

Two stages of interfacial reaction in B–Al composite

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Using an original technique, new data for the interfacial reaction in B–Al composites have been obtained. Two stages of the boron fibre/aluminium interface reaction were revealed. In Stage 1, due to the aluminothermal reduction of the oxide film on the boron fibre, fine-crystalline rhombohedral boron, alumina and dispersed aluminium borides are formed. The latter are formed by the reaction with the fine-crystalline boron and do not affect the fibre strength but can contribute to a more intensive interaction. In Stage 2, borides are formed by direct reaction with the fibres, thus seriously reducing their strength.

1. Introduction

The properties of fibre-reinforced metal matrix composites (MMCs) are mainly determined by the structure of the fibre/matrix interface which should provide a sufficiently adequate bonding without causing fibre weakening. It is known that the main cause of fibre weakening is the fibre/aluminium reaction which results in the formation of aluminium borides during the processes of production or thermal treatment [1–4].

There are different views in the literature on the interfacial process and the results of the fibre/matrix reaction. Some works [1–3] report the formation of AlB_2 borides at the interface. Hall *et al.* [5] also revealed two modifications of AlB_{12} boride and AlB_{10} boride. They showed that the formation of borides might be preceded by hemispherical intrusions of aluminium into the boron fibre.

Some authors [5, 6] are of the opinion that oxide films of a natural origin, being on the surfaces of the fibres and matrix, can considerably affect the development of the reaction, namely, its onset at the areas of oxide film degradation.

A number of works deal with the study of the fibre/matrix interface which occurs after long thermal exposure or at high temperature, whereas fibre weakening is already observed during early stages of composite production.

The purpose of the present work was to investigate the process of boron fibre/aluminium interface formation in the early stages of their interaction, and the effect of the products of the reaction on the tensile strength of the fibres.

2. Experimental procedure

The boron fibres used were 140 μm diameter with an average strength of 2.9 GPa. Single-fibre specimens were prepared by evaporating aluminium on to the fibres. The thickness of the evaporated aluminium layer was about 1 μm . The aluminium-coated single-

fibre specimens were annealed in a vacuum at 450 and 500 °C for various times from 5–60 min. The rate of cooling was the same in all cases.

The interface structure was studied using an extraction replica method [7]. This method, characterized by its high resolution ability, allows the study of rather large surface areas. For this purpose the evaporated aluminium was removed by using 10% NaOH solution. Then the carbon replicas were sputtered in a vacuum on to the fibre surface. Replicas were separated by plunging specimens in 10% NaOH + 10% $\text{K}_3\text{Fe}(\text{CN})_6$ solution. The products of fibre/aluminium reaction were studied in a transmission electron microscope JEM-2000EX (TEM). The replica taken from the surface of a pure boron fibre exactly repeats the relief of the fibre surface and contains a small number of microgrowths on its surface, these being assigned to the proper defects of fibres and easily identified later.

Tensile tests were conducted on 50 fibres for each thermal condition using an Instron-type machine. All fibres were tested with a gauge length of 20 mm and a strain rate of $8.3 \times 10^{-4} \text{ s}^{-1}$. The fracture surfaces of the boron fibres were examined in a scanning electron microscope (JSM-840A), operated at 20 kV.

To study the role of B_2O_3 in the process of interface formation, an additional experiment consisting in artificial growth of an oxide film was conducted. To this effect the fibres were annealed in air for 10 min at 400 °C [8–10]. Then a layer of aluminium was evaporated on to these fibres and on to those in the initial state. Subsequently, all these fibres were annealed in vacuum for 10 min at 500 °C. After removing the evaporated aluminium, the fibre surfaces were studied in a scanning electron microscope.

3. Results

3.1. Tensile tests

The measurement values of $\sigma_{fu}/\sigma_{fu}^0$ of specimens annealed at 450 and 500 °C for various times are shown

in Fig. 1, where σ_{fu}^0 is the original strength of fibre and σ_{fu} is the strength of fibre after annealing. At 500 °C, two regions are observed: region 1 (from 5–20 min), where no degradation is found, and region 2 (from 20–60 min), where the $\sigma_{fu}/\sigma_{fu}^0$ decreases with increasing annealing time. At 450 °C, no degradation is found (also in region 1).

3.2. Study of extraction replicas

After annealing at 450 °C, shapeless particles of fine crystalline rhombohedral boron were revealed on the replicas. Their amount differed in various areas. Particles of fine crystalline boron and a diffraction pattern from these particles are shown in Fig. 2a and b. Borides of two modifications have been revealed on replicas at 450 °C in addition to fine crystalline boron. Thus, after 5 min, small colonies of thin, rounded crystals were observed at the interface, as in Fig. 3a. The microdiffraction pattern from this particle, shown in Fig. 3b, is indexable as tetragonal AlB_{12} . With increasing annealing time, the number of crystals of this phase increases, but their sizes do not grow and remain in the range 0.1–0.4 μm (Fig. 3a,c). After 60 min, the colonies of this phase are 200 μm in size and more are observed on the replica. In addition, intergrowths of twins and tee-joints of orthorhombic AlB_{10} are revealed. Fig. 4a and b show an AlB_{10} particle and its diffraction pattern. Among the continuous signals from strongly curved faces of a crystal, the reflexes corresponding to $\{531\}$ planes may be distinguished. With increasing annealing time, the number of crystals of this phase also increases, but their sizes do not change and remain in the range

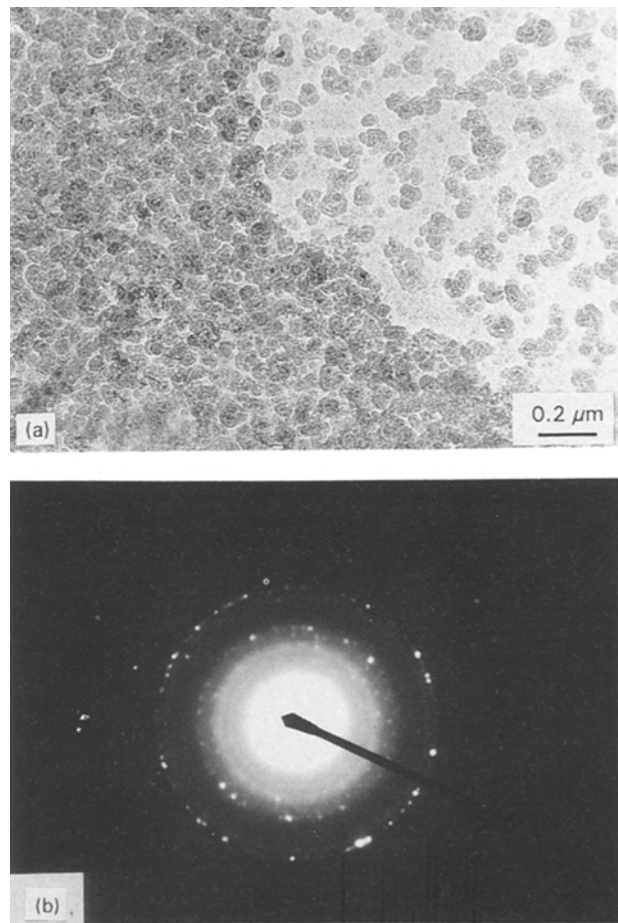


Figure 2 (a) Fine crystalline rhombohedral boron at the fibre/aluminium interface. (b) Diffraction pattern from particles in (a).

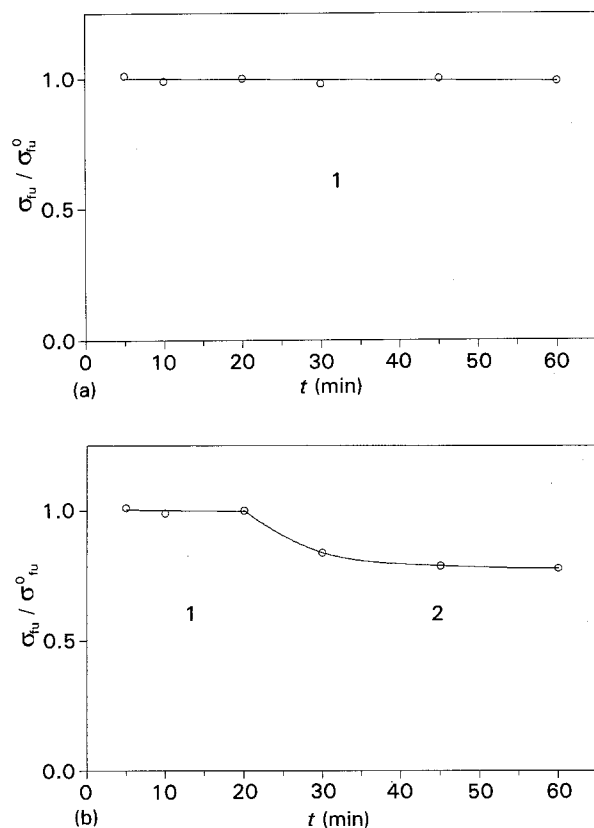


Figure 1 Measured values of $\sigma_{fu}/\sigma_{fu}^0$ of B/Al specimens annealed in vacuum at (a) 450 °C and (b) 500 °C for various times.

0.25–0.5 μm . It is typical that both of the phases are found in the area with a low concentration of boron particles. The areas where boron particles are aggregated into a continuous layer, occupy about 5% of the area of replica and no formation of boron phases was observed on them.

The study of extraction replicas from fibres annealed at 500 °C within region 1 (Fig. 1b) has shown a strong regularity in the distribution of fine crystalline boron at the surface (Fig. 5). Alongside the boron-rich and boron-poor areas, areas without any boron particles are observed.

As at 450 °C, small amounts of tetragonal AlB_{12} and orthorhombic AlB_{10} were observed in areas with a low concentration of boron. In addition, a new phase was revealed which was identified as hexagonal AlB_2 (Fig. 6a,b).

After 20 min holding (region 2, Fig. 1b), the appearance of the interface changed significantly. Active formation and growth of borides were observed on the surface without reflections from fine crystalline rhombohedral boron. At the same time, the formation of AlB_{12} phase with a tetragonal lattice was not revealed. Fig. 7a and b show the stages of nucleation, growth and mergence of hexagonal AlB_2 and orthorhombic AlB_{10} on the surface without fine crystalline boron.

Together with the phenomenon described above, areas of a continuous layer of boron particles were

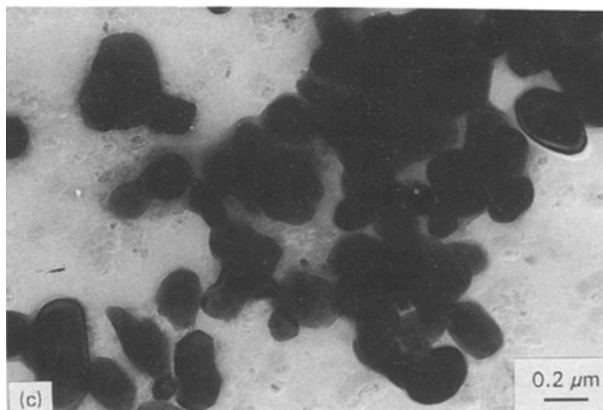
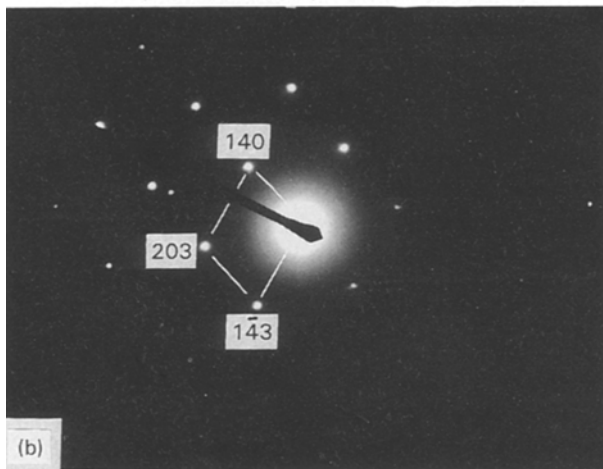
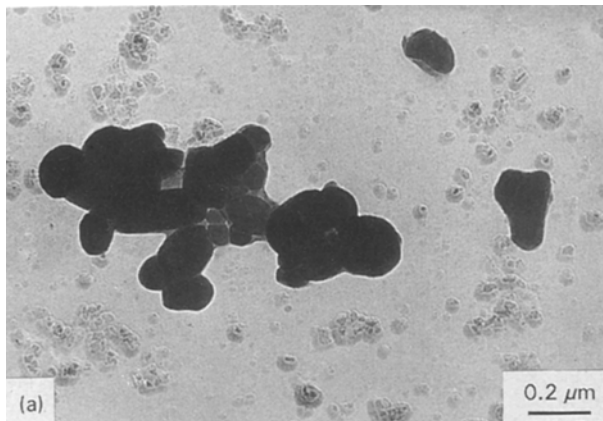


Figure 3 (a) Tetragonal AlB_{12} particles at the interface after 5 min annealing at $450\text{ }^{\circ}\text{C}$. (b) Diffraction pattern from tetragonal AlB_{12} . (c) Tetragonal AlB_{12} particles at the interface after 60 min annealing at $450\text{ }^{\circ}\text{C}$.

also observed. They occupy about 20% of the area of the replica. The nucleation of tetragonal AlB_{12} and orthorhombic AlB_{10} is occasionally observed in these areas, as a result of fine crystalline boron/aluminium reaction (Fig. 8).

3.3. Fractography

As Ochiai *et al.*'s work [1], two typical types of fracture surfaces were observed: type 1 fracture due to the defects inside the fibre (region 1), as in Fig. 9a, and type 2 fracture due to the defects at the fibre/aluminium interface for a "gull wing" pattern (region 2), as in Fig. 9b.

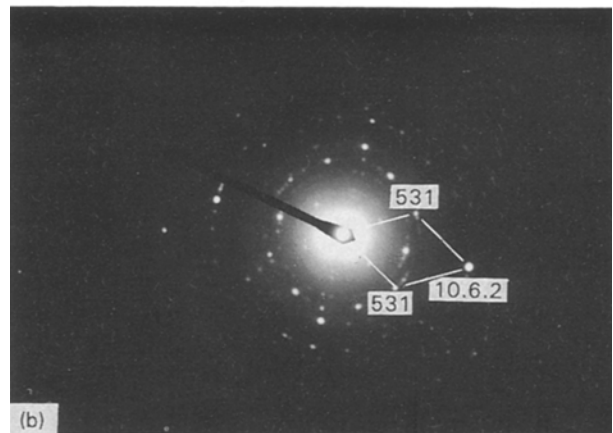
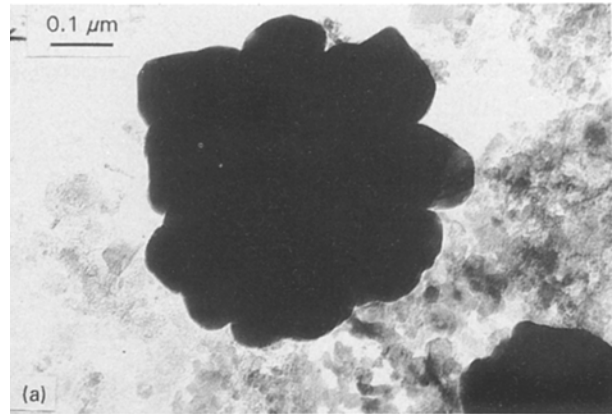


Figure 4 (a) Orthorhombic phase AlB_{10} at the interface after 5 min annealing at $450\text{ }^{\circ}\text{C}$. (b) Diffraction pattern from particles in (a).

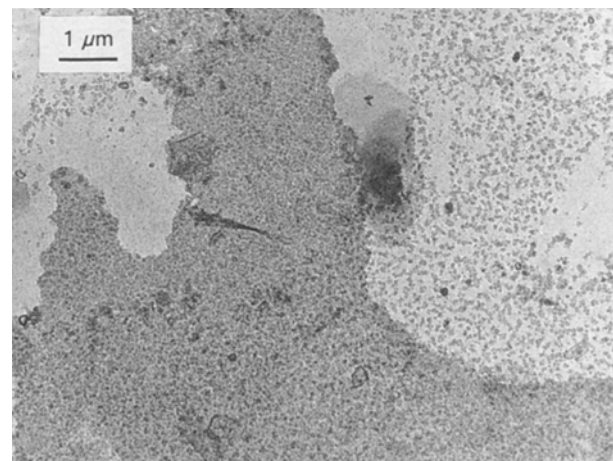


Figure 5 Fine crystalline rhombohedral boron at the interface after 5 min annealing at $500\text{ }^{\circ}\text{C}$.

3.4. Experiment with B_2O_3 film

After growing the oxide layer, the surface appearance of fibres did not differ from the initial one. However, after annealing, due to the interaction with aluminium, the amount of fine crystalline boron on the surface of extracted fibres increased, so that it could be observed in a scanning electronic microscope (Fig. 10b), whereas the fine crystalline boron formed on the surface of initial fibres can only be observed by the method of extraction replicas (Figs 2a, 10a).

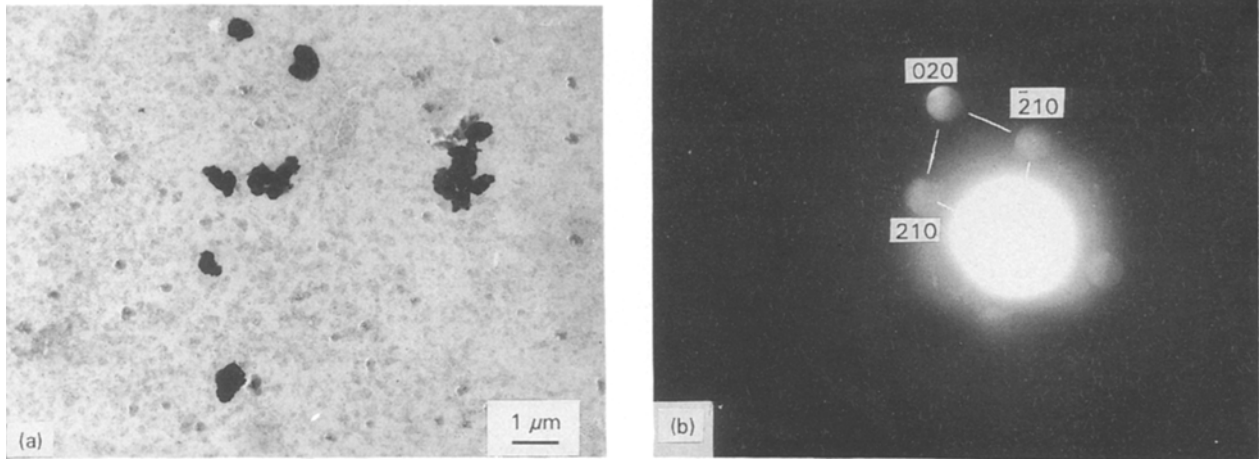


Figure 6 (a) AlB_2 particles at the interface at 500°C in region 1. (b) Convergent beam pattern from hexagonal AlB_2 .

The study of replicas taken from the surfaces of fibres with the grown oxide film has shown that the layer of reaction products on the surface of extracted fibres (Fig. 10b) consists of fine crystalline boron and aluminium borides.

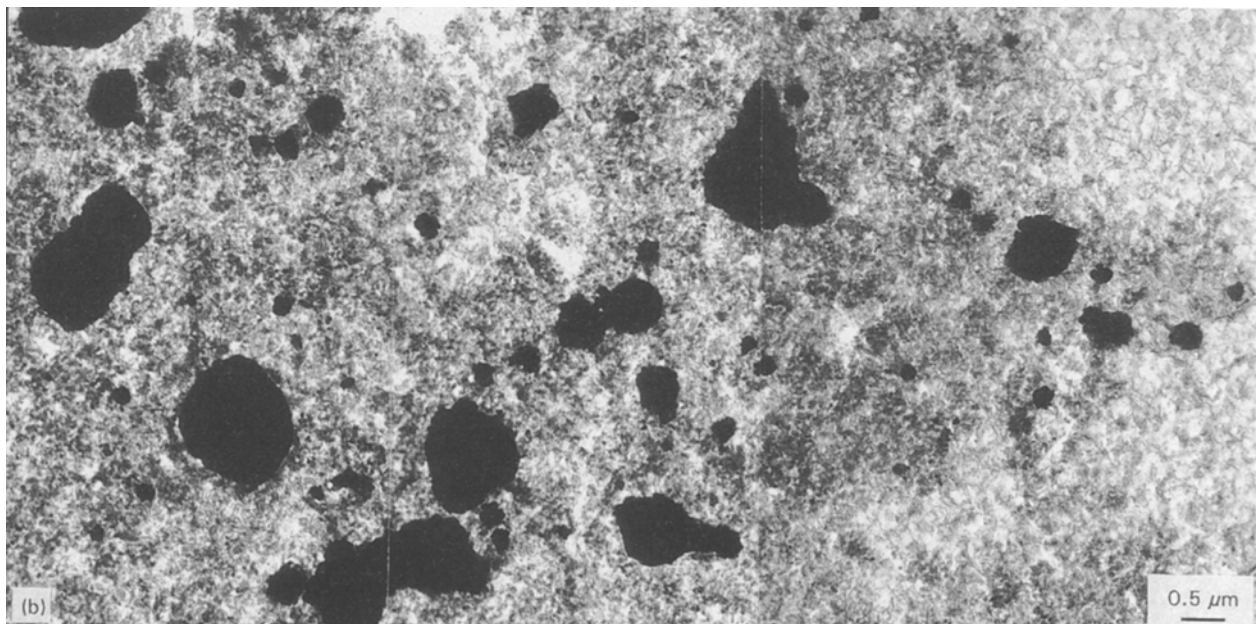
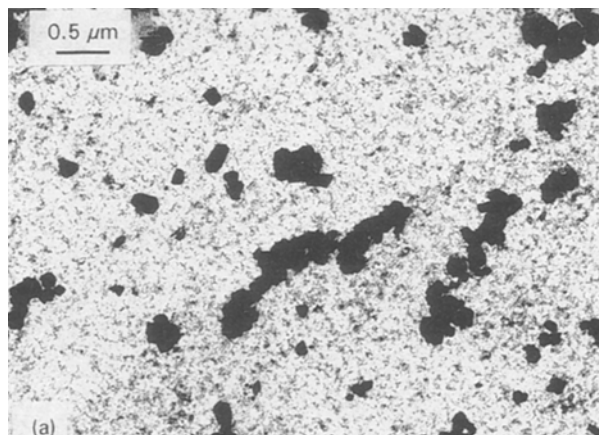


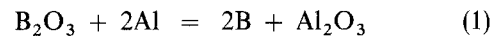
Figure 7 (a) Hexagonal AlB_2 and (b) orthorhombic AlB_{10} at the interface in region 2.

4. Discussion

The results of tensile tests are in good agreement with those from the work by Ochiai *et al.* [1]. It is seen that there is a permissible annealing time, below which no degradation occurs. After that, the state of fibres surface has changed significantly, and the decrease in boron fibre strength is evidently explained by this.

Using data known from the literature, let us represent the process of interface formation. For this purpose, consider the physico-chemical reactions which take place at the boron fibre–aluminium interface.

It is known that the oxide film of natural origin is initially present on the surface of boron fibres, its melting temperature being about 450°C . Consequently, the following reaction is possible at the boron fibre/aluminium interface



and then



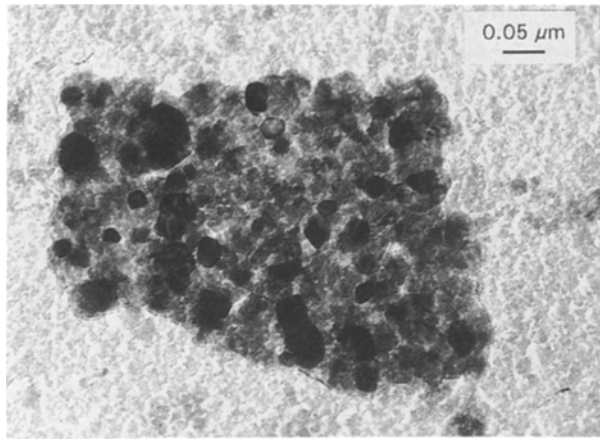


Figure 8 Tetragonal AlB_{12} particles formed in the area with a high concentration of boron particles in region 2.

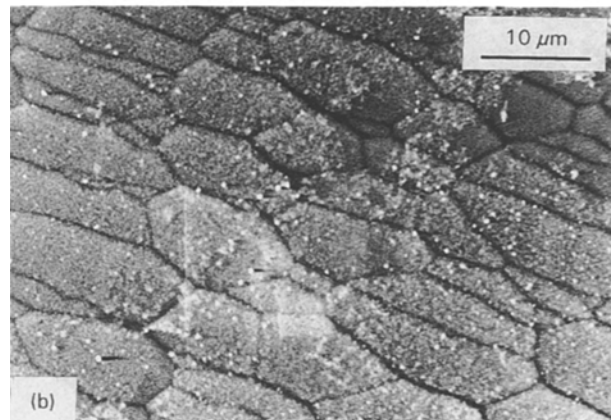
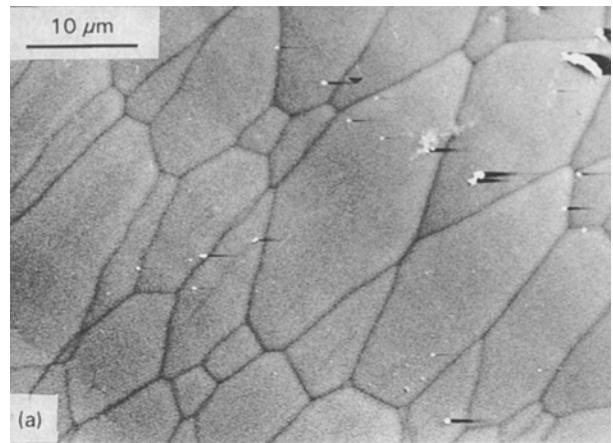


Figure 10 (a) Scanning electron micrograph showing the surface appearance of initial fibres after reaction with the evaporated aluminium layer. (b) The surface of fibres after growth of the oxide films and interaction with aluminium.

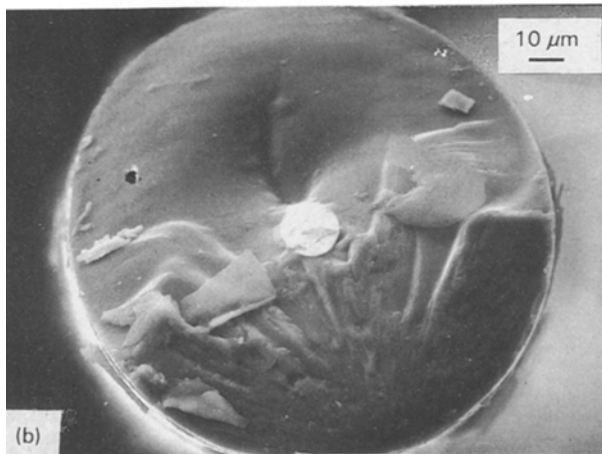
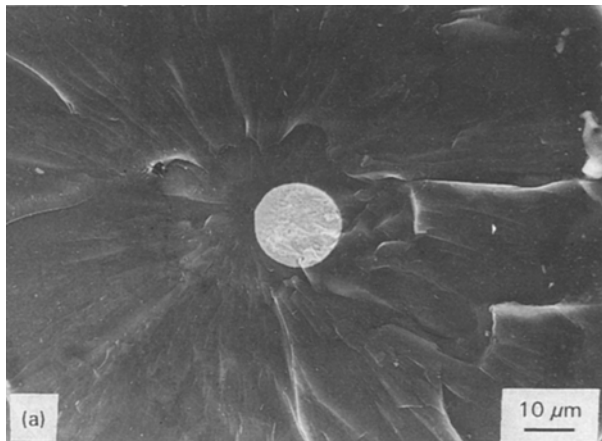


Figure 9 (a) Type 1 fracture surface, and (b) type 2 fracture surface, of boron fibre.

This is a well-known reaction of aluminothermal reduction of boron oxide, the reduction being often used to produce aluminium borides [11]. Consequently, the fine crystalline rhombohedral boron formed at the interface is most likely to be a product of B_2O_3 reduction. The experiment with the grown oxide film which leads to an increase in the amount of fine crystalline boron, confirms this conclusion.

Fig. 11 schematically shows the process occurring at the interface. Owing to the aluminium–melted boron

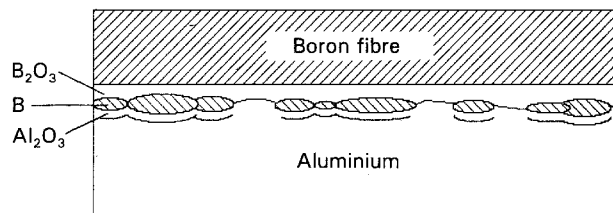


Figure 11 Schematic representation of the interphase interaction at the boron fibre/aluminium interface.

oxide reaction, the fine crystalline boron and alumina are formed according to Reaction 1. By diffusion through alumina, the aluminium reacts with this fine crystalline boron and forms aluminium borides by Reaction 2. With increasing exposure time, their amount increases but their growth is retarded because of the limited amount of fine-crystalline boron in the areas of their formation (Fig. 3a, c).

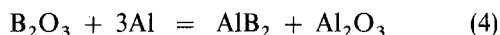
Alumina formed in a solid state can retard Reaction 2. Thus the formation of borides primarily occurs in areas with a small amount of fine-crystalline boron, because the layer of alumina is thinner there. The greater the amount of fine-crystalline boron formed, the thicker is the layer of alumina around it and thus the more time is required for the appearance of borides.

In fact, the formation of boride in the areas with a thick continuous layer of fine crystalline boron, begins only at 500 °C after 20 min exposure, as in Fig. 8. The process described above is confirmed by the fact that the fine crystalline boron and aluminium borides, having no firm bonds with the fibres, are easily separated from these fibres and then extracted on replicas. The alumina formed according to Reaction 1 is not extracted on the replica, because it dissolves completely in alkaline solution [12].

To discuss the regularities of the formation of particular boride phases, let us return to Equations 1 and 2. The reaction of the aluminothermal reduction of B_2O_3 is rather comprehensively studied elsewhere [11]. The thermodynamic analysis of the B_2O_3 -Al system has shown that deep restoration of B_2O_3 is possible and the process may be presented by the equation



An inconsiderable amount of composition AlB_2 crystallizes as an impurity to tetragonal AlB_{12} even when attempting to perform the following process



It is experimentally shown that an increase in the amount of aluminium and the decrease in the cooling rate contribute to the formation of aluminium diboride, and a decrease in the amount of aluminium and an increase in the cooling rate contribute to the formation of the AlB_{12} composition, rich in boron [11]. In the present work, the rate of cooling was similar in all cases; consequently, only the amount of aluminium at the interface at each moment in time affects the formation of a particular phase. A small amount of carbon affects the appearance of AlB_{10} phase, which is stable in the presence of carbon [13, 14].

Thus, at 450 °C, aluminium reacts with fine crystalline boron and under conditions of an aluminium deficit the boron-enriched AlB_{12} and AlB_{10} compositions are formed. On increasing the temperature up to 500 °C, the diffusion processes become stronger and the amount of excessive aluminium at the interface increases. Owing to this, the formation of AlB_2 phase with a hexagonal lattice becomes thermodynamically beneficial (Fig. 6a).

In region 2 (Fig. 1b), the growth of borides at the surface without reflections from fine-crystalline boron, is observed. This indicates that at this stage, the borides are formed by another method, namely, by fibre/aluminium reaction, thus seriously reducing the fibre strength. It is AlB_2 (stable under conditions of excess aluminium) and AlB_{10} (stable in the presence of a small amount of carbon) that cause fibre weakening. In this case, the carbon is in the form of an impurity.

AlB_{12} phase with a tetragonal lattice was not revealed. Under conditions of excess aluminium it is apt to transform into AlB_2 phase, as shown elsewhere [15, 16]. The fact that the arrangement of the AlB_{12} phase in region 1 is similar to that of AlB_2 phase in region 2, confirms this.

Evidently, the formation of aluminium boride by the second method becomes possible after fine-crystalline boron is used up, and primarily, in the areas with a low concentration of fine-crystalline boron. This formation is also likely to occur in the areas where the melted B_2O_3 -film coagulates and no fine-crystalline boron is formed.

From the above observation, it is clear that the two described methods of borides formation differently affect the strength of boron fibres. Thus, the formation of some boron phases at the interface in region 1 does not cause a weakening of fibres because they are formed by the reaction with the fine-crystalline boron and not with the fibre. In this case, the fracture of fibres is caused by defects within the fibres themselves (Fig. 9a). In contrast, the formation of borides by the direct reaction with boron fibres in region 2, weakens them considerably. In this case, the fracture of fibres is caused by defects at the fibre/aluminium interface, as in Fig. 9b.

It is seen that it would be wrong to connect the weakening of fibres only with the presence of borides, because much depends on the method of formation, sizes and disposition of borides. At the same time, both of these methods are important to form a cohesive bond.

Hence, it unexpectedly follows that in order to obtain the best properties of the composite, the use of a natural oxide film on the fibre surface is preferable but, in practice, it is desirable to have a uniform distribution and regeneration, for example during pressing under conditions of poor vacuum.

In our opinion, this approach to the study of the fibre/matrix interface, as shown by the example of B/Al composites, could be applied to another fibrous composites.

5. Conclusions

1. Interaction at the boron fibre/aluminium interface proceeds according to the reaction of the aluminothermal reduction of a B_2O_3 film. This reaction results in the formation of fine crystalline boron, alumina and aluminium borides.
2. Borides on the interface can be divided into two types: borides formed due to the fine crystalline boron/aluminium reaction and borides formed due to the boron fibre/aluminium reaction.
3. The direct fibre/aluminium reaction is preceded by the disappearance of fine crystalline boron and alumina from the interface.
4. Hexagonal AlB_2 and orthorhombic AlB_{12} formed by the second method weakens the fibre.

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