

Poly(borazinylamine): an excellent precursor for the preparation of low volume fraction metal-matrix composites containing metal borides and nitrides as ceramic phase

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Poly(borazinylamine) has been investigated as a binder and as an *in situ* source material for boron and nitrogen in the fabrication of low volume fraction metal–matrix composites. The representative matrix metals employed in this investigation were aluminium, copper, iron, titanium, nickel and tungsten. The resulting metal–matrix composites contained metal borides and metal nitrides as the ceramic phases in 10.0 mol%, with the exception of copper which does not react with poly(borazinylamine). Although, the composites were prepared at ambient pressure, the aluminium- and titanium-based composites attained close to theoretical densities. The surface analysis of the composites by SEM and XPS showed the presence of a protective oxide layer composed of metal oxide and refractories. © 1998 Chapman & Hall

1. Introduction

Metal–matrix composites (MMCs) are true “designer” materials because their properties can be tailored to specific needs [1, 2]. Since the early stages of research on MMCs, efforts have been focused on reinforcing metals with ceramics. For example, it was found that reinforcement of soft metals, such as aluminium, with relatively small amounts of a ceramic, improved strength, hardness, and fatigue properties of the metal. Improvement in wear-resistance was also seen. This is extremely important for the application of MMCs in the fabrication of engine components. The reinforcement of metals by ceramic fibres [3] or particles [4, 5] has been reviewed.

Low volume fraction MMCs containing 5%–30% by volume of ceramic phase are employed as structural materials. High volume fraction MMCs contain 45%–75% by volume of ceramic phase and are of interest in the electronic packaging industry. The common methods used for the fabrication of MMCs are liquid metal infiltration [6], cospraying [7], liquid metallurgy methods [8–10] semi-solid slurry processing [11] and powder metallurgy methods [12]. Regardless of the method of fabrication, the cost remains high and the applications of MMCs to date remain limited to aerospace-related industries. In recent years, a variety of automotive components such as drivershaft, brake rotors, engine block and cylinder liners, connecting rods, and pistons have been fabricated by molten metal routes using discontinuously reinforced aluminium (with SiC or alumina particles) [13–15]. Pistons for Toyota light diesel engines and

cylinder liners for Honda vehicles thus fabricated are in production [16, 17]. There is no doubt about the advantages of MMC-based components due to the resulting improved durability and quality, safety, fuel economy, reduced emissions, styling, performance, and recycling. However, the cost remains prohibitively high. Clearly, there is need for improvement in the fabrication processes to reduce cost either by reducing the amount of the reinforcing ceramic materials used or their cost, if MMCs are to find widespread use in civilian applications.

The application of a ceramic precursor, in principle, should reduce the amount of the ceramic component needed substantially, due to improved distribution of the latter throughout the metal matrix. The application of a polycarbosilane ceramic precursor as a binder in the consolidation of metal powders and as an *in situ* source of silicon carbide was first investigated by Yajima *et al.* in the fabrication of Fe–Cr alloy MMCs [18]. Recently, Seyferth and Czubarow have shown that organosilicon polymers, such as polysilanes, polycarbosilanes and polysilazanes, can be employed to fabricate a large variety of MMCs and they also described the advantages of this method [19]. A brief extension of this method is described by Narula *et al.* in the use of $(\text{CH}_3)_3\text{SiN-HTiCl}_3$ as a binder and as an *in situ* source of titanium nitride in the fabrication of TiN containing MMCs [20]. A common feature of all these reports is that heating results in the pyrolysis of the preceramic polymer dispersed within the metal matrix. During subsequent

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further heating, the ceramic thus formed reacts with the metal matrix. This is different from the use of ceramic precursors as binders for ceramic powders where precursors decompose to form ceramic materials but these do not react with the ceramic matrix [21–26].

In this paper, we describe the application of the poly(borazinylamine) [PBA] polymer reported by Narula *et al.* [27] in the fabrication of low volume fraction MMCs based on a variety of metals. Here, poly(borazinylamine) acts as a binder and as an *in situ* source of boron and nitrogen in the fabrication of boride- and nitride-containing MMCs. The identification of the crystalline phases in MMCs by X-ray diffraction methods (XRD) is presented. Selected MMCs have been examined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) to determine surface structure, and the results are discussed.

2. Experimental procedure

All experiments involving poly(borazinylamine) were carried out in a moisture-free inert atmosphere using standard Schlenk line or argon dry-box methods. Commercial metal powders were handled in a dry-box. Diethylether was dried over sodium benzophenone ketyl, and liquid ammonia was dried over sodium. Aluminium (–325 mesh), titanium (–325 mesh), iron (–325 mesh), copper (–325 mesh), and nickel (5 μm) were purchased from CERAC. Liquid ammonia, for use as a solvent, was dried over sodium metal.

Thermogravimetric analyses (TGA) were carried out on a Perkin–Elmer TA7 instrument. X-ray diffraction patterns were recorded on a Rigaku Rotaflex Ru-300 instrument. X-ray photoelectron spectra were obtained on a PHI 5100 ESCA. Scanning electron microscopic studies were carried out on a Hitachi S-530 instrument.

The sample was weighed and its volume was determined using a caliper and density was calculated from these values (density = mass / volume). Hardness tests were performed on a Rockwell Tester Model 4JR and the Superficial Model 4JS, both made by Acco Wilson Industry Division. Vickers microhardness was measured on a Leco DM 400 instrument. Between 10 and 15 hardness numbers were collected and the average was reported. Four-point bending tests were performed on a screw-type Instron 4505. Between 4 and 8 samples were broken in four-point bending and the average was reported.

2.1. Preparation of poly(borazinylamine)

Poly(borazinylamine) was prepared according to the method reported by Narula *et al.* [27]. 2,4,6-Trichloroborazene (16.7 g, 90.8 mmol) was dissolved in dry diethyl ether (170 ml) and cooled to -78°C . Hexamethyldisilazane (21.9 g, 136.2 mmol) was added slowly to the reaction mixture while stirring. After complete addition, stirring was discontinued and the reaction mixture was allowed to warm slowly to room temperature. The resulting gel was converted to a xerogel by removal of volatiles in vacuum. The characterization of the xerogel and its thermal decomposition can be found elsewhere [27]. The xerogel furnished turbostratic boron nitride in 59% ceramic yield on pyrolysis at 900°C *in vacuo* then at 1200°C in air.

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2.2. General method for the preparation of metal–matrix composite bodies

The metal particles were coated with the poly(borazinylamine) by the method described by Paine *et al.* [28]. For our studies, a round-bottomed flask was charged with the metal powder and poly(borazinylamine), and then dry ammonia (30 ml) was condensed into the reaction flask. After it had been stirred for 30 min, the mixture was allowed to warm which initiated evaporation of ammonia. After complete loss of ammonia, the residue was dried *in vacuo* to remove organics such as diethyl ether trapped in the gel structure and hexamethyldisilazane from the capping groups which are released due to dissolution of the poly(borazinylamine) in liquid ammonia with breakdown of the gel structure. The solid residue was ground to a fine powder. The thermogravimetric analyses of powders showed a small weight loss due to the decomposition of the ceramic precursor. A “green bar” (3.5 mm \times 1.2 mm \times 0.5 mm) was prepared by uniaxial pressing in a rectangular die at 13.5×10^3 p.s.i. (10^3 p.s.i. = 6.89 N mm^{-2}) for 1 h followed by isostatic pressing at 40×10^3 p.s.i. for 10 min. The green bar then was transferred to a boat in a tube furnace and heated (rate 5°C min^{-1}) in an argon atmosphere at a temperature shown in Table I.

The preparation of aluminium and titanium matrix composites also was carried out by a slightly modified method. The fine polymer-coated metal powders were fired at 500°C in an argon atmosphere prior to the fabrication of the “green bar”.

The experimental details of the metal–matrix composite preparation are summarized in Table I. The nomenclature of the samples reflects the matrix metal and temperature of the preparation of MMC.

3. Results and discussion

Poly(borazinylamine) gels can be easily prepared by the reaction of 2,4,6-trichloroborazene with hexamethyldisilazane in common organic solvents (Reaction 1).

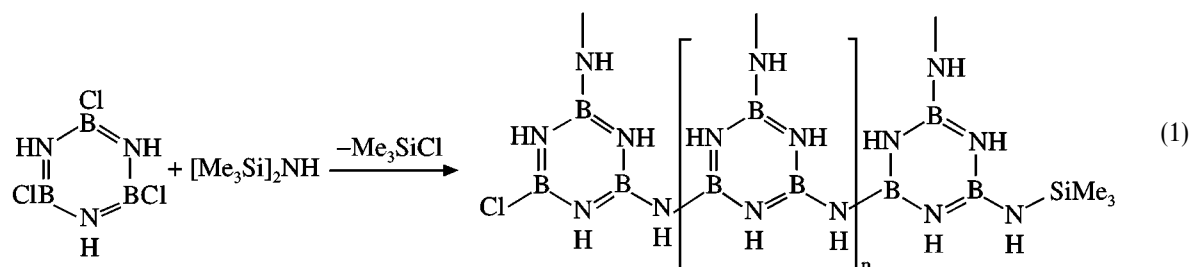


TABLE I Summary of the experimental procedure for fabrication of metal-matrix composites

Reactants		Temp. cycle		Phases observed by XRD	Density ^a	Hardness ^b	Sample																																																																																																												
Metal (g)	PBA (g)	(°C)	(h)																																																																																																																
Al (8.0)	(0.988)	250	2	Al, AlN	2.40	25.5 HV	Al/PBA/500																																																																																																												
		500	3					Al (8.0)	(0.988)	1000	3	Al, B, AlN, AlB ₂	2.55	51.2 HV	Al/PBA/1000	Al (8.0)	(0.988)	500	3	Al, AlN	2.09	23.5 HV	Al/PBA/500A ^c	Al (8.0)	(0.988)	1000	3	Al, B, AlN, AlB ₂	2.32	55.3 HV	Al/PBA/1000A ^c	Ti (8.0)	(0.556)	250	2	Ti, TiN, TiB	4.06	70.0 HRA	Ti/PBA/1200			1200	3	Ti (8.0)	(0.556)	1200	3	Ti, TiN, TiB	3.47	63.0 HRA	Ti/PBA/1200A ^c	Fe (8.0)	(0.477)	250	2	Fe, Fe ₂₃ B ₆	4.80	33.2 HV	Fe/PBA/800			800	3	Fe (8.0)	(0.477)	1200	3	Fe, B, Fe ₂₃ B ₆ , Fe ₃ N	6.60	25.0 HRA	Fe/PBA/1200	Cu (20.0)	(1.05)	250	2	Cu	6.47	37.0 HV	Cu/PBA/900			900	3	W (10.0)	(0.18)	250	2	W, W ₂ B, WN	12.1	35.0 HRA	W/PBA/1500			1500	3	Ni (16.0)	(0.91)	250	2	–	5.1	–	Ni/PBA/1000			1000	3	Ni (16.0)	(0.91)	250	2	Ni, Ni ₃ B	C	–	Ni/PBA/1200
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^a Density of metals: Al, 2.7; Ti, 4.5; Fe, 7.8; Cu, 8.9; W, 19.3; Ni, 8.9. C = too brittle to determine hardness. HV = Hardness, Vickers; HRA = Hardness, Rockwell (A).

^b Hardness of metals: Al, 150 HV (99.9%); Ti 70–74 HB (ingot), Fe, ~62.5 HV; Cu 37 HRA (cold drawn); W, ~350 HV; Ni, 64 HV (annealed).

^c Al/PBA/500A, Al/PBA/1000A and Ti/PBA/1200A were prepared by prepyrolysis method.

Further treatment of the gels with liquid ammonia has been shown to break down the gel structure, removing capping chloro- and trimethylsilyl- groups, and furnishing a solution. Evaporation of ammonia furnished a powder [27]. The pyrolysis of the poly(borazinylamine) has been proposed to involve elimination of amino groups. Facile exchange of exocyclic and ring amino groups was shown to occur by isotope labelling experiments, suggesting that ring opening also occurs during pyrolysis [29]. The resulting powder (ceramic yield 59%) is amorphous at 900 °C and crystallizes into a turbostratic phase of boron nitride at 1200 °C [27].

Thus, in the first stage, we expect the formation of a metal–matrix composite (MMC) with a highly dispersed, amorphous boron nitride ceramic phase. However, in the second stage, the reaction of amorphous boron nitride with the matrix metal also occurred at relatively low temperature, forming metal borides and nitrides as the final ceramic phases. We emphasize that the amount of poly(borazinylamine) employed in our work is 10 mol% and the resulting composites are low volume fraction MMCs with 10 mol% ceramic phase. This is different from earlier work [30,31] in which boron nitride precursors were reacted with metals in stoichiometric amount with the intention to prepare bulk powders of metal borides and/or nitrides. We would also like to point out that we report the value of ceramic content in mole per cent instead of volume per cent for simplicity. The value in mole per cent can be converted easily to the volume per cent employing the densities of ceramic phases formed. For example, Al/PBA contains 8.0 g Al and 0.988 g PBA. After pyrolysis of PBA, the sample contains 8.0 g Al (density of aluminium = 2.7) and 0.58 g amorphous

boron nitride [27] (density 2.0). A simple conversion to volume shows a 8.91 vol% ceramic phase. In another example, W/PBA contains 10.0 g W and 0.18 g PBA which converts to 0.10 g amorphous boron nitride on pyrolysis. A simple conversion shows 9.12 vol% amorphous BN in the composite.

The MMCs were prepared by suspending the metal powder of – 325 mesh particle size in a liquid ammonia solution of the poly(borazinylamine), removing volatiles and pyrolysing the samples at 500 °C or higher at a rate of 5 °C min⁻¹. The green bodies fabricated from this material did not exhibit any disintegration, even after storage for several hours in a polyethylene bag. In other experiments, the aluminium and titanium particles coated with poly(borazinylamine) were subjected to a slightly different thermal treatment to determine the effect of the evolving poly(borazinylamine) pyrolysis products on MMC formation. The coated particles were first pyrolysed at 500 °C in an argon atmosphere to complete the weight loss and then the “green body” was fabricated and sintered at high temperatures. Our results show that this procedure offers no advantages, because the *in situ* pyrolysis furnishes MMCs of higher density than those obtained from such prepyrolysed starting materials.

Traditional powder metallurgy processes generally involve hot-pressing for fabrication of dense bodies. Because our process did not involve hot pressing, we did not expect highly dense MMCs. To our surprise, aluminium- and titanium-based MMCs attained densities as high as 2.55 and 4.06 g cm⁻³, respectively, which compares very well to the theoretical densities of the metals (Al 2.7; Ti 4.5). Iron-, copper-, nickel-, and tungsten-based MMCs attained only ~65% of the theoretical densities of the matrix metals. We

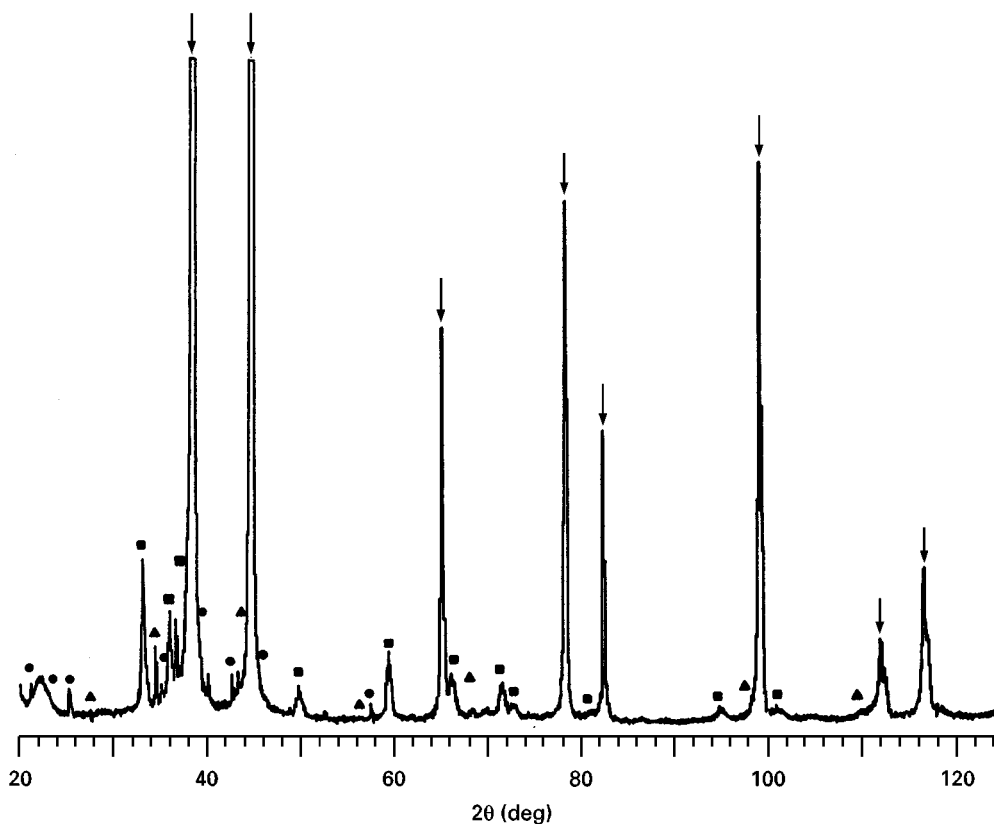


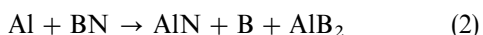
Figure 1 XRD of Al/PBA/1000. (↓) Al (JCPDS 4787), (●) B (JCPDS 17 788), (▲) AlB₂ (JCPDS 9154), (■) AlN (JCPDS 8262).

compare the densities of our MMCs with the density of the metals because the calculated densities of the MMCs with only 10 mol% ceramic phase are not significantly different.

The modulus of rupture of Al/PBA/1000 was found to be 14.5×10^3 p.s.i. The modulus of elasticity is 0.72×10^6 p.s.i. which is about ten times lower than that of aluminium or aluminium alloys. This is quite surprising, considering that an aluminium alloy containing 5%–6% alumina shows a modulus of elasticity comparable with that of aluminium.

3.1. X-ray powder diffraction (XRD)

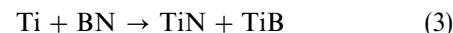
All diffraction patterns were interpreted on the basis of a complete match with diffraction patterns in JCPDS files. The XRD of Al/PBA/500 shows the diffraction pattern for aluminium metal (JCPDS card 4-787) and aluminium nitride (JCPDS card 25-1495) even at 500 °C. The presence of aluminium nitride suggests that nitridation of aluminium by amorphous boron nitride has occurred (Reaction 2). The resulting boron species are amorphous at this temperature.



The samples heated at 1000 °C, Al/PBA/1000, exhibit diffraction peaks (Fig. 1) due to elemental boron (JCPDS card 17-788) and aluminium boride (JCPDS card 9-154), in addition to the peaks due to aluminium and AlN.

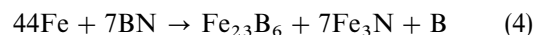
The XRD of Ti/PBA/1200 shows diffraction peaks due to titanium nitride (JCPDS card 38-1420) and titanium boride (JCPDS card 5-700) in addition to titanium (JCPDS card 5-682) from the matrix (Fig. 2),

which may be rationalized in terms of Reaction 3



The X-ray powder diffraction patterns of aluminium and titanium MMCs, Al/PBA/500A, Al/PBA/1000A and Ti/PBA/1200A prepared by the prepyrolysis routes are identical to those of Al/PBA/500, Al/PBA/1000 and Ti/PBA/1200, respectively.

The XRD of the iron-based MMC heated to 800 °C, Fe/PBA/800, shows diffraction patterns (Fig. 3) of iron (JCPDS card 6-696) and iron boride, Fe₂₃B₆ (JCPDS card 34-991). Although no nitrogen-containing species is seen, it is possible that nitrogen is occupying octahedral holes in the iron matrix [32]. Diffraction peaks due to crystalline Fe₃N (JCPDS card 1-1236) and elemental boron can be seen in the X-ray powder diffraction of a sample heated at 1200 °C, Fe/PBA/1200, supporting our explanation for the absence of iron nitride in Fe/PBA/800. The theoretical Reaction for the Fe/BN reaction is



Despite its low ceramic content, the composite showed high resistance towards rusting.

The X-ray diffraction pattern of the copper-based composite, Cu/PBA/900, shows diffraction peaks due to copper (JCPDS card 4-836) only (Fig. 4). Because copper does not react with nitrogen or ammonia at this temperature [33] and the only known copper nitride, Cu₃N, is unstable above 300 °C [34], it is unlikely that copper nitride was formed. Furthermore, copper borides are generally prepared at much higher

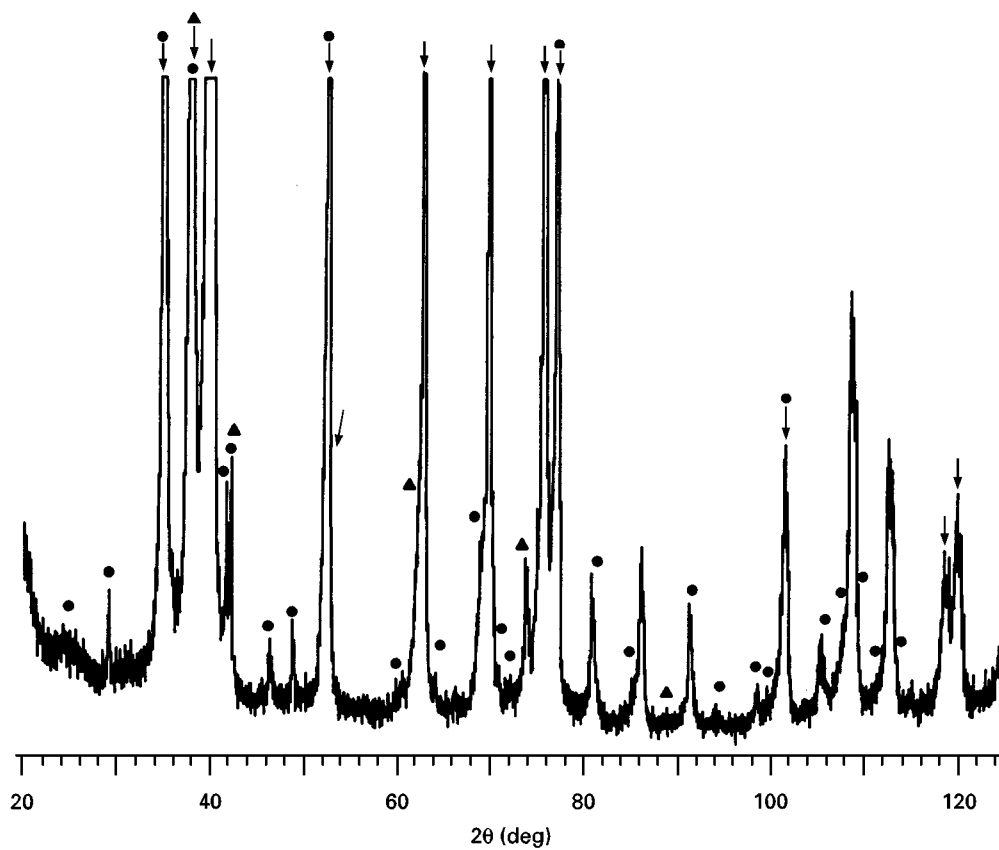


Figure 2 XRD of Ti/PBA/1200. (↓) Ti(JCPDS 5682), (●) TiB (JCPDS 5700), (▲) TiN (JCPDS 381420).

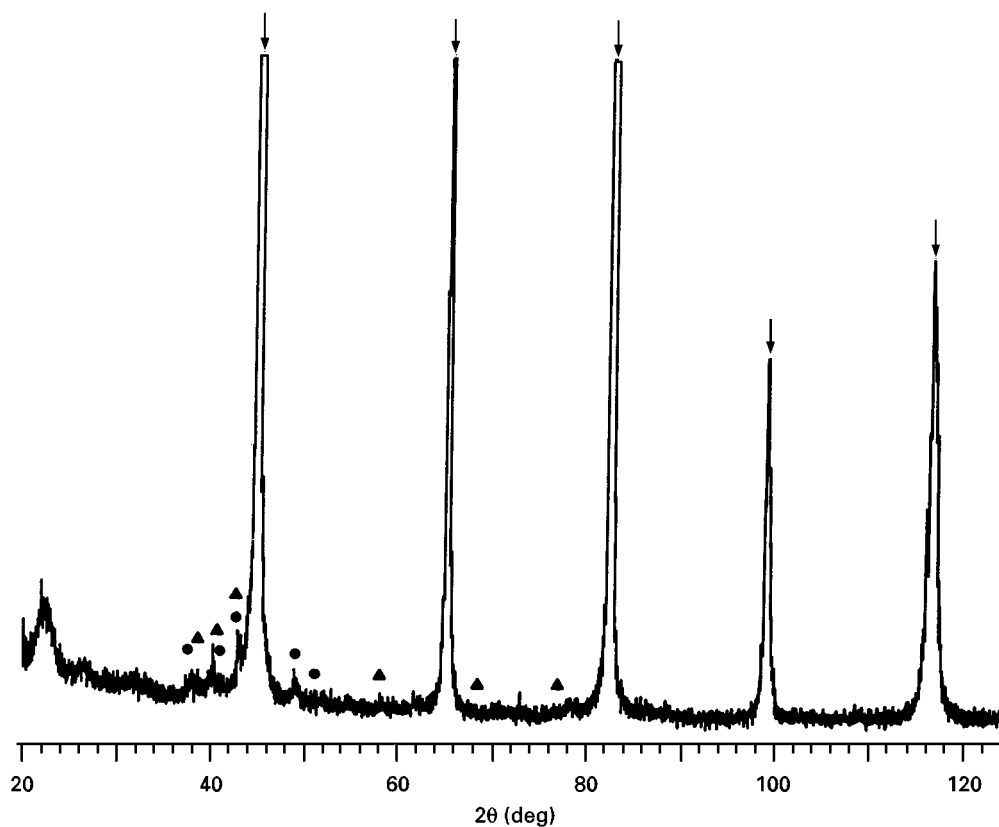


Figure 3 XRD of Fe/PBA/800. (↓) Fe (JCPDS 6696), (●) Fe₂₃B₆ (JCPDS 34991), (■) Fe₃N (JCPDS 11236).

temperatures [35]. Thus, the absence of copper boride, copper nitride, and elemental boron suggests that the Cu/PBA/900 composite comprises copper and amorphous boron nitride.

The X-ray diffraction pattern of W/PBA/1500 shows the diffraction peaks due to tungsten boride (JCPDS card 6-591) and nitride (JCPDS card 25-1256) (Reaction 5) (Fig. 5) which is not surprising, because

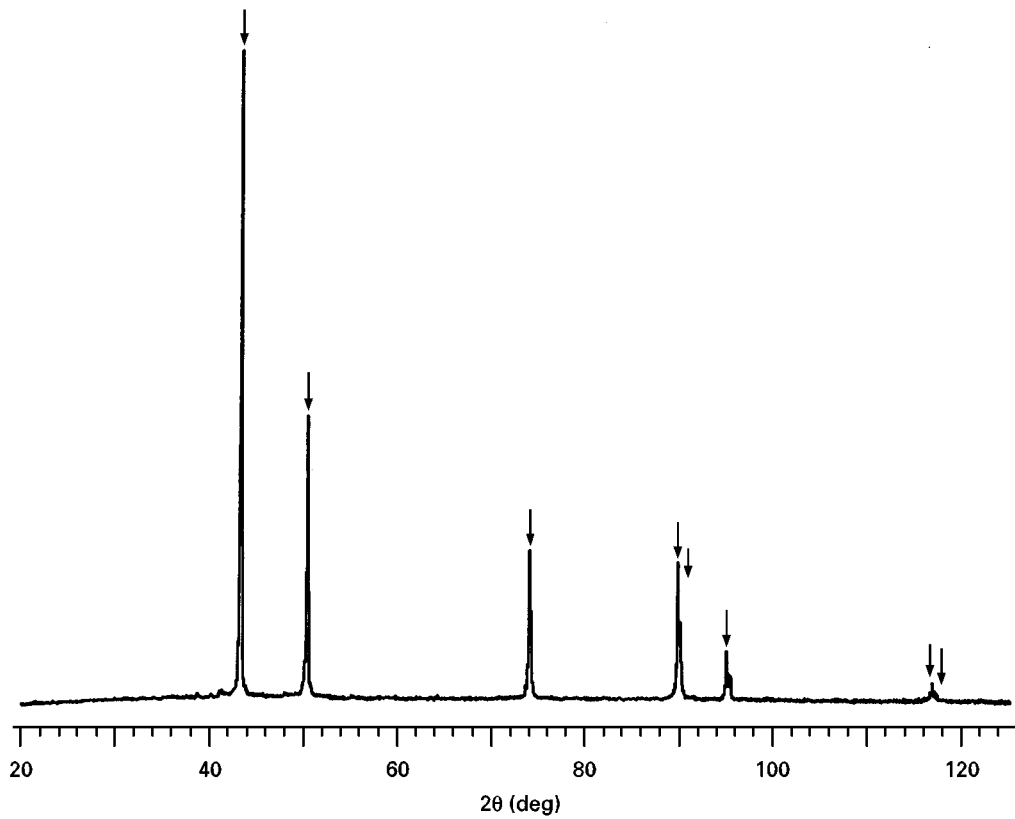


Figure 4 XRD of Cu/PBA/900. (↓) Cu (JCPDS 4367).

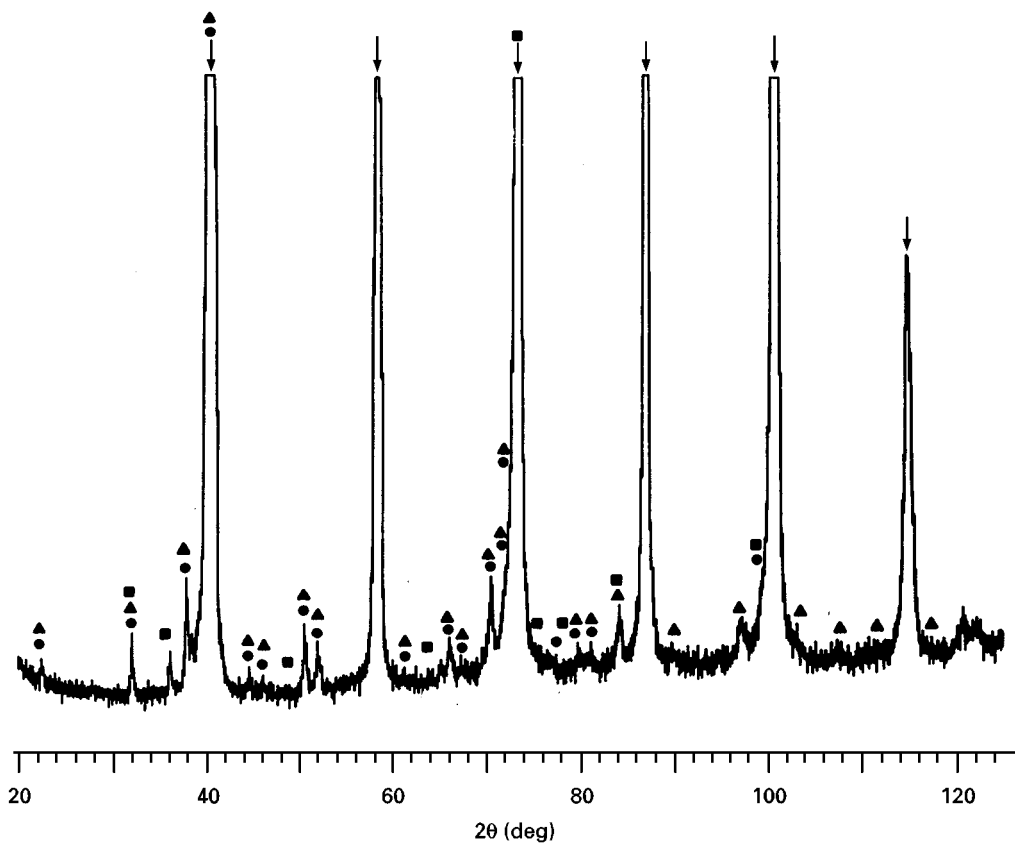
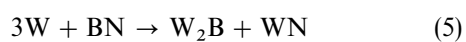


Figure 5 XRD of W/PBA/1500. (↓) W (JCPDS 4806), (●) W_2B (JCPDS 6591), (▲) W_2B (JCPDS 25930), (■) WN (JCPDS 251256).

both materials are stable at this temperature



The X-ray diffraction of Ni/PBA/1200 exhibits peaks due to nickel (JCPDS card 4-850) and nickel

boride, Ni_3B (JCPDS card 19-834), and there is no evidence of the presence of nitrides (Fig. 6).

These X-ray diffraction studies thus have shown that low volume fraction MMCs containing metal borides and nitride ceramic phases can be prepared at

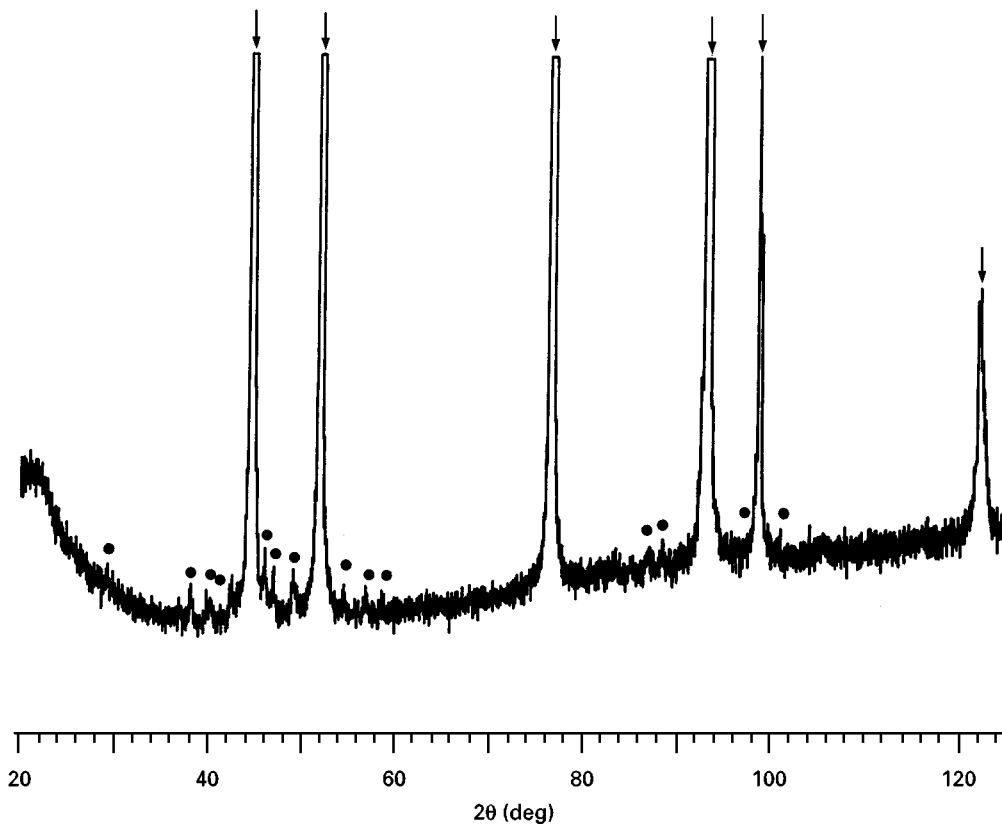


Figure 6 XRD of Ni/PBA/1200. (↓) Ni(JCPDS 4850), (●) Ni₃B (JCPDS 19834).

relatively low temperature from poly(borazinylamine) and a metal powder matrix. The exception is the copper–amorphous boron nitride MMC, where poly(borazinylamine) or amorphous boron nitride fail to react with the copper matrix. This is probably due to instability of copper nitrides.

3.2. SEM and XPS studies of selected MMCs

A scanning electron micrograph of Cu/PBA/900 shows loosely bonded ceramic grains in a copper matrix (Fig. 7a). This morphology is desirable for improving the fracture toughness of the composite by dissipating the crack growth energy through the open ceramic–metal interface [36]. The identity of the ceramic phase could not be determined by XRD. However, the XPS suggests that the ceramic phase is amorphous boron nitride, although on the surface, oxide species also are present. The XPS of Cu/PBA/900 exhibits Cu 2p₁, Cu 2p₃, Cu 3p, B 1s, and N 1s peaks. The B 1s window contains three peaks at 190.8, 192.0 and 194.0 eV (Fig. 8a) and there are two peaks in the N 1s window at 398.4 and 400 eV (Fig. 8b). The peaks at 190.8 and 194.0 eV correspond to the binding energies of B 1s for boron nitride [37] and boron oxide [38], respectively. The third peak at 192.0 eV most probably is due to boron nitride oxide [39]. This assignment is supported by the presence of two peaks in the N 1s window – the peak at 398.4 eV which is characteristic of nitrides [37] and the peak at 400 eV due to nitride oxides [40].

The scanning electron micrograph of Fe/PBA/800 failed to show any ceramic phase, although XRD showed the presence of iron boride in the sample (Fig.

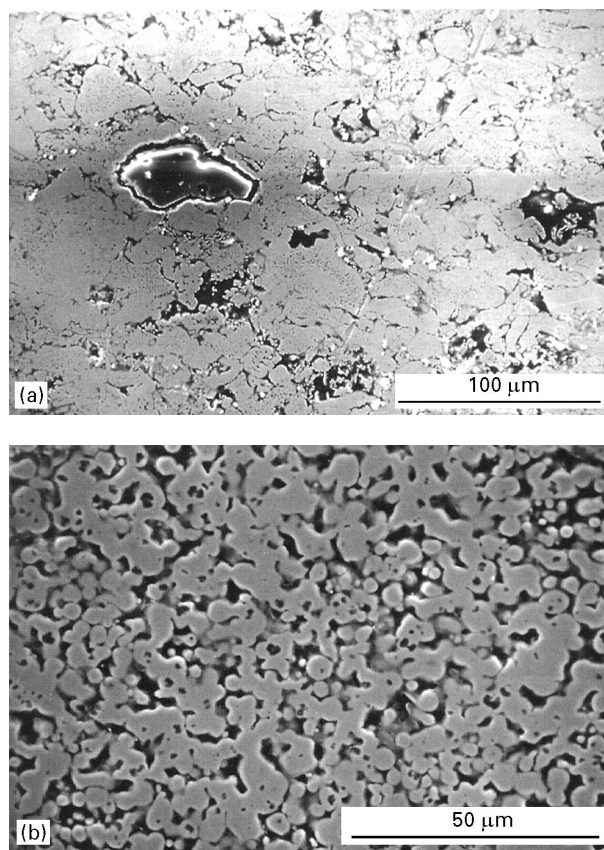


Figure 7 Scanning electron micrographs of (a) Cu/PBA/900, and (b) Fe/PBA/800.

7b). In addition, the composite is poorly sintered which is commensurate with its low density. The XPS of Fe/PBA/1200 shows Fe 2p₃, Fe 3s, Fe 3p, B 1s, and N 1s peaks. There is no evidence of iron borides on the

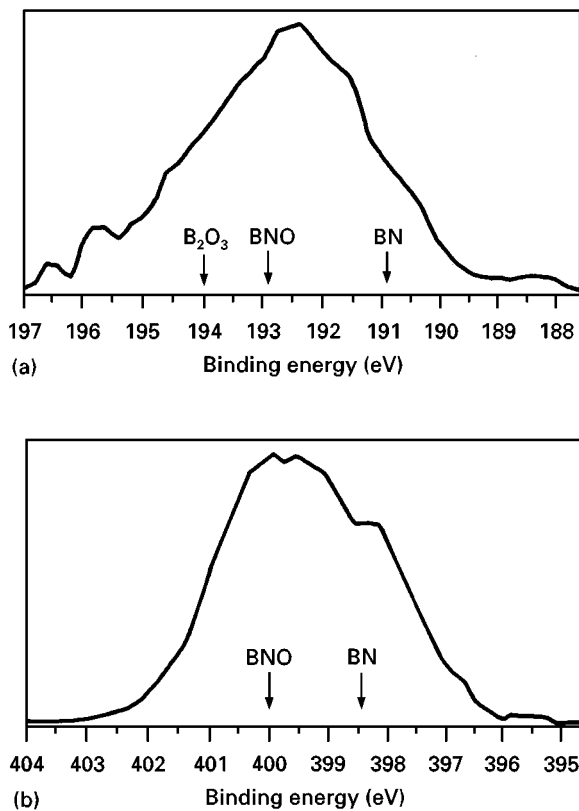


Figure 8 (a) Boron 1s window of the XPS of Cu/PBA/900. (b) Nitrogen 1s window of the XPS of Cu/PBA/900.

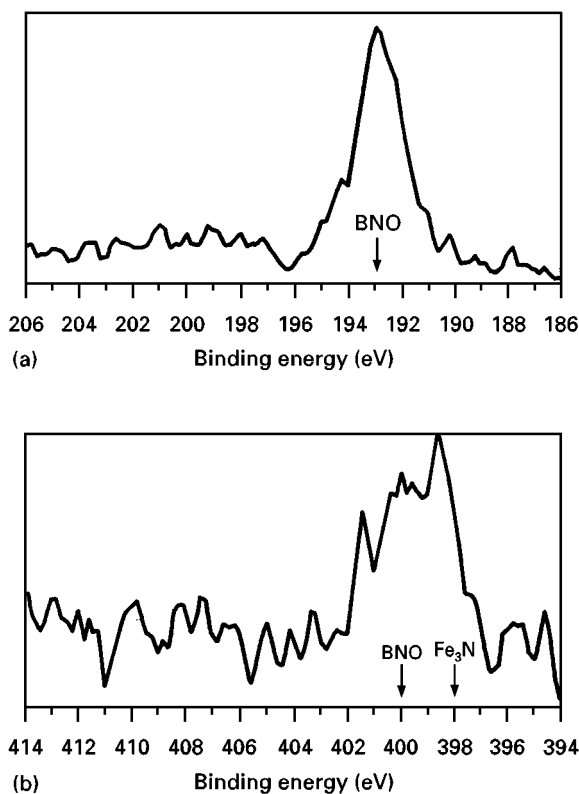


Figure 9(a) Boron 1s window of the XPS of Fe/PBA/1200. (b) Nitrogen 1s window of the XPS of Fe/PBA/1200.

surface. There is only one peak in the B 1s window at 192.8 which is assigned to boron nitride oxide (Fig. 9a). The N 1s window shows two peaks at 398 and 400 eV which can be assigned to iron nitride and boron nitride oxide, respectively (Fig. 9b).

The XPS of Al/PBA/1000 and W/PBA/1500 do not exhibit boron or nitrogen peaks, suggesting that the boron-containing species are not on the surface but beneath the metal oxide layers.

4. Conclusion

Poly(borazinylamine) is a suitable precursor for the fabrication of low volume fraction MMC bodies. It acts as a source of amorphous boron nitride or metal borides and metal nitrides, depending on the reactivity of amorphous BN towards the matrix metals. Although our method of fabrication did not involve hot pressing, the aluminium- and titanium-based MMCs prepared in this work show high density (90% of the theoretical density of aluminium and titanium metals) and hardness. Additionally, no other organic or inorganic binder is necessary in our fabrication process, and the minor weight loss that occurs during the conversion of poly(borazinylamine) into boron nitride or metal borides does not deteriorate the properties of MMCs. Finally, our method can be extended to prepare MMCs of alloys such as Al-Si, Al-Si-Cu, Al-Si-Mg, etc. (which are commonly used in the automotive industry) by a slight modification of the powder metallurgy route used to fabricate the alloys [1].

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