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On the fibre/matrix interface in boron/aluminium metal matrix composites

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The fibre/matrix interface of B/Al metal matrix composites (MMCs) has been examined by transmission and scanning electron microscopy (TEM and SEM). As-fabricated samples show no fibre/matrix reaction whereas isothermal exposure for increasing periods of time leads to the formation of at least four distinct borides. The extent and location of the fibre/matrix reaction is strongly influenced by the presence of an oxide layer which is present at all the interfaces. The effect of these reaction products upon mechanical properties is considered.

1. Introduction

It is well known that adequate bonding, either chemical or mechanical, is necessary to achieve good load transfer from matrix to fibre in metal matrix composites (MMCs) and that excessive fibre/matrix interface reaction is often implicated in property degradation. The B/Al MMC system has been the subject of many investigations and one of the principal subjects of interest has been the effect of thermal exposure and thermal cycling upon the mechanical properties [1–5]. Thermal exposure allows a greater degree of fibre/matrix reaction than is found in as-fabricated MMC's and consequent changes in mechanical properties, associated with fibre/matrix reaction, have been reported [2, 4].

Recently Kyono *et al.* [1] reported that thermal exposure for increasing periods of time at 500° C led to a decline in longitudinal tensile strength but a slight improvement in transverse tensile strength for the B/Al(1 1 0 0) MMC. A theoretical model was presented which attempted to account for the extent of fibre/matrix reaction and its influence upon mechanical properties. Other attempts have been made [6–8] to account for the effect of fibre/matrix reaction layers but the principal drawback to this type of model is that the interface must be assumed to be uniform, otherwise complex and imprecise modifications must be introduced to account for non-uniformity, variations in thickness and so forth. For this reason, detailed understanding of the fibre/matrix interface, and the effect of increased reaction at that interface, are of great importance.

Detailed analyses of the actual structure of the fibre/matrix interface are available for very few systems in spite of the large number of studies which have been performed to elucidate information about this critical region of MMCs and the major reason for this lies in the difficulty of studying a region which is typically much less than 0.5 μm in thickness. The B/Al system has already been studied quite extensively but detailed direct observation of the interface by transmission electron microscopy (TEM) was found to be lacking. Wright and Intwala [3] concluded that the fibre/matrix bond strength was degraded by thermal exposure and that this was partially responsible for the reduction in mechanical properties which accompanied thermal exposure of B/Al(6 0 6 1) at 600° C. Grimes *et al.* [2] proposed that a surface boride formed as a result of thermal cycling and led to embrittlement of the fibres through surface roughening. The boride which formed at the B/Al(1 1 0 0) interface was stated to have been identified by electron diffraction as AlB_2, a hexagonal phase, though no details concerning this identification were reported. Olsen and Tompkins [4] reported the occurrence of an acicular reaction product at the fibre/matrix interface in B/Al(6 0 6 1) and suggested, on the basis of two X-ray diffraction lines, that AlB_2 and MgB_2 were formed.

The most thorough recent consideration of the fibre/matrix reaction in the B/Al system has been presented by Kim *et al.* [9] on the basis of scanning electron microscopy (SEM) and X-ray data. They found that tetragonal AlB_{12} formed at the interface of B/Al(6 0 6 1) MMCs whereas AlB_2 formed in B/Al(1 1 0 0) MMCs.

The work reported below is an extension of the work previously reported by Kyono *et al.* [1] and concerns a TEM investigation into the effects of thermal exposure on the actual interface structure of the B/Al(1 1 0 0) MMC used in that study.

2. Experimental techniques

The MMC used in this study consisted of unidirectional B fibres in a matrix of commercially pure Al(1 1 0 0) fabricated by a diffusion bonding technique by AVCO Specialty Materials Division (Lowell, Massachusetts, USA). The fibres were 102 μm in diameter and the samples used in this present study contained 50 vol % of fibres. The samples were exposed for various lengths of time up to 72 h, at temperatures of 450 and 500° C. Samples for transmission electron

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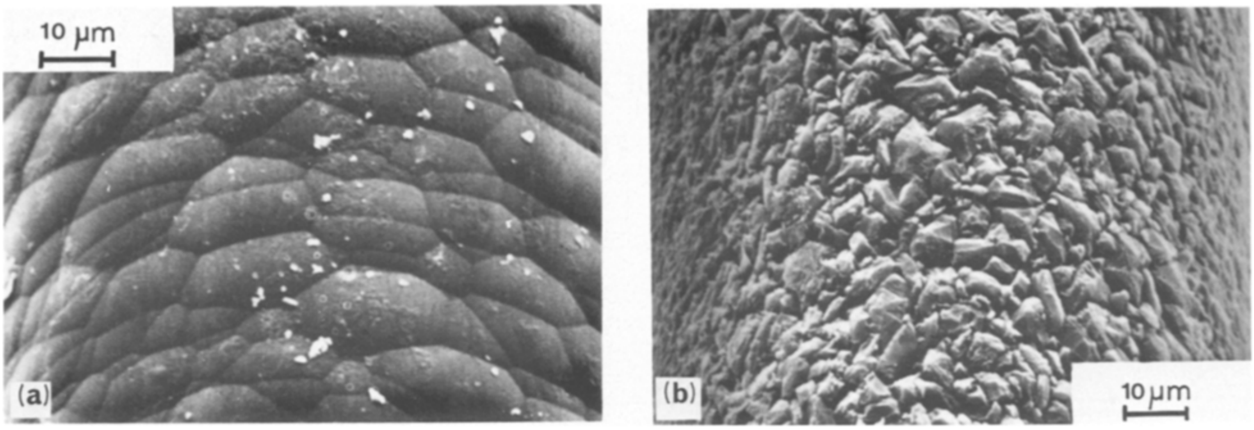

Figure 1 (a) Scanning electron micrograph showing general surface appearance of fibres extracted from as-fabricated composite. (b) Surface of fibres extracted from composite exposed 72 h at 500° C.

microscopy were prepared as 3 mm diameter discs which were mechanically thinned to 75 μm and then ion milled to perforation at 3.5 keV. Fibres were extracted for examination in the scanning electron microscope (SEM) by dissolving the matrix in 20% HNO_3. Further details of sample preparation and mechanical testing were given previously by Kyono *et al.* [1].

3. Results

Fibres extracted from as-fabricated samples showed the typical B fibre surface shown in Fig. 1a. After thermal exposure treatments the surface of extracted fibres began to exhibit angular particles after 24 h and, after 72 h at 500° C, a large fraction of the surface was covered by the particles as shown in Fig. 1b. The same angular reaction products also formed at 450° C, although much more slowly than at 500° C, and only the 500° C treatments will be detailed.

SEM examination of ion-milled samples of as-fabricated material revealed that the fibre/matrix and matrix/matrix interfaces were still clearly delineated (Fig. 2). Although it is evident that consolidation of this MMC does not approach ideality, the appearance of this sample is not atypical of that found in many B/Al MMCs and would not be regarded as unusual. TEM showed that the interfaces between adjacent sheets of 1 1 0 0 Al foil were marked by a continuous layer of fine particles, presumably oxide particles which were present at the start of the diffusion bonding procedure (Fig. 3a). This same type of oxide layer was also generally present between fibre and matrix. Although the fibre/matrix bond was generally poor, intimate contact had been achieved at occasional areas of the fibre/matrix interface, Fig. 3b, but there was no evidence of reaction.

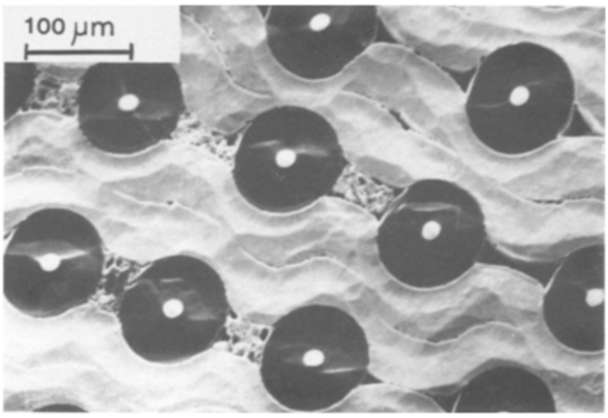

Figure 2 Ion-milled surface of as-fabricated composite showing incomplete diffusion bonding.

After 24 h at 500° C, significant fibre/matrix interfacial reaction had occurred. The original position of the interface was clearly marked by the thin oxide layer and diffusion had occurred across this interface to form hemispherical intrusions into the boron fibre. Where several such intrusions had formed close together they coalesced to form the type of feature labelled A in Fig. 4a. Energy dispersive X-ray micro-analysis (EDX) showed that the count rate for aluminium was the same in the matrix as in regions A and electron diffraction showed that these regions were aluminium. Fig. 4b shows a dark field micrograph which confirms not only that the intrusion and the matrix are indeed both aluminium but also that both are of the same orientation. Thus, it appeared that these intrusions were the result of growth of the matrix aluminium grains. At this stage, therefore, these intrusions do not correspond to precipitation processes. Occasionally, large angular particles were observed on the fibre side of the fibre/matrix interface, as in Fig. 5a. The microdiffraction pattern from this particle in Fig. 5b is indexable as orthorhombic AlB_{10}.

After 72 h at 500° C reaction was much more extensive and a significant fraction of the visible interface contained reaction products. The crystals which formed as a result of this reaction were angular, as shown particularly clearly in Fig. 6, and there is excellent correspondence between these crystals and those seen at the fibre surface by SEM (Fig. 1b). The particle in Fig. 6 has been indexed by electron diffraction as tetragonal AlB_{12}. It could often be seen, as in this example, that these large particles had grown by coarsening into both the matrix and the fibre at the same time. Nevertheless, the original fibre/matrix interface was still visible by virtue of its being decorated with fine oxide particles and could be found inside the boride reaction products.

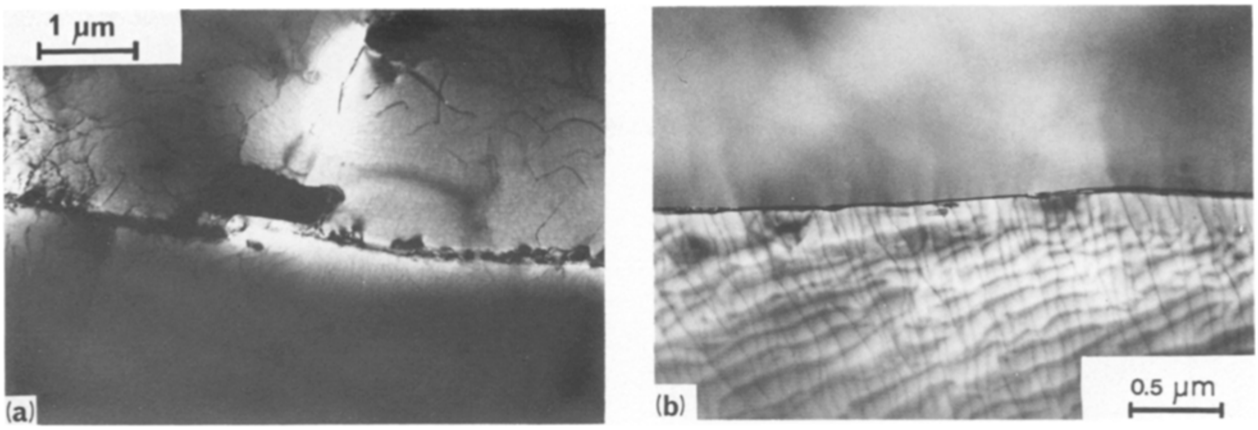

Figure 3 (a) Transmission electron micrograph showing a thin layer of oxide particles between adjacent sheets of 1 1 0 0 aluminium. (b) TEM micrograph showing an area of intimate contact between fibre (top) and matrix (bottom) in as-fabricated composite.

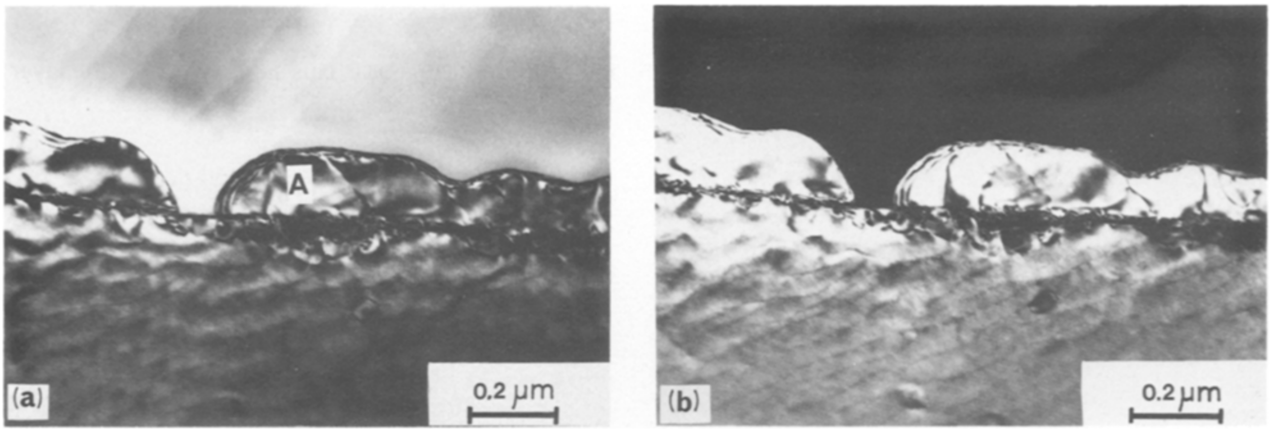

Figure 4 (a) Boron fibre (top)/matrix interface showing intrusion of aluminium, labelled A, across original boundary. (b) Dark field micrograph of Fig. 4a showing the intrusion to be aluminium of the same crystallographic orientation as the matrix.

Frequently the interfacial reaction layer exhibited several apparent layers between the fibre and the matrix as shown in Fig. 7a. Electron diffraction showed that these layers were all crystals of the same phase, namely hexagonal AlB_2. The indexed electron diffraction pattern from the central region of Fig. 7a is presented as Fig. 7b and gives only reflections from AlB_2 and the aluminium matrix.

A typical X-ray line scan for Al across the interfacial reaction layer, the region indicated by the contamination mark in Fig. 8a, is shown in Fig. 8b. It is quite evident that the aluminium content undergoes only two step-wise concentration increases, once at X, corresponding to the boron/boride interface, and once at Y, corresponding to the boride/aluminium interface. The small dip visible at Z corresponds to the intersection of the line scan with the original Al/B interface which is still marked by fine oxide particles. The general upward trend of the aluminium countrate is due to the wedge-shaped cross-section of the TEM sample used.

Convergent beam electron diffraction patterns were

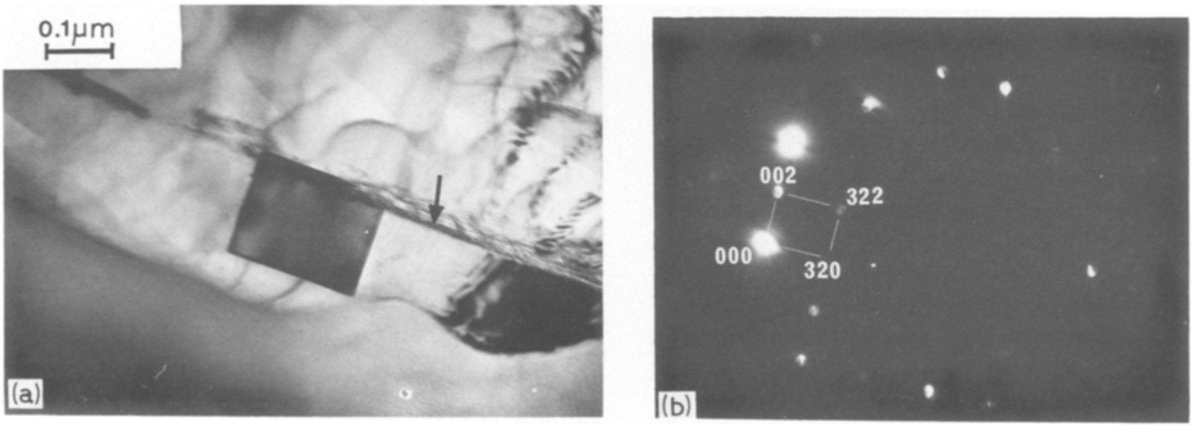

Figure 5 (a) AlB_{10} particle within an aluminium intrusion. The fibre/matrix interface is arrowed. (b) Microdiffraction pattern from particle of Fig. 5a.

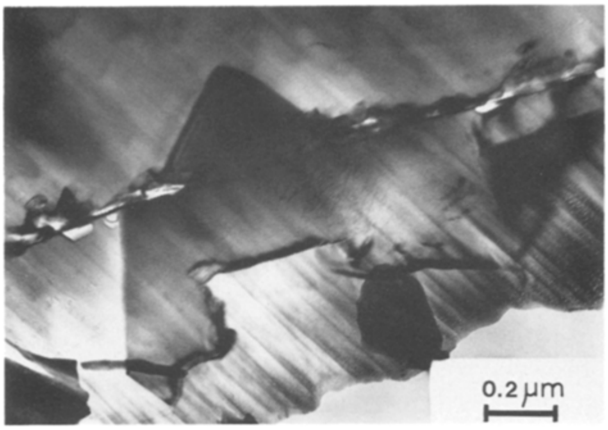

Figure 6 Tetragonal AlB_{12} particle growing into both matrix (top) and fibre. The original interface is still clearly visible.

obtained from many of the particles and low index zone axes commonly presented the 2 mm whole pattern symmetry as shown in Fig. 9. Many such large particles could be identified as hexagonal AlB_2 but occasional crystals could only be indexed on the basis of a tetragonal or an orthorhombic structure. This particular (composite) pattern comes from hexagonal AlB_2, with mirror planes $(1\,1\,\bar{2}\,0)$ and $(0\,0\,0\,1)$. The characteristic reciprocal lattice layer spacing perpendicular to the incident electron beam, H, can be calculated from the diffraction pattern using the expression:

$$H = \lambda G^2/2$$

given by Steeds [10] where G is the radius of the first order Laue zone (FOLZ) ring in reciprocal units and λ is the electron wavelength; this equation yields a value for H of $(1/0.529)\,\mathrm{nm}^{-1}$. The generalized solution of Raghavan *et al.* [11] for the hexagonal AlB_2 structure viewed along the $[1\,\bar{1}\,0\,0]$ zone axis predicts a value of H of $(1/0.52)\,\mathrm{nm}^{-1}$ and the good agreement between the two values is further support for the identification of this particular crystal as AlB_2. This value of 0.52 nm corresponds to twice the spacing of $\{1\,0\,\bar{1}\,0\}$ planes, i.e. it in fact arises from the second order Laue zone; the absence of the FOLZ may be attributed to a very low scattered intensity, symmetry effects for this particular space group, thermal effects or other effects as discussed by Raghavan *et al.* [11, 12].

Generally, the 2 mm symmetry seen in Fig. 9 could arise from cubic, tetragonal, hexagonal or orthorhombic systems but careful tilting experiments never led to the 3-fold symmetry zone axes which would be expected with cubic lattices. In addition, despite the large degree of tilt available (± 45°) it was frequently impossible to obtain the 4-fold or 6-fold symmetry axes expected from tetragonal or hexagonal lattices

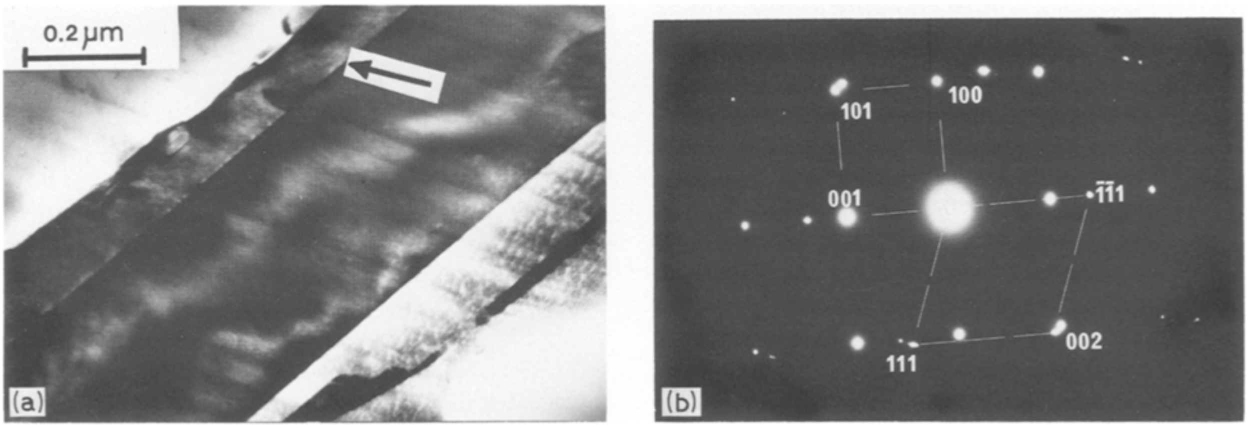

Figure 7 (a) Reaction product showing several apparent layers, all of which are AlB_2. The original fibre/matrix is marked and the matrix is at top left. (b) Diffraction pattern from central region of Fig. 7a, showing overlapping patterns of aluminium (lower right) and AlB_2 (top left).

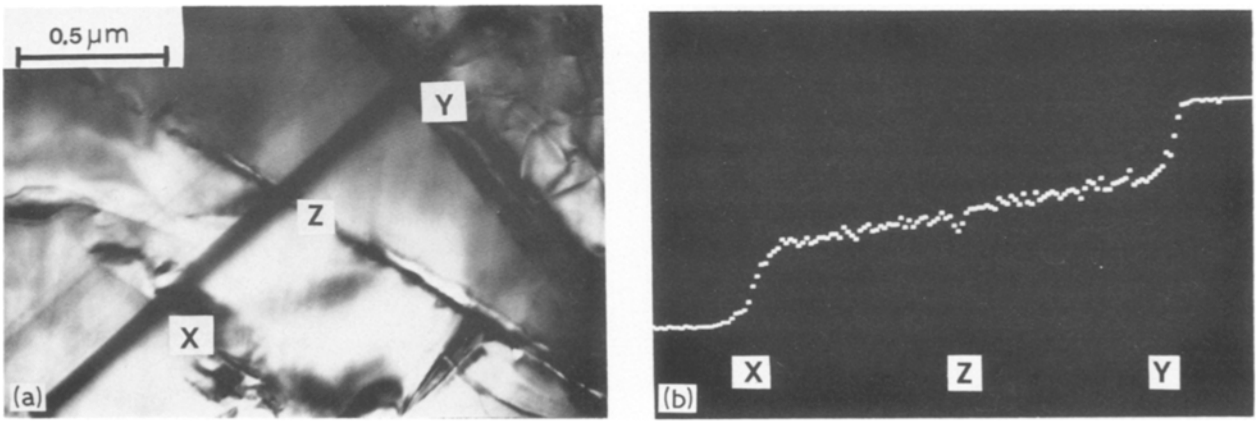

Figure 8 (a) Line scan across fibre/matrix interface showing the contamination mark. X represents the boron/boride interface, Y the boride/aluminium interface and Z the original B/Al interface. (b) Aluminium line scan from Fig. 8a, showing only two step-wise concentration increases and the original B/Al interface.

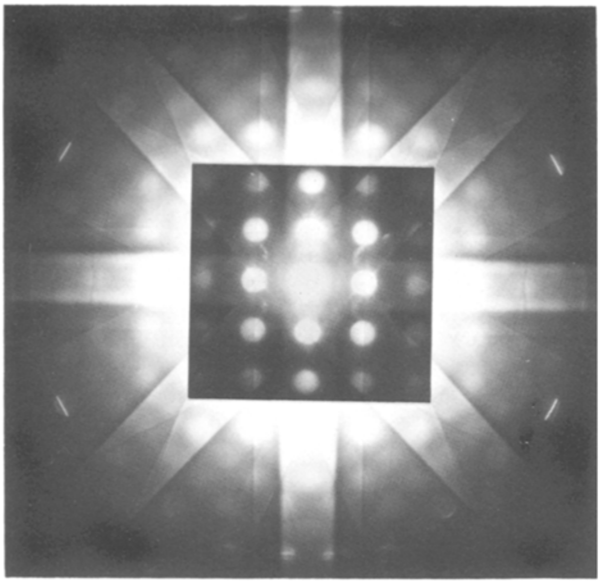

Figure 9 Typical convergent beam pattern from hexagonal AlB_2 showing characteristic 2 mm symmetry. (Micrograph is a composite of two micrographs)

and it was thus concluded that orthorhombic phases were also present. For example, Fig. 10 is one such diffraction pattern which can be indexed as orthorhombic AlB_{12} but not as hexagonal AlB_2, orthorhombic AlB_{10} or tetragonal AlB_{12}.

4. Discussion

The above observations confirm that the B/Al interfacial reaction is encouraged by exposure to high temperature and the typical thickness of the reaction layer is $< 1\,\mu m$ under the conditions used in this work. Considering firstly the mechanical properties of B/Al(1 1 0 0) MMCs, Kyono *et al.* [1] had noted that thermal exposure led to a change in fracture mode for the transversely tested MMC; as-fabricated material failed either by debonding at the fibre/matrix interface or by normal tensile failure of the matrix whilst after 72 h at 500° C failure occurred predominantly by fibre splitting. The reason for this behaviour is now clearly seen since it was found that in as-fabricated material a thin layer of oxide usually separated fibre from matrix (Fig. 2) and yielded a poor bond. After excessive thermal exposure, the interfacial reaction ultimately led to the formation of boride particles which were in intimate contact with both fibre and matrix and thus "keyed" the two together (Fig. 6). As discussed by Olsen and Tompkins [4], circumferential stress is likely to occur at the fibre surface on which the brittle boride particles are concentrated in thermally exposed B/Al composites and stress concentrations may also occur as a result of mechanical loading. Consequently, the high circumferential stress in the boron fibre can cause a splitting-type crack during transverse loading. In the case of longitudinal loading an initial crack would propagate into the fibre along the same plane and almost simultaneously propagate across the whole composite approximately perpendicular to the fibre axis. As a result, the longitudinal strength and work of fracture of thermally exposed composites would be found to be degraded, as has been shown in several investigations [2–6, 13–15].

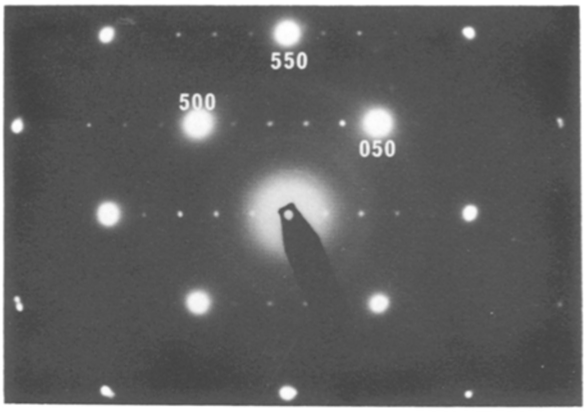

Figure 10 Diffraction pattern from orthorhombic AlB_{12}.

Kim *et al.* [9] had proposed a very reasonable model based upon consideration of the thermodynamically stable possible reaction products and the diffusive flux of the two species. They concluded that the boride reaction layer present would consist essentially of AlB_2 close to the matrix and AlB_{12}, if present at all, close to the fibre. The actual situation is seen to be more complex. The first effect noted after short thermal exposure treatments was the development of aluminium intrusions into the boron fibre. Since it has been conclusively demonstrated that these regions are aluminium and that they occur without any other signs of precipitation it must be assumed that this is a microscopic manifestation of the Kirkendall effect, i.e. the migration of an interface into the phase which consists of the more rapidly diffusing species. The fact that the oxide "markers" at the original interface do not move is due to the fact that they are massive compared with the diffusion length under consideration and diffusion initially takes place predominantly at gaps in the oxide layer. The diffusion of aluminium into the fibre implies that boron has diffused out into solution in the aluminium or possibly into the oxide layer but its location, at this stage, is unclear.

After formation of these intrusions, boride particles begin to form in them and the particle shown in Fig. 5 is an isolated crystal of orthorhombic AlB_{10}. This and the following micrographs show that the interfacial reaction layer is not a uniform region consisting of stratified layers arranged according to composition. Indeed, the four distinct aluminium borides which are listed in the JCPDS (ASTM Index) have all been identified within the reaction layer, frequently in isolation from each other. The total area of the specimen which may be viewed by TEM is, of course, very limited and it is not possible, therefore, to determine respective volume fractions of each boride phase. Nevertheless, the most commonly identified phase was undoubtedly tetragonal AlB_2 and this is in agreement with the previous results of Kim *et al.* [9]. The X-ray line scan of Fig. 8 shows only a constant aluminium content across the whole of the reaction layer and this may be interpreted as further evidence that the reaction layer is not a stratified layer with several phases of different composition but a single phase.

It is not clear from the present observations why there is such a variety of phases present in the reaction layer, although it might be expected that the boron-rich boride phases would form first and then be replaced by increasingly aluminium rich particles as the thermal exposure times increased and allowed aluminium to diffuse more extensively. However, it is evident that the diffusion paths are not straightforward, particularly in the vicinity of and across the oxide layer, and this factor will certainly complicate the precipitation processes. Furthermore, it is worth noting that the AlB_2 crystal visible in Fig. 5a has nucleated at the oxide layer within the aluminium intrusion and not at the boron itself. This probably indicates that there is also a problem in nucleating boride crystals and this may further account in some measure for the variety of phases present. Work is continuing in this area.

5. Conclusions

1. Several boride phases form as a result of thermal exposure of B/Al MMCs.
2. The oxide layer present almost unavoidably during fabrication is a formidable diffusion barrier and interfacial reaction is initiated at breaks in this layer.
3. The boride "keys" the matrix and fibre together.
4. The reaction layer is $< 0.5\,\mu m$ in thickness, even after 72 h at 500° C.

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