High Speed Nickel-Cobalt Alloy Electroforming by High Current Density with Flowing Electrolytes

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(Received June 30, 1976)

Abstract

High speed nickel-cobalt alloy electroforming witn high current density up to 120 A/dm^2 has been investigated. Deposits were made from a Watt type solution which contains cobalt as the sulfate, and rapid ion tranport is made by flowing electrolyte. The cobalt contents in electroformed alloy are in the range of 5% to 50% by weight. The stress of alloys are higher than those of electroformed nickel. The hardness of alloys are in the rang of 300 to 500 in Vickers hardness, which are higher than those of electroformed nickel. The tensile strength of alloys are in the range of 70 kg/mm^2 to 167 kg/mm^2, which are sufficient values for parctical usage. The tensile strength is generally proportional to the Vickers hardness.

High speed nickel-cobalt alloy electroforming is possible from the facts described above.

1. Introduction

Electroforming is based on the principle of electroplating techniques. The purpose of electroplating is to cover the surface of a substrate, but in electroforming deposits must have considerable thickness, for example, when the electroplated metal has a thickness in the range of 20 μm to 50 μm, that of electroformed metal is in a range of 200 μm to 2 cm. Nickel and copper are mainly used in the production of electroforming. Nickel is stronger than copper in mechanical properties and corrosion resitivity. Up to the present a number of studies on nickel electroforming have been carried out and the method of nickel electroforming has successfully been achieved. But the nickel electroforming can not satisfy the high level industrial technology requirement in tensile strength, corrosion resitivity and heat resitivity, and because of this, development of alloy electroforming, which has a higher quality than nickel, is to be promoted[1]. As alloy electroforming, nickel alloy electroforming is favourable; for instance, nickel-cobalt alloy and nickel-iron alloy. Nickel-cobalt alloy can be easily electrodeposited from an aqueous solution of nickel and cobalt sulfate.

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In this study, the possibility of high speed nickel-cobalt alloy electroforming is investigated with high current density and flowing electrolyte method.

2. Experimental

2-1 Experimental apparatus and measurement of stress

Details of the apparatus are shown in Fig. 1, and the cell for electroforming is shown in Fig. 2. This apparatus is composed of a electrolyte thank, a pump for circulating the electrolyte, a controller for electrolyte temperature and an electroforming cell made of acrylic acid resin. The electrolyte circulated by means of

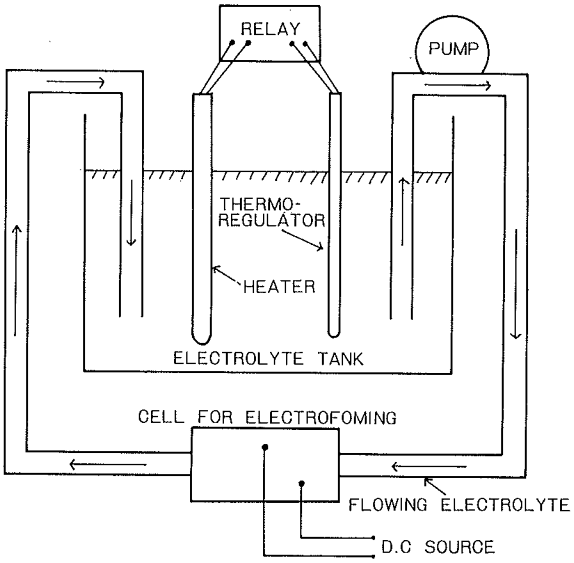

Fig. 1. Synopsis of apparatus for high speed electroforming

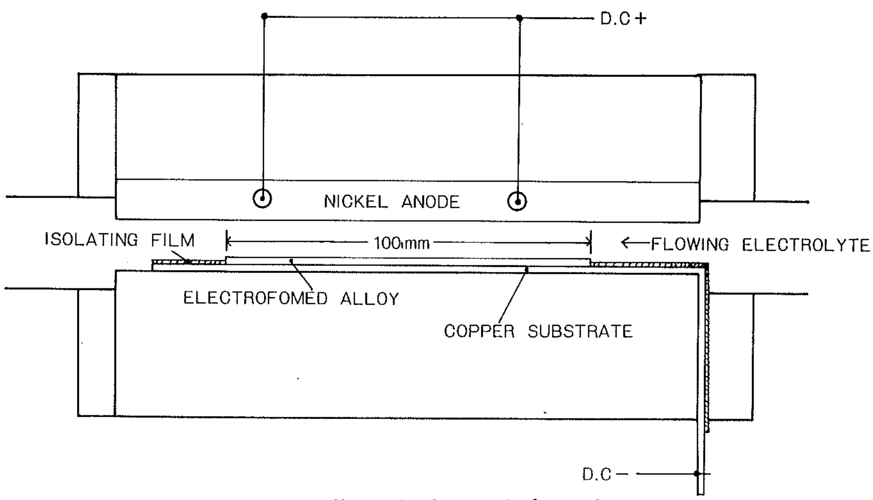

Fig. 2. Cell for high speed electroforming

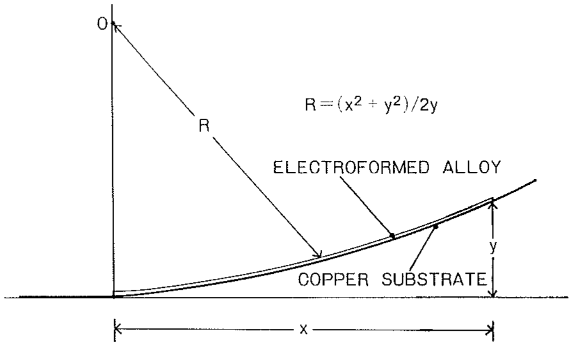

Fig. 3. Deformation of copper substrate by the stress in electroformed alloy

a pump flows through the gap between the anode and the cathode. The flowing electrolyte renders the diffusion layer thin, and because of this thin diffusion layer, the current density for electrofoming can be raised to over 100 A/dm^2.

A cathode substrate has a rectangle shape of 10 mm × 100 mm to be electroformed, and after the deposition, the substrate is deformed by the internal stress as shown in Fig. 3. The stress in electroformed alloy can be calculated through mesuring x and y (in Fig. 3) and from the following equation[2)];

$$\sigma = \frac{1}{R}\left[\frac{E_b}{2}(t_a+t_b)+\frac{\dfrac{t_a^3+(E_b/E_a)t_b^3}{6t_a t_b(t_a+t_b)}}{(E_a t_a+E_b t_q)}\right]$$

where σ : stress in electroformed alloy, R : curvature of deformed substrate, t_a : thickness of substrate (copper rolled, 0.4 mm), t_b : thickness of electroformed alloy, E_a : elastic coefficient of substrate (copper rolled, 12,000 kg/mm^2), E_b : elastic coefficient of electroformed alloy (assuming 21,000 kg/mm^2, this value is the same as nickel).

2–2 Electrolyte

A watt type solution containing cobalt was used as the electrolyte for nickel-cobalt alloy electroforming. The electrolyte composition is shown in Table. 1. Electrolysis with low current density (0.1 A/dm^2) to remove metallic impurities, activated carbon treatment to remove organic impurities, pH adjustment with nickel hydroxide and filteration were completed before cobalt was added to the Watt solution.

TABLE 1. Composition of Electrolyte

$NiSO_4$ $6H_2O$	330	g/ℓ
$NiCl_2$ $6H_2O$	45	g/ℓ
H_3BO_3	30	g/ℓ
Co (as metal)	1, 2, 3, 5, 7, 9	g/ℓ
pH	4	
Volume of Electrolyte	18,	ℓ

2-3 Experimental conditions

Experimental conditions are shown in Table. 2. The product of the current density and the electroforming time is fixed at 1,600 min·A/dm^2, at which time approximately a 200 μm thick alloy is deposited.

TABLE 2. Experimental Condition

Temperature of Electrolyte	60	°C
Flowing Speed of Electrolyte	5.4	m/s
Current Density	20, 40, 60, 80, 100, 120	A/dm^2

2-4 Quantitative analysis of cobalt in electroformed alloy and electrolyte

Cobalt concentration in electrolyte is quantitatively analysed, because the cobalt concentration in electrolyte showed a decrease after the deposition. The amount of decreased cobalt is deposited in the alloy. The ammount of cobalt which is equivalent to the decreased cobalt in the electrolyte is added to the electrolyte in the form of cobalt sulfate. The cobalt content in the alloy is also analysed quantitatively. Potentiometric titration with potassium ferricynide is used to analyse cobalt in the electrolyte and the electroformed alloy. This analytical method is easy and has the advantage of analysing cobalt without being influenced by nickel.

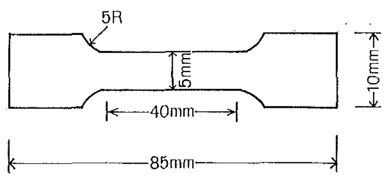

Fig. 4. Form of specimen for tention test

2-5 Measurement of tensile strength

Electroformed specimens are formed by electric discharge machining for tension test in Fig. 4. The specimens for tension test are dipped in aqueous solution of chromium trioxide and sulfuric acid to remove the copper substrate. This solution can not dissolve nickel.

The tenstion speed of specimen is 0.5 mm/min.

3. Experimental Results and Discussion

3-1 Cobalt content in electroformed alloy

The relation of cobalt content in electroformed alloy and that of electrolyte is shown in Fig. 5 where the current density is a parameter. As the cobalt concentration in the electrolyte increases, the cobalt content in the electroformed alloy increases for each current density.

Fig. 6 shows the relation between the current density and the cobalt content in the electroformed alloy where cobalt concentration in electrolyte is a parameter. As the current density increases, the cobalt content in the electroformed alloy decreases.

The cobalt contents in the electroformed alloys are in a range of 5% (1 g/ℓ cobalt concentration in electrolyte) to 50% (9 g/ℓ cobalt concentration in electrolyte) by weight.

In ordinary electroplating of nickel-cobalt alloy, under the conditions of cobalt concentration in electrolyte 10 g/ℓ, current density 0.1 A/dm² to 3 A/dm², cobalt content in the alloy is 30% to 70% by weight, and under the conditions

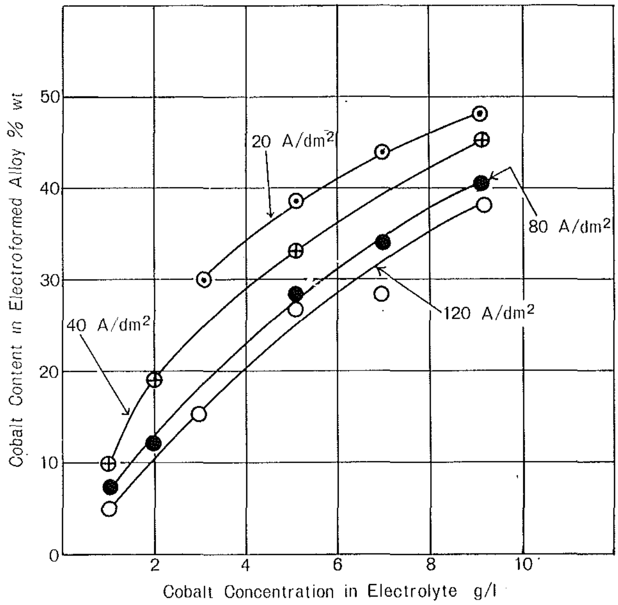

Fig. 5. Effect of Cobalt Concentration on Cobalt Content in Electroformed Alloy

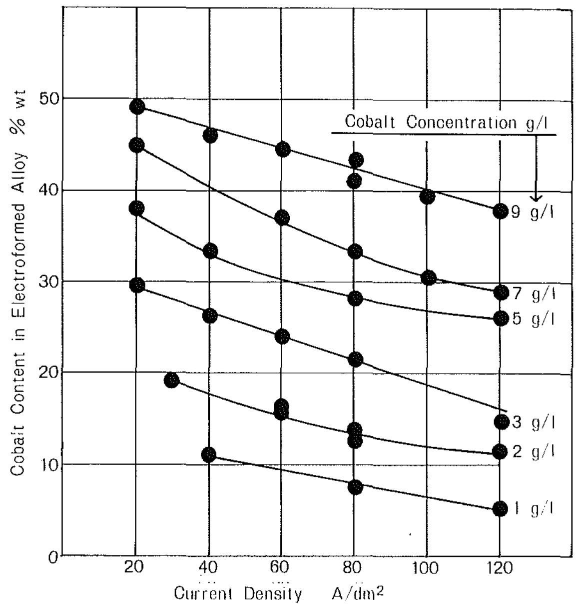

Fig. 6. Effect of Current Density on Cobalt Content in Electroformed Alloy

of cobalt concentration in electrolyte 1 g/ℓ, current density 0.1 A/dm^2 to 3 A/dm^2, cobalt content in the alloy is 10% to 20% by weight. Using the flowing electrolyte method, under the conditions of cobalt concentration in electrolyte 9 g/ℓ, current density 20 A/dm^2 to 120 A/dm^2, cobalt content in the electroformed alloy is 40% to 50% by weight, and under the conditions of cobalt concentration in electrolyte 1 g/ℓ, current density 20 A/dm^2 to 120 A/dm^2, cobalt content in the electroformed alloy is 5% to 10% by weight. It is considered that there is no essential difference in cobalt content in electrodeposited alloy between ordinary electroplating and high speed electroforming, when cobalt concentrations in electrolyte are the same in both cases. In consideration of the large difference of current density in the ordinary and the high speed electroforming, the electrochemical phenomena in alloy electrodeposition of the ordinary method (low current density) and the high speeed method (hight current density with flowing electrolyte) can be understood to be similar phenomena.

3–2 Stress in electroformed alloy

Fig. 7 shows the relation of stress in electroformed alloy and current density, where cobalt concentration in electrolyte is a parameter. As the cobalt concentration in electrolyte increases, the stress in electroformed alloy increases in tensile state.

Fig. 8. shows the relation of stress in the electroformed alloy and the cobalt content in the alloy, where the current density is a parameter. As the cobalt content in the electroformed alloy increases, the stress in the alloy increases gradually in tensile state. The stress in electroformed nickel-cobalt alloy is increased by cobalt contained in the alloy.

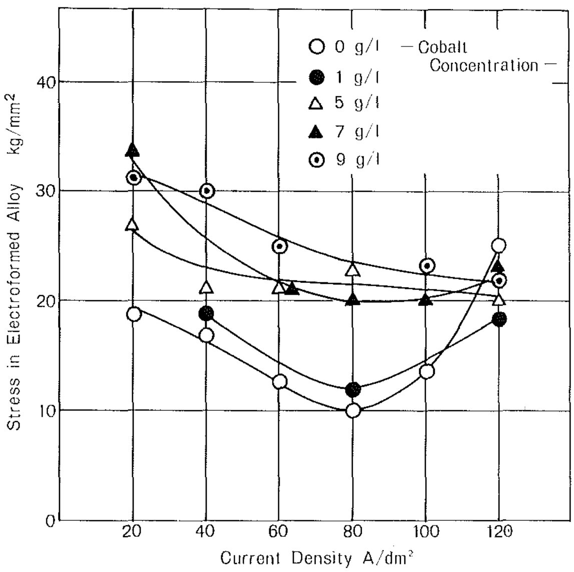

Fig. 7. Effect of Current Density on the Stress of Electroformed Alloy

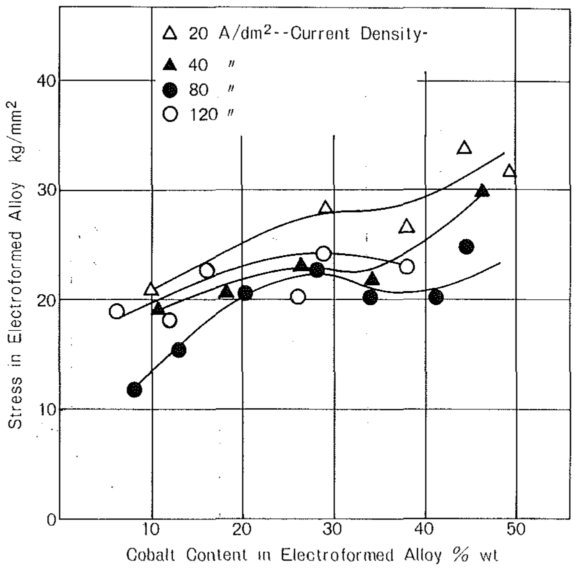

Fig. 8. Effect of Cobalt Content on the Stress of Electroformed Alloy

It is obvious that the cobalt contained in the electroformed alloy strongly affects the causes of the stress.

More detailed mechanism of origination of stress in electrodeposited metals should be investigated.

3-3 Hardness of electroformed alloy

Fig. 9 shows the relation of Vickers hardness and current density, where cobalt concentration in electrolyte is a parameter. Increasing cobalt concentration in electrolyte up to 3 g/ℓ, the hardness increases, but another addition of cobalt to the electrolyte hardly affects the hardness. Current densities, 40 A/dm^2 to 80 A/dm^2, give low stress to each cobalt concentration in electrolyte. As this result is similar to that of pure nickel electroforming, it may be considered that the essential phenomena of electrodeposition of nickel-cobalt alloy and that of pure nickel are the same.

Fig. 10 shows the relation of Vickers hardness and cobalt content in electroformed alloy, where current density is a parameter. In creasing the cobalt content in the alloy up to 20% or 30% by weight, the hardness increases, but in higher cobalt contents in the alloy, the hardness decreases. The curves in Fig. 10 have peaks in a range of 20% to 30% by weight of cobalt content in the alloy.

The hardness of the alloy is within a range of 300 to 500 in Vickers hardness, and this hardness is higher than that of electroformed nickel which has a hardness within a range of 200 to 300.

3-4 Tensile strength

Representative values of tensile strength of electroformed nickel-cobalt alloy

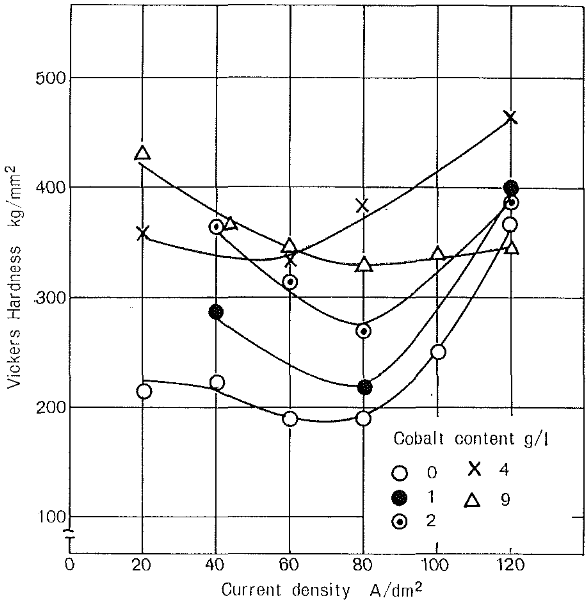

Fig. 9. Effect of Cobalt Concentration in Eelctrolyte on Hardness

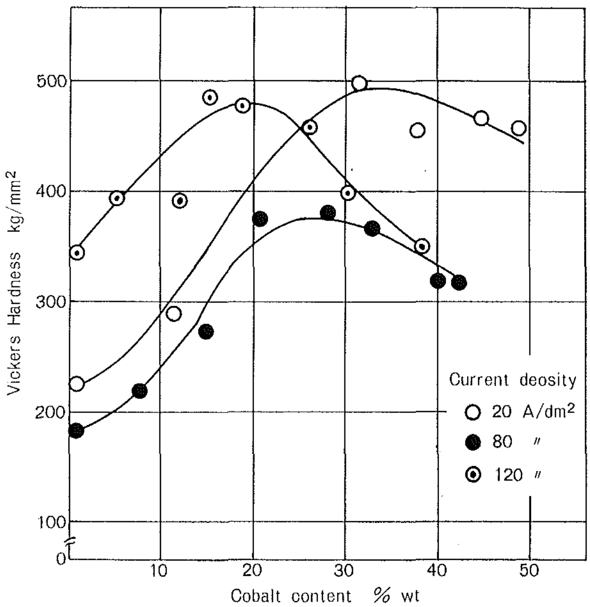

Fig. 10. Effect of Cobalt Content in Electroformed Alloy on Hardness

are as shown in Table. 3. with cobalt content in the alloy and Vickers hardness of the alloy. The tensile strength is within a range of 70 kg/mm² to 167 kg/mm². These values are higher than those of nickel, and have sufficient tensile strength for practical purposes[3].

Fig. 11 shows the relation of tensile strength and Vickers hardness. The tensile strength is proportional to the hardness of electroformed nickel-cobalt alloy. This relation has the advantage of forecasting the tensile strength from the hardness without tension test.

TABLE 3. Representative Tensile Strength of Electoformed Alloy

Current Density (A/dm^2)	Cobalt Content (% wt)	Tensile Strength (kg/mm^2)	Vickers Hardness (kg/mm^2)
20	44.7	132	461
20	48.3	167	437
40	33.4	89.6	322
40	10.6	88.0	280
60	15.3	91.8	314
60	37.2	87.5	312
80	7.6	70.0	217
80	12.7	85.7	270
80	28.1	105	383
80	40.5	93.9	325
120	5.3	107	395
120	12.4	110	391
120	28.7	112	394
120	37.7	107	349

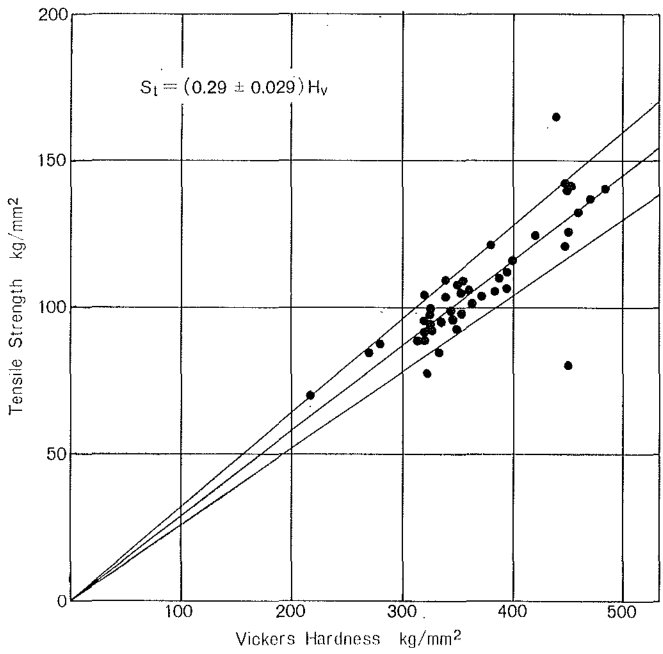

Fig. 11. Relation between Tensile Strength and Vickers Hardness of Electroformed Alloy
S_t: Tensile Strength, H_v: Vickers Hardness

4. Conclusions

1) High speed nickel-cobalt alloy electroforming is possible by high current density with flowing electrolyte which is a Watt type solution with added cobalt sulfate. The current density can be used up tp 120 A/dm^2.

2) The cobalt content in electroformed alloy increases as the cobalt concentration in electrolyte increases, and decreases as the current density increases. Cobalt content in electroformed alloy is in a range of 5% to 50% by weight in this investigation.

3) Stress in electroformed alloy is higher than that of electroformed nickel, but the aspect of stress change is simalar to that of nickel electroforming.

4) Hardness of electroformed alloy is in a range of 300 to 500 in Vickers hordness, and these values are higher than those of electroformed nickel.

5) Tensile strength of electroformed nickel-cobalt alloy is in a range of 70 kg/mm^2 to 167 kg/mm^2. The tensile strength is generally proportional to the Vickers hardness.

6) It is clear that electrochemical phenomena of high speed (high current density) nickel-cobalt alloy electrodeposit and ordinary (low current density) nickel-cobalt alloy electrodeposit are essentially equal, and phenomena of the high speed alloy electroforming are almost similar to that of the high speed nickel electroforming.

References

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