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The Fabrication of Fibre-Reinforced Metals by Filament-Winding and Electrodeposition: an Evaluation of some Electroplating Solutions

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The process of filament-winding and electroforming is a promising method for the fabrication of fibre-reinforcing metal composites. A simple test has been developed to evaluate some electroplating solutions of interest. It has been found that simple salt solutions work satisfactorily with the process but this was not the case with highly complexed solutions. The observed growth behaviour is explained in terms of the differences in micro-throwing power between the solutions investigated.

1. Introduction

In many respects the process of filament-winding used for fabricating sophisticated fibre-reinforced plastic components would also be ideal for fibre-reinforced metallic components. The difficulties in adapting this technique to metals lie in the method of metal matrix application. Whilst a resin system can be applied, either wet or tacky, to the fibres, and subsequently cured at low temperature, any comparable method for metals (e.g. melt impregnation or powder consolidation) requires temperatures which, because of the problem of fibre-matrix interactions, are unacceptably high. Another difficulty for metals, not met with to the same extent in resin systems, is the inherently low penetrating power of these techniques. This is a particularly important consideration when dealing with the very promising continuous fine multi-filament carbon fibres that have currently become available. These problems may be avoided to a large extent by applying the metal matrix in the molecular state. Two suitable methods of molecular transportation that could be used with a filament-winding process are chemical vapour deposition and electrodeposition.

Chemical vapour-deposition has the advantage of high penetrating power and that a wide range of metals and non-metals can be deposited, often at temperatures of only a few hundred degrees centigrade. Electrodeposition has the advantage over chemical vapour-deposition of being simple technologically, but is limited in the number of metals that can be deposited with satisfactory properties. Both methods are limited in their ability to deposit alloys.

For the reasons given, the electrodeposition process was chosen for some early studies on the fabrication of fibre-reinforced metals [1]. These studies were based on a combined process of filament-winding and electrodeposition†. It was found that good composites could be produced

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†This process is fully described by Baker *et al* [1]. Basically it consists of winding strong fibres (conducting usually) onto a conducting drum which is immersed in an electroplating solution. The resulting electrodeposit forms around the fibres as they are wound on the drum to give a continuous fibre-reinforced structure. The process is analogous in many respects to that of filament-winding glass fibres with a resin matrix.

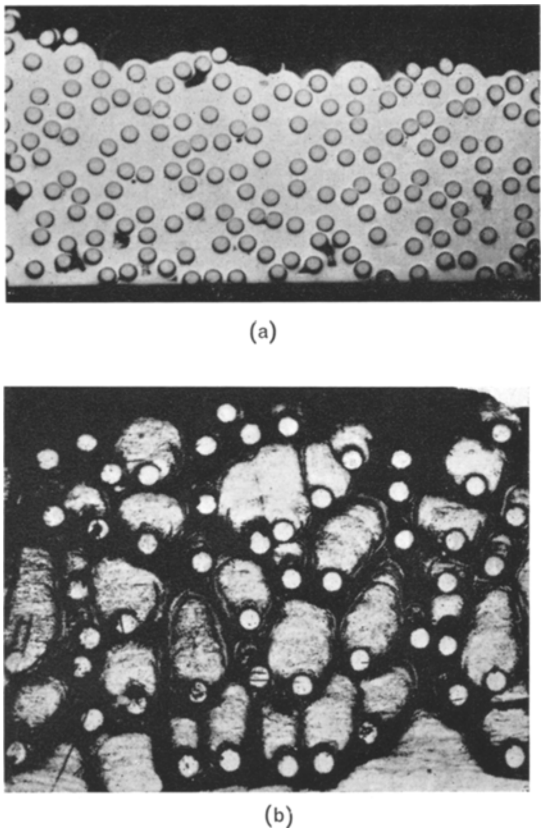

Figure 1 Filament-wound-electroformed composites. (a) Nickel matrix reinforced with 0.002 in. tungsten wires. Volume fraction of fibres – 25%. (b) Bronze matrix reinforced with 0.002 in. stainless steel wires. Volume fraction of fibres ~ 12%.

by the electrodeposition of nickel as a matrix from a sulphamate solution but not, for instance of bronze as a matrix from a cyanide solution, (see figs. 1a and 1b).

This paper describes the development of a simple static test using relatively small amounts of electrolyte to evaluate the applicability of some of the important electrodeposition solutions to the filament-winding process. The electrodeposited metals and alloys that are of interest for fibre-reinforcement can be categorised into those of interest (a) for structural applications such as Ni, Co, Ni/Co, Al and (b) for bearing applications, such as Pb, Sn, Pb/Sn, Cu, Cu/Sn, Ag. The difference in philosophy between these two applications of fibre-reinforcement is important: in the first case we are using the metal as a temperature-resistant binder for strong fibres; in the second case we are using the fibres as a method of improving the strength of a matrix with good bearing properties, without affecting its hardness.

2. Experimental—Electrolyte Evaluation

2.1. Model for the Filament-Winding-Electroforming Process

The initial stage of composite formation by the filament-winding process [1] is as shown diagrammatically in fig. 2a, i.e. conducting fibres rest (under tension) on the surface of a conducting drum. In fig. 2b a schematic representation is shown of a cross-section along a weft fibre of a single weave wire gauze (the wire is held in tension by frictional forces). The similarity between the two configurations is obvious; the gauze, therefore, constitutes a good model of the situation in the early stages of the winding process. Furthermore, other sections through the gauze represent other interesting situations. For instance fig. 2c shows diagrammatically the effect of making a taper section through the weft fibre. This gives the situation shown in fig. 2b, plus information on the effect of fibres of various spacings supported away from the drum surface.

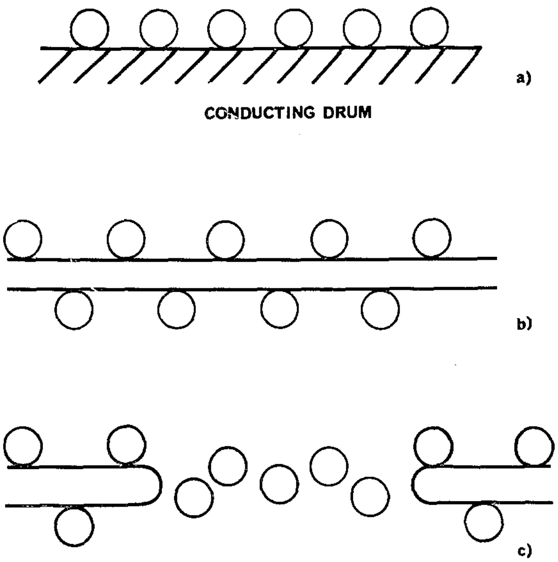

Figure 2 Schematic illustration of geometrical relationship between the filament-winding-electroforming process and the wire gauze model. (a) The initial stage in the filament-winding process. (b) Longitudinal section through a wire gauze along the weft fibre. (c) Longitudinal taper section through the weft fibre of the wire gauze.

2.2. Electrodeposition Experiments

Two types of test were carried out for most solutions: (1) a rough screening test to determine the effect of a wide range of current densities and (2) more controlled tests in the range of the most promising current-densities estimated from the rough screening tests.

2.2.1. Rough Screening Tests

The effect of current-density over a wide range was investigated using a Hull-Cell* test modified to allow for the relatively thick deposits required. The modification consisted of removing the bottom of the cell, suspending it in a three-litre tank of solution and providing efficient agitation within the cell space. The normal plain cathode was replaced by a wire gauze made from approximately 2.5×10^{-3} in. wires; this was stopped off around the edges with silicone rubber to prevent edge growth. In the use of the wire gauze cathode the assumption was made that the same 40:1 ratio of primary current density holds as for a plain cathode. The actual value of the current density is not easily determined because of the unknown and continuously changing effective surface area of the gauze. In the tests to be described two levels of current were used, 0.5 and 5 A, giving equivalent *plain cathode* current densities of 0.5 to 20 A/ft^2 and 5 to 200 A/ft^2.

2.2.2. Controlled Current-Density Tests

The controlled current tests were carried out with the wire gauze, in a perspex frame sealed with silicone rubber, suspended between two anodes about 8 in. apart.

The solutions investigated are listed in table I together with possible applications for the reinforced material. Detailed chemical compositions and recommended current-densities of use for these solutions are given in table I. To avoid end effects samples for metallographic examination were taken 0.25 to 0.5 in. from the edges.

3. Experimental Results

The results are reported in three subsections, the first dealing with simple salt solutions, the second with complex solutions, and the last with aluminium deposition from a non-aqueous solution.

3.1. Simple Salt Solutions

The results of the gauze tests on the metals deposited from simple salt solutions are shown in figs. 3a to e as a series of photomicrographs chosen from test at the optimum range of current-density†. A comparison of fig. 1a with 3a shows the relationship between the filament-winding-electroforming process and the gauze test for nickel from a sulphamate solution. This comparison may be used as a standard for evaluating the results of the gauze test on all other solutions. However, even without the benefit of this comparison the continuous deposit on the weft and warp fibres shown in fig. 3a, particularly at the point of contact between the fibres, strongly suggests that the process would work for this metal. Thus it can be concluded from figs. 3b to e that all of the other metals deposited from the simple salt solutions could successfully be used with the winding process.

3.2. Complex Electroplating Solutions

3.2.1. Copper

Typical results for copper electroplated from a cyanide solution at two levels of current density are shown in figs. 4a and b. It is seen that at a relatively high current density (fig. 4a) the deposit has not levelled‡ the notch formed by the intersection between the warp and weft wires of the gauze. In fact the angle of the notch at the intersection appears to have decreased to zero and a crack thus perpetuated. A superficial examination of the lower current density specimen (fig. 4b) would suggest that the notch has been removed or levelled out, as observed in the simple salt solutions. However, the presence of cracks emanating from some of the points of wire intersection makes this conclusion open to some doubt. Therefore this solution would not be expected to work successfully with the filament-winding process.

For comparison with the behaviour of the highly complexed copper cyanide bath and the simple salt copper sulphate or fluoborate bath, the copper pyrophosphate bath was investigated. This falls, in the degree of complexion of the copper ions, between the cyanide and the sulphate or fluoborate. The behaviour of this bath (fig. 4c) appears to be intermediate between that found for the sulphate or fluoborate (fig. 3b) and the

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*A Hull-Cell is a cell with a simple geometrical arrangement of anode and cathode which allows the evaluation of a large range of current densities in one test. [4].

†These tests were relatively insensitive to current-density.

‡Levelling or levelling power is the ability of the electroplating process to reduce surface irregularities [4].

TABLE I Classification and Operating Conditions of Electroplating Solutions

Deposited metal	Electrodeposition solution*	Solution composition and normal operating condition (CD = current density)		Possible application of composite
Nickel	Sulphamate(a)(1) (X)	Nickel Sulphamate	600 g/l	High temperature structural
		Nickel chloride	10 g/l	
		Boric acid	40 g/l	
		Temperature 60 to 70° C pH 3.8 to 4.2 CD up to 800 A/ft^2		
Nickel/cobalt alloy (60 / 40)	Sulphamate (X)	Nickel sulphamate	200 g/l	High temperature structural
		†Cobalt sulphamate	24 g/l	
		Boric acid	35 g/l	
		Temperature 45° C pH 3.8 to 4.2 CD 20 A/ft^2		
Copper	i) sulphate (X)	Copper sulphate	188 g/l	Bearings
		Sulphuric acid	74 g/l	
		Temperature 15 to 50° C CD 30 to 50 A/ft^2		
	ii) fluoborate (X)	Copper	120 g/l	
		Fluoboric acid	31 g/l	
		Temperature 27 to 49° C CD up to 400 A/ft^2		
	iii) pyrophosphate(b) (Y)	Copper pyrophosphate	94 g/l	
		Potassium pyrophosphate	300 g/l	
		Ammonia	2 ml/l	
		Temperature 50 to 60° C pH 8.0 to 8.6 CD up to 30 A/ft^2		
	iv) cyanide(a)(2) (Y)	Copper	38 g/l	
		Free potassium cyanide	28 g/l	
		Temperature 54 to 66° C pH 11.5 CD 20 A/ft^2		
Bronze (90 / 10)	i) Copper cyanide/stannate(a)(3) (Y)	Copper	32 g/l	Bearings
		Tin	16 g/l	
		Sodium hydroxide	10 g/l	
		Free sodium hydroxide	15 g/l	
		Temperature 60 to 65° C pH 8.5 to 9.0 CD 50 A/ft^2		
	ii) Copper cyanide/pyrophosphate(c) (Y) [3]	Copper	15 g/l	
		Stannous tin	0.5 g/l	
		Stannic tin	4 g/l	
		Free potassium cyanide	5 to 10 g/l	
		Temperature 60° C pH 9.5 CD 20 to 40 A/ft^2		
Lead	Fluoborate(a) (X)	Lead	100 g/l	Bearings
		Free fluoboric acid	44 g/l	
		Temperature 15° C CD 15 to 20 A/ft^2		
Lead tin alloy (70/30)	Fluoborate(a) (X)	Lead	62 g/l	Bearings
		Tin	28 g/l	
		Free fluoboric acid	40 g/l	
		Temperature 27 to 38° C CD 30 A/ft^2		
Silver	Cyanide (Y)	Silver cyanide	44 g/l	Bearings
		Potassium cyanide	45 g/l	
		Sodium carbonate	15 g/l	
		Potassium hydroxide	4 g/l	
		Temperature 38 to 47° C CD up to 100 A/ft^2		
Aluminium	Ethereal (Z)	Aluminium trichloride	16 g/l	Structural medium temperature
		Lithium aluminium hydride in ether		
		Temperature 23° C CD 15 to 100 A/ft^2		

*Anotation as follows

Manufacturer	Trade Name
(a) W. Canning and Co Ltd, UK	(1) Ni-Speed (2) Cuprax (3) Penybron
(b) Albright and Wilson (MFG) Ltd, UK	Pyrobrite
(c) The Enquist Chemical Co Inc, USA	Lustralite

(X) Simple salt solution. (Y) Complex salt solution. (Z) Non-aqueous solution.

†Made by dissolving cobaltous carbonate in sulphamic acid.

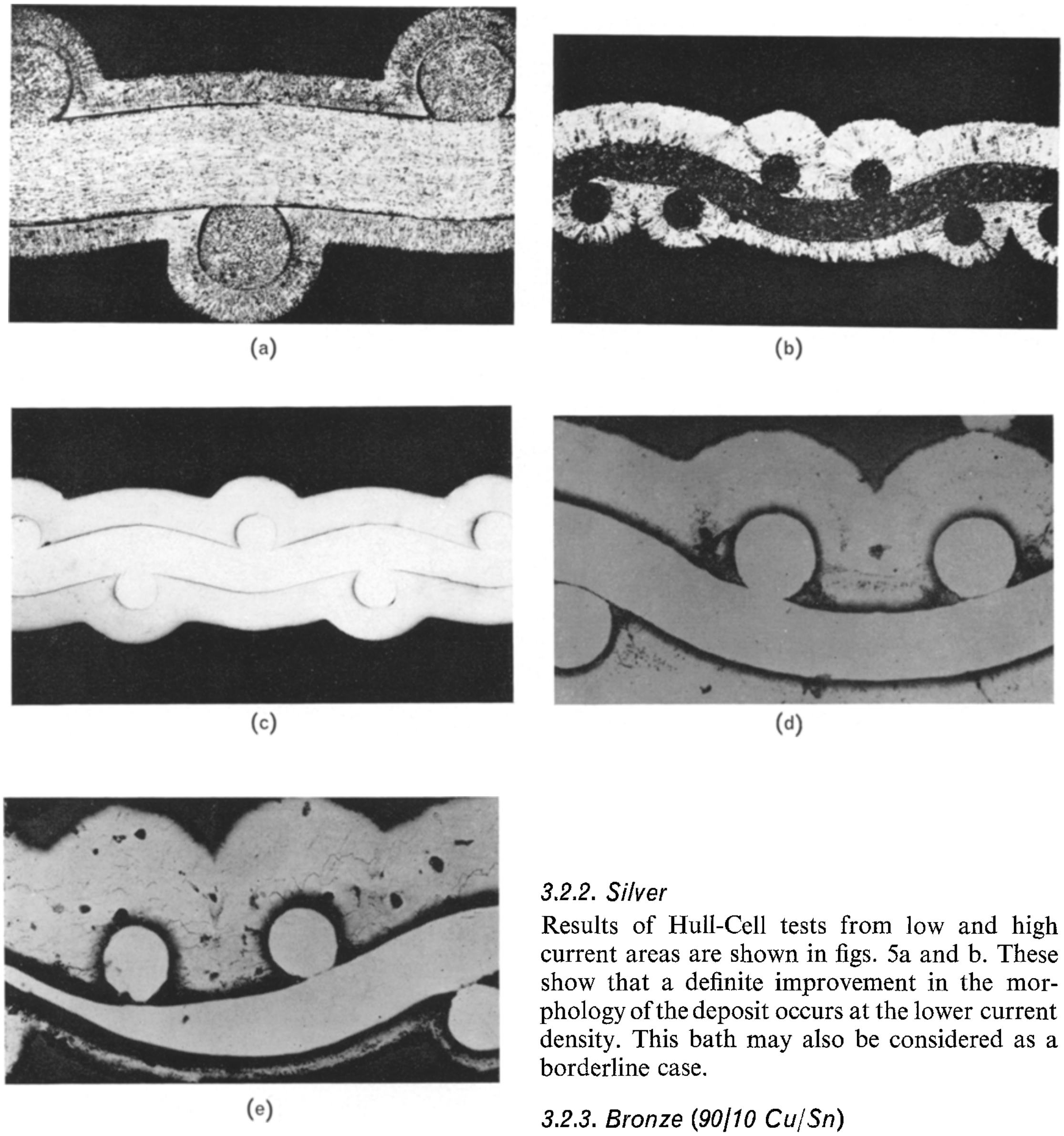


Figure 3 Longitudinal sections taken from wire gauzes which have been electroplated in a variety of simple salt solutions. (a) Nickel from sulphamate bath on to a copper gauze (×30). (b) Copper from a fluoborate bath on to a bronze gauze (×60). (c) Nickel-cobalt (60/40) from sulphamate bath on to a bronze gauze (×60). (d) Tin-lead (30/70) from fluoborate bath on to a stainless steel gauze (×120). (e) Lead from fluoborate bath on to a stainless steel gauze (×90). In all cases good levelling behaviour is exhibited.

cyanide bath (fig. 4a) and this solution may be considered as a borderline case

3.2.2. Silver

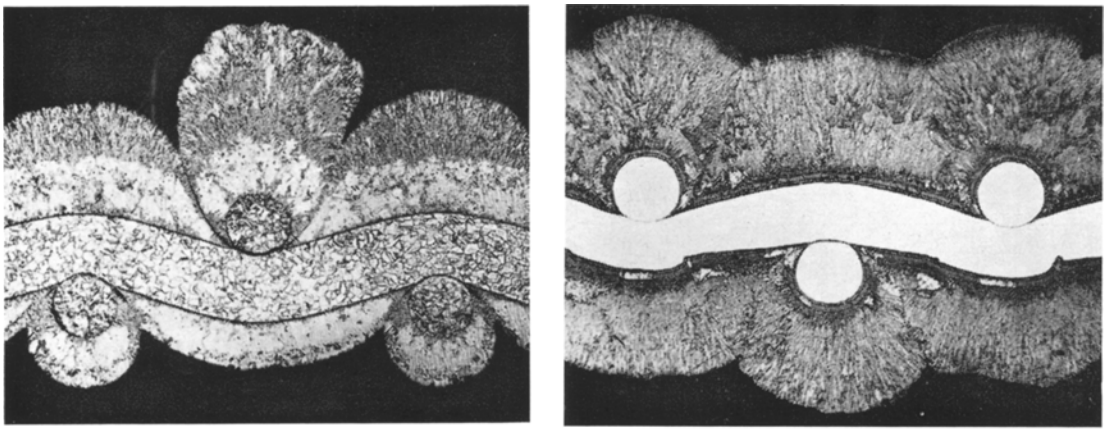
Results of Hull-Cell tests from low and high current areas are shown in figs. 5a and b. These show that a definite improvement in the morphology of the deposit occurs at the lower current density. This bath may also be considered as a borderline case.

3.2.3. Bronze (90/10 Cu/Sn)

Two proprietory bronze electroplating solutions were investigated (see table I): (a) a copper cyanide/stannate bath; (b) a copper cyanide/pyrophosphate bath.

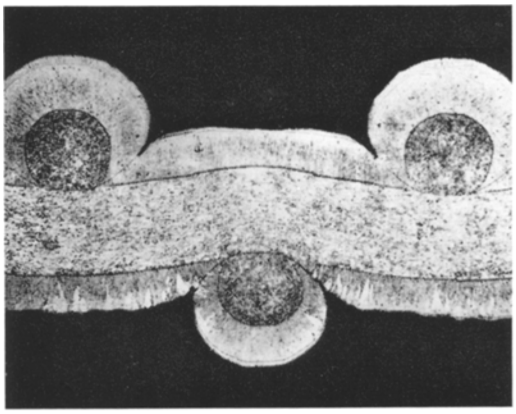
The copper cyanide/stannate bath is the standard bath used for deposition of bronze coatings; the copper cyanide/pyrophosphate bath is one developed by W. H. Safranek *et al* [2] of the Battelle Memorial Institute and was reported to have good electroforming properties.

Typical results from the cyanide/stannate solution are shown in figs. 6a and b and show an almost classical antilevelling or roughening



(a) (b)

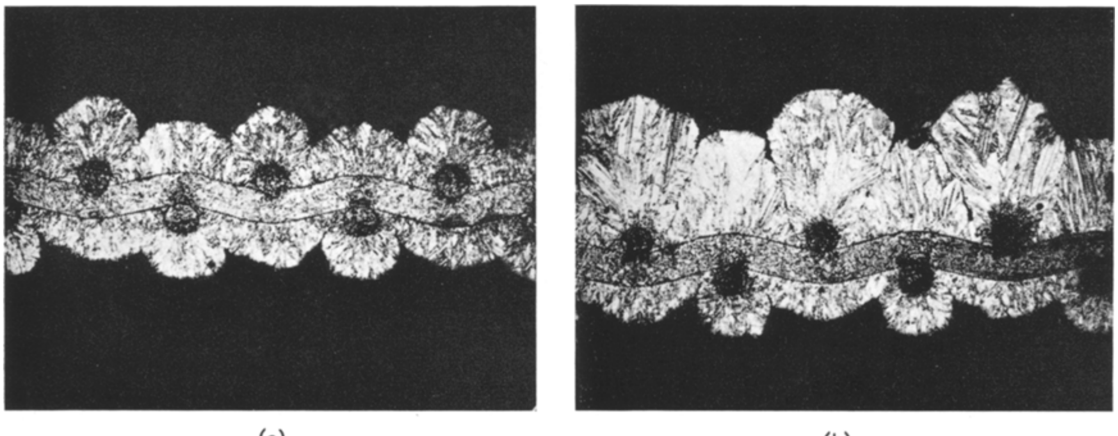
Figure 4 Longitudinal sections taken from gauze specimens which have been electroplated with copper deposited from complex solutions. The microsections from the Hull-Cell tests were taken from the centre of the gauze. (a) From a cyanide bath on to a bronze gauze at 5.0 A in Hull-Cell test (×80). (b) Same as (a) except current was 0.5 A. (c) From pyrophosphate bath on to a copper gauze at a current density, based on a plain cathode, of 40 A/ft^2 (×70).



(c)

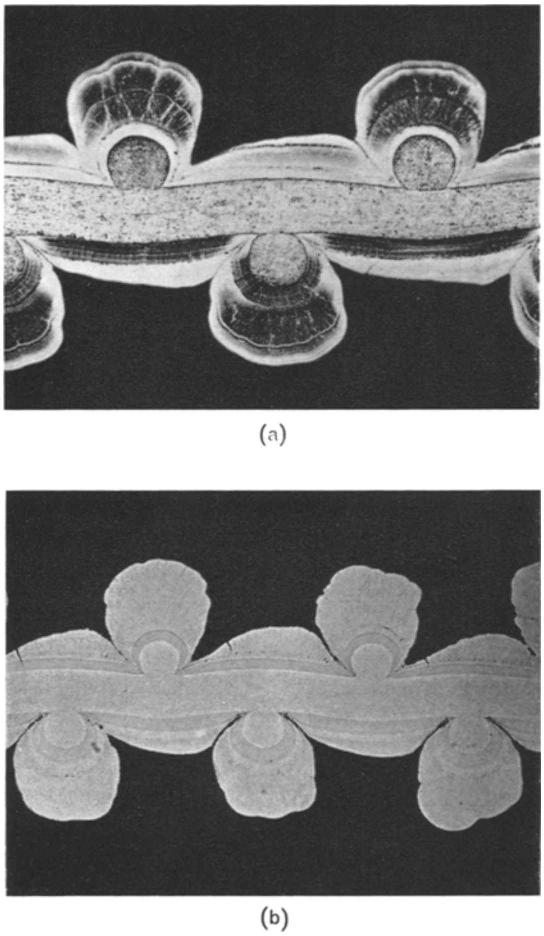
behaviour. This figure can be compared with fig. 1b to demonstrate the comparison between the test and the filament winding process for this solution. The angle of the notch formed by the intersection of the warp and weft fibre decreases almost to zero in some cases, but the sides of the crack or notch so formed are well separated.

The results obtained on Hull-Cell tests from the copper cyanide/pyrophosphate baths were more promising and some detailed tests were



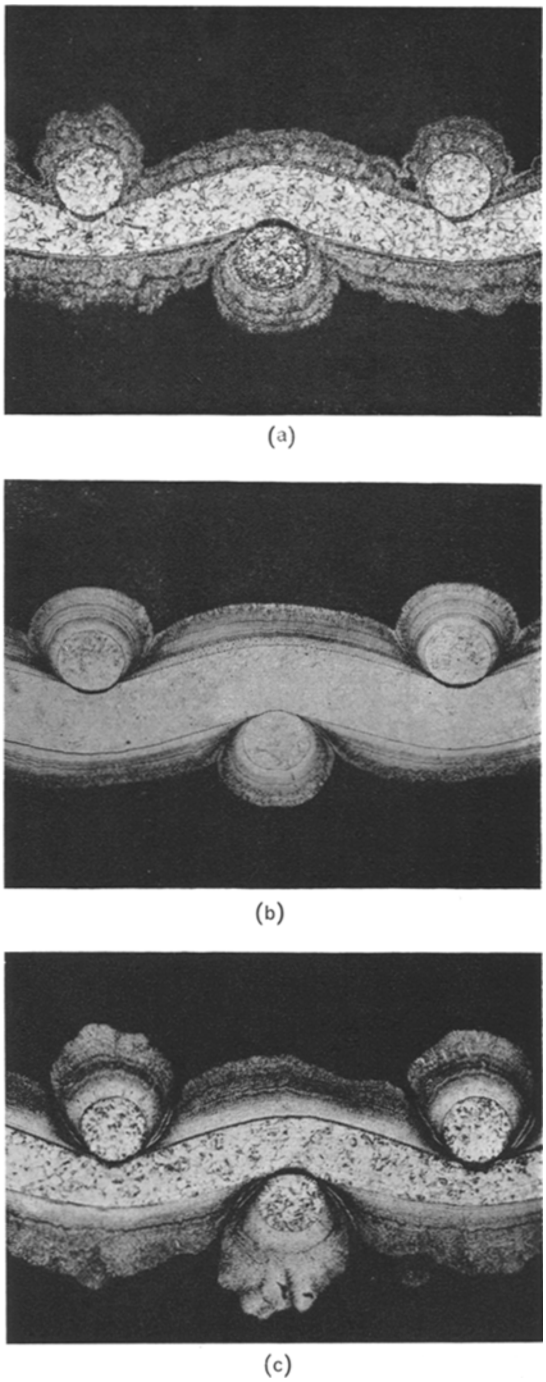
(a) (b)

Figure 5 Silver deposited from a cyanide solution on to a bronze gauze taken from Hull-Cell test at 0.5 A. (a) Low current density end of cell (×40). (b) High current density end of cell, (×40.)


(a)

(b)

Figure 6 Bronze deposited from a cyanide/stannate solution on to a copper gauze. (a) Etched (×40). (b) Unetched (×30).


(a)

(b)

(c)

Figure 7 Bronze deposited from a cyanide/pyrophosphate bath on to a bronze gauze at plain current-densities of (a) 2 A/ft^2, (b) 40 A/ft^2, (c) 160 A/ft^2. All at magnification of (×90).

carried out. The results of tests at plain cathode current densities of 2, 40 and 160 A/ft^2 are given in figs. 7a, b and c respectively, which show that at low current-densities reasonable levelling is obtained and that this degenerates with increasing current-density to roughening and crack-formation.

3.3. Aluminium Electrodeposition

Aluminium was deposited from the ethereal solution developed by Brenner. This electroplating solution has been used for producing 30 in. diameter, 30 × 10^{-3} in. thick parabolic mirrors by Schmidt and Hess and is reported in great detail by them [3]. The experimental work for this part of the investigation was carried out, at our request, at Bristol Aerojet, Ltd UK by Mr J. Leeson, to whom due acknowledgement is made. The resultant gauze is shown in fig. 8,

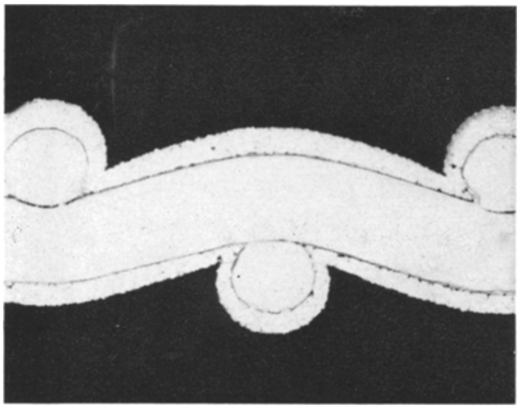
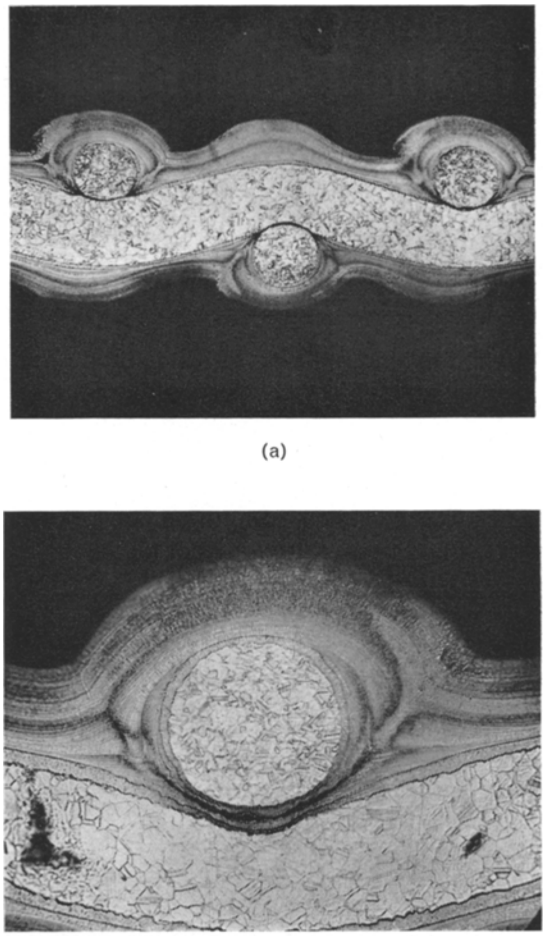


Figure 8 Aluminium deposited on to a stainless steel gauze from an ethereal solution. Good levelling behaviour is exhibited (×90).



(a)

(b)

Figure 9 Bronze deposited from a cyanide/pyrophosphate solution onto a bronze gauze at 160 A/ft^2 with a periodic current reversal of 4.4:1. (a) (×80) (b). (×225).

which compares extremely favourably with the metals deposited from simple salt solutions and the aluminium-plating bath would therefore be expected to work with the process.

3.4. Periodic Current Reversal—Bronze

In order to see if artificially promoted levelling by the use of periodic current reversal (experimental voltage reversal) would improve the behaviour of the copper cyanide/pyrophosphate solution at the highest current-density, tests were carried out at 160 A/ft^2 plain cathode current-density, with a plate-deplate cycle of 4.4:1. The two parts of the cycle lasted for approximately 1.2 and 0.3 sec in order to allow polarisation during the cathodic cycle and prevent it during the anodic cycle. A typical result from these experiments is given in figs. 9a and b, where it is seen that the morphology of the deposit has been considerably improved (compare fig. 7). This improvement by periodic current reversal may be expected to make an otherwise unfavourable solution work with the process.

4. Discussion

4.1. General Summary of Findings

The experimental results have shown that a wire gauze test can predict the behaviour of an electroplating solution with the filament-winding and electroforming process. This test provides a very simple and rapid method of evaluation of electroplating solutions for the process and requires very small quantities of solution.

In general, it has been shown that the simple salt solutions investigated and the non-aqueous aluminium plating solution would produce satisfactory composites. In most cases the complex solutions would not. Silver from the cyanide solution at low current-densities and copper from the pyrophosphate solution may be borderline cases.

The effect of periodic current reversal in the range investigated would appear to be beneficial for the complex solutions. This has yet to be proven with an actual electroforming and filament-winding test.

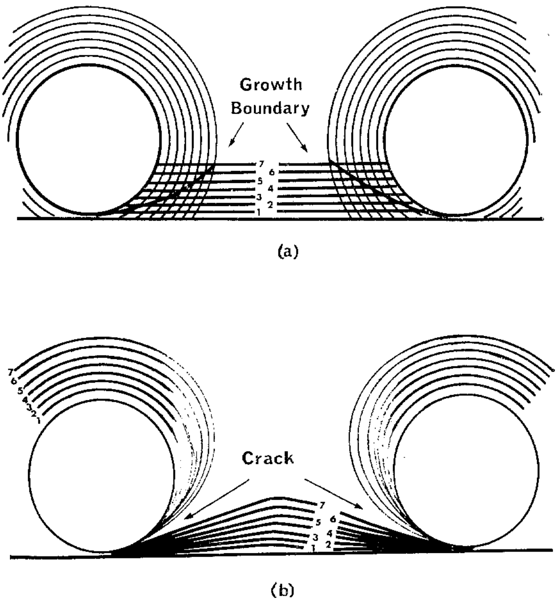
4.2. Reasons for the Observed Behaviour

It is difficult to define exactly what growth properties are required from the electroforming process, but levelling or smoothing power is probably the most important. This decides whether or not a continuous deposit can be produced, in particular at the point of fibre intersection. This ability is related to the micro-throwing power which ultimately is dependent on the thickness of the cathode diffusion-layer [4]. This is because on cathode surface irregularities of the same order of size as the diffusion-layer, the diffusion-layer will vary in thickness with the result that the rate of mass transport of the depositing ions will be less in the recessed regions. Thus the deposit will not reproduce the contours of the cathode surface satisfactorily, which in the gauze model shows up as a lack of bonding at the point of fibre intersection. The thickness of the diffusion layer is determined largely by the activity of the depositing ions, the current density and the degree of agitation of the electrolyte. Thus the simple salt solutions, if all other factors were equal, would be expected to be better than the complex solutions and the latter should be improved by reducing the current density. Solutions such as the silver cyanide bath and the copper pyrophosphate, in view of their lower degree of complexity, would be expected to be intermediate in behaviour. This fits in very well with the experimental observations.

4.3. Model for the Behaviour During Deposition onto the Wire Gauze

If ideal micro-throwing power is assumed [4]—equal thicknesses of deposition on all surfaces—then levelling can only be of a geometrical nature. This situation is shown schematically in fig. 10a, assuming growth on all surfaces. The point of schematic cross-over of the growth fronts results in an impingement boundary (heavily drawn in) representing the point of intersection of each incremental layer. This situation is shown clearly in fig. 3a where the presence of the "impingement" boundary can be seen. This behaviour obviously results in a continuous structure.

If the levelling is less than ideal, the recessed regions, i.e. the point of fibre intersection, will have less metal deposited than on the remainder of the surface. The resulting situation is shown schematically in fig. 10b and in the photomicrographs of fig. 6. It is apparent that in this situation a continuous structure could appear to have been produced if the angle of the crack emanating from the point of fibre intersection is reduced to zero; i.e. if the levelling is very poor. In fact of course the reverse is the case and a non-continuous structure is produced.



(a)

(b)

Figure 10 Schematic illustration of the effect of (a) geometrical levelling, (b) anti-levelling behaviour, on the geometry of deposition in the wire gauze test. (The sequences of growth on the surface concerned are indicated by the numbers 1 to 7).

4.4. The Effect of Periodic Current Reversal

The effect of periodic current with a complex electrolyte is to improve the micro-throwing power [4]. This is because during the anodic part of the cycle the rate of dissolution is greater in the peaks of the cathode profile where the diffusion layer is thinnest. Thus on this basis the situation of fig. 10b may be expected to revert to fig. 10a. However, the actual effect of periodic reversal on the morphology of the structure (fig. 10a and b) suggests that the actual mechanism is more complicated than is suggested in this simple model.

4.5. The Penetrating Power of the Molecular Forming Process

So far we have been considering the ability of the electrolyte to deposit a continuous matrix in a filament-wound composite consisting of continuous conducting monofilaments, such as metal wires. It was mentioned earlier that the potentially attractive carbon fibres are available only as very fine multifilament tows and that under these conditions the penetrating power of the forming process was also of great importance. The penetrating power refers to the ability of the process to provide circulation of the depositing medium into the deeply recessed areas. Obviously factors such as the surface tension, viscosity, and rate of diffusion impose a limit on the penetrating ability of a liquid medium. This can be offset to a limited extent by efficient solution agitation. Attempts to produce carbon fibre composites using a modified form of the filament winding process were found to be promising provided the number of fibres in the tow were kept to a minimum. In contrast, the penetrating power would be expected to be very much better with chemical vapour-deposition owing to the very high rates of diffusion which can be obtained [5]. These conditions may make chemical vapour-deposition a more attractive molecular forming process to use in conjunction with the filament-winding technique when multi-fibre tows are being dealt with.

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