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Synthesis of Al_3BC in Air from Mechanically Activated Al/B/C Powder Mixtures

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Abstract

A ternary aluminum borocarbide, Al_3BC was prepared for the first time by self-propagating high-temperature synthesis (SHS) induced by mechanical activation of Al/B/C powder mixtures in air. The effect of mixing molar ratio of Al/B/C and grinding time on the formation of Al_3BC was investigated. On the other hand, Al_3BC was also formed by mechanical activation and subsequent annealing of Al/B/C = 3/1/1 powder mixture. The lattice constants of Al_3BC obtained in two methods were compared. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: milling, borides, carbides, nitrides, Al_3BC, SHS.

1 Introduction

Many phases of the system Al/B/C have been the topic of several recent investigations as promising ceramic materials of high hardness and toughness in lightweight structures.[1–3] Among them, a ternary aluminum borocarbide Al_3BC is the most recently synthesized and characterized. According to the structural determination of Al_3BC single crystal, which was synthesized from the elements Al, B and C under an atmosphere of argon at 850°C for 160 h, Meyer and Hillebrecht[1] gave a hexagonal unit cell with $a = 0{\cdot}34840(7)$ nm and $c = 1{\cdot}15202(18)$ nm.

Mechanical activation or mechanosynthesis is pointed out to be a potential process for the production of new materials, particularly advanced materials such as metal carbides and nitrides. We have recently developed a technique combining mechanical activation by grinding and self-propagating high-temperature synthesis (SHS). This technique is based on SHS induced by exposing the metal–graphite powder mixtures mechanically activated to air and has been successfully applied to the synthesis of carbides and nitrides of Al, Zr and Nb.[4–10] In this study the development of this technique for preparation of ternary borocarbides of Al, Zr and Nb has been attempted for the first time. It is well known that the mechanical activation enhances the reactivity of solids and lowers remarkably reaction temperature. Therefore, another traditional technique was also used for the formation of aluminum borocarbide, in which the powder mixture of Al/B/C = 3/1/1 was mechanically activated by grinding and subsequently annealed at temperatures above 500°C. The lattice constants of Al_3BC obtained in two processes were compared.

2 Experimental Procedures

The procedures of mechanical activation of metal (Al, Zr and Nb)–graphite (C) powder mixtures have been in detail described in the previous papers.[4–10] Aluminum metal (particle size varying between 61 and 104 μm, 99·9% purity, Kojundo Chemical Laboratory), amorphous boron (practical grade, Sigma Chemical Company) and natural graphite (mean flake size 5 μm, 97% carbon, 2% ash and 1% volatile component, Nippon Kokuen Industry) were used as starting materials. These powders were mixed in various molar ratios of Al/B/C in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany), and then ground for about 30 min. The grinding was interrupted every 15 min and the sample was scraped from the balls and the side walls of the jar and then reloaded to continue grinding. A 25 ml jar and seven balls of tungsten carbide (12 mm diameter) were used for grinding.

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The ground sample was transferred into a graphite crucible (inner diameter of 30 mm and depth of 40 mm) and exposed to air. It self-ignited instantly and the exothermic reactions propagated into the powders. As soon as the reactions started, the graphite crucible was covered with another one to prevent the sample from oxidizing. After the reaction, the surface of the product lump was removed and the bulk was ground in an agate mortar and then supplied to XRD examination. Some experiments were carried out using zirconium metal ($< 150\,\mu$m, 98% purity, Kojundo Chemical Laboratory) and niobium metal ($< 45\,\mu$m, 99·9% purity, Kojundo Chemical Laboratory) instead of aluminum metal. Another experiments for the low temperature synthesis of Al_3BC were also carried out as follows. The powder mixture of Al/B/C = 3/1/1 was at first mechanically activated by grinding in air for 0, 30, 60 and 90 min. In order to avoid self-ignition the ground samples were taken out of the jar after the temperature dropped to around room temperature, compacted into a pellet and then heated at 500, 800 and 1000°C for 3 h in static air and in flowing argon of 100 ml min^{-1}, respectively. Powder X-ray diffraction (XRD) patterns were obtained with a RINT-2000 (Rigaku Denki) using Ni-filtered CuK_α radiation.

3 Results and Discussion

3.1 Mechanically induced SHS of Al_3BC in air

When the mechanically activated Al/B/C powder mixtures were exposed to air, the exothermic reactions spontaneously occurred in the successive steps, evolving red heat initially and then white heat. The self-ignition reaction in the SHS is estimated to be the oxidation of the disordered carbon formed by grinding in air as well as in the Al/C system.[4–6]

Figure 1 shows the XRD patterns of the reaction products obtained by SHS induced by mechanical activation of the Al/B/C powder mixtures with various molar ratios. The formation of ternary compounds, Al_3BC and $Al_8B_4C_7$ can be seen from the figure. Compared with Al/B/C system, the reactions in the systems of Zr/B/C = 1/1/1 and Nb/B/C = 1/1/1 were also investigated. These results are summarized in Table 1.

In the systems of B/Al $\geqq$ 0·3, the formation of aluminum borocarbide Al_3BC is observed. With increasing boron content, the amount of Al_3BC formed increases and a single phase of Al_3BC is obtained in Al/B/C = 1/2/1 system. In contrast, with decreasing boron content, the amount of Al_4C_3 and AlN formed increases. The unreacted Al and C are detected in all systems as shown in Fig. 1. Surprisingly, in the least B content system of Al/B/C = 1/0·1/1·1, boron-rich ternary compound, $Al_8B_4C_7$ (B = 4/19 in mol) is formed instead of Al_3BC (B = 1/5 in mol). In this system, as quoted in Table 1, the violent emission of white heat was detected just after self-ignition. Furthermore, with increasing boron content the grinding time

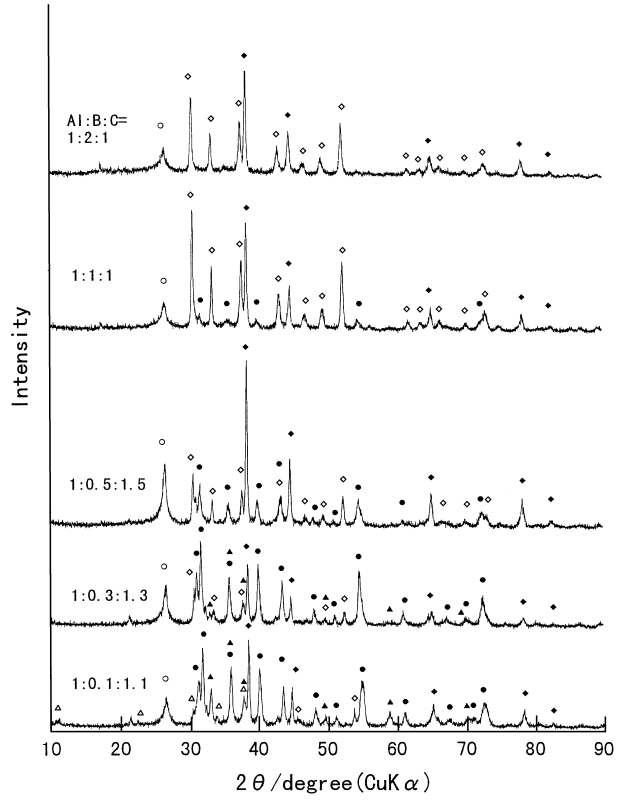

Fig. 1. The XRD patterns of the reaction products obtained in air by SHS induced by mechanical activation of the Al/B/C powder mixtures with various molar ratios. ◇: Al_3BC; ○: C; ◆: Al; ●: Al_4C_3; ▲: AlN; △: $Al_8B_4C_7$.

Table 1. Phases of main products, grinding times and reaction behavior with heat emission in self-ignition high-temperature synthesis (SHS) in M/B/C(M = Al, Nb, Zr) powder mixtures with different molar ratios

M	*Mixing molar ratio of M:B:C*	*Main products*	*Grinding time (min)*	*Reaction behavior with heat emission*
Al	1:2:1	Al_3BC	30	Only red heat
	1:1:1	$Al_3BC \gg Al_4C_3$	30	Only red heat
	1:05:15	$Al_3BC \cong Al_4C_3$	29	Red heat and then white heat
	1:0·3:1·3	$Al_4C_3 > Al_3BC$,AlN	27	Red heat and then white heat
	1:0·1:1·1	$Al_4C_3 > AlN \gg Al_8B_4C_7$	25	White heat just after self-ignition
Nb	1:1:1	$NbC > \varepsilon$-NbB_2	75	White heat just after self-ignition
Zr	1:1:1	$ZrC > ZrB_2$	45	White heat just after self-ignition

required to self-ignite and the emission time of red heat became longer, and only the reaction with red heat emission occurred in the systems of Al/B/C = 1/1/1 and 1/2/1, where the lowering of reaction temperature is clearly expected. Therefore, the maximum reaction temperature reached during SHS is considered to have affected the kinds of aluminum borocarbide formed. In fact, it is reported that $Al_8B_4C_7$ was prepared by the heating of Al_4C_3 and B_4C powder mixture to 1800°C, corresponding to white heat emission region, at 50°C min^{-1} in Ar atmosphere.[11]

On the other hand, as shown in Table 1, in the systems of Zr/B/C = 1/1/1 and Nb/B/C = 1/1/1 the grinding times taken to self-ignite were 45 and 75 min, and not zirconium and niobium borocarbides, but ZrC and ZrB_2, and NbC and ε-NbB_2 were formed, respectively. This difference seems to be attributable to the difference in the formation free energies of borocarbides, borides and carbides of Al, Zr and Nb. Although the formation free energies of aluminum, zirconium and niobium borocarbides have not been reported yet, it is known that the free energies of the formation of ZrB_2 and ε-NbB_2 are very smaller than those of ZrC and NbC.[12]

3.2 Formation of Al_3BC by mechanical activation and subsequent annealing of Al/B/C = 3/1/1 powder mixture

Figure 2 shows the XRD patterns of the powder mixtures of Al/B/C = 3/1/1 ground for different periods of 0~90 min. A strong decrease in intensity of graphite 002 line after 30 min-grinding results from the disappearance of ordered stacking of graphite layers. With further increased grinding time, the intensity of each diffraction line of aluminum is decreased and the full-width at the half-maximum is increased, indicating the decrease in particle size and increase in strain energy. These mechanically activated samples were compacted into a pellet and then annealed at 500, 800 and 1000°C in air or Ar. After reaction, the pellet was ground into powder and supplied to XRD measurement. The XRD patterns of the products obtained in air and Ar were almost identical, hence the XRD patterns obtained in the latter case are shown in Fig. 3. At 500°C Al_3BC is detected in the 30, 60 and 90 min-ground samples, increased with an increase in grinding time. When annealed at 800°C, the formation of Al_3BC is ultimately noticed in the unground sample as well, and the 90 min-ground sample was converted to almost a single phase of Al_3BC, though with a trace amount of unreacted Al. When further annealed at 1000°C, in addition to Al_3BC the formation of Al_4C_3 was also observed. From the above results, therefore, it was found that the mechanical activation by grinding enhanced remarkably the rate of Al_3BC formation compared to the unground sample, and the process of mechanical activation for 90 min and subsequent annealing at 800°C is suitable conditions for the Al_3BC formation.

3.3 Comparison of lattice constants of Al_3BC obtained in two methods

Table 2 shows lattice constants, a and c of Al_3BC obtained in SHS induced by mechanical activation in air, and by mechanical activation and subsequent annealing in Ar. These values were determined by using (102), (103), (104) and (110) lines of Al_3BC. Compared to a and c reported in the references, i.e. $a = 0{\cdot}34840(7)$ nm and $c = 1{\cdot}15202(18)$ nm,[1] and $a = 0{\cdot}3491(2)$ nm and $c = 1{\cdot}1541(4)$ nm,[3] the a values are almost identical, but c values are somewhat larger, in particular in Al_3BC obtained in SHS induced by mechanical activation in air. Meyer *et al.*[1] synthesized a single crystal of a black-bluish hexagonal platelet of Al_3BC at 850°C for 160 h in Ar atmosphere, and tried structure analysis. According to them, the crystal structure of Al_3BC was described as a closest packing of Al (sequence ABACBC) with alternating layers of edge-sharing BAl_6 octahedra and trigonal bipyramids CAl_5, linked by common corners. This leads to a pronounced two dimensional character as

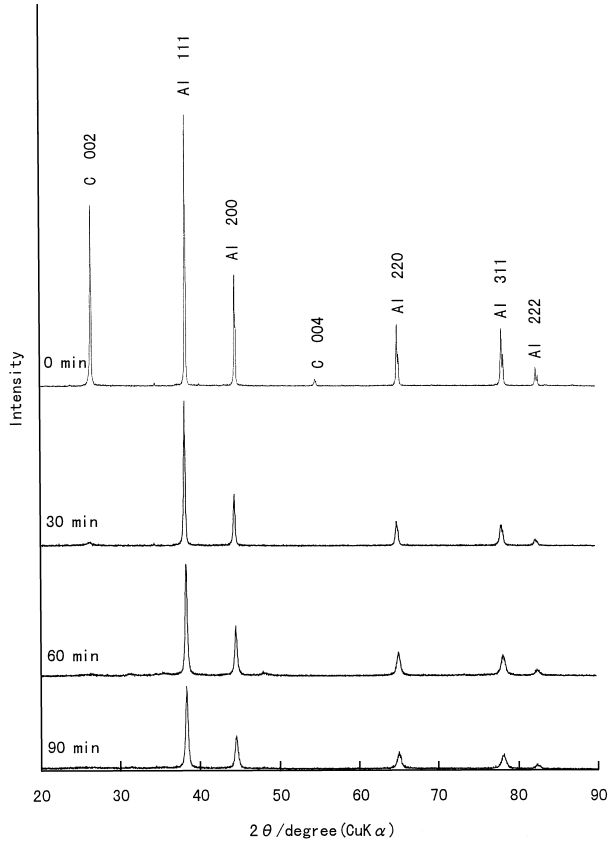

Fig. 2. The XRD patterns of the powder mixtures of Al/B/C = 3/1/1 ground for different periods of 0~90 min.

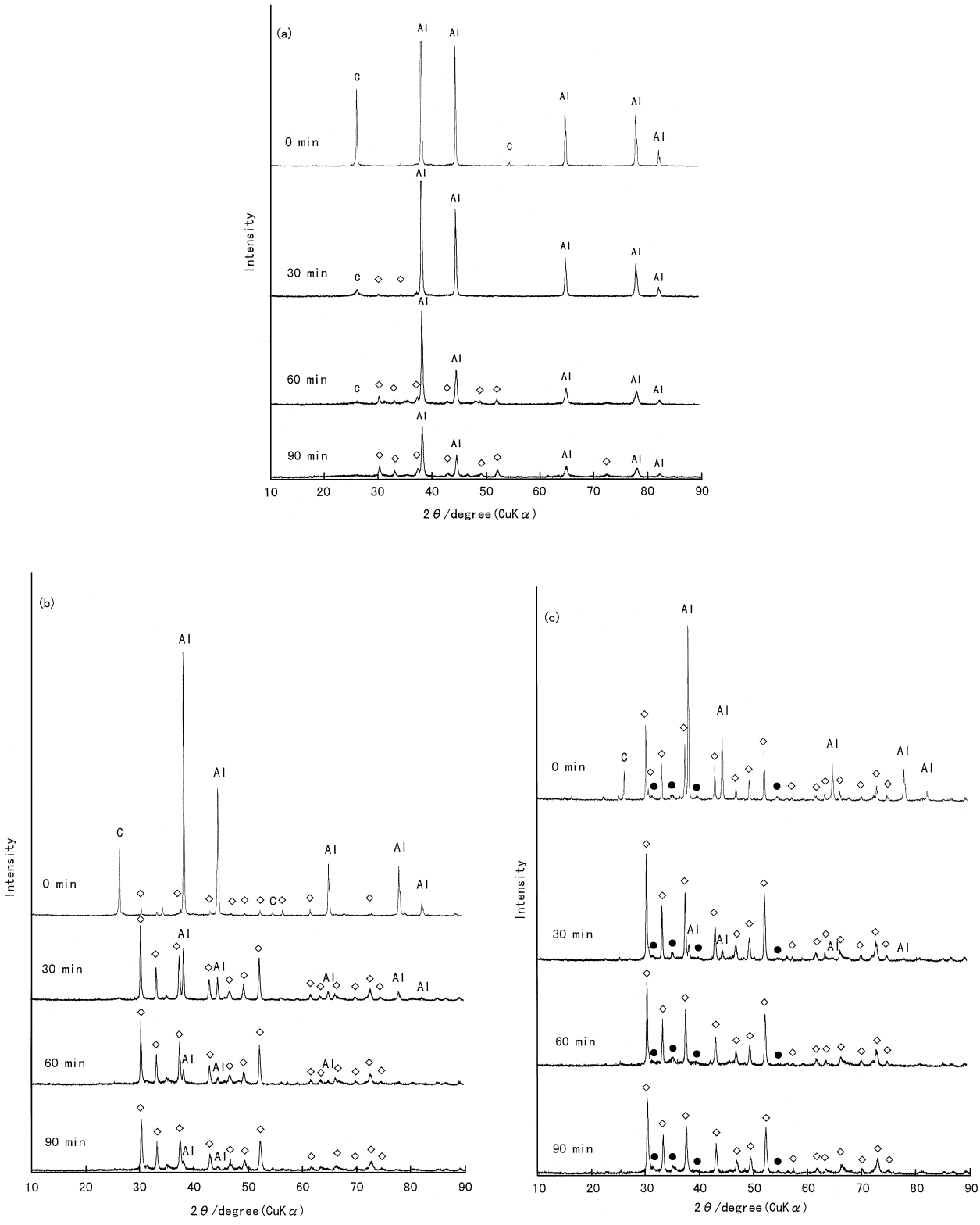

Fig. 3. The XRD patterns of the products obtained by mechanical activation for 0∼90 min and subsequent annealing at (a) 500, (b) 800 and (c) 1000°C for 3 h in Ar. ◇: Al_3BC; ●: Al_4C_3.

Table 2. Comparison of lattice constants, *a* and *c* of Al_3BC obtained in two methods with those reported in Refs. 1 and 3

	Self-propagation high-temperature synthesis induced by mechanical activation in air			*Mechanical activation and subsequent annealing at 1000°C for 3 h in Ar*				*Ref. 1*	*Ref. 3*
	Al/B/C = 1/2/1	*Al/B/C = 1/1/1*	*Al/B/C/ = 1/0·5/1·5*	*0 min grinding*	*30 min grinding*	*60 min grinding*	*90 min grinding*	—	—
a (Å)	3·49	3·48	3·48	3·48	3·47	3·50	3·49	3·48	3·49
c (Å)	11·75	11·65	11·66	11·59	11·59	11·63	11·61	11·52	11·54

layer structure. The insertion of additional boron and/or carbon between these layers or the boron/carbon substitution may result in the expansion of lattice constant of *c*. The dissolution of O into the structure of Al_3BC cannot be neglected in the experiments carried out in air. Further study is needed to discuss quantitatively the expansion of *c* shown in Table 2.

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