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In vacuo production of α-AlB_{12}, C_4AlB_{24}, $AlB_{12}C_2$ and $Al_3B_{48}C_2$ powders

Ahmet Koroglu[a,*], Derek P. Thompson[b]

[a] *Department of Physics, Science and Art Faculty, University of Ondokuzmayis, Kurupelit, Samsun 55139, Turkey*
[b] *Advanced Materials Group, School of Chemical Engineering & Advanced Materials, Merz Court, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK*

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Abstract

The production of pure powder samples of boron-rich ternary Al–B–C phases was investigated in vacuum at temperatures between 1400 °C and 1600 °C, using a range of different starting powders. Compacted powder mixes of B–AlB_2–B_4C, Al–B–C, Al–B–B_4C, B–C–AlB_2, B–AlB_2 and Al–B were heated for 1–2 h under vacuum in a carbon resistance furnace and the products characterised by X-ray diffraction. It was found impossible to produce significant quantities of C_4AlB_{24} under these conditions, but >95% pure samples of α-AlB_{12}, $AlB_{12}C_2$ and $Al_3B_{48}C_2$ were obtained. This study is a precursor to further research aimed at producing dense B_4C-type materials which might offer the advantages of easier densification and fabrication as compared with B_4C itself.

Keywords: Aluminium boron carbides; Powder-chemical preparation; Firing; X-ray methods; Borides; Armour

1. Introduction

Boron carbide is a unique material which combines the properties of low density ($d\approx2500\,\mathrm{k\,gm^{-3}}$), a hardness just below that of diamond (>9.5 on Mohs' scale), excellent thermal stability and remarkable chemical inertness.[1] It is a potential substitute for silicon carbide (SiC) in applications where good wear resistance is a major requirement, but where low mass is also important. A currently topical application where boron carbide has shown considerable promise is as a body armour material, where its low density (>30% less than competitive materials such as silicon carbide) is a unique advantage. However, boron carbide is not a user-friendly material, and cannot easily be made into samples of high density, or fabricated into complex shapes. Moreover the temperatures needed for densification (>2000 °C) automatically result in a high-cost final product. In addition, for body armour applications, B_4C experiences localised amorphisation when impacted with high velocity projectiles,[2,3] and alternative ways of reinforcing the structure to improve impact resistance are needed. An excellent review of boron carbide has been given recently by Domnich et al.[4]

Due to the specific ability of the ^{10}B isotope to capture neutrons, Al–B_4C materials also find application in the nuclear industry[5]; in addition, B_4C is used as a hardening/strengthening agent for aluminium based materials. Boron carbide fibres have not been widely developed, but studies done on such materials show promise for composites or cermets prepared using B_4C particles or fibres.[6–9] Boron carbide can also be used as a surface coating on fibres as a thin protective film, and for example, B_4C coatings on 100 μm boron filaments are an excellent reinforcement for aluminium based composites.[10] Improved methods for depositing uniformly thin layers of B_4C on 5–10 μm carbon fibres have also been developed[11–14] for the reinforcement of aluminium alloys.[15] However, the most important factor in the development of high-performance composite materials is correct design of the matrix–reinforcement interface, and in particular the avoidance of chemical reactions taking place at in-service temperatures. Despite many studies of the Al–B–C system reported in the literature, there is considerable scope for further work to clarify the reactions taking place and the relative stabilities of the various ternary phases at high temperatures.

A theoretical study of Al–B_4C equilibria, combined with experimental work up to 1000 K provided some data[16] and more extensive investigations have been carried out on the high temperature thermal behaviour of Al–B_4C cermets.[7,9,17] Of the various Al–B–C phases reported in the literature, Table 1 shows data for those whose existence can be considered as definitively

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[*] Corresponding author. Tel.: +90 3623121919/5426125116; fax: +90 3624576081.
E-mail address: kahmet@omu.edu.tr (A. Koroglu).

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Table 1
Binary and ternary compounds reported in the Al–B–C system.

Formula	Thermal stability (K)	Crystal system (space group – if known)	Unit cell parameters (nm)	ICDD file no. [Reference no.]
Al_4C_3	Decomposes 2429	Rhombohedral ($R\bar{3}m$)	$a = 0.33388$ $c = 2.4996$	35-799 [19,20]
B_4C	Decomposes 2723 Range 8.8–20 at % C	Rhombohedral ($R\bar{3}m$)	$a_{8.8} = 0.5672$ $c_{8.8} = 1.225$ $a_{20} = 0.5607$ $c_{20} = 1.209$	35-798 [1,21,22]
AlB_2	Decomposes 1438	Hexagonal (P_6/mmm)	$a = 0.30054$ $c = 0.32528$	39-1483 [17,23]
AlB_{12}	High T α-form, decomposes 2323	Tetragonal ($P4_12_12$ or $P4_32_12$)	$a = 1.016$ $c = 1.428$	12-640 [23,24,25]
	Low temperature γ-form	Orthorhombic ($P4_12_12_1$)	$a = 1.656$ $b = 1.753$ $c = 1.016$	[23,24,25]
$Al_3B_{48}C_2$ (β-AlB_{12})	High T form decomposes ∼2300	Tetragonal (P4/nmm)	$a = 0.882$ $c = 0.509$	19-269 [26,27]
	Low temperature form A	Orthorhombic (Cmma)	$a = 1.234$ $b = 1.263$ $c = 0.508$	19-270 [26,27]
	Low temperature form B	Orthorhombic (Ammm)	$a = 0.617$ $b = 1.263$ $c = 1.016$	19-271 [26,27]
C_4AlB_{24} (Orig. AlB_{10})	Decomposes >2370	Orthorhombic (Bbmm)	$a = 0.8881$ $b = 0.9100$ $c = 0.5690$	15-617 [26,29–31]
$AlB_{12}C_2$		Rhombohedral ($R\bar{3}m$)	$a = 0.565$ $c = 1.239$	[32]
$Al_8B_4C_7$	Decomposes ∼2383 Small composition range	Hexagonal ($P6_3$/mcm)	$a = 0.59118$ $c = 1.5915$	35-1216 [33,34]
Al_3BC (X, Al_4BC)	Stable up to at least 1273	Hexagonal	$a = 0.6046$ $c = 1.1541$	[17,18]

established, along with their thermal and structural characteristics where known. In addition to Al_3BC, there are arguments for the existence of a more Al-rich ternary compound (Al_4BC) sometimes referred to as phase X.[8,17,18] Phase equilibria in the Al–B–C system at 1273 K are shown in Fig. 1 (after [17]). Here, the solid–liquid data at 1273 K are shown as bold lines, whereas solid–solid phase equilibria are represented by thin lines because the results of some of the experiments were not completely convincing. It is interesting that the $Al_3B_{48}C_2$ phase was found to readily occur at this temperature, whereas the C_4AlB_{24} phase did not.

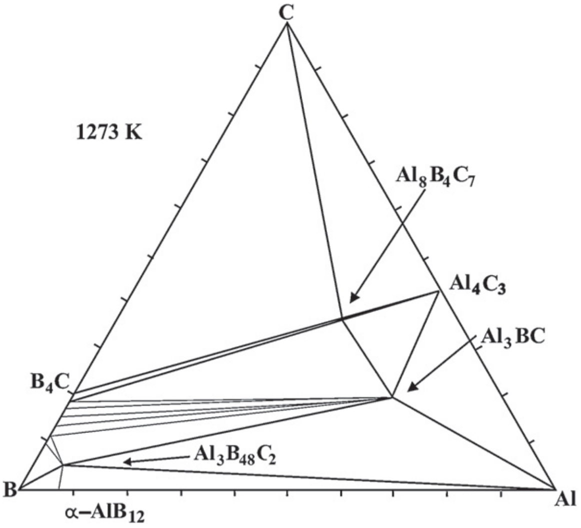

Fig. 1. Phase equilibria in the Al–B–C system at 1273 K.[16]

In early literature, AlB_{12} was reported to occur in three forms, α-, β- and γ-[23–25] but of these, the γ-form is rare and the β-form has now been more correctly characterised as $Al_3B_{48}C_2$, occurring in one high-temperature and two low-temperature forms[26,27]; the powder X-ray diffraction pattern of the tetragonal boron type α-AlB_{12} form is still correctly described by its original ICDD card (12-640). Of the compounds originally described as having the composition AlB_{10},[28] the one described in ICDD card 22-2 as rhombohedral with equivalent hexagonal dimensions of $a = 0.7835$, $c = 1.591$ nm has not been reproduced by subsequent researchers and was not observed in the present work. The other form of AlB_{10} originally reported,[28] having orthorhombic unit cell dimensions of $a = 0.888$, $b = 0.910$, $c = 0.569$ nm, is now known to be carbon-containing with the composition of either C_4AlB_{24}[29] or $C_8Al_{2.1}B_{51}$,[30] and here the former formula will be used; it is known to decompose into a B_4C-type phase above 2000 K.[31] Finally, there is the compound $AlB_{12}C_2$, for which a B_4C type X-ray diffraction pattern was provided in ICDD card 19-4[32] and even though it