The Al-B (Aluminum-Boron) System

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Equilibrium Diagram

Due to contradictory evidence and misleading speculations, evaluation of the Al-B system has hitherto proven unsatisfactory. Early investigations of the constitution of the system Al-B by [26Hae], later discussed by [26Mei], claimed the existence of a eutectic L ↔ Al + AlB_2 at 560 °C at 30 to 35 at.% B. AlB_2 was said to form peritectically from Al(L) and AlB_{12} at 1100 °C. The assessed Al-B phase diagram is presented in Fig. 1. The Al-rich portion (>33 at.% Al) is essentially based on a review by [84Sig], who reported the eutectic L ↔ (Al) + AlB_2 at a maximum solid solubility of 0.0045 at.% of B in Al at 659.6 °C, the temperature corroborated by DTA experiments of [93Ips]. Agreement exists on the peritectic mode of formation of AlB_2 from the dodecaboride and the liquid. Whereas the peritectic point and temperature were given at 0.55 at.% B and 975 °C by [61Ser] and [84Sig], at ~2.4 at.% B and 980 °C by [90Car], and at 0.74 at.% B and ~927 °C by [76Mon], results of [36Hof2], [53Lih], [66Gru], and [72Sir] claimed the existence of AlB_2 up to temperatures between 1350 and 1500 °C. Differential thermal analysis experiments (Al_2O_3 crucibles, 5 K/min, Ar + 5% H_2 atmosphere) [93Ips] confirmed the peritectic formation of AlB_2 at 1030 ± 5 °C; this value is used throughout this assessment. The boron-rich (>66 at.% B) part of the phase diagram refers to a review by [89Ner] including some features from [84Sig], [89Hig], and [90Car] and results from a reinvestigation of the Al-B binary by [93Dus] including Pirani melting point measurements with a calibrated microoptical pyrometer and confirming the incongruent melting of αAlB_{12} at 2050 ± 35 °C.

Attempts to establish the solubility of Al in β-boron from X-ray powder and single crystal studies on an arc-melted alloy with nominal composition AlB_{12} revealed a maximum solubility of ~3 at.% Al [89Hig, 93Dus].

Despite the continuing controversy on the existence of "βAlB_{12}" and "AlB_{10}," all the experimental evidence leads to the conclusion that these phases are impurity (carbon) stabilized and that AlB_2 and AlB_{12} are the only true binary aluminum boride compounds. Experimental evidence from the formation of ternary aluminum borides $Al_{1-x}M_xB_{12}$ (M = Be, Mg, V, Cr, Mn, Fe, Co, Ni, Cu) with the γAlB_{12}-type structure [81Hig, 87Hig1, 87Hig2] furthermore backs the conclusion that αAlB_{12} is the only thermodynamically stable modification of the aluminum dodecaboride. Binary γAlB_{12} might thus be accepted as a metastable compound or as a ternary product stabilized by the small amounts of M present in Al flux grown crystallized material. The stability of αAlB_{12} at 850 °C confirmed by [93Dus] is in contrast to observations by [67Ato], who claimed no formation of AlB_{12} below 920 °C. A similar instability of AlB_2 at room temperature reported by [53Lih], however, is believed to arise from chemical attack rather than from thermodynamic instability.

A new phase in the Al-B system was formed after implantation of aluminum by boron ions at peak concentrations between 6 and 60 at.% [92Var]. The composition of this phase Al_2B_3 is near 60 at.% B. It is stable to at least 525 °C after heat treatment in vacuum. The accepted invariant reactions in the Al-B binary are listed in Table 1.

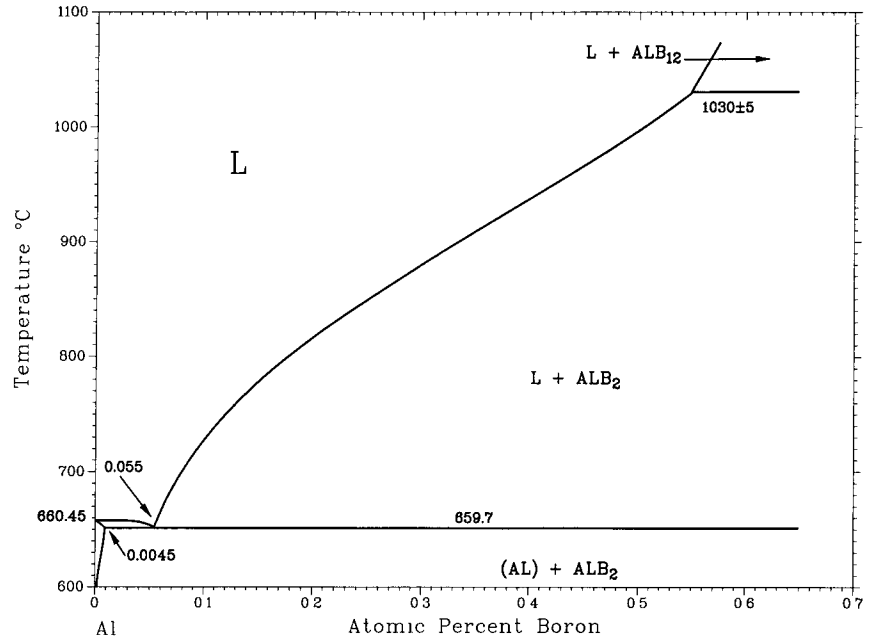
Table 1 Reaction Scheme in the Al-B System

Reaction	Composition, at.% B			Temperature, °C	Reaction type	Reference
L ↔ Al		0		660.452	Melting	[90Car]
(Al) + AlB_2 ↔ Al_3B_2	0.004	66.7	60.0	525	Peritectoid	[92Var]
L ↔ (Al) + AlB_2	0.055	0.0045	66.7	659.7	Eutectic	[84Sig]
L + αAlB_{12} ↔ AlB_2	0.6	92.3	66.7	1030	Peritectic	[84Sig],[93Dus]
L + βB ↔ AlB_{12}	<92.3	~97.0	92.3	2050	Peritectic	[93Dus]
L ↔ βB		100		2092	Melting	[90Car]

Table 2 Al-B Crystal Structure Data

Phase	Pearson symbol	Space group	Strukturbericht designation	Prototype
Al	*cF*4	$Fm\bar{3}m$	*A*1	Cu
αB	*hR*12	$R\bar{3}m$	...	αB
βB	*hR*111	$R\bar{3}m$	...	βB
Al_2B_3	*hR**	. .	...	Al_2B_3
AlB_2	*hP*3	*P*6/*mmm*	*C*32	AlB_2
αAlB_{12}	*tP*216	$P4_12_12$	...	αAlB_{12}
γAlB_{12}(a)	*oP*384	$P2_12_12_1$	..	γAlB_{12}

(a) Metastable or metal impurity stabilized.



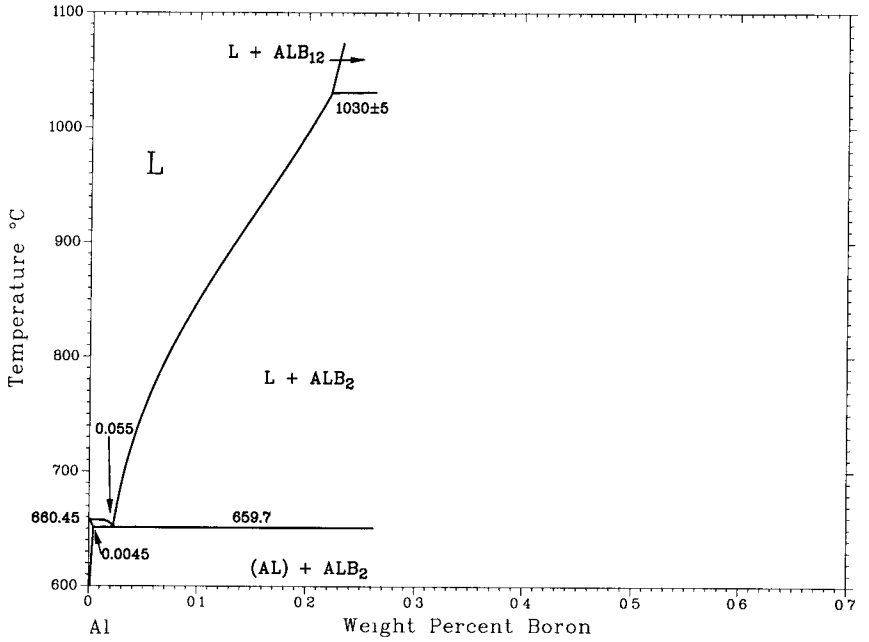


Fig. 1 Assessed Al-B phase diagram.

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data for Al-B phases are given in Tables 2 and 3, respectively. Table 4 results from an attempt to resolve the existing confusion about true and/or impurity-stabilized Al-B phases. Thus Table 4 lists the original phase name in contrast to the phase name accepted throughout this assessment based on proper characterization. Table 4 in chronological sequence reflects on the various methods of preparation and characterization of the "Al-B" phases mentioned in the literature including information on the aluminum

Table 3 Al-B Lattice Parameter Data

Phase	Composition, at.% B	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
Al	0	0.404954	...	...	...	[59Str]
αB	100	0.4908	...	1.2567	...	[59Dec]
βB	100	1.09251	...	2.38143	...	[77Cal]
	96.9	1.0965	...	2.3868	At $AlB_{\sim 31}$	[89Hig]
Al_2B_3	60	1.840	...	0.896	...	[92Var]
AlB_2	66.7	0.3006	...	0.3252	...	[56Fel]
αAlB_{12}	92.3	1.0158	...	1.4270	...	[77Hig]
γAlB_{12}(a)	92.3	1.6573	1.7510	1.0144	...	[83Hig]
	92.3	1.6623	1.7540	1.0180	...	[77Hug]
AlB_2	ρ_{exp}:	3.09×10^6 g/m^{-3} [61Ser], 2.955×10^6 g/m^{-3} [64Mat1].				
αAlB_{12}	ρ_{exp}:	2.557×10^6 g/m^{-3} [60Koh1], 2.62×10^6 g/m^{-3} [61Ser], $26.5(8) \times 10^6$ g/m^{-3}[77Kas], 2.54×10^6g/m^{-3}[80Oka], 2.56×10^6 g/m^{-3}[91Gos].				
γAlB_{12}(a)	ρ_{exp}:	2.56×10^6 g/m^{-3} [77Hug], 2.5×10^6 g/m^{-3} [83Hig].				

(a) Metastable or metal impurity stabilized.

Table 4 Preparation and Crystal Structures of Aluminum Borides

Reference	Phase name in reference	Proper phase name	Crystal system	Lattice parameters, nm *a*	*b*	*c*	Preparation	Comment
[1857Woh1]	Boron	$Al_3B_{48}C_2$	...	...	...	...	Graphite-crucible	"Diamond-like" boron
	Boron	αAlB_{12}	...	...	...	...	Graphite-crucible	"Graphite-like" boron
[1857Woh2]	Boron	$Al_3B_{48}C_2$	Tetragonal	...	...	...	...	"Diamond-like" boron
[1867Woh]	Boron	αAlB_{12}	Monoclinic	...	...	...	Melt. of Al in amorphous B	"Graphite-like" boron
[1876Ham]	AlB_{12}	αAlB_{12}	Monoclinic	...	...	...	...	Black crystals, absence of C is necessary
	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	Tetragonal	...	...	...	Graphite-crucible	Yellow crystals
[08Bil]	AlB_{12}	αAlB_{12}	Orthorhombic or monoclinic		a:b:c = 0.7130:1:0.7139		...	Black crystals, chemical analysis: $AlB_{12.22}$
[10Bil]	$Al_3B_{44}C_2$	$Al_3B_{48}C_2$	Tetragonal	...	...	...	Graphite-crucible	Yellow crystals, chemical analysis: $Al_{3.03}B_{44.82}C_2$
[36Hof1]	AlB_2	AlB_2	Hexagonal	0.300	...	0.324	...	Bronze-colored crystals
[36Hof2]	AlB_2	AlB_2	Hexagonal	0.300	...	0.324	...	$L + AlB_{12} \rightarrow AlB_2$ at T_p = 1350 °C
[36Nar]	AlB_{12}	$Al_3B_{48}C_2$	Tetragonal	1.255	...	1.018	...	Yellow-brown crystals, at least 0.7 wt.% C, later called βAlB_{12}
	AlB_{12}	αAlB_{12}	Orthorhombic	1.764	2.500	1.026	Produced by MERCK	Crystal structure may be monoclinic, but β ≈ 90°
[39Hal1]	AlB_{13}	βB	Monoclinic	1.701	1.098	1.880	...	β = 110°54'
[39Hal2]	AlB_{12}	βB	Monoclinic	0.850	1.098	0.737	Preparation without C	β = 143°29', modification I, [39Hal1] corrected to AlB_{12}
	AlB_{12}	$Al_3B_{48}C_2$	Tetragonal	...	...	...	Preparation with C	...
	AlB_{12}	αAlB_{12}	Tetragonal	1.028	...	1.430	Preparation without C	Modification II

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Table 4 Preparation and Crystal Structures of Aluminum Borides (continued)

Reference	Phase name in reference	Proper phase name	Crystal system	Lattice parameters, nm *a*	*b*	*c*	Preparation	Comment
[53Lih]	AlB_2	AlB_2	...	...	...	. .	Starting materials: Al, B_2O_3, S, $KClO_3$, 1350 to 1450 °C	L + AlB_{12} → AlB_2 at T_p > 1400 °C, at *RT*: 2 AlB_2 → "AlB_4" + Al
[55Sam]	AlB_{12}	αAlB_{12}	Tetragonal	1.01	...	1.43	...	..
[56Fel]	AlB_2	AlB_2	Hexagonal	0.3009	...	0.3262	Graphite-crucible, 800 °C	Impurities: Al, C, B_4C
[58Par]	βB	βB	Rhombohedral	1.014	..	.	...	α = 65°, cell of monoclinic AlB_{12} [39Hal2] is transformed into βB
[58Koh]	AlB_{12}	βB	Monoclinic	...	...	...	...	Comparison of monoclinic AlB_{12} with βB
	αAlB_{12}	αAlB_{12}	Tetragonal	1.028	...	1.430	Graphite-crucible	...
	βAlB_{12}	$Al_3B_{48}C_2$	Tetragonal	1.255	...	1.018	Graphite-crucible	...
	AlB_{10}	$AlB_{24}C_4$	Orthorhombic	0.8881	0.9100	0.5690	Graphite-crucible	Chemical analysis: 0.37 wt.% C
[60Koh1]	αAlB_{12}	αAlB_{12}	Tetragonal	1.0161	...	1.4283	Graphite-crucible	Melting point at 2150 ± 50 °C
	βAlB_{12}	$Al_3B_{48}C_2$	Orthorhombic	1.2340	1.2631	1.0161	Graphite-crucible	...
			Pseudotetragonal	1.255	...	1.018	...	...
[60Koh2]	AlB_2	AlB_2	Hexagonal	0.3009	...	0.3262	...	No details of preparation
	AlB_{10}	$AlB_{24}C_4$	Orthorhombic	0.888	0.910	0.569	Graphite-crucible	...
	αAlB_{12}	αAlB_{12}	Tetragonal	1.016	...	1.428	Graphite-crucible	...
	βAlB_{12}	$Al_3B_{48}C_2$	Orthorhombic	1.234	1.263	1.016	Graphite-crucible	...
	γAlB_{12}	γAlB_{12}	Orthorhombic	1.66	1.75	1.02	Graphite-crucible	Observed at single-crystal examinations of αAlB_{12}
[61Bec]	AlB_2	AlB_2	Hexagonal	...	...	...	Al_2O_3-crucible, H_2, Ar, vac., 900 °C	Starting materials: 98% Al, 96 to 99% B, above 950 °C: AlB_2 → Al(L) + βAlB_{12}
[61Koh]	γAlB_{12}	γAlB_{12}	Orthorhombic	1.656	1.753	1.016	Graphite-crucible	...
[61Ser]	αAlB_{12}	αAlB_{12}	Tetragonal	1.015	...	1.429	Al_2O_3-crucible, He	...
	βAlB_{12}	$Al_3B_{48}C_2$	Orthorhombic	1.255	...	1.018	Preparation without C	No chemical analysis for C
	AlB_2	AlB_2	Hexagonal	0.301	...	0.326	...	Claimed to be stable below 975 °C
[63Wil]	AlB_{10}	$AlB_{24}C_4$	Orthorhombic	0.888	0.910	0.569	Graphite-crucible	Single-crystal obtained from [58Koh]
[64Mat1]	AlB_2	AlB_2	Hexagonal	..	...	...	...	Chemical analysis: $Al_{0.9}B_2$
	αAlB_{12}	αAlB_{12}	Tetragonal	.	...	...	Graphite-crucible, 1700 °C, cooling rate ~450 °C/h	Chemical and crystallographic analysis as [36Nár]
	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	Orthorhombic	1.234	1.263	0.508	...	Low-temperature phase (LT - mod. A)
			Orthorhombic	0.617	1.263	1.016	...	Low-temperature phase (LT - mod. B)
			Tetragonal	0.882	...	0.509	...	High-temperature phase (HT)
	$AlB_{24}C_4$	$AlB_{24}C_4$	Orthorhombic	0.888	0.910	0.569	...	Earlier called "AlB_{10}"

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Table 4 Preparation and Crystal Structures of Aluminum Borides (continued)

Reference	Phase name in reference	Proper phase name	Crystal system	Lattice parameters, nm			Preparation	Comment
				a	*b*	*c*		
[64Mat1]	γAlB_{12}	γAlB_{12}	Orthorhombic	...	...	...	Graphite-crucible, 1400 °C, cooling rate ~100 °C/h	Contains 0.7 wt.% C
[64Mat2]	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	...	...	...	...	...	Comparison of the high-temperature phase with tetragonal boron (a = 0.874, c = 0.509), temperature of reversible transformation HT → LT(A, B) at 850 °C
[65Eco]	$AlB_{24}C_4$	$AlB_{24}C_4$	Hexagonal	0.563	...	1.229	BN-crucible, Ar, 1900 to 2000 °C	Composition range from $Al_{0.5}B_{24}C_4$ to $Al_{1.5}B_{24}C_4$
[66Gie]	$AlB_{24}C_4$	$AlB_{24}C_4$	Hexagonal	0.563	...	1.229	BN-crucible, Ar, 1700 to 2000 °C	Rhombohedral: a = 0.523 nm, α = 65°10' (B_4C-type), irreversible high temperature transformation of $AlB_{24}C_4$, composition range from $Al_{0.5}B_{24}C_4$ to $Al_{1.5}B_{24}C_4$
[66Wil]	AlB_{10}	$AlB_{24}C_4$	Orthorhombic	0.8881	0.9100	0.5680	Graphite crucible	Single-crystal obtained from [58Koh]
[67Ato]	AlB_2	AlB_2	...	...	...	...	Graphite crucible	Formed above 600 °C up to 1000 °C
	αAlB_{12}	αAlB_{12}	...	...	...	...	Graphite crucible	Formed above 920 °C up to 1900 to 2000 °C, no observation of βAlB_{12}, γAlB_{12}, and AlB_{10}
[67Wil]	AlB_{10}	$AlB_{24}C_4$	Orthorhombic	0.8881	0.9100	0.5680	Graphite crucible	Convolution molecule method
[67Ser]	...	...	...	...	...	...	Al_2O_3-, BeO-crucible	Reactions with the crucibles above 1500 °C, no chemical analysis for C
	AlB_2	AlB_2	Hexagonal	...	...	...	...	AlB_2 → Al(L) + αAlB_{12} at T_p = 980 °C
	αAlB_{12}	αAlB_{12}	Tetragonal	1.015	...	1.429	...	Decomposition at 2075 °C
	βAlB_{12}	$Al_3B_{48}C_2$	Tetragonal	1.255	...	1.018	...	Stable between 1550 °C and 1660 °C
	AlB_{10}	$AlB_{24}C_4$	...	...	...	...	...	Stable between 1660 °C and 1850 °C
[68Ner]	χ	?	...	...	...	...	...	Stoichiometric formula AlB_2, stable between 1450 and 1550 °C
[69Lam]	βAlB_{12}	$Al_3B_{48}Si$	Tetragonal	0.891	...	0.505	Preparation with Si	Conclusion that βAlB_{12} is a ternary compound

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Table 4 Preparation and Crystal Structures of Aluminum Borides (continued)

Reference	Phase name in reference	Proper phase name	Crystal system	Lattice parameters, nm a	b	c	Preparation	Comment
[69Per]	$Al_{2.1}B_{51}C_8$	$AlB_{24}C_4$	Orthorhombic	0.569	0.8881	0.910	No details about preparation	...
[69Wil]	$AlB_{24}C_4$	$AlB_{24}C_4$	Orthorhombic	0.888	0.910	0.569	...	Single-crystals from [64Mat1], doubts in the existence of AlB_{10}
[72Sir]	AlB_2	AlB_2	Hexagonal	...	...	...	Graphite crucible	$AlB_2 \leftrightarrow Al(L) + \alpha AlB_{12}$ at $T_p >$ 1500 °C
[77Gol]	AlB_2	AlB_2	...	...	...	...	Al_2O_3-, BN-crucible, Ar	$AlB_2 \leftrightarrow Al(L) + \alpha AlB_{12}$ at $T_p >$ 1200 °C
	αAlB_{12}	αAlB_{12}	Tetragonal	...	...	...	Cooling rate 100 °C/h in the range 1700 to 1300 °C	...
	βAlB_{12}	$Al_3B_{48}C_2$	...	...	...	...	...	At introduction of C and Si impurities only
[77Hig]	αAlB_{12}	αAlB_{12}	Tetragonal	1.0158	...	1.4270	Al_2O_3-crucible, 1 h, 1550 °C, Ar	...
[77Kas]	αAlB_{12}	αAlB_{12}	Tetragonal	1.0161	...	1.4283	Al_2O_3-crucible, 1 h, 1500 °C, Ar	...
[77Hug]	γAlB_{12}	γAlB_{12}	Orthorhombic	1.6623	1.7540	1.0180	Crystal from J.A. Kohn	...
[79Sam]	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	...	...	...	...	Preparation in graphite-crucible or with C	Preparation without C impossible
	$AlB_{24}C_4$	$AlB_{24}C_4$	...	...	...	...	Preparation in graphite-crucible or with C	Preparation without C impossible
[81Hig]	αAlB_{12}	αAlB_{12}	Tetragonal	...	...	...	Preparation from Al-M-B melts (M = Li, Ti, V, Cr, Mn, Fe, Co, Ni, Cu), 1500 °C, Ar, cod. rate 10 °C/min	Atomic ratio Al:B = 1:13.1
	γAlB_{12}	γAlB_{12}	Orthorhombic	1.6573	1.7510	1.0144	Preparation from Al-M-B melts (M = V, Cr, Mn, Fe, Co, Ni, Cu), 1500 °C, Ar, cooling rate 10°C/min	Unit cell $Al_{25.2}B_{352}$, chemical analysis of crystal-twins shows Ni-atoms incorporated in the structure
[83Hig]	γAlB_{12}	γAlB_{12}	Orthorhombic	1.6573	1.7510	1.0144	Crystal from [81Hig]	Investigation of the crystal structure
[86Pes]	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	Orthorhombic	1.2382	1.2630	0.50767	1300 to 1100 °C, Al_2O_3-crucible, Ar	Low-temperature phase A from [64Mat1]
				1.2302	1.2620	0.50799	1650 °C, Al_2O_3-crucible, Ar	...
			Orthorhombic	0.6191	1.26293	1.01549	1300 to 1100 °C, Al_2O_3-crucible, Ar	Low-temperature phase B from [64Mat1]
				0.61459	1.2622	1.0161	1650 °C, Al_2O_3-crucible, Ar	Postulation of homogeneity range of $Al_3B_{48}C_2$
[87Kis]	AlB_2	AlB_2	Hexagonal	0.3004	...	0.3246	(a)	...
	αAlB_{12}	αAlB_{12}	Tetragonal	1.018	...	1.4343	(a)	...
	γAlB_{12}	γAlB_{12}	Orthorhombic	1.666	1.769	1.0195	(a)	...
	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	Orthorhombic	1.2325	1.2647	0.5081	(a)	Low-temperature phase A
			Orthorhombic	0.6164	1.2621	1.0164	(a)	Low-temperature phase B
	$AlB_{24}C_4$	$AlB_{24}C_4$	Orthorhombic	0.8914	0.9095	0.5676	(a)	

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Table 4 Preparation and Crystal Structures of Aluminum Borides (continued)

Reference	Phase name in reference	Proper phase name	Crystal system	Lattice parameters, nm a	b	c	Preparation	Comment
[87Kro]	$AlB_{24}C_4$	$AlB_{24}C_4$	Orthorhombic	0.8914	0.9095	0.5676	...	Morphologic studies
	$Al_3B_{48}C_2$	$Al_3B_{48}C_2$	Tetragonal	0.884	...	0.506	...	High-temperature phase from [64Mat1]
[89Pug]	AlB_{10}	$AlB_{24}C_4$	Orthorhombic	...	..	...	Oxidation of B_4C-Al, surface etching in ethanol solution of iodine with perhydrol	Melting point at 2100 °C, oxidation starts above 700 °C
[89Ner]	γAlB_{12}	γAlB_{12}	Orthorhombic	...	...	...	...	Assumption that γAlB_{12} is no binary phase
	AlB_2	AlB_2	..	...	...	...	...	Claimed to be stable up to 1450 °C
[89Hig]	AlB_{31}	βB	Hexagonal	1.0965	...	2.3868	Arc melting of αAlB_{12}	Solubility of ~3 at.% Al in βB
[92Var]	Al_2B_3	Al_2B_3	Hexagonal	1.840	...	0.896	Ion implantation of Al by B	After vacuum heat treatment a nonequilibrium precipitate is stable up to 525 °C

(a) All compounds obtained from monocrystal specimens grown from B-C solution in Al melt.

Table 5 Electrical Conductivity of Compounds in the Al-B System by [87Kis]

Phase	Temperature, K	E, eV
αAlB_{12}	100 to 192	0.18
	192 to 227	0.23
	227 to 357	0.363
γAlB_{12}	100 to 203	0.217
$Al_3B_{48}C_2$	200 to 400	0.6 to 1.2
$AlB_{24}C_4$	110 to 119	0.18
	119 to 238	0.28
	238 to 435	0.075

boron carbides as carbon usually was the major source of impurity. Comparison of the lattice parameter data given in Table 4 reveals the various attempts towards a proper and unambiguous crystallographic description of the individual and in many cases mislabeled phases.

Miscellaneous

Melting points of AlB_2, $AlB_{24}C_4$("AlB_{10}"), αAlB_{12}, and $Al_3B_{48}C_2$ ("βAlB_{12}") were found by [60Gia] to be 1655 ± 50 °C, 2423 ± 50 °C, 2163 ± 50 °C, and 2214 ± 50 °C, respectively. No details, however, were given concerning the correction for black body condition.

Vickers (HV) and Knoop (KV) microhardness as well as crack resistance for single crystal faces of αAlB_{12}, γAlB_{12}, $AlB_{24}C_4$ ("AlB_{10}"), and $Al_3B_{48}C_2$ ("βAlB_{12}") were studied in detail by [86Dub]. The authors used the fracture toughness K_{Ic} as a criterion for crack resistance. These mechanical properties increase in the following order: $\alpha AlB_{12} \rightarrow \gamma AlB_{12}$ 2 $AlB_{24}C_4$("AlB_{10}") $\rightarrow Al_3B_{48}C_2$ ("βAlB_{12}"). The Young modulus E (for 100% dense pellets) of αAlB_{12} is similar to B_4C (400 to 600 GPa) [91Gos]. Knoop hardness was measured for various crystal faces by [60Gia] under a load of 100 g for AlB_2 (9.6 GPa for (00.1)), αAlB_{12} (22.45 GPa for (110), 23.8 GPa for (101), 22.1 GPa for (221)), and γAlB_{12} (23.55 GPa for (100)). These values have to be compared with 22.9 GPa for the (100) face of α and γAlB_{12} at a load of 2 N [86Kis] and with the values of Knoop-microhardness on (101) faces of αAlB_{12} between 20.2 and 22.6 GPa found by [80Oka]. Under a load of 30 g, [55Sam] found 36.2 ± 1.7 GPa as Knoop hardness for αAlB_{12}. Fracture toughness was reported by [86Kis] for α and γAlB_{12} to be 2.2 MPa $m^{1/2}$ for (100).

Thermal conductivity λ of α and γAlB_{12} is reported by [86Kis] to be 38.7 W/m·K at 315 K in contrast to ~14 W/m·K measured and calculated by [91Kek] and ~5 W/m·K measured by [91Gos].

Experimental values for the electrical resistivity at room temperature are between 3.1×10^{-2} and 7.7×10^{-2} Ωm for AlB_2 [72Sir], 5.92×10^2 Ωm for αAlB_{12}, 3.85×10^5 Ωm for γAlB_{12}, 2.64×10^3 to 1×10^6 Ωm for $Al_3B_{48}C_2$ ("βAlB_{12}"), and 2.02×10^5 Ωm for $AlB_{24}C_4$ ("AlB_{10}") [87Kis]. Resistivity of αAlB_{12} as a function of temperature and porosity was reported by [55Sam]. No superconductivity was observed for AlB_2 as low as 1.5 K [72Sir]. All phases in the Al-B system are *p*-type semiconductors [86Kis]. According to [72Sir], the measured values of the Hall coefficient (R) are positive, ranging from 1×10^{-3} to 1.5×10^{-4} cm^3/C. [87Kis] also calculated the activation energy of electrical conductivity E_a in various temperature ranges from measurements of the temperature dependence of E_a. The results are listed in Table 5.

Table 6 Thermodynamic Data in the Al-B System

Phase	Temperature, K	$\Delta_f H^0_T$, kJ/mol	$\Delta_f S^0_T$, J/mol·deg	Reference
AlB_2	298	-66.9 ± 12.6	...	[67Dom]
	298	-66.9	34.7	[76Jon]
αAlB_{12}	0	-146.4 to -154.8	...	[77Kan]
	298	-200.8 ± 41.8	...	[67Dom]
	298	...	88.4	[88Kap]
	1673 to 2273	-171.5	50.2	[77Kan]
"AlB_{40}"	0	-196.6 to -209.2	...	[77Kan]
	1673 to 2273	-223.8	49.4	[77Kan]

Oxidation of αAlB_{12} single crystals in air starts at 1000 °C forming $9Al_2O_3 \cdot 2B_2O_3$ and B_2O_3 [80Oka].

The dissolution of αAlB_{12} was studied as a function of dispersity in hydrochloric, sulfuric, nitric acids, KOH in various concentrations and in hydrogen peroxide at room temperature and at the boiling point of the solvent [87Ner].

From infrared (IR) and electron spin resonance (ESR) spectroscopy on single crystals of αAlB_{12} and γAlB_{12}, the refractive index was determined; the Al-B compounds can be regarded as wide zone semiconductors [88Pri].

The energy of an interstitial solid solution of boron in aluminum and the energy of mixing were calculated using the pseudopotential method by [81Bog].

A calculation of the band structure of AlB_2 in all main symmetry directions was performed by [77Arm] with the LCAO technique in order to discuss the stability and bonding in metallic diborides. A density-of-states calculation confirmed that electrons are transferred from Al into B orbitals, which are mainly π bonding in the two-dimensional boron layer.

A calculation of the electronic structure of AlB_2 using the LAPW method is currently in progress [93Rip].

Thermodynamics

Thermodynamic data have been assembled by various research groups [67Dom, 76Jon, 77Kan, 81Bat, 84Sig, 87Kis, 88Kap]. They are given in Table 6.

Measurements of the enthalpy of AlB_2 in the temperature range 310 to 1200 K by [87Kis] give the temperature dependence $H^0(T) - H^0(298) = -12\,335.54 + 34.75153T + 22.2118 \times 10^{-3}T^2$ (J/mol).

The heats of combustion are -3711.2 kJ/mol for AlB_2 and -14 916.0 kJ/mol for αAlB_{12} [67Dom].

The coefficients for the specific heat are $C_p = a + bT - cT^2$ (J/mol·K). For AlB_2, $a = 50.17$, $b = 22.3 \times 10^{-3}$, $c = 7.87 \times 10^5$ [76Jon], and $a = 34.75$, $b = 44.4 \times 10^{-3}$, $c = 0$ [87Kis]. For αAlB_{12}, $a = 211.28$, $b = 115.07 \times 10^{-3}$, $c = 85.34 \times 10^5$ [88Kap].

The calculated Gibbs energy for the reaction $AlB_2(s) \rightarrow 2B(\text{polycrystalline}) + Al(L)$ equals $201\,133.25 - 152.143\,T$ J/mol. For the reaction $Al(s) + 2B(\beta) \rightarrow AlB_2$, ΔG equals $-66\,944 + 5.335\,T$ J/mol [84Sig].

The integral heat of dissolution of boron in molten aluminum at 1773 K was examined by [81Bat] between 0 and 18 at.% B; the composition dependence was claimed to be $\Delta H_{soL} = 9292.7\,x_B$ (J/g-atom).

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Addendum

The Al-B System, contributed by O.N. Carlson, was published in *Bulletin of Alloy Phase Diagrams, 11*(6), 560-566 [90Car]. The present evaluation supersedes the earlier evaluation.

Cited References

1857Wöh1: F. Wöhler and H. Sainte-Claire Deville, "About Boron - Part I," *Ann. Chem. Pharm., 101*, 113-118 (1857) in German. (Crys Structure)

1857Wöh2: F. Wöhler and H. Sainte-Claire Deville, "About Boron - Part II," *Ann. Chem. Pharm., 101*, 347-355 (1857) in German. (Crys Structure)

1867Wöh: F. Wöhler, "About the So-called Graphite-Like Boron," *Liebigs Ann., 141*, 268-270 (1867) in German. (Crys Structure)

1876Ham: W. Hampe, "About the Boron," *Ann. Chem., 183*, 75-101 (1876) in German. (Crys Structure)

08Bil: H. Biltz, "About Crystallized Boron I," *Chem Ber., 41*, 2634-2645 (1908) in German. (Crys Structure)

10Bil: H. Biltz, "About Crystallized Boron II," *Chem. Ber., 43*, 297-306 (1910) in German. (Crys Structure)

26Hae: P. Haenni, "Boron in Aluminium and Aluminium Compounds," *Rev. Met., 23*, 342-352 (1926) in French. (Equi Diagram)

26Mei: K.L. Meißner, "Aluminium-Boron Compounds," *Z. Metallkd., 10*, 324-325 (1926) in German. (Equi Diagram)

36Hof1: W. Hofmann and W. Jäniche, "The Structure of Aluminiumboride AlB_2," *Z. Phys. Chem. B, 31*, 214-222 (1936) in German. (Crys Structure)

36Hof2: W. Hofmann and W. Jäniche, "Contribution to the Knowledge of the System Aluminium-Boron," *Z. Metallkd., 28*, 1-5 (1936) in German. (Equi Diagram, Crys Structure)

36Nár: S. von Náray-Szabó, "X-Ray Examination of the Aluminiumdodecaboride AlB_{12}," *Z. Kristallogr., 94*, 367-374 (1936) in German. (Crys Structure)

39Hal1: F. Halla and R. Weil, "The Lattice of the Aluminiumboride AlB_{13}," *Naturwissenschaften, 27*, 96 (1939) in German. (Crys Structure)

39Hal2: F. Halla and R. Weil, "X-Ray Examination of Crystallized Boron," *Z. Kristallogr., 101*, 435-450 (1939) in German. (Crys Structure)

53Lih: F. Lihl and P. Jenitschek, "About the Decomposition of the Hexagonal Aluminiumboride AlB_2," *Z. Metallkd., 44*, 414-417 (1953) in German. (Equi Diagram, Crys Structure)

55Sam: G.V. Samsonov and N.N. Zhuravlev, "Aluminium Boride, AlB_{12}" *Fiz. Met. Metalloved., 1*, 564-565 (1955) in Russian. (Crys Structure)

56Fel: E.J. Felten, "The Preparation of Aluminium Diboride, AlB_2," *J. Am. Chem. Soc., 78*, 5977-5978 (1956). (Crys Structure)

58Koh: J.A. Kohn, G. Katz, and A.A. Giardini, "AlB_{10}, a New Phase, and a Critique on the Aluminium Borides," *Z. Kristallogr., 111*, 53-62 (1958). (Crys Structure)

58Par: E. Parthé and J.T. Norton, "Note on the Cell and Symmetry of So-Called Monoclinic AlB_{12}," *Z. Kristallogr., 110*, 167-168 (1958). (Crys Structure)

59Dec: B.F. Decker and J.S. Kasper, "The Crystal Structure of a Simple Rhombohedral Form of Boron," *Acta Crystallogr., 12*, 503-506 (1959). (Crys Structure)

59Str: M. Straumanis, "Absorption Correction in Precision Determination of Lattice Parameters," *J. Appl. Phys., 30*, 1965-1969 (1959). (Crys Structure)

60Gia: A.A. Giardini, J.A. Kohn, L. Toman, and D.W. Eckart, "Vector Hardness Properties of Boron and Aluminium Borides," *Boron-Synthesis, Structure and Properties*, Plenum Press, New York, 140-158 (1960). (Crys Structure)

60Koh1: J.A. Kohn and D.W. Eckart, "Aluminium Boride, AlB_{12}," *Anal. Chem., 32*, 296-298 (1960). (Crys Structure)

60Koh2: J.A. Kohn, "Crystallography of the Aluminium Borides," *Boron-Synthesis, Structure and Properties*, Plenum Press, New York, 75-82 (1960). (Crys Structure)

61Bec: H.J. Becher, "Preparation and Stability of Aluminium Diboride," *Z. Anorg. Allg. Chem., 308*, 13-22 (1961) in German. (Crys Structure)

61Koh: J.A. Kohn and D.W. Eckart, "γAlB_{12}, a New Structure, and its Relation to αAlB_{12} as Shown by Twinned Space Groups," *Z. Kristallogr., 116*, 134-142 (1961). (Crys Structure)

61Ser: V.T. Serebryanskii, V.A. Eipelbaum, and G.S. Zhdanov, "Concerning the Constitutional Diagram of the System Aluminium-Boron," *Dokl. Akad. Nauk SSSR, 141*, 884-886 (1961) in Russian TR: *Proc. Akad. Sci. USSR, Chem. Sect., 141*, 1244-1246 (1961). (Equi Diagram, Crys Structure)

63Wil: G. Will, "On the Crystal Structure of AlB_{10}," *J. Am. Chem. Soc., 85*, 2335-2336 (1963). (Crys Structure)

64Mat1: V.I. Matkovich, J. Economy, and R.F. Giese, Jr., "Presence of Carbon in Aluminium Borides," *J. Am. Chem. Soc., 86*, 2337-2340 (1964). (Crys Structure)

64Mat2: V.I. Matkovich, R.F. Giese, Jr., and J. Economy, "Phases and Twinning in $C_2Al_3B_{48}$ (β-AlB_{12})," *Z. Kristallogr., 122*, 108-115 (1964). (Crys Structure)

65Eco: J. Economy, V.I. Matkovich, and R.F. Giese, Jr., "Crystal Chemistry of Alpha-Boron Derivatives," *Z. Kristallogr., 122*, 248-258 (1965). (Crys Structure)

66Gie: R.F. Giese, Jr., J. Economy, and V.I. Matkovich, "Topotactic Transition in C_4AlB_{24}," *Acta Crystallogr., 20*, 697-700 (1966). (Crys Structure)

66Gru: G.A. Grulke, "Refractory Bodies Composed Chiefly of Aluminium Nitride and Boride," U.S. 3,261,701 (C1.106-65) July 19 1966, Appl. July 19 1961. (Equi Diagram).

66Wil: G. Will, "Crystal Structures of Higher Aluminium Borides," *Nature, 212*, 175-176 (1966). (Crys Structure)

67Ato: T. Atoda, I. Higashi, and M. Kobayashi, "Process of Formation and Decomposition of Aluminium Borides," *Sci. Papers Inst. Phys. Chem. Res., 61*, 92-99 (1967). (Equi Diagram; Crys Structure)

67Dom: E.S. Domalski and G.T. Armstrong, "Heats of Formation of Aluminium Diboride and α-Aluminium Dodecaboride," *J. Res. Natl. Bur. Stand A, Phys. Chem., 71*, 307-315 (1967). (Thermo)

67Ser: V.T. Serebryanskii, V.A. Eipelbaum, and G.S. Zhdanov, "Phase Diagram of the Aluminium-Boron System," *Zh. Neorg. Khim., 12*, 2486-2493 (1967) in Russian. (Crys Structure)

67Wil: G. Will, "Crystal Structure Analysis of AlB_{10} by the Convolution Molecule Method," *Acta Crystallogr., 23*, 1071-1079 (1967). (Crys Structure)

68Ner: V.A. Neronov, "Phase Diagram of the Aluminium-Boron System," *Zh. Neorg. Khim., 14*, 1704-1705 (1968) in Russian. (Crys Structure)

69Lam: L.K. Lamikhov, V.A. Neronov, V.N. Rechkin, and T.I. Samsonova, "The β-AlB_{12} Phase in the Silicon-Aluminium-Boron System," *Izv. Akad. Nauk SSR, Neorg. Mater., 5*, 1214-1217 (1969) in Russian; TR: *Inorganic Mater., 5*, 1034-1036 (1969). (Crys Structure)

69Per: A.J. Perotta, W.D. Townes, and J. Potenza, "Crystal Structure of $C_8Al_{2.1}B_{51}$," *Acta Crystallogr. B, 25*, 1223-1229 (1969). (Crys Structure)

69Wil: G. Will, "The Crystal Structure of C_4AlB_{24}" *Acta Crystallogr. B, 25*, 1219-1222 (1969). (Crys Structure).

72Sir: E. Sirtl and L.M. Woerner, "Preparation and Properties of Aluminium Diboride Single Crystals," *J. Cryst. Growth, 16*, 215-218 (1972). (Equi Diagram, Crys Structure)

76Jon: G.P. Jones and J. Pearson, "Factors Affecting the Grain-Refinement of Aluminium using Titanium and Boron Additives," *Metall. Trans. B, 7*, 223-234 (1976). (Thermo)

76Mon: L.F. Mondolfo, *Aluminum Alloys: Structure and Properties*, Butterworths, London-Boston (1976). (Equi Diagram)

77Arm: D.R. Armstrong, A. Breeze, and P.G. Perkins, "On the Electronic Structure of Aluminium Diboride," *J. Chem. Soc., Faraday Trans. II, 73*, 952-957 (1977). (Crys Structure)

77Cal: B. Callmer, "An Accurate Refinement of the β-Rhombohedral Boron Structure," *Acta Crystallogr. B, 33*, 1951-1954 (1977). (Crys Structure)

77Gol: O.A. Golikova, V.M. Orlov, T. Khomidov, M.M. Usmanova, and A.S. Umarov, "Preparation of Single Crystals of AlB_{12}," Izv. Akad. Nauk SSR, Neorg. Mater., 13, 1097-1098 (1977) in Russian; TR: Inorganic Mater., 13, 894-895 (1977). (Crys Structure)

77Hig: I. Higashi, T. Sakurai, and T. Atoda, "Crystal Structure of α-AlB_{12}," *J. Solid State Chem., 20*, 67-77 (1977). (Crys Structure)

77Hug: R.E. Hughes, M.E. Leonowicz, J.T. Lemley, and L.-T. Tai, "Icosahedral Boron Frameworks. The Structure of γ-AlB_{12}," *J. Am. Chem. Soc., 99*, 5507-5508 (1977). (Crys Structure)

77Kan: A. Kant and K.A. Moon, "Mass-Spectrometric Study of the Aluminium-Boron System," *High Temp. Sci., 9*, 131-145 (1977). (Thermo)

77Kas: J.S. Kasper, M. Vlasse, and R. Naslain, "The α-AlB_{12} Structure," *J. Solid State Chem., 20*, 281-285 (1977). (Crys Structure)

79Sam: G.V. Samsonov, V.A. Neronov, and L.K. Lamikhov, "The Conditions, Structure and some Properties of Phases in the Al-B System," *J. Less-Common Met., 67*, 291-296 (1979). (Crys Structure)

80Oka: S. Okada and T. Atoda, "Growth Condition, Oxidation, Hardness and Density of AlB_{12} Single Crystals," *Yogyo-Kyokai-Shi, 88*, 547-553 (1980) in Japanese. (Crys Structure)

81Bat: G.I. Batalin, E.A. Beloborodova, V.V. Nerubashchenko, and A.N. Shlapak, "Heats of Dissolution of Titanium, Zirconium and Boron in Molten Aluminium," *Metally, 1*, 69-71 (1981) in Russian. (Thermo)

81Bog: V.I. Bogdanov, D.L Fuks, A.V. Mikhaylov, and L.B. Protopopova, "Energy of Mixing of Interstitial Aluminium-Based Solutions," *Phys. Met. Metall., 52*, 98-103 (1981). (Crys Structure)

81Hig: I. Higashi and Y. Takahashi, "Boron-Rich Phases Grown from Al-M-B Melts (M = Li, Ti, V, Cr, Mn, Fe, Co, Ni, Cu)," *J. Less-Common Met., 81*, 135-142 (1981). (Equi Diagram, Crys Structure)

83Hig: I. Higashi, "Aluminium Distribution in the Boron Framework of γ-AlB_{12}," *J. Solid State Chem., 47*, 333-349 (1983). (Crys Structure)

84Sig: G.K. Sigworth, "The Grain Refinement of Aluminium and Phase Relationships in the Al-Ti-B System," *Metall. Trans. A, 15*, 277-282 (1984). (Equi Diagram, Thermo)

86Dub: S.P. Dub, T.A. Prikhina, and O.N. Il'nitskaya, "Mechanical Properties of Crystals of Compounds of the Al-B-C System," *Sverkhtverd. Mater., 8*, 12-18 (1986) in Russian; TR: *Sov. J. Superhard Mater., 8*, 14-21 (1986). (Crys Structure)

86Kis: P.S. Kisley, T.A. Prikhna, and L.S. Golubyak, "Properties of High-Temperature Solution-Grown Aluminium Borides," *J. Less-Common Met., 117*, 349-353 (1986). (Crys Structure)

86Pes: P. Peshev, G. Gyurov, and M. Khristov, "Preparation and Some Properties of Aluminium Carboboride Single Crystals," *J. Less-Common Met., 117*, 341-348 (1986). (Crys Structure)

87Hig1: I. Higashi and T. Ito, "Structure and Electron Density Distribution of Icosahedral B_{12} Compounds," Proc. 9th Intern. Symp. on Boron, Borides and Related Compounds, 21st - 25th Sept., Duisburg, 41-52 (1987). (Equi Diagram)

87Hig2: I. Higashi, J. Sida, Y. Timura, and Y. Takahashi, "Preparation of Icosahedral B_{12} Borides $Al_{\sim 1.4}Mg_{\sim 0.55}B_{22}$ and $BeB_{9\text{-}12}$ from Molten Metallic Solutions," Proc. 9th Intern. Symp. on Boron, Borides and Related Compounds, 21st - 25th Sept., Duisburg, 271-276 (1987). (Equi Diagram)

87Kis: P.S. Kisly, T.A. Prikhna, A.N. Gontar', and O.V. Podarevskaya, "Structure and Properties of Monocrystals of the Al-B-C System Compounds," Proc. 9th Intern. Symp. on Boron, Borides and Related Compounds, 21st - 25th Sept., Duisburg, 273-274 (1987). (Crys Structure, Thermo)

87Kro: V.M. Krochuk, T.A. Prikhna, V.S. Mel'nikov, and P.S. Kislyi, "Morphological Characteristics of Aluminium Carbide Boride (AlC_4B_{24}) and Aluminium Carbide Boride ($Al_3C_2B_{48}$) Crystals," *Dokl. Akad. Nauk USSR, Ser. B: Geol., Khim. Biol. Nauki, 11*, 10-11 (1987) in Russian. (Crys Structure)

87Ner: V.A. Neronov, K.A. Matasova, T.I. Serebryakova, V.I. Lyashenko, and E.M. Dudnik, "Chemical Properties of α-AlB_{12} of Different Dispersity," Proc. 9th Intern. Symp. on Boron, Borides and Related Compounds, 21st - 25th Sept., Duisburg, 305-306 (1987). (Crys Structure)

88Kap: G. Kaptay, S.N. Akhmadov, and Yu.V. Borisoglebskii, "Thermodynamic Evaluation of the Reactions of Metal-like Refractory Compounds with Molten Aluminium," *Izv. V.U.Z., Tsvetn. Metall.*, 70-77 (1988). (Thermo)

88Pri: T.A. Prikhna, T.A. Nachal'naya, and V.G. Malogolevets, "IR and ESR Spectroscopy of Single Crystal Compounds of the Al-B-C System," *Sverkhtverd. Mater., 10*, 24-27 (1988) in Russian; TR: *Sov. J. Superhard Mater., 10*, 31-34 (1988). (Crys Structure)

89Hig: I. Higashi, H. Iwasaki, T. Ito, T. Lundström, S. Okada, and L.-E. Tergenius, "Single-Crystal X-Ray Diffraction Study of AlB_{31} of the β-Rhombohedral Boron Structure," *J. Solid State Chem., 82*, 230-238 (1989). (Equi Diagram)

89Ner: V.A. Neronov, "Review of Data on the Al-B Phase Diagram," *Poroshkov. Metall., 10*, 58-62 (1989) in Russian; TR: *Sov. Powder Metall. Met. Ceram., 28*, 789-792 (1989). (Equi Diagram Crys Structure)

89Pug: E.A. Pugach, Ya.V. Ivas'kevich, G.G. Postolova, and V.V. Ogorodnik, "Effect of Titanium and Aluminium on the Scaling Resistance of Boron Carbide," *Sov. J. Superhard Mater., 11*, 31-35 (1989); TR: *Sverkhtverd. Mater., 11*, 26-29 (1989). (Crys Structure)

90Car: O.N. Carlson, "The Al-B System," *Bull. Alloy Phase Diagrams, 11*, 560-566 (1990). (Equi Diagram)

91Gos: D. Gosset, M. Guery, and B. Kryger, "Thermal Properties of Some Boron-Rich Compounds ("B_nC" and AlB_{12})," Boron Rich Solids, August 1990, Albuquerque, NM, D. Emin, T.L. Aselage, A.C. Swilendick, B. Morosin, and C.L. Beckel, Ed., AIP Conf. Proc., 231, p 380-383, AIP, New York (1991). (Crys Structure)

91Kek: L.I. Kekelidze, I.A. Bairamashvili, V.N. Kovtun, I.I. Petrov, and D.K. Tavartkiladze, "The Effect of Structural Defects, on Thermal Conductivity of Polycristalline AlB_{12} and EuB_6," *Boron Rich Solids*, August 1990, Albuquerque, NM, D. Emin, T.L. Aselage, A.C. Swilendick, B. Morosin, and C.L. Beckel, Ed., AIP Conf. Proc., 231, p 371-375, AIP, New York (1991). (Crys Structure)

92Var: R.G. Vardiman, "Microstructures in Aluminum Ion Implanted with Boron and Heat Treated," *Acta Metall. Mater., 40*, 1029-1035 (1992). (Equi Diagram, Crys Structure)

93Dus: H. Duschanek, thesis, Univ. Wien (1993). (Equi Diagram)

93Ips: H. Ipser, research at Univ. Wien (1993). (Equi Diagram)

93Rip: H. Ripplinger, thesis, Techn. Univ. Wien (1993). (Crys Structure)

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