

Effects of anode materials in the electroforming of iron-nickel alloy foil

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Received 29 April 1980

The effects of soluble and insoluble anodes upon the composition and mechanical properties of iron-nickel alloy foil of thickness about 0.1 mm have been studied. The soluble materials include stainless steels, main constituents 17.5–19% Cr, 9–11% Ni or 16–18% Cr, 0.5% Ni, and iron-nickel alloys of composition 60% Fe, 40% Ni or 30% Fe, 70% Ni. The performance of these materials is compared with graphite, an insoluble anode. The presence of chromium as a constituent in soluble anodes has an adverse effect on the electroforming process: the current efficiency of metal deposition is reduced, as is the working current density for the production of foil of acceptable quality and with satisfactory mechanical properties. The nickel content of the alloy foil can be increased, and the quality of the foil improved, by using iron-nickel anodes which are free of chromium.

1. Introduction

In electroforming, the well-known electroplating process is utilised in the production of finished components or articles [1]. However, electroforming differs significantly from electroplating in the following ways. Firstly, the thickness of the electroformed metal is much greater than electroplated coatings, which seldom exceed 25 μm . Secondly, a cathode mandrel of predetermined shape and with dimensions representative of the component to be electroformed is needed; cf. electroplating which is usually used simply to alter the surface characteristics or dimensions of a component. Thirdly, the electroformed metal has to be removed from the mandrel after electrodeposition to yield the finished component. In contrast, electroplated metals have to adhere to their substrate.

An example of electroforming which demonstrates these characteristics involves the production of foil, that is, metal strip of thickness about 0.1 mm. The material can be electroformed in individual sheets by means of plane or cylindrical cathode mandrels. Continuous formation of foil may be obtained by use of a rotating cylindrical cathode. Recent industrial interest in the electroforming of iron foil has

stemmed from three main features:

(a) Thinner foils cost proportionally less than thicker gauges. The process is therefore attractive as a cheaper alternative to rolling. The latter process becomes exceedingly expensive when thin gauges are required [2].

(b) Foil may be electroformed from a ferrous chloride electrolyte solution, obtained by the dissolution of waste steel swarf in hydrochloric acid.

(c) The capital cost of electroforming plant is low.

Although graphite has been adopted as the anode material in these industrial operations for the electroforming of iron foil, other experimental investigations of the process have revealed the difficulties which arise with the use of this material [3, 4]. First, the pH of the ferrous chloride electrolyte solution may not remain constant during electrolysis; secondly the concentration of metal ions in solution is reduced as metal deposition takes place. Nevertheless, these studies have shown that the electroforming process can be satisfactorily maintained by the regular addition of iron salts, hydrochloric acid or ammonia solution to the electrolyte to keep the bath at a constant pH and concentration [3]. These procedures are tedious, however, and can be avoided by the use of soluble, pure iron anodes. Recently, a study of

iron foil electroforming has been reported in which such a material has been used [5].

Since electroformed iron–nickel–chromium and iron–nickel alloy foils offer an even wider range of industrial applications [6], the production of such materials has also been studied [7]. Electroforming of ternary iron–nickel–chromium alloy foil was unsuccessful, however, because of microcracking of the deposited metal. The failure was attributed to the deleterious effects created by electrodepositing from an electrolyte containing chromium metal in solution [7]: the very low current efficiencies with which the chromium was co-deposited resulted in severe hydrogen embrittlement, the cause of the microcracking. The electroforming was then attempted without chromium salts in solution, i.e. with a binary electrolyte containing only iron and nickel salts, and smooth, bright iron–nickel alloy foil was produced.

One limitation encountered, however, was the unacceptable quality of foil containing more than about 6% nickel, because of hydrogen embrittlement. The occurrence of this condition was partly attributed to the need to increase the nickel chloride concentration in solution as the only effective way of raising the percentage of co-deposited nickel; and that increase was associated with a rise in the amount of hydrogen evolution at the cathode, and hence in the degree of hydrogen embrittlement of the foil.

The use of soluble anodes composed of the three metals, iron, nickel and chromium, as an alternative way of co-depositing chromium with iron and nickel and of increasing the percentage of co-deposited nickel, is explored in this paper. In addition to regular co-deposition at the cathode of metal ions from the electrolyte, a further prospect is then provided that dissolution of the anode may be accompanied by migration of the ions of the alloying elements through the electrolyte, with their subsequent deposition at the cathode. Although the benefits of soluble iron anodes in the direct replenishment of the metal salts in the electrolyte for iron foil electroforming are well established, the corresponding role and effects of soluble anodes in the production of alloy foil have not yet been clearly defined. Thus in this paper the influence of different soluble anodes on the composition and mechanical proper-

ties of the alloy foil is discussed. The performance of the soluble anodes is compared with that of insoluble graphite, which is commonly used in industry for the electroforming of iron foil.

2. Experimental apparatus and procedure

Fig. 1 shows the apparatus for electroforming iron–nickel alloy foil. The electrolyte solution consists of aqueous ferrous chloride (of concentration 400 g l^{-1}) into which are dissolved 80 g l^{-1} of calcium chloride, 30 g l^{-1} of nickel chloride and $2 \text{ cm}^3 \text{ l}^{-1}$ of a commercial anti-pitting agent. The solution, which has a pH of 0.5, was housed in a 100 litre tank, and was maintained at a temperature of 95° C by means of six 1 kW thermostatically controlled, quartz-sheathed immersion heaters. In addition to thermal insulation of the tank, two layers of 45 mm diameter polypropylene spheres floating on the surface of the solution helped to prevent heat loss.

Rectangular sheets of stainless steel (grades EN58E and EN60), 80 mm by 200 mm by 0.9 mm thick, were used as the cathode materials. The anodes were plane, and fixed parallel to the cathode with an interelectrode gap of 90 mm. The soluble anode materials investigated were stainless steel, types EN58E and EN60 (the main respective constituents of which are 17.5–19% Cr, 9–11% Ni, and 16–18% Cr, 0.5% Ni), an iron–nickel alloy (containing approximately 60% Fe, 40% Ni) and the same iron–nickel alloy together with an auxiliary anode of pure nickel (which in effect raised the total proportion of nickel present at the anode to about 70%). No significant change in electrolyte solution composition was observed over a period of 12 months from the use of these soluble anode materials.

By means of a rectifier of capacity 150 A at 12 V, current (current density 5 to 20 A dm^{-2}) was passed between the electrodes in order to electrodeposit the iron–nickel alloy. The current efficiency (the percentage ratio of the experimental to theoretical Faradaic metal deposition rates) was determined by weighing the cathode before and after each experiment. The electroformed alloy foils were then obtained by peeling them from the cathode. The constituents and mechanical properties of the alloy foil were determined by procedures described elsewhere [3, 4 7].

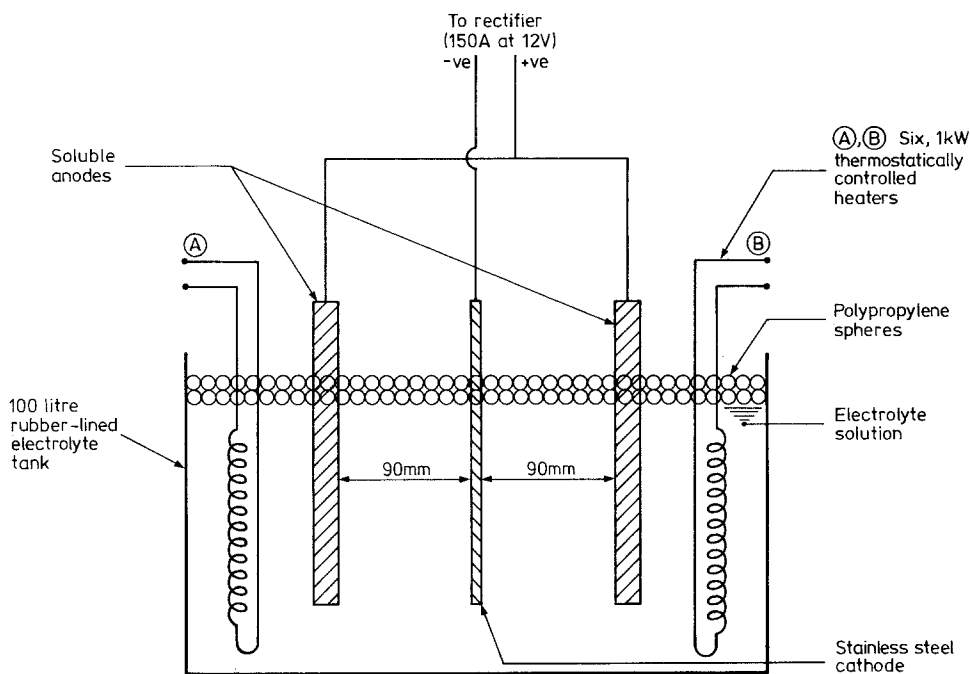


Fig. 1. Apparatus for electroforming iron–nickel alloy foil with soluble anode electrodes.

3. Results and discussion

Table 1 shows that the composition of the alloy foil obtained with EN58E steel anodes is comparable with that produced with graphite anodes. Evidently the dissolution of the steel anodes merely replenishes the iron and nickel contents of the electrolyte, without significantly influencing the deposition of these metals at the cathode.

Although chromium metal would also have been introduced into the electrolyte from the anode, its deposition at the cathode would have been strongly dependent on induced co-deposition [8], resulting from the rate of reduction there of the iron and nickel ions. Since the latter mechanism was retarded, as confirmed by the reduced current efficiencies indicated in Table 1 (cf. graphite), little means were available by which chromium could have been co-deposited as a further alloying element. (Note: the terms 'current density' and 'current efficiency' used in this section refer respectively to conditions at the cathode and for metal deposition, unless otherwise specified.)

Although the composition of the alloy foils obtained with both types of anode material was comparable, the mechanical properties of the foils

produced with the EN58E anodes were generally slightly inferior. This effect may be linked with the lower current efficiency of deposition with this anode material. The low current efficiency would in turn be associated with increased hydrogen evolution, and hence with greater hydrogen embrittlement of the alloy foil.

For the EN60 steel anodes, Table 1 indicates a net increase in the percentage of co-deposited nickel over the same current-density range. This behaviour contrasts with that observed for the graphite and EN58E anodes. With the latter materials, the process of alloy deposition takes place by regular co-deposition in which an increase in current density leads to a decrease in the percentage of the more noble metal in the deposit, as explained in earlier work [7]. With the EN60 steel anodes, the increase is not to be expected, especially since this metal only contains a maximum nickel content of 0.5%. Instead, the effect appears to be due to the phenomenon of 'depolarization' discussed by Vagramyan [9]. When this condition arises, the potential for the discharge of hydrogen ions at the cathode changes towards a more noble value, which results in increased hydrogen evolution and hence a decrease in the current efficiency for alloy deposition (see

Table 1. Effects of cathodic current density on current efficiency and deposited alloy foil

Anode material	Cathodic current density (A dm ⁻²)	Current efficiency of deposition (%)	Percentage of co-deposited nickel	Percentage of co-deposited iron
EN58E	5	65	5.65	94.20
	10	64	4.23	95.72
	15	59	3.98	95.95
	20	58	3.98	95.97
EN60	5	64	5.0	95.97
	10	59	4.30	95.68
	15	48	6.88	93.04
	20	46	6.41	93.47
Graphite	5	70	5.87	93.95
	10	69	4.95	94.83
	15	65	4.56	92.38
	20	61	3.87	95.21
Iron-nickel	10	80	5.31	94.49

Table 1). The phenomenon is apparently accompanied by a shift in the potential for the reduction of iron and nickel ions towards less noble values; this change is more pronounced in the case of iron deposition, so that the electroformed alloy contains a relatively higher nickel content.

Despite this apparently attractive trend of an increase in the nickel content with increasing current density, 10 A dm⁻² was found to be the highest working value for which smooth, bright foil could be electroformed with this anode material. At greater current densities, the alloy foil obtained was cracked and blistered. This behaviour is consistent with the decrease in current efficiency of alloy deposition noted in Table 1, with which would be associated greater hydrogen embrittlement and its consequential detrimental influence on the quality of the alloy foil.

These experiments demonstrated the adverse effect of electroforming with chromium as a constituent of the anode materials. Further studies were therefore carried out with other soluble anodes which did not contain chromium, to assess their effect on the amount of co-deposited nickel and current efficiency of alloy deposition, using the upper working current density of 10 A dm⁻² previously established. The results in Table 1 show that with the iron-nickel anode, the amount of co-deposited nickel in the alloy foil is greater than that obtained with the two previous soluble

anodes (for the same current density). The magnitude of the increase, however, indicates that the dissolution of the iron-nickel anode material still serves mainly to sustain the amount of iron and nickel ions in the electrolyte solution without contributing significantly to the deposition of these metals at the cathode. That is, regular co-deposition is still the main mechanism for alloy electroforming. Nevertheless, the experimental evidence does indicate an increase in the amount of nickel co-deposited. The effect may be attributed to the absence of chromium from the anode material. The previous part of this investigation has shown that the presence of chromium, especially in the EN60 anode, promotes an increase in hydrogen evolution, and that the alloy foil suffers increasingly from hydrogen embrittlement. In contrast Table 1 shows that the current efficiency of alloy deposition with the chromium-free anode is higher than that obtained with the EN58E materials. The former alloy foil is then less likely to be so affected by hydrogen embrittlement. Indeed Table 2 shows that the percentage elongation (a property especially susceptible to hydrogen embrittlement) of the foil produced with the iron-nickel anode is superior to that of the foils (of similar nickel content) produced with the two previous soluble anodes, whilst the other mechanical properties are comparable.

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Table 2. Current efficiencies of deposition and average mechanical properties of iron-nickel alloy foil

Anode material	Percentage composition of deposited alloy		Current efficiency of deposition (%)	Percentage elongation (%)	Tensile strength (MN m ⁻²)	0.2% proof stress (MN m ⁻²)	Young's modulus (GN m ⁻²)	Micro-hardness (VHN)	Thickness (μm)	Cathodic current density (A dm ⁻²)	Deposition time (min)
	Ni	Fe									
Iron-nickel	5.31	94.49	80	0.6	447	394	189	225	79	10	45
Iron-nickel + auxiliary nickel	5.64	94.17	79	0.5	436	392	200	223	79	10	45
EN58E	5.65	94.20	65	0.3	443	420	186	245	64	5	90
EN60	5.00	94.97	64	0.2	443	450	183	244	63	5	90
Graphite	5.27	94.70	76	0.7	503	437	252	224	75	10	45

soluble iron–nickel anode, further tests were performed in which the nickel content of the anode was increased by the addition of an auxiliary, pure nickel anode. Such a practice is well known in electroforming, and has been described by Lowenheim [10]. Table 2 shows that a further, small rise in the nickel content of the alloy foil is then obtained. This effect is probably due to the more ready supply of nickel ions to the cathode layer (promoted by the greater amount of nickel at the anode): the reduction of nickel ions to the metallic state is then increased. Nevertheless regular co-deposition would still seem to be the main mechanism by which the alloy foil is electroformed. However since the nickel content of the foil only increases by about 0.3% when the auxiliary anode is employed, little change in most of the mechanical properties of the alloy material occurs, in comparison with that formed with the iron–nickel anode alone.

Finally, from Table 2 it is noted that the higher current efficiencies of deposition attained with the iron–nickel anodes lead to a shorter time of electroforming compared with those obtained with the steel anodes, for alloy foils containing similar amounts of nickel.

4. Conclusions

The presence of chromium as a constituent of soluble anodes affects adversely the electroforming of iron–nickel alloy foil, by lowering both the current efficiency for metal deposition and the maximum working current density at which foil of acceptable surface quality and mechanical properties can be produced. With iron–nickel anodes which are free of chromium, increases in the nickel content in the alloy foil, faster deposition rates (for comparable percentages of co-deposited metal) and higher current efficiencies

of alloy deposition are achieved in comparison with those attainable with soluble anodes containing chromium. This investigation, and previous work, show that iron–nickel alloy foil of satisfactory quality can be produced with a variety of anode materials ranging from insoluble graphite to soluble electrodes.

Acknowledgements

This work has been supported by a Science Research Council grant, No. B/RG 8037.3. The authors are grateful to Professor T. M. Charlton for his interest and support, and by courtesy of whom an Aberdeen University Engineering Department Research Studentship was held by one of them (SHFL). The tenure of a research fellowship by Dr Lai under SRC Grant No. G/RA 5850 is also gratefully acknowledged.

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