JOURNAL OF MATERIALS SCIENCE 2 (1967) 409-414

Electroformed Composite Materials

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Received 26 January 1967 (originally submitted to "Applied Materials Research" 7 November 1966)

Electroforming has been used as a method of incorporating fibres in a metal matrix. Studies on both conducting and non-conducting fibres formed the basis of a critical assessment of the potentialities of this technique for making composite materials. Examples of the application of the method to the forming of various materials are given.

1. Introduction

Electroplating as a means of incorporating a reinforcing fibre in a metal matrix has not been widely studied. Experiments by Sautter [1] and Smith [2] on the incorporation of submicroscopic alumina particles in electro-nickel showed how substantial hardening could be obtained, but their results have tended to be eclipsed by work on thoria-dispersed nickel, which has attracted more interest [3]. More recently, however, Withers has reported making nickel composites reinforced with tungsten wire [4] or with boron fibres [5]. Sutton and coworkers report the use of electroforming techniques to incorporate alumina whiskers in nickel, obtaining a strength of 1.95×10^5 lb/in.^{2} (1 lb/in.^{2} = 7×10^{-2} kg/cm^2) with 39 vol % of fibres at room temperature [6]; while Baker [7] and Williams [8] have made tungsten-reinforced nickel and copper composites by electrodeposition techniques. However, most of these workers have been concerned with the properties of the composites produced, and relatively little attention has been paid to the technique of electroforming itself.

This paper presents some results obtained in studies with both conducting and non-conducting fibres, and forms a basis for the assessment of electroforming as a general technique for the manufacture of composite materials. It is emphasised that these results are of a preliminary nature only, and that further improvement of composite properties must follow development of the method.

Electroplating offers a number of advantages over other methods for fabricating composite materials. It is carried out at temperatures below 100° C, so there are no furnace or atmosphere considerations. The problems of compatibility are minimal, and systems may be made by electroforming which might prove reactive at higher temperatures. Alternatively, composites in which the two phases are completely unreactive may be made: there is no necessity, for example, for good wetting by a molten infiltrant; an advantage which may become increasingly significant as more ceramic-fibre/metal-matrix composites are made. This latter property, allowing control to be exercised over the strength of the fibre/matrix bond, may prove valuable in making materials which are tough and resistant to notches, by having a weak fibre/matrix bond [9, 10].

2. Apparatus

Composites with both copper and nickel matrices were made, the former deposited from an acid copper sulphate solution, and the latter from a Watts-type bath. The results presented here were obtained from composites with a copper matrix, but similar properties were found when nickel was used. The electroplating apparatus is sketched in fig. 1. The cathode was in the form of a copper drum, interchangeable with the winding drums on a silica-fibre drawing machine [13]. This arrangement enabled silica fibres to be incorporated in the electroplated matrix with the minimum of handling. It also provided a convenient method for making composites containing metal wires. The cathode drum was mounted on a spindle provided with a pulley-wheel, by which the drum was rotated via a belt drive from above the electrolyte. The axis of the driving pulley also formed a pivot on

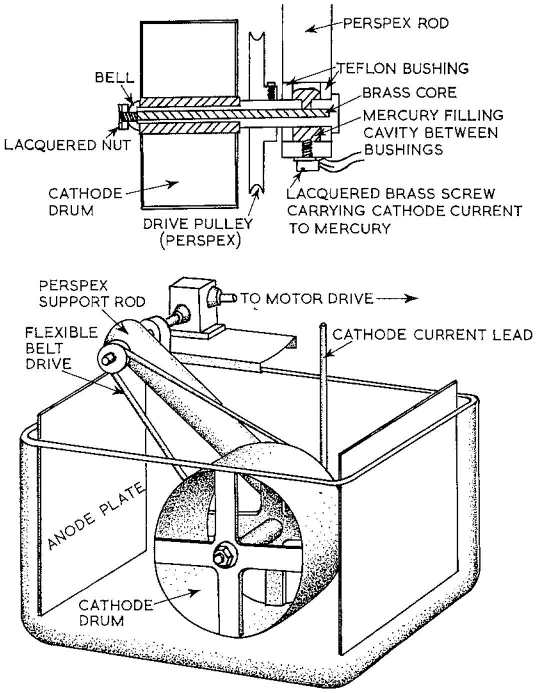

Figure 1 Electroplating apparatus used for making composite specimens.

which the whole cathode assembly was hinged. Thus it could be raised out of the plating tank for removal or inspection of the cathode without deranging the driving mechanism.

Electrical contact to the cathode was made through the driving spindle, which had a Perspex exterior but a brass core. The spindle was carried in a hollow Teflon bearing, which contained a pool of mercury, through which the current was conducted from an external lead into the core of the spindle. This design was able to carry currents up to 50 A. All parts of this assembly, except the core of the cathode spindle, were made of various plastics, so the current was conducted to the cathode without ever coming in contact with the electroplating solution.

This whole construction enabled the cathode drum to be rotated while plating was in progress; a function which had two advantages. Not only did the rotation (about 100 rev/min) cause a considerable degree of agitation in the solution, enabling high current densities to be used, but also the deposit on the cathode was much more uniform and was circularly symmetric. The two anodes, which were plates of high-conductivity copper, were placed vertically in the bath on either side of the cathode drum. In early experiments, the anodes were wrapped in nylon cloth, to prevent the particles of copper and copper oxide which fall from the anode surface during dissolution attaching to the cathode, where the particles formed unpleasant excrescences. Later, it was found that these excrescences could be avoided if the cathode rotation speed was sufficiently high, so the practice was discontinued.

The electrical supply was via a variable transformer and rectifier. Some experiments were conducted with a device for the periodic reversal of the plating current, which has been shown to produce, in some circumstances, a more even cathode deposit [11, 12]. It was found, however, that equally good results could be obtained by decreasing the continuous plating current without periodic reversal, and that, in terms of the effective deposition rate, the continuous plating method was marginally superior.

When making a composite, first the cathode drum was covered with a thin layer of colloidal graphite. A flash of copper was struck onto this by commencing with an abnormally high current density. Then plating was continued at the normal rate until 5 to 10 μm of copper were deposited. The drum was removed, and a layer of silica fibre or metal wire was wound onto the drum. Plating was recommenced, and the process continued until a composite of the required dimensions had been built up. The composite was removed by making an axial cut in the surface of the drum and peeling it away from the graphite coating.

3. Growth Profiles

To determine something of the growth characteristics of material made in this way, and to assess the maximum volume-fraction attainable with conducting and non-conducting fibres, two experiments were made.

In the first experiment, a composite was made with a single row of irregularly spaced, 50 μm, glass fibres. After plating for some time, the composite was sectioned and examined (fig. 2). It will be seen that the electroplate has been unable to grow between fibres which are touching, but is able to grow satisfactorily through gaps of half a fibre-diameter or less (about 20 μm). Once past this barrier, the surface expands, and, meeting other bodies of growing matrix metal, amalgamates with them. It should be noted, however, that the rejoining of the

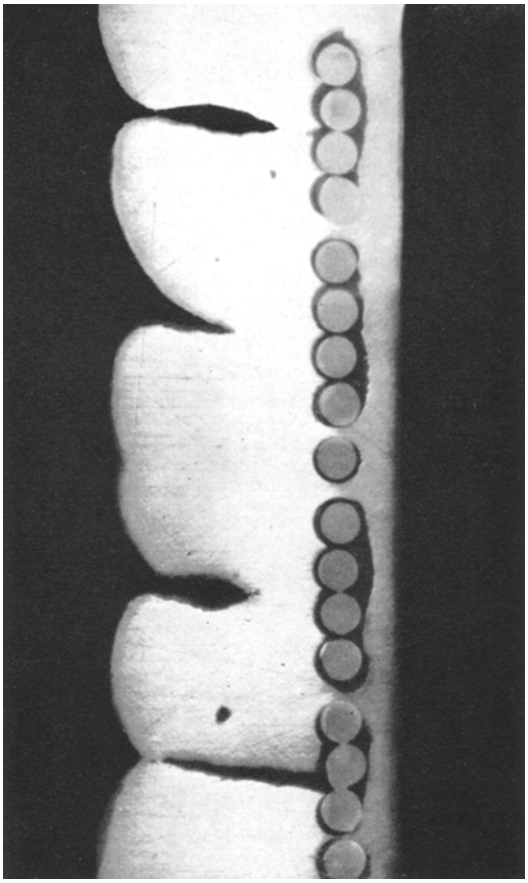

Figure 2 Section of an electroformed composite with a single row of closely spaced non-conducting fibres (×150).

electroplate surface is by no means rapid, and large voids are formed above continuous rows of more than a few fibres.

In the second experiment, growth contours for the electroplated matrix were calculated by computer for a particular fibre geometry, with both conducting and non-conducting fibres. For the purposes of the calculation, perfect throwing power was assumed for the electroplating process, and the rate of growth was made to depend inversely upon the instantaneous surface area of the matrix metal (i.e. constant current, rather than constant current density, was used). These are, of course, first approximations, but may be adequate for small fibres. The results were then compared with observed fibre dispositions in composites containing 40 μm silica fibres, in both the conducting and non-conducting conditions. The fibres were rendered conducting by a coating of carbon. This was applied by passing the fibre, while it was still hot from the drawing process, through a chamber containing heated acetylene. The hot acetylene cracked on contact with the fibre, depositing a thin, coherent, and protective coating of carbon onto the fibre surface. As well as being electrically conducting, the coating protects the fibre from adventitious damage, and preserves its high nascent strength [13]. The results of the observations are shown in figs. 3 and 4. Both show an initial geometry of a plane surface, on which were placed three fibres: two touching, and the third spaced one fibre-radius away. The electroplate was allowed to grow for some time, and then a further two fibres were laid down so as to occupy the grooves in the upper surface of the electroplate. Examination shows that the accidental touching of two fibres causes a much more severe disturbance later in the case of non-conducting fibres than in the case of conducting fibres. It also leads (in the case shown) to a total discontinuity of matrix metal across the specimen, leading to

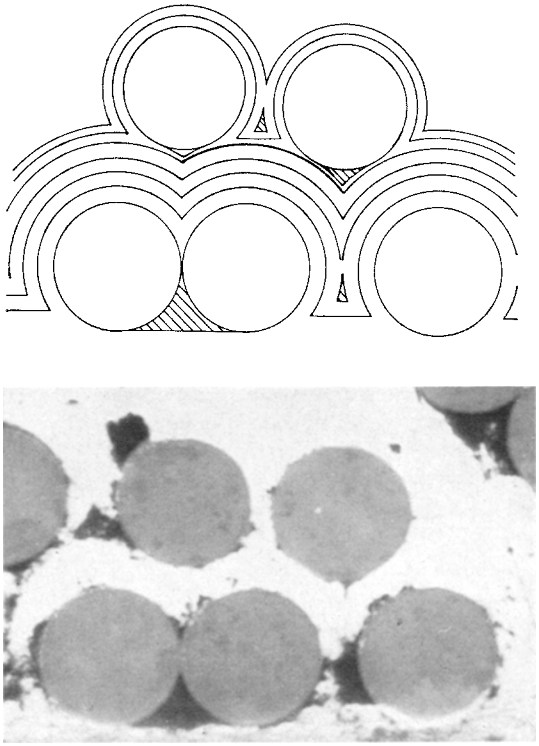

Figure 3 Comparison of experimental and computed fibre distributions for conducting 40 μm diameter fibres.

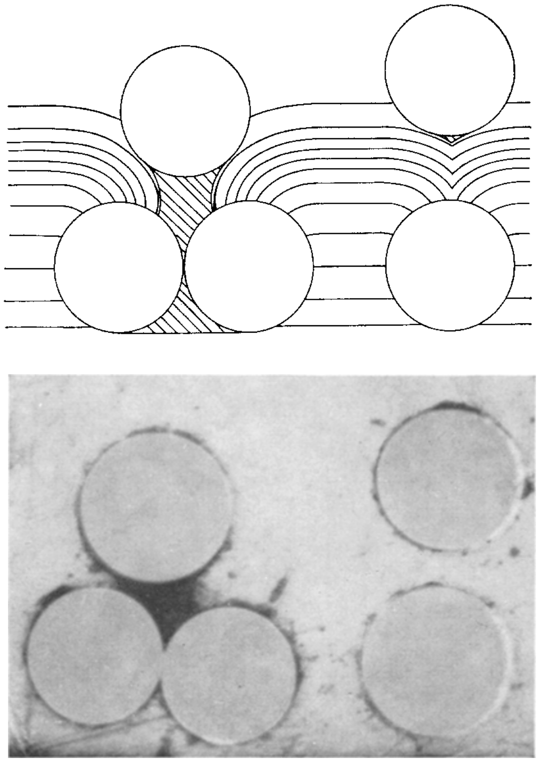

Figure 4 Comparison of experimental and computed fibre distributions for non-conducting 40 μm diameter fibres.

voids and a corresponding loss of transverse strength.

The similarity between the calculated and observed fibre dispositions is quite good, and shows that the assumption of perfect throwing power is adequate for calculations of this type.

The maximum volume-fraction of non-conducting fibres is dictated by the need to maintain a continuous body of matrix metal. The minimum practical gap between fibres in any row is approximately one fibre-radius (see above). The minimum amount of matrix metal, which must be deposited to ensure complete burial of a row of fibres, requires the subsequent row of fibres to be again approximately one fibre-radius above the previous row. On this basis, therefore, volume-fractions of up to 40% should be attainable with non-conducting fibres.

For the case of a conducting fibre, the limiting factor is the transverse strength of the composite: even if the bond between the fibre and the metal plated onto it is very good, it is unlikely that a bond will develop between the fibre and the pre-existing matrix surface onto which it is wound. The strength of the composite determined in the direction of growth will therefore be governed largely by the size of the gaps between fibres in any row, and by the strength of the matrix bridges in these gaps. The maximum volume-fraction achieved in practice with silica fibre (non-conducting) was 20%, and with tungsten was 55%.

4. Applications of the Technique

Various composites made by electroforming are now described to illustrate the potentialities of this method of fabrication – none of these materials has been successfully made by other means.

4.1. Silica/Copper

Composites containing both conducting and non-conducting silica fibres were made by drawing 40 μm filament directly onto the cathode drum of the plating apparatus. Maximum volume-fractions of 20 and 25% were attained with plain and coated fibres respectively. The volume-fractions obtained with silica fibres are low by comparison with those obtained using tungsten; this is probably due to the less orderly packing of the finer silica fibres.

The measured mean strength of individual coated fibres (4.9×10^5 lb/in.^{2}) was compared with that deduced from measurements of the composite breaking strength. Allowing for statistical effects [10], the mean strength of the fibres in the composite was estimated to be 4.7×10^5 to 5.3×10^5 lb/in^2. It was concluded that the fibre had not been damaged significantly by the incorporation process, indicating an advantage of this technique over such methods as hot-pressing of powder compacts, or vacuum-infiltration; these methods almost invariably cause degradation of fibre strength.

4.2. Tungsten/Copper

A series of electroformed composites containing 0.1 mm tungsten wire was made. Material made in this way has a poor fibre/matrix bond, in comparison with material made by vacuum-casting. It was used in experiments on fracture toughness and on the variation of composite strength with orientation [10, 14].

The properties of the fibre/matrix bond were measured in shear and in tension, using clean, electropolished tungsten wire. The tensile strength of the interface was determined for composites containing a single row of tungsten fibres. The transverse breaking strength was measured as a function of specimen thickness, and was found to extrapolate to zero at a thickness equal to one fibre-diameter (fig. 5). The tensile strength of the interface was concluded to be not measurably different from zero. The shear strength of the interface was found by measuring the fraction of fibres which were pulled out rather than broken, when wires were embedded to various depths in the matrix. The results are shown in fig. 6, and give a mean value for the shear strength of the interface of 1.1 × 10^3 lb/in^2.

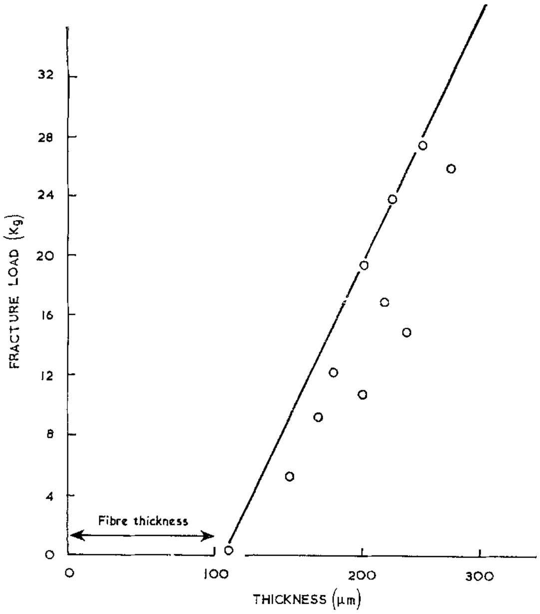

Figure 5 Plot of transverse failure load versus specimen thickness for tungsten-wire-reinforced composites.

The apparent inconsistency of these results may perhaps be explained by assuming that the shear resistance arises not from an actual interfacial bond, but by the effect of interlocking irregularities in the tungsten and copper surfaces which form the interface. It should be noted, however, that the bond strength may be subsequently increased by heat-treatment, if desired.

4.3. Niobium/ 25 wt % Zirconium/Copper

A further application of the technique may be in the field of superconductor technology. It is of interest to enclose the superconductor in a jacket of a high-conductivity copper, so that, in the event of the superconductor going critical, a part of the current may be carried in the copper jacket.

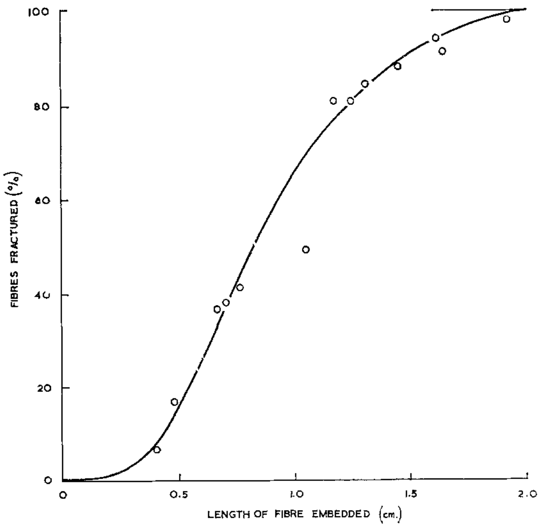

Figure 6 Variation of number of fibres fractured when composites reinforced with tungsten wire were gripped over varying distances.

To this end, a series of superconducting composites was made by the author and Dr C. Baker*. These were in the form of tapes, containing a single row of between five and twenty, 0.1 mm diameter, niobium/25 wt % zirconium wires. The volume-fraction of superconductor was 25%.

The electroplating method is again ideal for fabricating composites of this type, in which freedom from interaction is more important than great mechanical strength. Our material shows distinct advantages over composites made by hot-pressing, which suffer from the presence of a brittle, copper/zirconium intermetallic phase which forms at temperatures above 500° C. This does not, however, preclude the annealing of the electroformed composite below this temperature to improve the conductivity of the matrix, which, in the "as-plated" condition, has a very fine grain size and considerable internal strain.

5. Conclusions

In this paper, we have examined the technique of electroplating as a means for fabricating various fibrous composite materials. We have noted that electroforming has particular ad-

*Now at Central Electricity Research Laboratories, Leatherhead, Surrey, UK vantages, by reason of the low temperatures and absence of mechanical working involved in making composites. We have also estimated the maximum quantities of fibre which may be incorporated in an electroformed composite, and have reported measurements on the strength of the tungsten/electro-copper bond. We conclude that electroforming may be a valuable technique if composites with a low fibre/matrix bond strength are required, or if it is necessary to minimise the fibre/matrix interaction.

Acknowledgements

The author would like to thank J. C. Viner of the University Mathematical Laboratory for assistance in writing the computer programmes. The work forms part of a programme of research into "strong materials" under the supervision of Dr A. Kelly, to whom the author is indebted for constant advice and encouragement. The author also thanks the Science Research Council for a maintenance grant received while this work was executed.

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