal Structure Data

Phase	Composition, at.% Br	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(In).....	0	<i>tI2</i>	<i>I4/mmm</i>	A6	In	[King1]
InBr.....	50	<i>oC8</i>	<i>Cmcm</i>	B33	TII	[50Ste]
In <sub>5</sub> Br <sub>7</sub> .....	58.3	<i>tP192</i>	<i>P4<sub>2</sub>2<sub>1</sub>2</i>	...	...	[65Bra]
In <sub>4</sub> Br <sub>7</sub> .....	63.4	...	...	...	...	[61Wal]
InBr <sub>2</sub> .....	66.7	...	...	...	...	[04Thi]
InBr <sub>3</sub> .....	75	...	...	...	...	[04Thi]
(Br).....	100	<i>oC8</i>	<i>Cmca</i>	...	Cl	[Massalski]

Table 3 In-Br Lattice Parameter Data

Phase	Composition, at.% Br	Lattice parameters, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
(In).....	0	0.32512	...	0.49467	...	[Pearson3]
InBr.....	50	0.446	1.239	0.473	...	[50Ste]
In <sub>5</sub> Br <sub>7</sub> .....	58.3	1.322	...	3.727	...	[65Bra]
In <sub>4</sub> Br <sub>7</sub> .....	63.4	...	...	...	...	...
InBr <sub>2</sub> .....	66.7	...	...	...	...	...
InBr <sub>3</sub> .....	75	...	...	...	...	...
(Br).....	100	0.668	0.449	0.874	At -150 °C	[King1]

[62Mor]. The result of [62Mor] is accepted in Fig. 1, because it is based on 18 well-defined data points (for clarity, not all points are shown in Fig. 1).

### InBr<sub>2</sub>

The congruent melting point of InBr<sub>2</sub> is 197.1 °C [62Mor]. Due to limited data, the type of melting is not clear in the diagram of [61Wal].

### InBr<sub>3</sub>

The melting point of InBr<sub>3</sub> is 436 [26Kle] or 419.7 °C [62Mor]. The latter value is accepted.

### (Br) Terminal Phase

The triple point and boiling point temperatures of Br<sub>2</sub> are -7.25 and 59.1 °C, respectively [Massalski].

## Crystal Structures and Lattice Parameters

In-Br crystal structure and lattice parameter data are summarized in Tables 2 and 3, respectively. The struc-

tures of InBr and In<sub>5</sub>Br<sub>7</sub> are known. [40Bro] attempted to determine the Br-Br interatomic distance in InBr<sub>3</sub>, but because the crystal structure is uncertain, a few different values were reported to be possible.

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# Br-In Cl-In

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\* Indicates key paper.

# Indicates presence of a phase diagram.

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## The Cl-In (Chlorine-Indium) System

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### Equilibrium Diagram

The assessed In-Cl phase diagram (Fig. 1) is based primarily on the works of [63Pal], [68Fed], and [87Dmi]. The data of [58Cla], [66Cha], and [77Saf] are in reasonable agreement (Fig. 1). The intermediate phases existing in the assessed diagram are (1)  $\beta$ InCl and  $\alpha$ InCl; (2)  $\text{In}_3\text{Cl}_4$ ; (3)  $\beta$ In<sub>2</sub>Cl<sub>3</sub> and  $\alpha$ In<sub>2</sub>Cl<sub>3</sub>; (4)  $\text{In}_5\text{Cl}_9$  with a possible polymorphic transition; (5)  $\beta$ InCl<sub>2</sub> and  $\alpha$ InCl<sub>2</sub>; and (6) InCl<sub>3</sub>. Special points of the assessed diagram are given in Table 1.

#### (In) Terminal Solid Solution

The melting point of In is 156.634 °C [Melt]. In(L) and InCl(L) are immiscible [63Pal]. The monotectic temperature is 216 °C [63Pal].

#### $\beta$ InCl(red) and $\alpha$ InCl(yellow)

Two modifications exist in solid InCl, with a transition temperature of 120 °C [66Ber]. Syntectic melting point of

InCl is 212 °C [87Dmi]. [64Fed] and [68Fed] proposed diagrams with a congruent melting point at about 225 °C. Because a critical data point in a diagram of [68Fed] does not agree with the tabulated value, the result of [87Dmi] is accepted.

On the Cl-rich side of InCl, [63Pal] observed a monotectic reaction at about 254 °C (see data points in Fig. 1). However, [58Cla] and [68Fed] observed the L/(L +  $\text{In}_3\text{Cl}_4$ ) liquidus in the same composition range. The latter relationship is shown in Fig. 1. The L  $\leftrightarrow$   $\beta$ InCl +  $\text{In}_3\text{Cl}_4$  eutectic point is 50.5 at.% Cl and 210 °C [87Dmi].

#### $\text{In}_3\text{Cl}_4$

The peritectic melting point of  $\text{In}_3\text{Cl}_4$  is shown at 265 °C in Fig. 1, based on thermal arrest data given by [63Pal] and [68Fed]. However, [63Pal] considered this temperature to correspond to a polymorphic transformation of an unknown compound ( $\text{In}_x\text{Cl}_y$ ).

Table 1 Special Points of the Assessed In-Cl Phase Diagram

Reaction	Compositions of the respective phases, at.% Cl		Temperature, °C	Reaction type
L $\leftrightarrow$ In		0	156.634	Melting point
L $\leftrightarrow$ (In) + $\beta$ InCl	~0	0	156	Eutectic
L <sub>1</sub> + L <sub>2</sub> $\leftrightarrow$ $\beta$ InCl	?	50.24	212	Syntectic
$\beta$ InCl $\leftrightarrow$ $\alpha$ InCl		50	120	Polymorphic
L $\leftrightarrow$ $\beta$ InCl + $\text{In}_3\text{Cl}_4$	50.5	50	210	Eutectic
L + $\alpha$ In <sub>2</sub> Cl <sub>3</sub> $\leftrightarrow$ $\text{In}_3\text{Cl}_4$	55	60	265	Peritectic
L $\leftrightarrow$ $\beta$ In <sub>2</sub> Cl <sub>3</sub>		60	325	Congruent
L + $\beta$ In <sub>2</sub> Cl <sub>3</sub> $\leftrightarrow$ $\alpha$ In <sub>2</sub> Cl <sub>3</sub>	57	60	302	Peritectic?
$\beta$ In <sub>2</sub> Cl <sub>3</sub> $\leftrightarrow$ L + $\alpha$ In <sub>2</sub> Cl <sub>3</sub>	?	63	284	Catatectic
L + $\alpha$ In <sub>2</sub> Cl <sub>3</sub> $\leftrightarrow$ $\beta$ In <sub>5</sub> Cl <sub>9</sub>	64.5	60	258	Peritectic
$\beta$ In <sub>5</sub> Cl <sub>9</sub> $\leftrightarrow$ $\alpha$ In <sub>5</sub> Cl <sub>9</sub>		64.3	224	Polymorphic
L $\leftrightarrow$ $\beta$ In <sub>5</sub> Cl <sub>9</sub> + $\beta$ InCl <sub>2</sub>	65.8	64.3	236	Eutectic
L + InCl <sub>3</sub> $\leftrightarrow$ $\beta$ InCl <sub>2</sub>	66	75	239	Peritectic
$\beta$ InCl <sub>2</sub> $\leftrightarrow$ $\alpha$ InCl <sub>2</sub>		66.7	186	Polymorphic
L $\leftrightarrow$ InCl <sub>3</sub>		75	580	Congruent
Cl <sub>2</sub> (g) $\leftrightarrow$ Cl <sub>2</sub> (L)		100	-100.97	Boiling point
L $\leftrightarrow$ Cl		100	-34.05	Triple point