JOURNAL OF MATERIALS SCIENCE 13 (1978) 1841–1848

Interface reactions during preparation of aluminium-matrix composites by the sodium process*

D. M. GODDARD
The Ivan A. Getting Laboratories, The Aerospace Corporation, El Segundo, California, USA

A process has been developed in which aluminium matrix composites, reinforced by either graphite or polycrystalline alumina (FP) fibres, are prepared by immersing the fibres sequentially in molten baths of sodium, tin, and aluminium. The experimental details of this process are presented, and the theory behind the process is explained. In essence, sodium wets the fibres, and is then reacted to form stable intermetallic compounds at the fibre–matrix interface; these compounds are then wetted by the aluminium. Composites with full theoretical strength can be prepared by means of this process if rayon-base graphite, Pan I graphite, or FP fibres are used. Composites containing an intimate mixture of two or more types of fibres are also possible.

1. Introduction

Several processes currently exist that can be used to produce graphite–aluminium composites with near rule-of-mixtures strengths. The most successful of these involves the infiltration of bundles or tows of graphite fibres with molten aluminium. Unfortunately, molten aluminium does not wet graphite, except at elevated temperatures where carbide formation promotes wetting but causes severe degradation of the fibre strength. In order for these processes to be successful, therefore, some agent must be present on the fibres that protects the fibres but also induces wetting by the aluminium. Dependent upon its nature, this agent may be deposited by electrodeposition, by chemical vapour deposition, or by immersion of the fibres in a liquid bath of the wetting agent. The last process is the easiest to control and duplicate because it requires neither elaborate reaction chambers nor close control over experimental conditions, and there is no problem in depositing the desired material uniformly throughout the fibre bundle. In a process developed at The Aerospace Corporation [1], molten sodium is used as the wetting agent. It has been found that this "sodium process" can be used to prepare not only graphite–aluminium composites, but also aluminium matrix composites containing the newly developed DuPont FP (polycrystalline alumina) fibre. The process, therefore, not only is versatile, but can be used to prepare hybrid composites consisting of more than one fibre type in the metal matrix. The desirable characteristics of two types of fibres, e.g., the tensile strength of graphite and the compressive strength of alumina, thus can be combined in one material.

Although the sodium process is simple in operation, it depends for its success on some rather interesting and significant metallurgical reactions at the fibre–matrix interface. The purpose here is to identify and explain these interface reactions.

2. Basic steps in the process

The process consists of sequentially immersing graphite or alumina fibres in three molten metal baths. The first bath is sodium, the second is tin, and the third is aluminium or an aluminium alloy.

---

*This research was Company funded.

Magnesium, in a concentration of approximately 2 at.%, should be present in either the sodium or the tin bath. The best results have been obtained with the following bath temperatures: sodium, 550 ± 20° C; tin, 600 ± 20° C; aluminium alloys, from 20 to 50° C above the liquidus temperature. Immersion times of 10 minutes per bath can be considered typical but vary with sample size. For example, a single bundle or tow consisting of 10 000 graphite filaments, each filament with a diameter of 7 μm, can be processed successfully with immersion times of 1 minute per bath, whereas multi-strand tape may require the full 10-minute immersions.

3. Process mechanism

3.1. The function of sodium

It is a well established fact that molten sodium wets graphite. Work at The Aerospace Corporation has indicated that wetting and infiltration of a tow (approximately 10 000 fibres) of graphite yarn by sodium, in a helium atmosphere, can be accomplished in 10 minutes at sodium temperatures above 450° C. However, although higher temperatures promote faster wetting, temperatures above 600° C may result in visible corrosion of the graphite by the sodium [2]. A sodium temperature of 550° C has been found to produce a combination of rapid wetting and no attack on the graphite.

It has also been determined that liquid sodium penetrates graphite, which causes swelling of the solid. This penetration may be by intergranular diffusion [2], or by intercalation in which such compounds as $C_{64}Na$ may be formed [3, 4]. Studies at Aerospace, which involved the use of the ion microprobe mass analyser (IMMA), have indicated that sodium is present within the graphite fibres of graphite–metal composites produced by the sodium process. In these studies, the ion beam was used to "bore through" a graphite fibre, in a direction approximately perpendicular to the fibre axis. This method of analysis, as it pertains to graphite–metal composites, has been described by Harrigan [5]. Essentially, the IMMA monitors only the elements present within the graphite fibre until the bored hole is deep enough, i.e., until enough material has been sputtered away by the ion beam, to have fully penetrated the fibre. At this point, elements present at the fibre–matrix interface or in the matrix itself can be detected. Thus, on a plot of element concentration versus time of ion sputtering (depth of hole), the location of the fibre–matrix interface can be determined quite accurately. A plot for sodium and aluminium in a graphite–aluminium composite produced by the sodium process is shown in Fig. 1. Later discussion will verify that the first measurable increase in aluminium concentration closely corresponds to the location of the fibre–matrix interface; i.e., there is not a thick aluminium-free interfacial layer through which the beam must penetrate before aluminium is detected. Note that there is an appreciable concentration of sodium within the graphite fibre. This concentration reaches a peak at the fibre–matrix interface, then it falls off to a low level in the matrix itself. In some IMMA studies, the sodium concentration within the fibre appeared actually to exceed that at the fibre–matrix interface.

If the short times and moderate temperatures used in the process are considered, it is probable that the sodium enters the graphite at the crystal boundaries rather than between the C-planes of the graphite crystal lattice. In either event, the

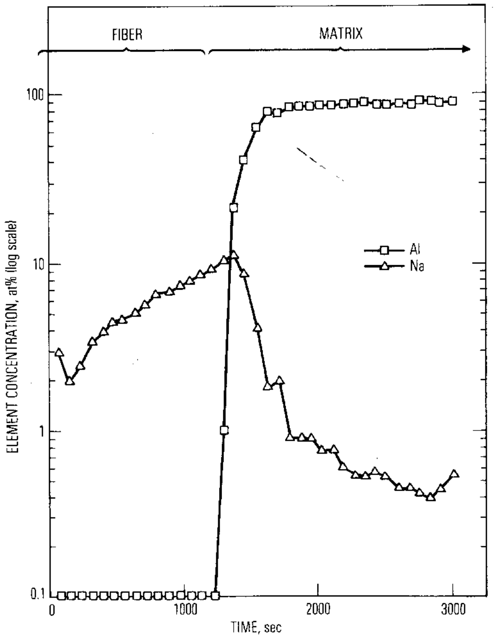

Figure 1 IMMA plot of sodium and aluminium concentrations as a function of time (depth of sputtered hole) in graphite–aluminium composite prepared by the sodium process. (Analysis starts in graphite fibre and proceeds into aluminium matrix).

structure of the graphite fibre must influence its interaction with the sodium. Rayon, pitch, Pan I, and Pan II fibres all differ from each other with regard to C-plane spacing, degree of preferred orientation of the C-planes, crystallite size, impurity content, and fibre geometry. In fact, different manufacturers' fibres of the same type may differ in these respects. The effects of these differences on sodium absorption have not been fully defined. It is known that sodium wets all varieties of graphite fibres equally well. On the other hand, the strength of the rayon-base and the Pan I fibres tends not to be degraded by the sodium, whereas Pan II fibres are weakened by the treatment.

The electrically nonconducting nature of the alumina fibres makes it extremely difficult to use the IMMA to analyse the composition of the fibre interior. Thus, no data exist to establish whether or not these fibres absorb sodium. Sodium does wet the fibres, but whether this wetting is simply the result of favourable surface free energies or whether the sodium chemically reacts with the aluminium oxide is not known. If chemical reaction does occur, it is probably limited to a very thin surface layer. Excessive reaction would undoubtedly cause an uneven attack, or roughening, of the fibre surface. Such an attack would cause a decrease in fibre strength, which is not observed. Furthermore, when alumina fibres are first wetted with sodium, and then the sodium is removed by reaction with ethyl alcohol, the resulting bare fibres show no change in appearance due to surface roughening.

It was originally thought that the function of the sodium was to "clean" the fibres, i.e., remove adsorbed gases and other surface impurities, thereby allowing subsequent metal baths to wet the fibres. The evidence now indicates, however, that a thin film of sodium remains on the fibres throughout the processing (and is present in the finished composite) and that this film is essential to the success of the process. In other words, sodium acts as a protective and wettable coating on the fibres; subsequent metal baths must wet the sodium, rather than the fibres, without destroying this coating. It has been found that if the sodium coating is removed, such as by vacuum evaporation, before the fibres are immersed in the second bath, the second bath metal will not wet the fibres.

3.2. The function of tin

The major function of the tin bath is to dissolve and displace the sodium. Mixing and diffusion between liquid tin and sodium result in a composite that, when solidified, consists of a nearly pure tin matrix with a thin layer of sodium-rich metal remaining at the fibre–matrix interface.

In the preparation of fibre-reinforced aluminium composites by the sodium process, it would be advantageous if the aluminium bath could be used to displace the sodium, thus eliminating the necessity for the tin bath. This procedure unfortunately does not produce an infiltrated fibre composite, but rather only an aluminium "skin" on the periphery of the fibre bundle, with bare fibres throughout the remainder of the sample. This phenomenon can be explained on the basis of the fact that sodium and tin are completely miscible at the temperature of the tin bath (600° C), whereas sodium and aluminium are almost completely immiscible at all temperatures [6]. Apparently, the second metal bath must be capable of establishing a continuous sodium concentration gradient from a high-sodium region at the fibre surface to a low-sodium region between the fibres. In the case of sodium–aluminium, the higher density of aluminium presumably displaces the sodium from the region of the fibres without permitting the necessary fibre coating to remain in place. Another way of stating the problem is that the second bath must be capable of forming a liquid alloy with sodium. It may be noted that, in the preparation of fibre-reinforced lead composites by the sodium process [7], the sodium-infiltrated fibres can be immersed directly in the lead bath since sodium and lead are miscible.

3.3. The function of magnesium

It was stated earlier that a small amount of magnesium should be present in either the sodium bath or the tin bath. Magnesium and sodium are nearly immiscible; a saturated sodium bath at 550° C would contain less than 1.5% magnesium [6], an amount that has been found to be sufficient. Magnesium and tin are completely miscible, but a similar magnesium content (approximately 2 at.%) in the tin bath has been found to produce the same effect.

The function of the magnesium appears to be the stabilization of the fibre coating necessary for successful aluminium infiltration. Unlike tin, the

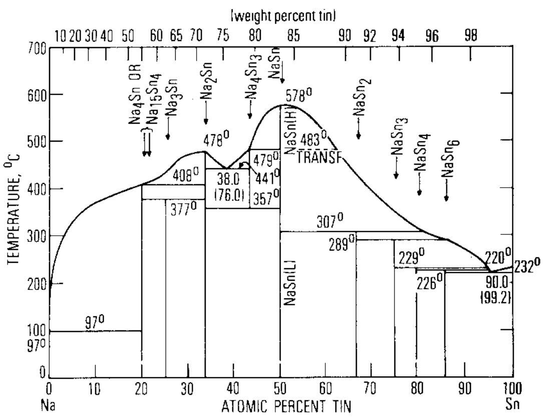

Figure 2 Sodium–tin phase diagram, after Hansen [6].

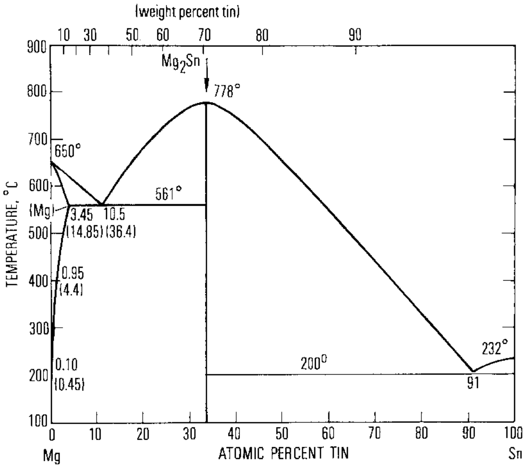

Figure 3 Magnesium–tin phase diagram, after Hansen [6].

absence of magnesium will not necessarily prevent the sodium process from working. However, experience has shown that the process works better and more consistently when magnesium is present. Without magnesium in either the sodium or tin baths, incomplete infiltration of the fibre bundle by aluminium is likely to occur.

Sodium and tin form a series of intermetallic compounds, several with higher melting temperatures than either pure component (Fig. 2). When a sodium-infiltrated fibre bundle is immersed in a molten tin bath, the concentration gradient from the high-sodium region adjacent to a fibre to the low-sodium region between fibres may well produce a small region with a melting temperature as high as 578° C. Obviously, such a region would tend to stay solid longer when immersed in molten aluminium, at nearly 700° C, than would a similarly sized region of pure tin or sodium. Since solid diffusion is much slower than liquid diffusion, it follows that a solid coating on a fibre is more likely to remain intact than a liquid coating.

Consider now the addition of magnesium to the system. Magnesium and tin form an intermetallic compound, Mg_2Sn, with a melting temperature of 778° C (Fig. 3). If a small layer of Mg_2Sn could be formed around each fibre, such a layer would remain solid (in the absence of diffusion) up to a temperature above that of the aluminium bath. Thus, the presence of Mg_2Sn could help stabilize the sodium-rich fibre coating during immersion in the aluminium, to an even greater extent than any of the sodium–tin intermetallics. Unfortunately, no information is available on possible intermetallic compounds in the sodium–tin–magnesium ternary system. However, IMMA studies conducted on FP–aluminium composites produced some interesting results. In these studies, analysis was made of a polished surface of the composite; no attempt was made to use the ion beam to bore through the material. The composites were purposely processed in metal baths that had been significantly contaminated by previous processing operations, so that higher (and thus more easily measurable) quantities of sodium, tin, and magnesium would be present in the finished composite. Element "maps", showing the locations of these three elements plus aluminium (light-coloured areas) in a section of the composite parallel to the fibre axis are presented in Figs. 4 to 7. (The fibres appear as horizontal dark regions in all of these figures; this effect occurs even on the aluminium map, for reasons associated with the electrically insulating nature of aluminium oxide.) The relatively high concentrations of sodium, tin,

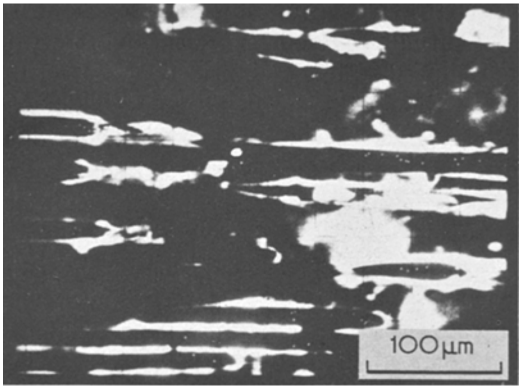

Figure 4 IMMA sodium map, FP–aluminium composite.

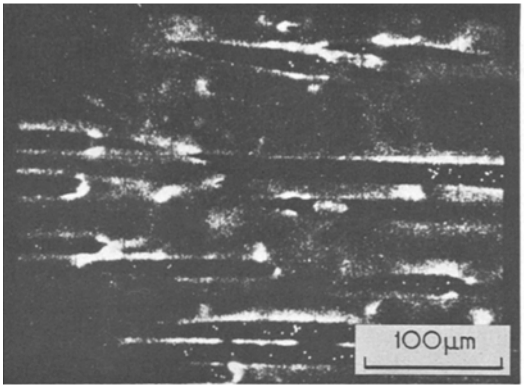

Figure 5 IMMA tin map, FP–aluminium composite.

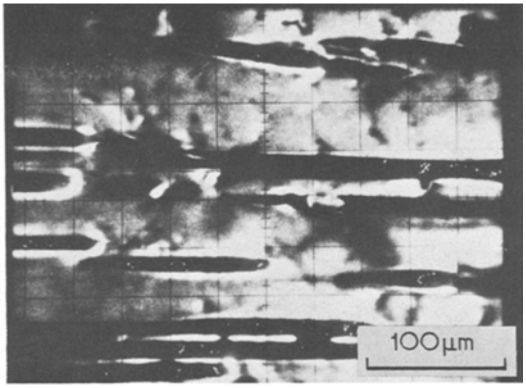

Figure 7 IMMA aluminium map, FP–aluminium composite.

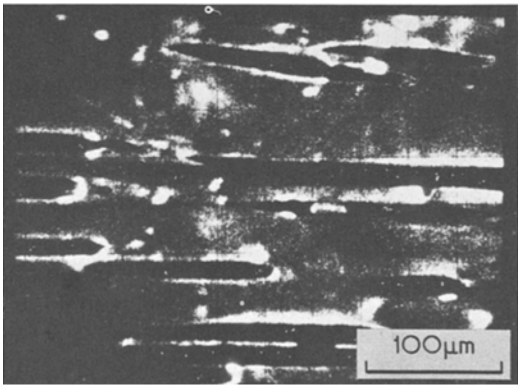

Figure 6 IMMA magnesium map, FP–aluminium composite.

and magnesium at the fibre–matrix interfaces are evident. Quantitative IMMA analysis was performed at selected locations within the microstructure; the results are given in Table I. The nearly constant Na:Mg:Sn ratio in regions near the fibre–matrix interface certainly suggests that a ternary intermetallic compound may be present; thus, such a compound may be responsible for stabilizing the interface. Another significant feature of the data in Table I is the relatively low contaminant level in the bulk matrix, even in a purposely contaminated alumimium composite, which demonstrates that sodium, tin, and magnesium do tend to remain segregated at the fibre–matrix interface.

Further evidence that high melting temperature compounds promote interface stability was provided by experiments involving graphite–lead composites. Sodium and lead are totally miscible, and the two elements form a series of compounds, several of which have melting temperatures near 400° C [6]. Molten lead at normal temperatures (350 to 400° C) displaces and dissolves sodium from the graphite fibre bundle, as does tin, to form a fully infiltrated graphite–lead composite upon solidification. If the lead bath is heated to 800° C, the resulting composite contains a considerable portion of bare graphite fibres, which indicates a breakdown of the fibre coating and resultant lack of wetting by the lead. If, however, immersion in the 800° C lead bath is preceded by immersions in both the sodium and the tin–magnesium baths, dewetting does not occur.

3.4. The function of aluminium

Just as the tin bath dissolves and displaces the sodium, the aluminium bath dissolves and displaces the tin, which is possible because aluminium and tin are completely miscible. The resultant composite, when solidified, should therefore consist of graphite or alumina fibres imbedded in

TABLE I Aluminium–FP composite compositions

Location	Na (at.%)	Sn (at.%)	Mg (at.%)	Al (at.%)	Mg/Sn	Na/Sn	Mg/Na
Between close fibres	9.0	8.8	27.0	55.2	3.1/1	1.0/1	3.0/1
Adjacent to single fibre	2.0	2.5	5.3	90.2	2.1/1	0.8/1	1.7/1
Matrix	0.18	nil	0.36	balance	–	–	–

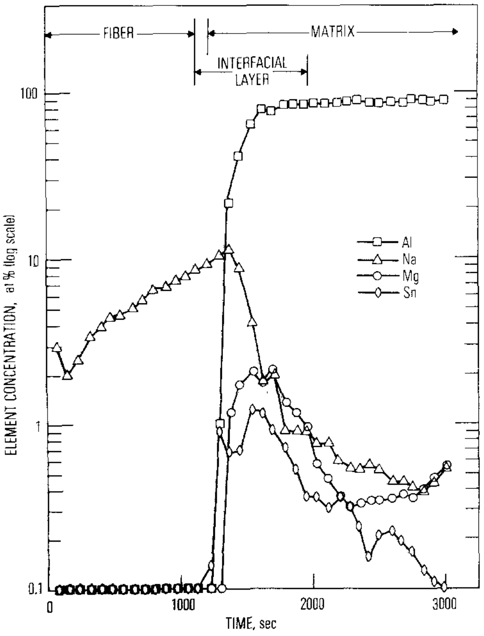

Figure 8 IMMA plot of sodium, tin, magnesium, and aluminium concentrations as function of time (depth of sputtered hole) in graphite–aluminium composite prepared by the sodium process. (Analysis starts in graphite fibre and proceeds into aluminium matrix).

a pure aluminium (or the desired aluminium alloy) matrix, with a thin layer rich in sodium, tin, and magnesium existing at the fibre–matrix interface.

IMMA "boring" experiments conducted on a graphite–aluminium (Thornel 50 fibres in a 6061 alloy matrix) composite confirm the presence of this thin interfacial layer. The results of one such experiment are shown in Fig. 8, which is actually a duplicate of Fig. 1 with the tin and magnesium concentration traces shown in addition to those of sodium and aluminium. In spite of the fact that the 6061 alloy itself contains magnesium, the concentration of this element is much higher at the fibre–matrix interface than in the matrix itself. Sodium and tin also reach their maximum concentrations at the interface. There is an indication that the fibre may be coated first with a sodium–tin intermetallic and then with a magnesium–tin intermetallic, but this apparent result may be due to the geometric effects of the irregular surface of the Thornel 50 fibre, or to minor concentration fluctuations at the interface. Thus, although it cannot be determined positively whether binary or ternary intermetallic compounds exist, the presence of some form of compound at the interface appears to be very probable. The aluminium matrix, not surprisingly, appears to alloy with the interfacial layer, except, perhaps, for a very thin portion immediately adjacent to the fibre. It is known that the rate of penetration of the ion beam through an aluminium alloy is approximately 6.5 Å $\sec^{-1}$. If this rate is assumed to be valid throughout the interfacial layer, the thickness of the layer can be estimated from Fig. 8. It must be pointed out that the IMMA will analyse elements present, not only at the bottom of the hole being bored by the ion sputter-

TABLE II Room temperature tensile strengths of sodium process aluminium composites

Composite type (fibre/matrix)	Fibre type	Fibre content, (vol. %)	Composite fracture stress (MPa)	Composite strength (% theoretical[a])
HM-3000/ 1100 Al	Pan I Graphite	9.3	210	87.7
Thornel 50/ 1100 Al	Rayon Graphite	13.3	317	96.9
Thornel 300/ 1100 Al	Pan II Graphite	11.3	98	31.8
FP/1100 Al	Alumina	13.5	173	117.0
Thornel 50/ A413 Al [8]	Rayon Graphite	28.0	731	105.0

[a] These values were determined from the equation

$$\sigma_c = \sigma_f V_f + \sigma'_m (1 - V_f)$$

where σ_c = theoretical strength of composite,
σ_f = tensile strength of fibres, as determined from strength of epoxy-infiltrated fibre bundle,
V_f = volume fraction fibres,
and σ'_m = stress on matrix at breaking strain of fibres; this value was assumed to be 34.5 MPa for 1100 Al and 207 MPa for A413 Al.

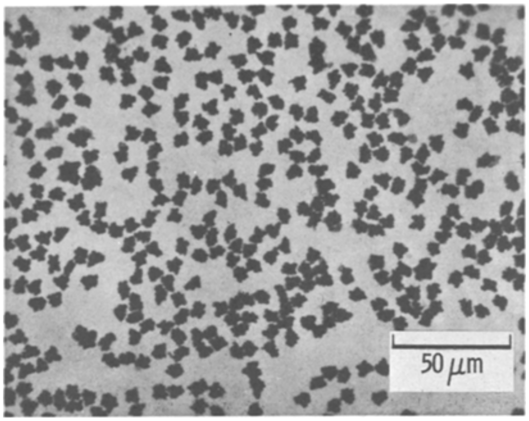

Figure 9 Photomicrograph of Thornel 50–aluminium composite prepared by the sodium process.

ing, but from the sides of the hole as well. Thus, the apparent concentrations of sodium, tin, and magnesium do not drop to zero when the interfacial layer has been fully penetrated. It may therefore be estimated that the interfacial layer is between 0.45 and 0.55 μm thick, of which the inner (adjacent to the fibre) 0.06 μm contains no aluminium. These values undoubtedly vary from sample to sample, and may be expected to be significantly larger if aluminium baths containing appreciable quantities of the interfacial elements are used in the preparation of the composite. However, IMMA studies on several types of graphite fibre–aluminium composites indicate that the thickness values determined from Fig. 8 are quite typical.

4. Mechanical properties and microstructures

Typical tensile strengths of fibre-reinforced aluminium composites produced by the sodium process are shown in Table II. Most studies of this process have employed batch rather than continuous processing so that experimental conditions could be more readily controlled or changed. A somewhat unfortunate consequence of batch processing is that fibre volume fractions, and hence composite tensile strengths, tend to be low. However, the data in Table II demonstrate that most fibres retain essentially full theoretical strength when incorporated into aluminium matrix composites by this method. The notable exception is the Thornel 300 fibres; apparently, the lesser degree of graphitization of these Pan II fibres makes them more susceptible to attack and degradation during processing. It is not clear, however, that the sodium treatment is the major culprit. Lead–Thornel 300 composites, prepared by immersing the fibre first in sodium at 550 and then in lead at 360° C, have retained up to 90% of their theoretical strength. Thus, the higher temperature tin–magnesium and aluminium baths may be largely responsible for the strength loss of these fibres. The alumina (FP) fibres, although initially much lower in tensile strength than the graphite fibres, are not degraded by the processing treatment. Composites containing these fibres may therefore perform quite satisfactorily under service conditions, such as compressive loading or oxidizing atmosphere, where ceramic fibres may be preferable to graphite. All of the composites, except those with Pan II fibres, should exhibit much more impressive tensile strengths with fibre contents in the more usual range of 30 to 50 vol.%.

Typical microstructures of aluminium composites produced by the sodium process are shown in Figs. 9 and 10. Note completeness of wetting of the fibres and infiltration of the fibre bundles by the aluminium matrix. The sodium process produces equally good results for both graphite and alumina fibres, even when the two fibre types are intimately mixed during processing (Fig. 10). This feature, together with complete flexibility in the selection of a matrix alloy, means that the process is adaptable to the production of a wide variety of composite types.

The preceding mechanical property and microstructure information is presented primarily to show that the sodium process is a useful procedure for preparing aluminium matrix composites. The

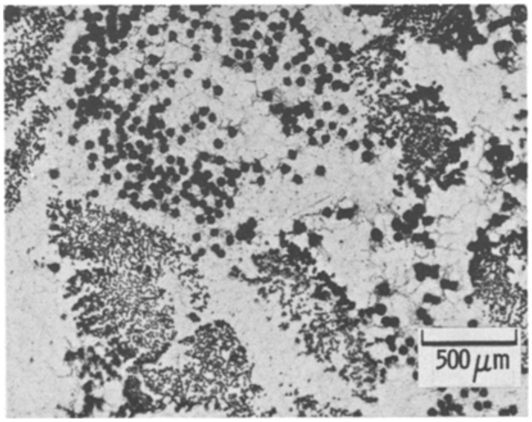

Figure 10 Photomicrograph of Thornel 50 plus FP-A 356 aluminium composite prepared by the sodium process.

process does have its drawbacks, most notable of which are the difficulty in handling molten sodium and the possible contamination of the aluminium matrix with sodium and tin. However, the process does offer the opportunity to study a rather interesting and potentially significant sequence of events that occurs at the fibre–matrix interface. It is quite possible that an understanding of the reasons for the success of the sodium process may provide the ground work for the successful development of other fibre–matrix composite combinations.

5. Summary

The sodium process for the preparation of fibre-reinforced aluminium composites consists first of wetting the fibres with molten sodium, then forming protective intermetallic compound fibre coatings by reacting the sodium with one or more other molten metals, and finally by displacing all metal except the fibre coating with a final bath of molten aluminium or aluminium alloy. This process is suitable for use with either graphite or alumina fibres, or a combination thereof. Rayon-base graphite, Pan I graphite, and alumina fibres exhibit no appreciable strength loss as a result of the processing, whereas Pan II fibres are significantly degraded. The metallurgical reactions that occur at the fibre–matrix interface during this process may provide insight into potential methods of forming other protective fibre coatings suitable for other fibre–matrix composite systems.

References

1. R. T. PEPPER and E. G. KENDALL, US Patent No. 3 770 488, Assigned to the United States of America as represented by the Secretary of the United States Air Force, Washington, D.C., November 6, 1973.
2. S. C. CARNIGLIA, Proceedings of the French–American Conference on Graphite Reactors, Document No. BNL 489 (Brookhaven National Laboratory, Upton, New York, 1957) pp. 159–167.
3. A. R. UBBELOHDE and F. A. LEWIS, "Graphite and its Crystal Compounds" (Clarendon Press Oxford, 1960).
4. G. M. WOLTEN Report No. NAA-SR-4545, Atomics International, Canoga Park, California (1960.
5. W. C. HARRIGAN Jr, ATR-76 (8162)-2, The Aerospace Corporation, El Segundo, California (1976).
6. M. HANSEN, "Constitution of Binary Alloys" (McGraw–Hill, New York, 1958).
7. D. M. GODDARD and E. G. KENDALL, *Composites* 8 (1977) 103.
8. R. T. PEPPER, J. W. UPP, R. C. ROSSI and E. G. KENDALL, *Met. Trans.* 2 (1971) 117.
9. R. C. ROSSI, R. T. PEPPER, J. W. UPP and W. C. RILEY, *Ceram. Bull.* 50 (1971). 484.

Received 31 August 1977 and accepted 17 January 1978.