RECENT TRENDS IN ELECTROFORMING

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ABSTRACT

The recent developments in the field of electroforming of metals have been discussed with reference to the techniques, bath formulations, properties of the electroforms, applications and economics.

INTRODUCTION

The process of electroforming, namely, the production or reproduction of articles by electrodeposition, has a striking feature in that it involves the separation of the deposit from the base on which it is produced. Further, the electroform is often obtained on non-metallic bases. The applications of the method to electrotyping is well known for a long time. This is essentially an art whose success depends upon the skill and experience of the operator. The earliest reference to electroforming appears to be the work by Jacobi in the U.S.S.R., and Spencer and Jordan in England about the same time[1]. Quite a number of patents have been taken during the early period for mounting artificial teeth[2], for headlight reflectors by Garrett, manufacture of hollow, seamless articles by Edison, and cartridge cases by Cowper-Coles[3]. The developments were quite rapid in the U.S.A. In 1924 and 1925 about 35,000 reflectors were made by electroforming every month. The first bright rhodium plate was made in 1927, and a dental plate of electroformed palladium was invented 8 years later. During the last war more than 6,000 anti-aircraft searchlight mirrors were produced[4].

TECHNIQUES

The design engineer has to choose the metal of which the electroform is to be made, keeping in view the following factors: (1) mechanical and physical properties required, (2) corrosion resistance, (3) plating bath, and (4) cost of the metal and speed of its deposition. The metals commonly used are copper, nickel and iron, and for specialized applications silver and gold. The method for preparing a matrix for plating and parting depends upon the matrix material and the parting method to be used. Table I gives the various types of matirx materials, together with the preparation for plating or parting, and the parting method.

The materials have their own advantages and disadvantages, and a proper selection has to be made depending upon the requirements. The matrix must be within the dimensional tolerance of the finished part and also retain dimensional stability in high temperature baths. Where necessary, low temperature solutions such as acid copper or sulphamate nickel can be chosen. Proper consultation between the design engineer and the electroformer will facilitate to a great extent a minimum adequate design in keeping with the question of costs. Bottomley[1] has discussed in detail the use of masters, mandrels and matrices. Depending upon the type of matrix it is properly prepared either for plating or for the separation of the electroform from it. The forming process is more difficult as compared with conventional plating because: (1) the plating period is longer and the current densities are higher, (2) a minimum thickness is required and the metal distribution should be uniform ,and (3) roughness in the deposit should be minimized. All these warrant a proper control of the operating conditions. To avoid deformation, any necessary machining or other mechanical finishing operations are usually preferred before the electroform is parted from the matrix.

In permanent matrices the electroform is separated by a combination of several methods such as impact, gradual force, heating or cooling. Expendable molds are dissolved out in solutions like hydrochloric acid or sodium hydroxide, or melted in the case of low-melting alloys. Plastics are generally softened by heating so that the matrix may be withdrawn and the electroform then cleaned. New techniques such as aluminium mandrel removal, silver receiver and metallurgical conditioning have been discussed by Turns[5]. In the electroforming of molds and printing plates it is necessary to back the electroform with some other material.

TABLE I: Types of Matrix Materials

Types	*Matrix Materials*	*Preparation for Plating*	*Preparation for Parting*	*Method for Parting*	*Remarks*
Expendable conductor	low-melting alloys	cleaning	nil	melt	generally for producing a single piece or when a close tolerance is not required
	aluminium, zinc	,,	zincate for aluminium	dissolve	
Permanent conductor	passive alloys: nickel, stainless steel, Invar, Kovar or other suitable metal	,,	chemical filming; graphite or parting compound	mechanical	for accuracy and high production runs
Semi-permanent non-conductor	glass, plastic, wood, etc.	clean and metallize	any of the above methods	,,	

PLATING SOLUTIONS

The electrolyte chosen for electroforming has to satisfy the following requirements: (1) properties such as hardness, internal stress, ductility, electrical and thermal conductivity, corrosion resistance, coefficient of friction and performance over a wide range of temperature, (2) speed of deposition, (3) stability, maintenance and control of the bath, and (4) the costs as compared with the conventional methods of fabricating the material.

Experimental data are available for the electroforming of copper, nickel, iron, gold, silver, palladium, platinum and rhodium. Tables II and III give the operating conditions for copper and nickel, which are most commonly used in electroforming, from important types of baths. The sulphate bath for copper was the first to be used in electroforming and is chiefly employed at the present time. Further, it is advantageous in most respects. The initial cost of the fluoborate bath is higher than that of sulphate. Electroforming from the pyrophosphate is of comparatively recent origin, and the solutions have excellent tolerance to impurities, whereas the latter have to be carefully controlled in the sulphate type. Organic addition agents have been developed to obtain an electroform with desired properties for the sulphate as well as pyrophosphate baths. The most widely used metal in this field is nickel, and by a proper choice of the plating solution and the operating conditions it is possible to obtain an electroform of practically any required design. In addition to the baths mentioned in Table III the following can also be used: hard nickel, chloride, and chloride-acetate. The deposits from the chloride bath are more highly stressed, but there is a savings in the power costs. Control of the fluoborate bath is simple as in copper. The sulphamate type has displaced most of the older types of baths, chiefly because of the low internal stress in the deposits. Detailed data are available on the effect of the variables on the properties of the deposit as well as the cathode efficiency [17-19].

Iron can be used in place of copper or nickel for many applications. A chief disadvantage is the tendency for surface oxidation or rusting which can be eliminated by coating with nickel or chromium. Chloride, sulphate and fluoborate solutions are used, and they are comparatively stable and easy to operate. Difficulties such as those due to the build up of ferric iron can be taken care of by normal methods. The first two types of baths are more commonly employed, and the sulphate type for low temperature operations. Gold can be deposited

TABLE II: Copper

	Sulphate[6-7]		*Fluoborate*[8-9]		*Pyrophosphate*[10-15]	
Bath composition, g/l						
	Copper sulphate	225-240	Copper fluoborate	693	Copper pyrophosphate	94
	Sulphuric acid	45-75	Fluoboric acid	10.8	P_2O_7 : Cu	5.5-7.0
			Boric acid	46	Ammonium hydroxide	2.5ml/l
					Addition agent as recommended by supplier	
pH	—			0.2-0.8		8.1-8.6
Temperature, °C		27-43		27-49		54-60
Voltage, V	Usually < 6			4-12		4-7
Filtration	continuous preferred for heavy deposit			—	Continuous	
Agitation	cathode rocking (upto 30 amp./dm² with special equipment), air agitation preferred,and high solution flow		air or mechanical		air preferred, cathode rocking at lower c.ds.	
Anode	rolled, cast, phosphorized or oxygen-free high conductivity copper		bagged electrolytic or rolled		various types oxygen free high conductivity copper preferred	
Cathode c.d., amp/dm²	3.2-16.2		8.1-32.4		1.1-8.6	
Anode c.d., amp/dm²	3.2-16.2		8.1-32.4		1.6-4.9	
Cathode efficiiency, %	99-100		99-100		100	
Anode efficiency, %	—		99-101		—	
Deposit						
Hardness, pyramid diamond	250-275		44-74 Rockwell 15 T		150-200	
Stress, psi.	0-5,000		—		10,000 at 40 amp/dm² upto 0.001" deposit	
Tensile strength. psi	35,000-42,000		17,100-32,500		60,000	
Elongation in 2", %	5-25		3.2-14.5		Elongation of massive deposit at break 10	

TABLE III: Nickel

	Sulphate-chloride[9,14]		*Fluoborate*[13,16]		*Sulphamate*[9]	
Bath composition, g/l						
	Nickel chloride	45	Nickel fluoborate	300	Nickel sulphamate	338
	Nickel sulphate	330	free Fluoboric acid	3.7-37.5	Nickel chloride	6-15
	Boric acid	38	free Boric acid	30	Boric acid	30
pH		1.5-4.5		2.0-3.5		3.5-4.2
Temperature, °C		46-60		40-80	Range: 28-60, Optimum:49	
Agitation		——		——	Air from low-pressure blower preferred; cathode rocker or solution agitation can be employed.	
Cathode c.d., amp/dm²		2.7-10.8		4.3-10	Range: 2.2-6.5 Optimum: 4.3	
Deposit						
Hardness, Vickers		140-160		183	140-190	Diamond pyramid
Stress, psi		18,000		16,000-26,000	1500-10,000	
Tensile strength, psi		51,000		74,500	108,000	
Elongation in 2", %		30		16.6	15-20	

from the cyanide and acid baths. In spite of the relativley higher cost, it has found use in high reliability electronics. Silver electroformed from the cyanide bath finds application in electrical and electronics fields where the highest electrical conductivity is required. For magnetic properties duplex coatings of iron and silver or nickel and silver are used. Substances like thiosulphate, nitrate and formulations containing carbon disulphide or selenium compounds have been added to the plating bath in order to obtain the desired type of deposit. In view of the high cost, electroforming of the precious metals is confined to the electronics and aerospace industries. The baths used are: chloride for palladium, sulphamate for platinum and sulphate-sulphamate for rhodium[9].

Alloy electroforming is of very recent origin and has been taken up in order to meet some specialized requirements as in aerospace. Alloy deposition of many systems is fairly well established, but the progress on the forming side has been rather slow due to lack of developmental work on the one hand and industrial utility on the other. The sulphate-chloride type of nickel has been modified with the inclusion of a small quantity of cobalt sulphate for the producion of nickel electrotypes. This corresponds to bright nickel deposition with cobalt as the minor ingredient in the alloy. Turns[5] has described a sulphate bath for the electroforming of a nickel alloy containing 5% manganese. The molar ratio of manganese to nickel was about 12.

Recent investigations indicate that reliable aerospace structures of cobalt-tungsten alloys can be electroformed. Electroforming of a ternary alloy of cobalt-tungsten-nickel also appears promising. Table IV gives the essential data for the production of these alloy electroforms. The inclusion of anti-pit addition agents in the plating bath is helpful. The solution is insensitive to small traces of zinc, manganese or cadmium, but copper is not desirable. Sulphur compounds decrease the tungsten content as in deposition. In the ternary alloy bath addition agents are used for stabilization as well as decreasing the stress and pitting.

APPLICATIONS

Electroforming has many advantages: (1) properties of the deposited metal can be controlled over a wide range by choosing a proper metal and plating bath and variation in the operating conditions, (2) parts can be produced, practically to any size, with a very high order of dimensional accuracy, being limited only by the accuracy obtainable in machining the matrix which may be of the order of 0.001 inch, (3) the process is equally applicable to the making of single pieces or large mass production runs, and (4) in case of large runs, many pieces may be processed at one time for a relatively very small increase in plant investment, which is not true in the case of expensive machine tool equipment.

There are, however, some disadvantages: (1) the cost is often relatively high, and in such cases the process may become competitive when large number of reproductions are required. For example[6], an electroformed filter for a missile originally cost $ 125 each in small quantities, but when the number rose to several thousand, the unit price dropped to $23; (2) the production rate may be comparatively slow ; (3) limitations in design; and (4) scratches and imperfections in the master will also be reproduced in the pieces. Amongst the problems encountered in alloy electroforming mention may be made of pitting, due to hydrogen evolution, and anode corrosion. The first one is eliminated by adding a wetting agent to the solution. During the electroforming of cobalt-tungsten, cobalt anodes are substituted for tungsten after sometime in order to prevent excessive corrosion.

A large number of applications can be cited for the electroforming process, the more important and recent ones being: copper for producing masters and nickel for stampers in the manufacture of disk records; nickel in plastic molds for automotive industry, manufacture of typing wheels, aerospace vehicles, and pitot static tubes; nickel or copper in the production of Venturi type nozzles[24]; nickel/copper/nickel in molds and die-castings[21], and copper in the production of precise wave-guide pieces[24]. Alloy electroforming of cobalt-tungsten and cobalt-nickel-tungsten finds itself in aerospace applications[22]. There is a mention of cobalt-molybdenum alloy[25]. Electroforming is being used to make nickel-copper reflectors for ticker tape projectors. After deposition the reflector is plated with rhodium[26]. The development of a new process for electroforming the refractory metals—tungsten, tantalum, molybdenum, columbium, hafnium, vanadium, zirconium and chromium, is no doubt a welcome sign that this technique will extend its sphere of applications[27].

TABLE IV:

	Cobalt-tungsten[20,21]	Nickel-cobalt-tungsten[21]
Bath composition, g/l		
Cobaltous sulphate	86-115	110-115
Sodium tungstate	40-45	38-43
Nickel sulphate	—	5-8
Rochelle salt	350-380	375-385
Ammonium chloride	50-60	50-55
Addition agent	—	0.5-0.8
pH	8.5-9.0	8.0-9.0
Temperature, °F	190 ± 5	190 ± 5
Anodes	tungsten or cobalt-tungsten	tungsten or cobalt-tungsten
Current density, amp/dm²	2.0-8.0	4.0-5.0
	5 for deposits of high integrity	
Deposition rate, mils/hr	—	1.5-2.0
Deposit		
Composition, % of metal	35 tungsten	30 tungsten, 65 cobalt
Hardness	825 Vickers after 256 hr. at 700 °C	546, Knoop, as electroformed
Tensile strength, psi	92,500	47,600-52,100

CONCLUSION

It is seen from the above discussion that electroforming has established itself as a convenient and useful tool in the hands of the design engineer. The subject has been one of great interest in recent times. At a recent Symposium on "Nickel Deposition in the Engineering Industries", three out of the seven papers covered electroforming for nickel screens, moulds and dies, and all-nickel shell electrotype printing plates. In spite of its limitations, electroforming holds promise for further developments and new applications in the future. A wider field is open for exploitation with the development of new types of mandrels, metals and alloys, electrolytes and improved techniques[2-4]. The applications may well be extended to household articles such as coffee jugs, frying pans, switch-plates, wash-basins and so on. Electroformed nickel, for example, has a very high corrosion resistance similar to that of stainless steel, but in addition combines the ability to reproduce raised patterns and to be produced in a great variety of finishes. It can be confidently hoped that electroforming will play a very significant role in these days of mass production.

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