

The microstructure and mechanical properties of Al-Si-B₄C metal matrix composites

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B₄C particles have been added to molten Al-7wt% Si-0.3 wt% Mg alloys, at levels of 5 and 10 wt%, using a proprietary K-Al-Ti-F flux. The resulting composites were examined metallographically and mechanically tested in the as-manufactured condition and after heat treatment for 48 hours at 500°C and 700°C. During incorporation into the melt, a complex Ti-B-C reaction layer was formed on the particle surfaces. The reaction layer remained intact during heat treatment and the stable, protective nature of this layer gave rise to a significantly reduced rate of particle degradation compared to other Al-B₄C composites. Significant increases in stiffness were observed; modulus increases per volume percent of particles added were similar to those for the Al-TiC system where strong interfacial bonding occurs. Improved adhesion between the solidified matrix and the B₄C reinforcement was encouraged by the enhanced metallic character of the reaction layer. Solid state reaction at 500°C produced little change in mechanical properties. Heat treatment and reaction at 700°C resulted in an increase in the volume fraction of stiff, brittle reinforcing phases, leading to an increase in stiffness and a decrease in ductility. © 2002 Kluwer Academic Publishers

1. Introduction

Boron carbide is an attractive reinforcement for aluminium and its alloys. It shows many of the mechanical and physical properties required of an effective reinforcement, in particular high stiffness, 445 GPa, and hardness, 3700 Hv, [1] matching and even surpassing those of conventional reinforcements such as Al₂O₃ and SiC. These factors, combined with a density, 2510 kg m⁻³ [1], less than that of solid aluminium, 2700 kg m⁻³ [2], indicate that large specific property improvements are possible and specific properties will improve with increasing particle addition. The small density difference between B₄C and molten Al, 2385 kg m⁻³ [2], means that particle sedimentation rates are low, minimising settling problems observed during solidification processing. The main reason B₄C is not always an obvious choice of reinforcement for MMCs is its high cost compared to SiC.

Since B₄C has a similar free energy of formation to SiC, -69 kJ mol⁻¹ and -65 kJ mol⁻¹ at 727°C respectively [3], there are concerns over its chemical stability and hence its suitability as a reinforcement for Al. Work focussed on the fabrication of B₄C-Al cermets has shown that B₄C and Al do react [4–6]. The exact compositions of the reaction products are, however, in some doubt. Reactions occurring between 600°C and 900°C are thought to produce AlB₂ and either an Al₄BC [4, 5] or Al₃BC [6] phase.

B₄C particles were also found to be unstable in Al-Si-Mg-Ti matrices [7]. In the solution treated and aged condition, reaction products were identified either at

or near the particle-matrix interface [7, 8]. No such reaction was observed for SiC particles. In a separate study, the rate of dissolution of B₄C in pure Al was found to be four times that of SiC [9].

Few studies have investigated the mechanical property advantages offered by adding low volume fractions, less than 30 vol%, of B₄C particles to Al; most of the previous research in this area having been focussed on producing cermets [4, 5, 10–14]. Those studies that have measured mechanical property improvements have shown increases for B₄C to be greater than those for similar additions of SiC particles [8, 15]. In the case of Al-Si-Mg-Ti alloys, this is in spite of extensive reaction [8]. Differences in mechanical properties between Al-SiC and Al-B₄C composites, in particular those manufactured by a liquid route, have been attributed to improved wetting, and hence interfacial bonding, in the Al-B₄C system [10, 15, 16].

2. Experimental procedure

B₄C particles were added to molten Al-7wt% Si-0.3 wt% Mg alloy metal charges heated to 800°C in clay-bonded SiC crucibles. The particles, supplied by Boride Ceramics Ltd, Newport, UK, were, on average, 25 μm in diameter but varied widely in size from 2 to 60 μm. In order to facilitate the incorporation of B₄C particles into molten aluminium, a proprietary K-Al-Ti-F flux was co-added with B₄C powder to the surface of the melt. After addition of the powder mixture, a liquid flux was formed which was left on the

melt surface for no more than 10 minutes before being removed, after which the melt was immediately cast.

The total mass of the flux was always equal to the mass of B_4C added and the flux composition was such that the mass ratio of Ti to B_4C in the powder mixture was 0.07. In this way 100% of the particles added were transferred to the metal. Additions were made at levels of 5 and 10 wt% (5.4 and 10.7 vol% respectively). Composites were cast into a cylindrical, cast iron mould. Sections from cast samples were heat treated in the solid state, at $500^\circ C$, and in the liquid state, at $700^\circ C$, for 48 hours.

Specimens for metallographic examination were dry ground on SiC wheels and polished using diamond wheels to a $1 \mu m$ finish. Care was taken not to grind, polish or clean the samples with water because of reaction with Al_4C_3 , which may be present as a reaction product, to produce Al_2O_3 and methane gas. Optical microscopy, scanning electron microscopy (SEM), in backscattered mode, and energy dispersive x-ray anal-

ysis (EDX) were used to identify the presence and approximate composition of reaction products.

Mechanical testing was performed on composites and un-reinforced alloys, to determine the effect of particle additions. Specimens heat-treated in the solid-state were also tested to explore the possible effects of reaction on mechanical properties. The modulus was measured and averaged over three loading cycles using a twin strain gauge method outlined by Clyne and Withers [17]. The 0.2% proof stress, ultimate tensile stress and ductility were also measured. The results represent an average of four samples tested.

3. Results

3.1. Microstructure in the as-cast composite

Fig. 1 shows an optical micrograph and Fig. 2 an SEM micrograph of a composite containing 5 wt% of B_4C reinforcement. It can be seen from these two micrographs that small-scale clustering of the reinforcing

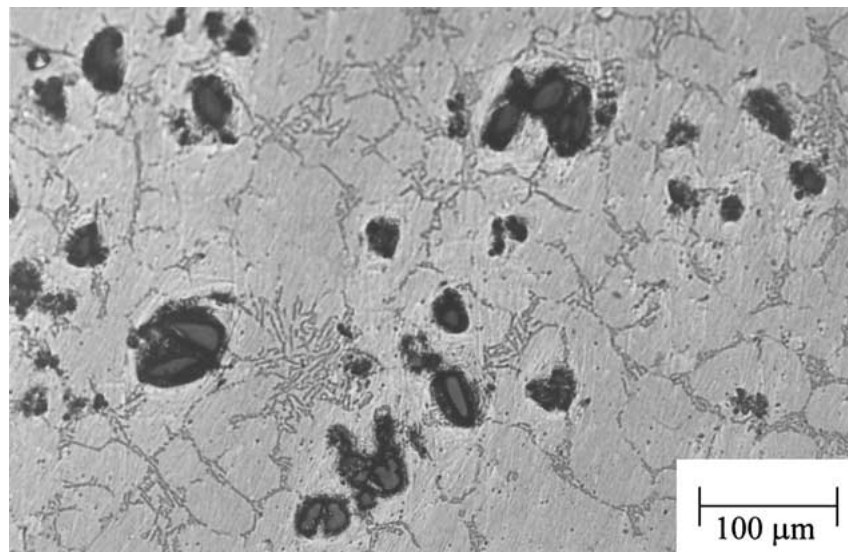


Figure 1 Optical micrograph showing the microstructure of an Al- B_4C composite in the as-manufactured condition.

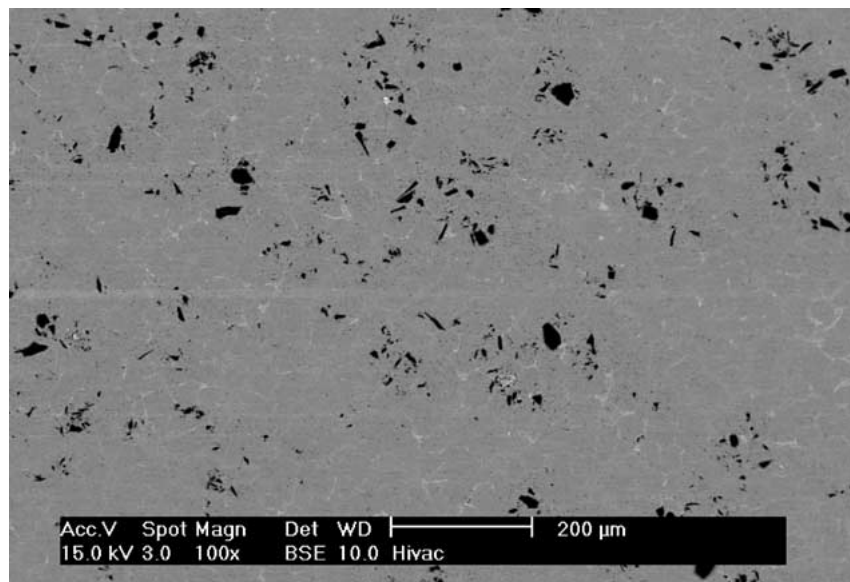


Figure 2 SEM image showing the distribution of B_4C particles in a composite in the as-manufactured condition.

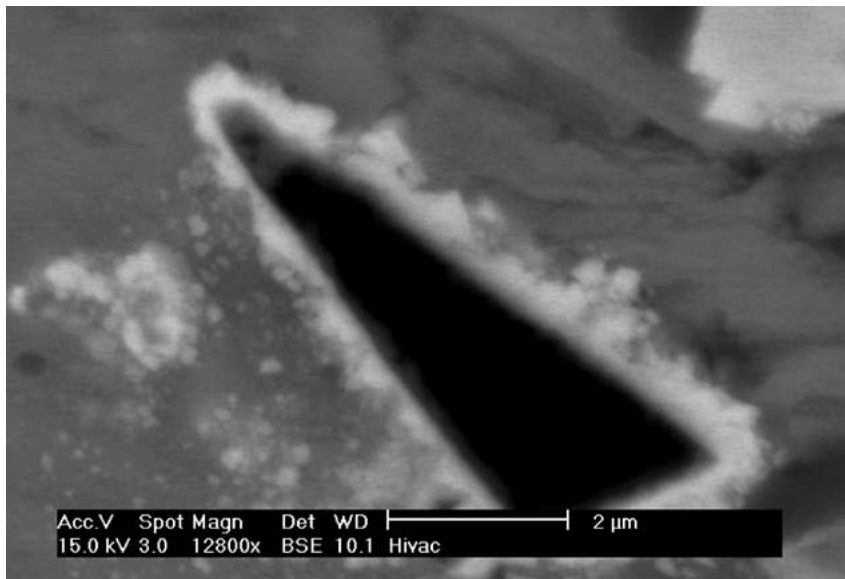


Figure 3 SEM image highlighting the interface between the matrix and the B₄C reinforcement in a composite in the as-manufactured condition.

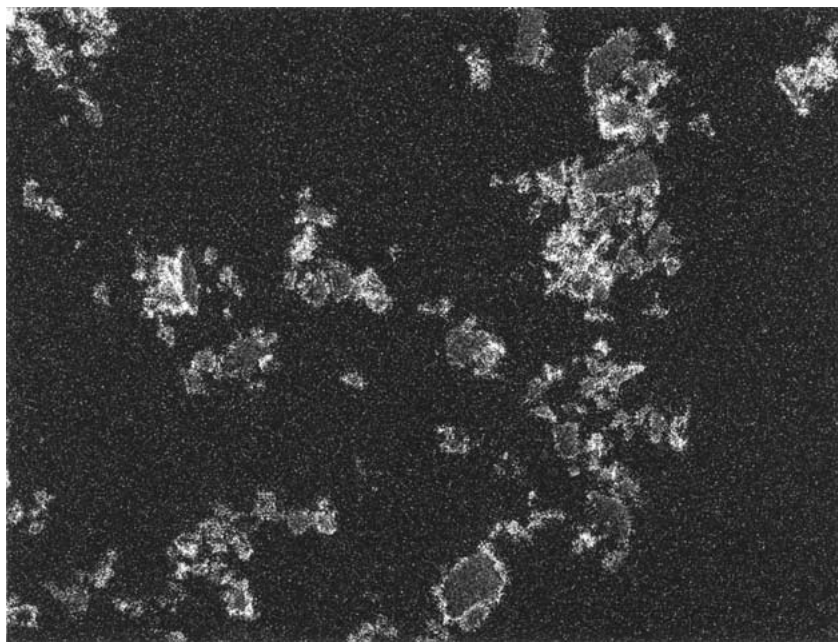


Figure 4 An elemental map of titanium (light) and boron (grey) in an as-manufactured composite.

phase occurs, although this is not severe, and that the particles are associated with the eutectic phase. There is some relief at the particle-matrix interface generated during polishing and hence the presence of interfacial reaction products is better studied in the SEM.

Fig. 3 presents higher magnification SEM micrographs that more clearly highlight the interface between the B₄C particles and the matrix. In these backscattered electron images a lighter phase, of higher atomic mass, surrounds the particles. For most particles this phase appears to be continuous; in others some fragmentation has occurred, possibly as a result of mechanical grinding and polishing. Elemental mapping for boron, grey, and titanium, light, presented in Fig. 4, indicates that a Ti-rich layer surrounds the particles. The Ti-containing layer is too thin compared to the spot size to enable energy dispersive X-ray analysis using the SEM. Preparation and analysis of the fragile interface

by transmission electron microscopy also proved very difficult.

Besides the Ti-containing layer there was little evidence of other inter-metallic, carbide or boride compounds either at the particle-matrix interface, or in the bulk of the matrix, suggesting that limited reaction occurs between B₄C and Al during manufacture.

3.2. Microstructure in heat treated composites

Figs 5 and 6 show the microstructures of composite heat-treated at 500°C for 48 hours. It is clear that the eutectic Si has spheroidised during heat treatment. The reinforcement is still, of course, associated with the eutectic phase. There are some signs of reaction products, shown more clearly in the SEM micrograph in Fig. 6. Reaction products, which appear as dark grey blocks, are present both in the bulk of the matrix

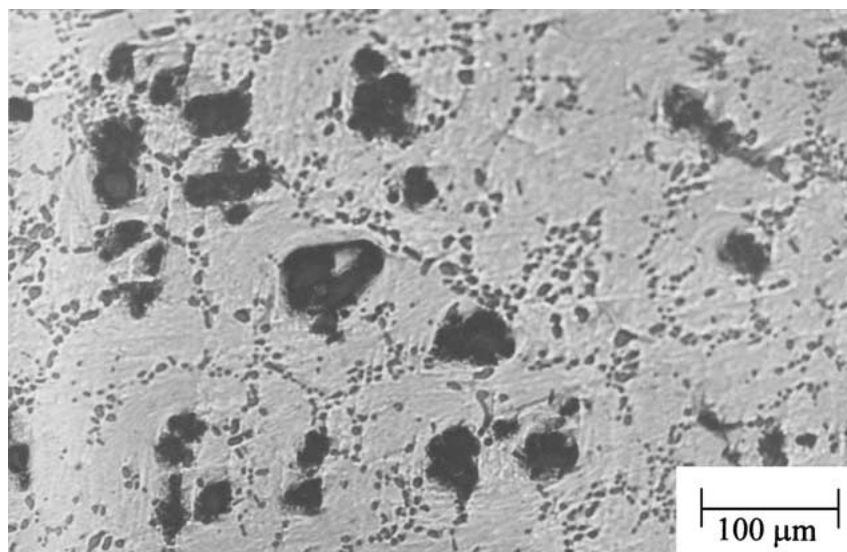


Figure 5 Optical micrograph showing the microstructure of an Al-B₄C composite heat-treated at 500°C for 48 hours.

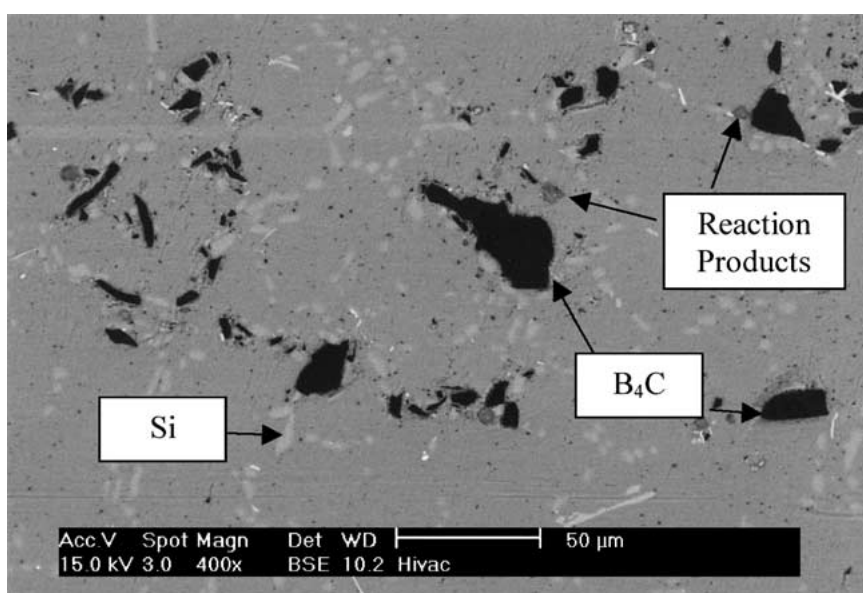


Figure 6 SEM image showing an Al-B₄C composite heat-treated at 500°C for 48 hours.

and attached to the carbide particle surfaces. EDX revealed these blocks to be AlB₂. Al₄C₃ particles were not observed. The light needles were identified as a Fe-rich inter-metallic often observed in cast Al-Si-Mg alloys. The micrograph in Fig. 7 shows that for many of the particles, the Ti-rich layer is still intact after heat treatment.

Fig. 8 presents an optical micrograph of the microstructure of the composite heat treated at 700°C for 48 hours. In this sample the eutectic Si is present as needles and the dendrite structure is coarser than that observed in the as-fabricated material. The particles are still associated with the eutectic phase. The SEM micrograph in Fig. 9 indicates that there are signs of reaction products, again with some particles in the bulk of the matrix and others attached to the carbide particle surfaces. Partial coverage of the reinforcement with a Ti-rich layer can be observed in this figure. EDX analysis of the reaction products revealed the grey blocks to be AlB₂, and the light blocky phases to be TiB₂. There

was no evidence of Al₄BC, Al₃BC or Al₄C₃ reaction products growing on the particle surfaces. It should be noted that there were insufficient concentrations of any of the reaction products for identification using X-ray diffraction.

3.3. Mechanical properties

From mechanical property data in Table I it can clearly be seen that, with the exception of the ductility, the addition of B₄C particles improves the mechanical properties of the resulting composite compared to the base alloy. Whilst the increases in yield and tensile stresses are relatively modest, the improvements in stiffness are large, corresponding to approximately 2 GPa per volume percent of particles added. Since the addition of boron carbide lowers the density of Al, the specific modulus values are also high, roughly 30 and 34 MNm kg⁻¹ and increase with increasing particle addition.

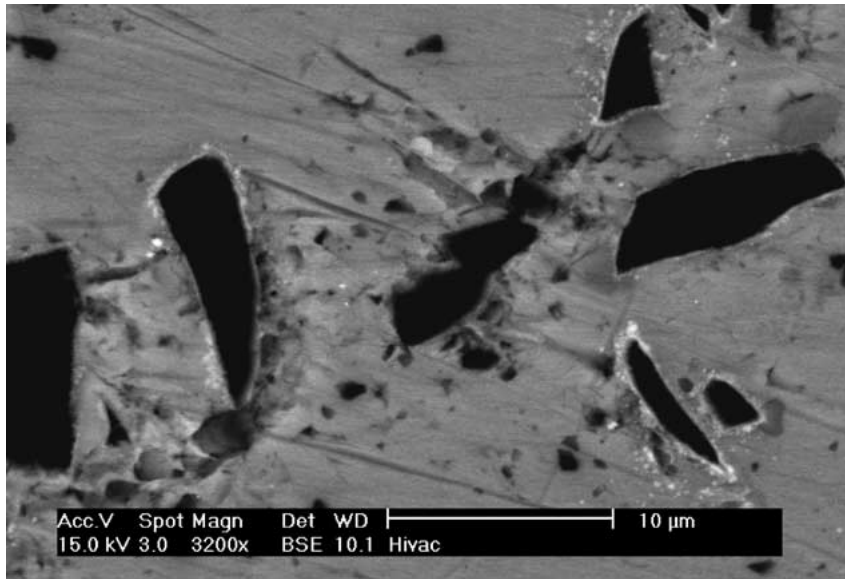


Figure 7 SEM micrograph showing the presence of a Ti-rich layer on many of the B₄C particles after heat treatment at 500°C for 48 hours.

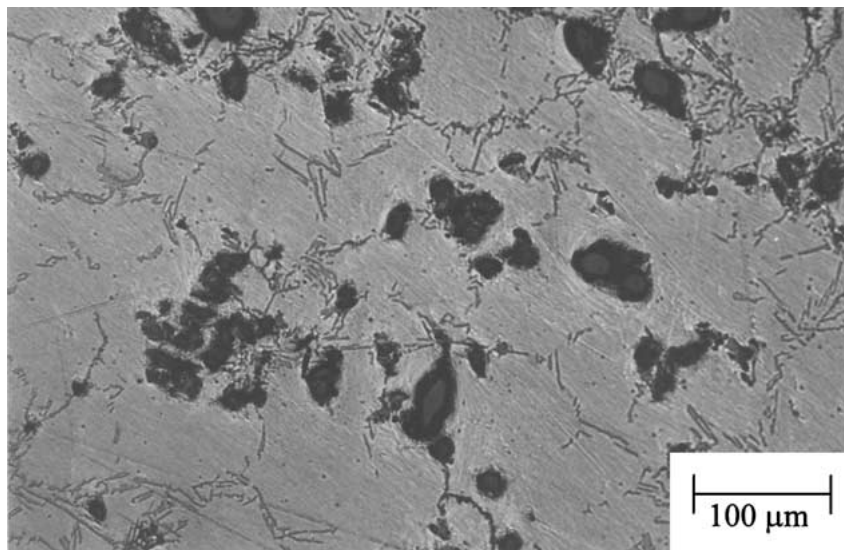


Figure 8 Optical micrograph showing the microstructure of an Al-B₄C composite heat-treated at 700°C for 48 hours.

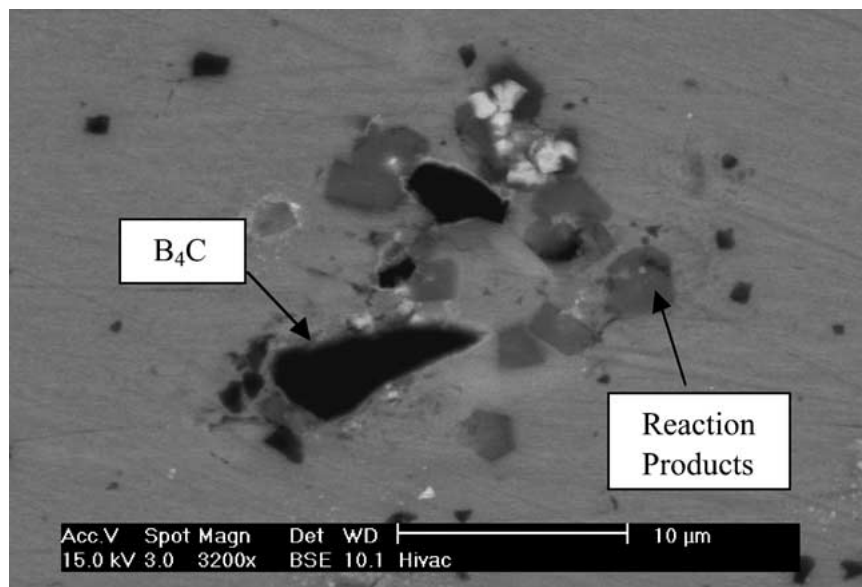


Figure 9 SEM image showing an Al-B₄C composite heat-treated at 700°C for 48 hours.

TABLE I Mechanical properties for the base alloy and composites in the as-manufactured condition

	σ_y (MPa)	σ_{UTS} (MPa)	Elongation (%)	Modulus (GPa)	E/ρ (MNn kg ⁻¹)
Al-7Si-0.3Mg	99 ± 3	138 ± 5	3.5 ± 0.5	70 ± 1.0	25.9
Al-7Si-0.3Mg-5wt% B ₄ C	106 ± 4	165 ± 7	2.8 ± 1	81 ± 1.5	30.1
Al-7Si-0.3Mg-10wt% B ₄ C	120 ± 7	188 ± 9	1.6 ± 1	90 ± 2.0	33.6

TABLE II Mechanical properties for the base alloys and composites in the as-manufactured and heat-treated conditions

	σ_y (MPa)	σ_{UTS} (MPa)	Elongation (%)	Modulus (GPa)
Al-7Si-0.3Mg	99 ± 3	138 ± 5	3.5 ± 0.5	70 ± 1.0
Al-7Si-0.3Mg (500°C, 48 hrs)	92 ± 2	120 ± 3	4.7 ± 1.0	70 ± 1.5
Al-7Si-0.3Mg (700°C, 48 hrs)	88 ± 3	110 ± 3	3.8 ± 0.5	70 ± 1.5
Al-7Si-0.3Mg-5wt% B ₄ C	106 ± 4	165 ± 7	2.8 ± 0.5	81 ± 1.5
Al-7Si-0.3Mg-5wt% B ₄ C (500°C, 48 hrs)	97 ± 3	145 ± 8	2.6 ± 0.5	82 ± 2.0
Al-7Si-0.3Mg-5wt% B ₄ C (700°C, 48 hrs)	98 ± 2	151 ± 6	1.6 ± 0.5	87 ± 2.0

Heat treatment at 500°C for 48 hours results in similar decreases in yield and tensile strengths in both the composite and the base alloy. The ductility increases slightly in the heat-treated base alloy whereas the ductility of the heat-treated composite is similar to that in the as-manufactured state. In the composite a small increase in stiffness was measured after heat treatment.

Holding the un-reinforced alloy at 700°C for 48 hours results in decreases in yield and tensile strength and a slight increase in ductility. The modulus remained unchanged. Decreases in the yield, tensile strength and ductility, and a significant increase in the modulus of the composite, were observed after holding in the liquid state.

4. Discussion

B₄C particles were incorporated into the melt with a Ti-rich layer covering their surfaces. It is thought that this layer is generated during manufacture by reaction between the B₄C particles and Ti from the flux as they are added to the surface of the melt. Reaction between Ti and B₄C is energetically favourable and highly exothermic [3]. The reaction products that surround the B₄C particle are likely to comprise a mixture of titanium borides (TiB₂ and TiB) and titanium carbide [18].

The compounds in the reaction layer have more metallic character [19] to their bonding than covalently-bonded B₄C and this aids wetting by molten Al. Without Ti in the flux it is impossible to incorporate B₄C particles into Al but it is possible to incorporate TiB₂ and TiC particles using this method [20]. Thus, when sufficient coverage with the reaction layer has been achieved, wetting is possible and the particles are incorporated into the bulk of the melt.

The particles do not stimulate grain refinement and, as such, do not become engulfed into the primary Al during solidification. The result is that the particles reside in the eutectic regions between the dendrites with the last liquid to freeze. This type of structure is similar to that observed for TiB₂ particles in Al-Si alloys [21]. Since the partition coefficient in the Al-Ti system is greater than unity, the last liquid to freeze will be depleted rather than enriched in solute and it is, therefore,

highly unlikely that any Ti at the particle surfaces is due to local solute enrichment during solidification.

In other Al-B₄C studies, reactions at 530°C [7] and at 727°C [6] were extensive even for short holding times. In the Al-Si-Mg-Ti system [7], for particles similar in size to those used here, a 17 hour hold at 530°C produced a continuous, 5 μm thick reaction zone around all the particles. In these composites 0.2 wt% Ti was present, but was ineffective at protecting the particles. For an Al-B₄C composite, 48 hours at 727°C resulted in over half the B₄C being consumed [6].

In the composites produced in this study, where the Ti level is close to 0.4 wt%, the only reaction product detected was AlB₂. Al-B-C compounds and Al₄C₃ particles were not observed. Clearly if the boron carbide particles are dissolving, reaction products containing carbon should also be detected, as the solubility of carbon in Al is extremely small. It is possible that because the extent of reaction was limited, detection of these reaction phases is very difficult.

The rate of reaction observed for B₄C particles in these composites is much reduced compared to those made by powder metallurgy or infiltration [6, 7] and it is thought that this is due to the presence of the Ti-containing surface layer which acts as a barrier coating. TiB₂, unlike B₄C has a very negative free energy of formation [3] and TiB₂ particles are known to be stable in Al-Si alloys [21]. For some particles, however, the protective layer does not appear to be continuous, this is perhaps not a requirement for wetting and incorporation into the liquid, and hence some reaction does occur. It is possible that the reaction layer may degrade with time, either due to erosion in the melt during processing or degradation of the TiC component in the reaction layer, as there are questions over the stability of TiC in Al-Si alloys. Reaction is, as expected [6], faster in the liquid state than in the solid state.

Significant increases in stiffness were observed with the addition of reinforcement to the matrix. Modulus increases per volume percent of particles added are similar to those measured in the Al-TiC system, where strong interfacial bonding is thought to occur, and significantly higher than those in the Al-Si-SiC system [22] and Al-B₄C composites made by powder

metallurgy [23]. Interfacial reaction layers thinner than one micron are thought to be beneficial to mechanical properties [24] since they usually enhance both the chemical and mechanical bonding between the particle and the matrix giving, in particular, improved stiffness. The thin reaction layer observed in these composites is likely to improve the adhesion, and hence load transfer between the solidified matrix and the reinforcement, due to the enhanced metallic character of the coating which encourages strong chemical bonding at the interface [19].

Decreases in strength after holding the base alloy at 500°C are expected, due to recovery and grain growth. Increases in ductility are a result of spheroidisation of the brittle, needle-like Si phase. Long holds at 700°C also result in decreases in strength and a slight increase in ductility. In this case, changes in properties are thought to be due to the loss of Mg from the alloy by evaporation during holding in the molten state. The stiffness of the base alloy, as expected, is invariant with heat treatment.

The composite exhibits similar decreases in strength after holding at 500°C and 700°C and the same explanations for the behaviour of the base alloy are expected to apply. The ductility does not, however, increase even though the Si needles spheroidise. It is expected that the brittle ceramic phase dictates the failure of the composite more strongly than the morphology of the Si.

The formation of reaction products is thought to be responsible for the increase in stiffness with heat treatment at 700°C and the decrease in ductility. Stiffness increases are only likely to occur, either by an increase in reinforcement volume fraction, or an improvement in load transfer to the particles as a result of enhanced interfacial bonding. It is possible that holding for long periods at high temperature enables a more uniform reaction layer to be established, thus improving wetting and load transfer. It is more likely, however, that the formation of an increased volume fraction of stiff, brittle phases, in this case AlB₂, through reaction between the particles and the matrix, facilitates the changes in mechanical properties. Heat treatment in both the Al-TiC [25] and Al-B₄C systems [5] has been observed to promote increases in stiffness at the expense of ductility through particle-matrix reaction. The quantity of reaction products formed at 500°C is thought to be too small to have a noticeable effect on the stiffness and ductility of the composite.

5. Conclusions

B₄C particles have been incorporated into molten Al using a Ti-containing flux, resulting in the formation of a complex Ti-B-C reaction layer on the particle surfaces.

The reaction layer remains intact during heat treatment and the stable, protective nature of this layer gives rise to a reduced rate of reaction compared to other Al-B₄C composites.

Significant increases in stiffness were observed with the addition of reinforcement to the matrix. Modulus

increases per volume percent of particles added are similar to those for the Al-TiC system where strong interfacial bonding occurs.

It is thought that improved adhesion between the solidified matrix and the reinforcement has been encouraged due to the enhanced metallic character of the reaction layer.

Solid state reaction at 500°C produces little change in mechanical properties. Heat treatment at 700°C results in an increased volume fraction of stiff, brittle phases, through reaction between the particles and the matrix, and an increase in stiffness and a decrease in ductility.

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