JOURNAL OF MATERIALS SCIENCE LETTERS 11 (1992) 711–714

Composition and lattice parameters of a new aluminium-rich borocarbide

J. C. VIALA, G. GONZALES, J. BOUIX
Laboratoire de Physico-chimie Minérale 1, URA CNRS n° 116, Université Lyon 1, 43 boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

High-strength and low-weight composite materials or cermets have been prepared by reinforcing an aluminium-base matrix with boron carbide particles or with boron carbide-coated boron fibres [1–3]. In the former case boron carbide (B_4C) is the strengthening agent, whereas in the latter the role of B_4C coating is to protect the fibres against a too severe attack by aluminium during processing or use of the composites. Recently B_4C-coated carbon fibres have been produced on a pilot plant in our laboratory [4, 5]. A general study is now in progress with the aim of employing these treated fibres for the manufacture of aluminium-base matrix composites. The development of such materials and improvement of their performances require, however, a thorough understanding of the metal–carbide interface chemistry and, primarily, a detailed description of the phases likely to be formed by chemical reaction in the Al–B–C system.

In a general study on the processing of B_4C–Al cermets, Halverson *et al.* observed the formation of a new ternary compound, which they called phase X, at every temperature between 800 and 1400 °C [1]. Attempts were made by Sarikaya *et al.* [6] to characterize that phase by electron diffraction and energy-loss spectroscopy: those authors proposed a hexagonal symmetry with the lattice parameters $a_0 = 0.3520$ nm and $c_0 = 0.5820$ nm and the chemical formula Al_4BC. This letter reports the composition and lattice parameters of an aluminium-rich borocarbide that was prepared by direct synthesis from the elements and discusses the possible relationship between this compound and the foregoing phase X.

Commercial powders of aluminium (purity 99.8 wt %, grain size $d < 50$ μm, Alfa Ventron), boron (99.4 wt %, $d < 250$ μm, Alfa Ventron) and carbon (spectrographic grade, $d < 25$ μm, Le Carbone Lorraine) were ball-mixed in a steel mortar at the atomic ratio Al:B:C = 80:10:10 and cold-pressed under 272 MPa into small rods (dimensions 4 mm × 6 mm × 30 mm and weight about 2 g). These rods were placed on an alumina boat and heated for 160 h at 1273 K in a closed silica tube under atmospheric-pressure purified argon. Under these conditions the weight losses were <5%. After air-cooling the resultant samples were characterized by X-ray powder diffraction (XRD), using standard Philips equipment: a PW1720 generator, PW1390 channel-control unit and PW1050/25 two-circle goniometer supplied with a step-scanning motor monitored by an Apple II microcomputer [7]. The investigated spectral range was $6 < 2\theta < 86°$ for filtered CuK_α radiation ($\lambda = 0.154\,18$ nm), the step being 0.025 (2θ) for a 15 s counting time. Further characterization of the treated samples was carried out on diamond-polished sections by optical metallography and electron-probe microanalysis (EPMA). A Cameca Camebax apparatus equipped with a wavelength-dispersive spectrometer and an energy-dispersive Tracor Northern 2000 analyser was used. An accelerating voltage of 5 kV, a regulated beam current of about 30 nA and a counting time of 10 s were retained as standard operating parameters. In every case the background was substracted from the recorded counting rates that were referred to pure or complex standards (Al, B, C, AlB_2, Al_4C_3, B_4C and SiC) and corrected for atomic number, absorption and fluorescence (ZAF correction).

Metallographic observation of the treated samples (Fig. 1) revealed that, apart from some small dark crystals ($d \approx 3$ μm), only two phases were distinguishable: a bright grey phase with a metallic lustre

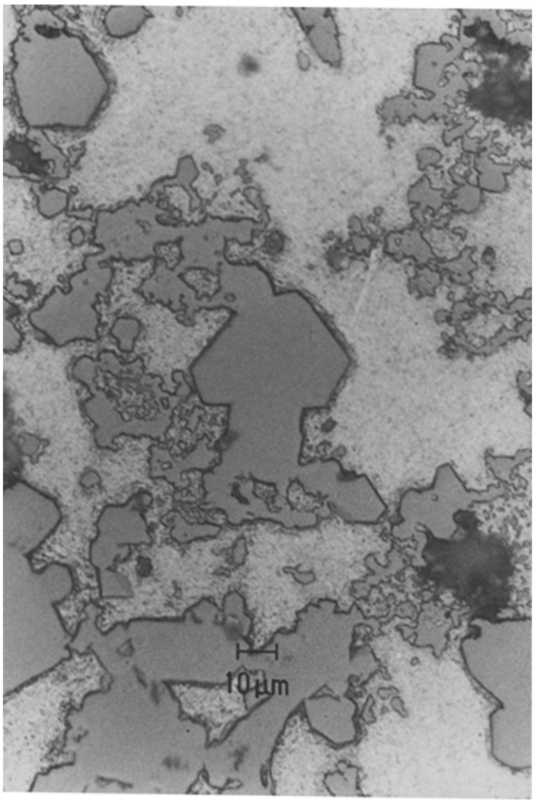

Figure 1 Optical metallography of an Al:B:C powder mixture (atomic ratio 80:10:10) heat-treated for 160 h at 1273 K.

and, embedded in it, bluish grey crystals with sizes varying from 2 to 40 μm; some of these crystals exhibited hexagonal shapes. EPMA showed that the bright phase consisted of almost pure aluminium, whereas the small dark crystals were pure aluminium oxide, Al_2O_3. As for the bluish grey crystals, EPMA revealed that they all contained aluminium (major constituent), boron and carbon; no oxygen, nitrogen or any other element could be detected. It was not possible, however, to determine simultaneously the abundances of Al, B and C present in these crystals by a classical analytical procedure (comparison of the counting rates with those of pure or complex standards and ZAF correction). Non-consistent values were indeed found, due to excessive correction factors for atomic number and absorption. At most, indications were obtained for a B:C atomic ratio of about unity. Consequently, only the aluminium content could be obtained with a reasonable accuracy: successively assuming that B and C were the sole elements present with Al in the crystals, the Al content calculated after ZAF correction and by referring to a pure aluminium standard was 59.04 and 62.84 at %, respectively. It was then concluded that the bluish grey crystals contained 60.9 ± 2 at % aluminium.

In order to determine more precisely the B:C ratio, mixtures with different Al:B:C proportions were reacted under the same experimental conditions as previously (160 h at 1273 K). Fig. 2 shows the typical appearance of a sample prepared from a mixture with the atomic ratio Al:B:C = 80:9:11. A third phase, which was analysed by EPMA as Al_4C_3, is clearly visible (dark zones). On the other hand, a sample prepared from a mixture with Al:B:C = 80:11:9 also contained a third phase, but the latter was characterized as incompletely transformed β-AlB_{12} crystals (Fig. 3). At this point it must be remembered that when only two or three condensed phases are obtained by reaction under a constant pressure in a ternary system, equilibrium conditions are reached (application of the phase rule). Consequently, if the impurity Al_2O_3 is neglected, the foregoing results prove, first, that the reaction has gone to completion under our experimental conditions and, secondly, that the B:C atomic ratio in the bluish grey crystals is higher than 9:11 and lower than 11:9. These results, summarized in Table I, are in good agreement with the chemical formula Al_3BC, which will be used to describe the aluminium-rich borocarbide crystals prepared in the present work.

Fig. 4 shows the typical diffraction pattern obtained for samples prepared from Al–B–C mixtures with the atomic ratio Al:B:C = 80:10:10. Apart from the four strong diffraction peaks characteristic

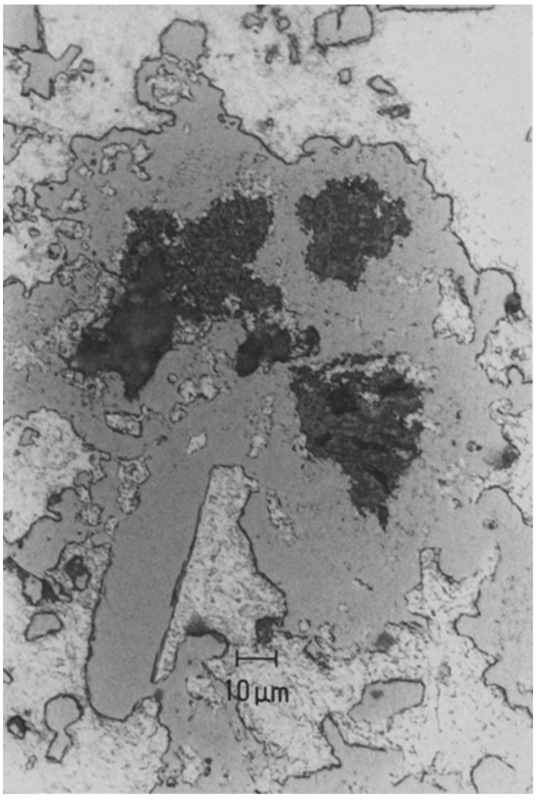

Figure 2 Al_4C_3 crystals (dark areas) formed with Al_3BC by reacting an Al:B:C mixture (80:9:11) for 160 h at 1273 K.

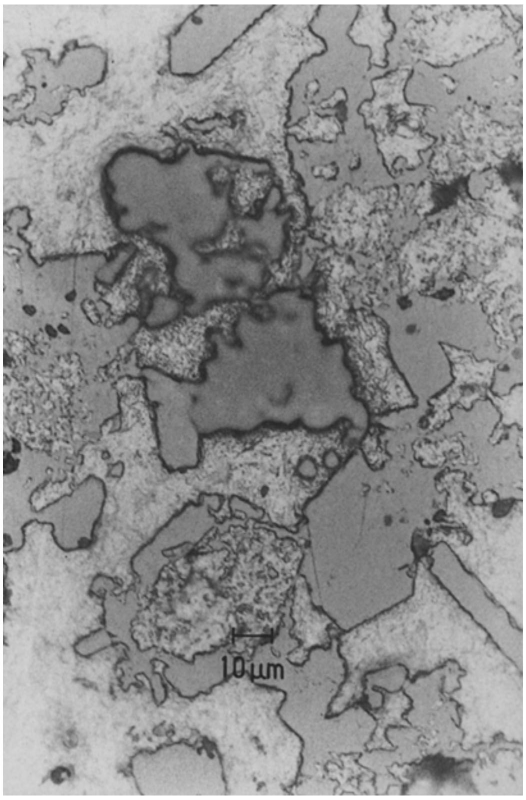

Figure 3 β-AlB_{12} crystals (with blurred outlines) formed with Al_3BC in an Al:B:C mixture (80:11:9) heated for 160 h at 1273 K.

TABLE I Analytical and structural data for the new borocarbide Al_3BC

Chemical composition	Al 60.9 ± 2 at % B + C 39.1 ± 2 at % $0.45 < B/B+C < 0.55$
Symmetry	Hexagonal
Lattice parameters	$a_0 = 0.3491(2)$ nm $c_0 = 1.1541(4)$ nm
Cell volume	$V = 0.1218(2)$ nm^3
Molecules/unit cell	$Z = 2$

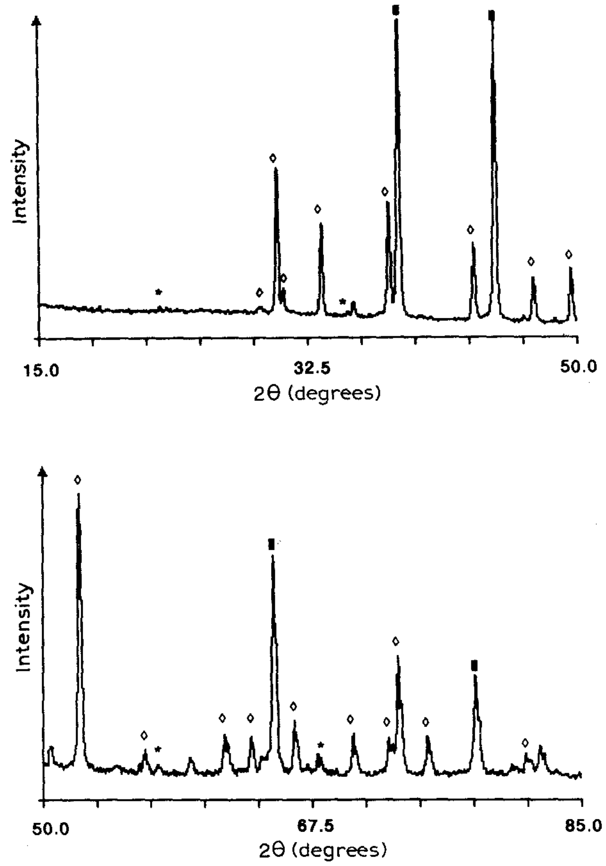

Figure 4 X-ray powder diffraction pattern of an Al:B:C mixture (80:10:10) reacted for 160 h at 1273 K (CuK_α radiation): (◇) Al_3BC, (■) Al and (★) Al_2O_3.

for aluminium in excess and very weak lines corresponding to α-Al_2O_3 reflections, the observed lines could not be attributed to any known reported compound. These lines, which must be characteristic for the bluish grey crystals because of the previous observations, are listed with their relative intensities in Table II. They were analysed using Bunn charts and were found to be consistent with a hexagonal symmetry, the c/a ratio being of about 3.3. Further refinement of the cell parameters a_0 and c_0 (Table I) was realized using a classical least-squares computer program: the resultant values, with their standard deviation, were $a_0 = 0.3491(2)$ nm and $c_0 = 1.1541(4)$ nm (2 0 1 and 1 1 4 reflections were not considered for final refinement, due to an overlapping problem). The d-spacings calculated with these refined parameters were in excellent agreement with the experimental data (Table II). Particular reflection rules were observed to be $l = 2n$ for $h\,h\,l$ and $l = 2n$ for $0\,0\,l$ (no condition for $h\,k\,l$).

Density calculations were worked out for the new ternary phase on the basis of the analytical and structural results listed in Table I. With two Al_3BC molecules per unit cell the calculated density was 2.83. This value is acceptable since it is intermediate between the densities of Al (2.7), Al_4C_3 (2.97) and α-AlB_{12} (2.56). On the contrary, densities calculated with the chemical formula Al_4BC were not consistent with those of other Al–C or Al–B compounds: they were too low with $Z = 1$ or too high with $Z = 2$.

TABLE II X-ray powder diffraction data for Al_3BC

2θ (degrees)	d_{obs} (nm)	d_{calc} (nm)	$h\,k\,l$	I/I_0
		0.577 05	0 0 2	
29.45	0.3030	0.302 33	1 0 0	5
30.57	0.2923	0.292 46	1 0 1	100
30.97	0.2885	0.288 52	0 0 4	17
33.45	0.2676	0.267 80	1 0 2	61
37.825	0.2376	0.237 71	1 0 3	76
43.325	0.2087	0.208 73	1 0 4	51
47.225	0.1923	0.192 35	0 0 6	30
49.675	0.1834	0.183 46	1 0 5	37
52.40	0.1745	0.174 55	1 1 0	69
		0.167 07	1 1 2	
56.70	0.1622	0.162 29	1 0 6	6
		0.151 16	2 0 0	
61.875	0.149 82	(0.149 88	2 0 1	10
		(0.149 35	1 1 4	
63.60	0.146 17	0.146 23	2 0 2	10
		0.144 75	1 0 7	
		0.144 26	0 0 8	
66.40	0.140 67	0.140 69	2 0 3	13
70.225	0.133 91	0.133 90	2 0 4	10
72.525	0.130 22	0.130 20	1 0 8	5
73.15	0.129 26	0.129 26	1 1 6	30
75.05	0.126 46	0.126 46	2 0 5	10
		0.118 85	2 0 6	
81.475	0.118 03	0.118 05	1 0 9	4

d-Spacings calculated with Cu$K_{\alpha 1}$ radiation, $\lambda = 0.154\,0.56$ nm.

The question now arises of whether the borocarbide Al_3BC prepared from the elements in the present work is different from the phase X obtained earlier as a reaction product between aluminium and boron carbide by Halverson *et al.* [1]. Both phases appear as an aluminium-rich ternary compound of the Al–B–C system, but they differ in synthesis conditions, composition and lattice parameters. With the aim of providing a response to this question, mixtures containing various amounts of boron carbide and aluminium were cold-pressed and reacted for 162 h at 950–1273 K. Characterization of these samples by X-ray diffraction and EPMA showed [9] that crystals having the same lattice parameters and the same composition as those reported in Table I were obtained as major reaction product with AlB_2 ($T < 1100$ K) or β-AlB_{12} ($T > 1150$ K). This constitutes a strong argument for supporting the assumption that Al_3BC and X (Al_4BC) would actually correspond to the same compound. However, it must be noted that the samples of Halverson *et al.* were initially densified at high temperature ($T = 1453$ K) before being isothermally heat-treated at lower temperatures. Moreover, some weak lines appearing in the diffraction pattern reported in Fig. 1 remained unindexed. These lines are located at the 2θ values 35.52, 46.55, 48.62, 50.52, 55.1, 59.6 and 82.35°. They correspond neither to Al_2O_3 modifications nor to any known compound of the Al–B–C system (Al_4BC included). Attempts made to index these lines in hexagonal superlattices derived from the basic cell of Al_3BC also failed. Thus the existence of several crystalline modifications for Al_3BC or of several aluminium-rich borocarbides having slightly different compositions must not be ruled out. A similar problem has recently been encountered in the Al–Mg–C system, where a ternary carbide Al_2MgC_2 has been found to exist with two different structures [8].

Further work is now in progress with the aim of preparing Al_3BC single crystals for structural determination and obtaining a better insight into the thermodynamic and kinetic aspects of the chemical interaction between aluminium and boron carbide.

References

1. D. C. HALVERSON, A. J. PYZIK, I. A. AKSAY and W. E. SNOWDEN, *J. Amer. Ceram. Soc.* **72** (1989) 775.
2. W. KAI, J. M. YANG and W. C. HARRIGAN, JR, *Scripta Metall.* **23** (1989) 1277.
3. J. LECOMTE-BECCKERS and E. DIDERRICH, *ATB Metall.* **27** (1987) 3.
4. J. BOUIX, C. VINCENT, H. VINCENT and R. FAVRE, in "Chemical vapor deposition of refractory metals and ceramics", MRS Symposium Proceedings, Vol. 168, edited by T. M. Besman and B. M. Gallois (Materials Research Society, Pittsburgh, Pennsylvania, 1990) p. 305.
5. H. VINCENT, B. BONNETOT, J. BOUIX, H. MOURICHOUX and C. VINCENT, *J. Phys.* **50** (1989) 249.
6. M. SARIKAYA, T. LAOUI, D. L. MILIUS and I. A. AKSAY, in Proceedings of the 45th Annual Meeting of the Electron Microscopy Society of America, edited by G. W. Bailey (San Francisco Press, San Francisco, 1987) p. 168.
7. B. F. MENTZEN, *J. Appl. Crystallogr.* **21** (1988) 266.
8. J. C. VIALA, F. BOSSELET, G. CLAVEYROLAS, B. F. MENTZEN and J. BOUIX, *Eur. J. Inorg. Solid St. Chem.* **28** (1991) 1063.
9. G. GONZALEZ, J. C. VIALA and J. BOUIX, 17th Journées d'Etude des Equilibres entre Phases, Utrecht, 3–4 April 1991 edited by H. A. J. Oonk (Utrecht University, 1991) p. 199.

Received 2 July
and accepted 12 September 1991