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[illegible] WITH ALLOYS

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CHAPTER III

NICKEL ALLOYS

10. COATING WITH A NICKEL-COBALT ALLOY

With respect to their physical, chemical, and mechanical properties nickel-cobalt coatings are of considerable interest. The advantage of nickel-cobalt coatings lies in the fact that they are harder and more resistant to corrosion than nickel.

Since the deposition potentials of nickel and cobalt in solutions of simple salts differ negligeably from each other, from the electrochemical point of view the combined deposition of nickel and cobalt on the cathode from sulfate electrolytes is fully possible.

The relationship between the composition of the electrolyte and the composition of the cathode deposit, and the influence of different factors on the cathode process have been described in detail in scientific reports (8).

The authors note that the deposition of cobalt on the cathode has an advantage over the deposition of nickel.

Thus with only 15% Co in a solution (as compared with the total percentage of nickel and cobalt, which is taken to be 100) with a current density of 1 amp/dm^2 and a temperature of 50°C, an alloy with an equal amount of both metals is obtained. With increase in current density, and with increase in temperature of pH the nickel content in the cathode deposite increases.

Measurement of the hardness of nickel-cobalt coatings (1) shows that already with only about 25% Co in a coating maximum hardness is obtained, equal to the hardness of pure cobalt.

Corrosion tests in a 2% solution of NaCl enable us to draw the conclusion that alloys with an identical content of nickel and cobalt in the coating have the greatest chemical stability.

11. SPECIAL CASES OF DEPOSITION OF A NICKEL-COBALT ALLOY

Deposition of a nickel-cobalt alloy as a protective and decorative coating.

An alloy containing 1-4% cobalt has been widely used abroad as a lustrous nickel coating (for more details see No. 5 "Bibliotechka").

An alloy containing 15-20% cobalt is used to shorten the time required or the mechanical preparation of the surface before application of the nickel coating. A peculiarity of this alloy is that in applying it as a sublayer on coarsely treated surfaces of components, the surface of the coating becomes smoother.

Considerable smoothing action is obtained in an electrolyte with the following composition:

Nickel sulfate	360 g/l
Nickel chloride	30 g/l
Formic acid	25 g/l
Boric acid	27.5 g/l
Cobalt sulfate	2.5 g/l

Formaldehyde .... 0.6 g/l

Cathode current density D_k .... 4.1 amp/dm^2

Temperature .... 77-77° C

The anodes are made of an alloy with the same composition as the cathode deposit. Stirring and filtering the electrolyte are essential.

Deposition of magnetic alloys. Electrodeposition of magnetic alloys is used to advantage in sound recording and in the recording of non-sound signals instead of powder sound-carriers, which, when compared to alloys, possess a number of defects (less mechanical strength, greater noise level, difficulty in obtaining a uniform layer, etc.).

However, electrodeposited alloys may also be used to make permanent magnets of a given configuration or on a given base.

Alloys of nickel with cobalt and alloys of nickel with cobalt and phosphorus are used as magnetic coatings.

To obtain the best characteristics of a nickel-cobalt alloy (coercive force [illegible]-460 oersteds and residual induction 4000-6000 gauss), it is necessary to keep the percentage of nickel in the alloy between 15 and 35%. A highly coercive Ni-Co-P alloy (coercive force 600-700 oersteds, residual induction 4000-6000 gauss) may be obtained with a phosphorus content of about 3% in the alloy.

The technology of deposition of these alloys was worked out in the Institute of Sound Recording (9). For this purpose the coating is applied on the surface of drums or on wire.

Drums coated with a cobalt-nickel alloy are used for recording speech and music.

Drums coated with a triple alloy Ni-Co-P are used as memory devices in electronic calculating machines.

To deposit a magnetic alloy Ni-Co, the following conditions are recommended:

Nickel chloride	130-140 g/l
Cobalt sulfate	110-120 g/l
Boric acid	20-30 g/l
Potassium chloride	10-15 g/l
Cathode current density D_k	1-2 amp/dm^2
pH of the electrolyte	4.0-5.0
Temperature	50-60° C

To deposite a triple alloy Ni-Co-P, the following conditions are recommended:

Nickel chloride	120-140 g/l
Cobalt chloride	120-140 g/l
Ammonium chloride	80-100 g/l
Sodium Hypophosphite	8-10 g/l
Cathode current density D_k	10-15 amp/dm^2
pH of the electrolyte	0.3-4.5
Temperature	40-60° C

In both cases, in order to obtain alloys of uniform thickness, it is necessary to rotate the cathode.

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For an Ni-Co alloy a high current density of 5 amp/dm^2 is recommended for 20 seconds, after which the strength of the current is reduced to 1 amp/dm^2. The purity of the electrolyte is of very great significance, thus requiring that the salts used in it be marked either "chemically pure" or "pure for analysis" and that the electrolyte be purified periodically by filtration through activated charcoal.

To obtain uniform results, the surfaces of the drums should be coated with copper. If the drum is made of steel or has steel components, it is necessary to demagnetize the steel before applying the coating.

In coating wire, it is convenient to work on a conveyor installation, which makes it possible to coat wire of great length.

The wire must have a small coefficient of elongation (brass, steel, nickeline, phosphorus and beryllium bronze). The optimum thickness of a wire coating is 6-8 microns. An alloy of nickel with cobalt may be used for anodes, in which case, it is desirable that the cobalt content in the anodes be higher than 70%, or else pure cobalt may be used, if we periodically correct the bath with respect to nickel.

A defect in the galvanic method of applying a magnetic coating is the necessity of coating the drum, not on the spot (in a machine), but in dismantled form, which makes it hard to set the parts in place accurately, afterwards.

However, this defect is fully compensated by the strength of the resulting alloy under operational conditions, thus ensuring greater reliability than powder carriers.

12. COATING WITH A NICKEL-PHOSPHORUS ALLOY

Alloys of nickel with phosphorus are harder and more corrosion-resistant than nickel coatings. The hardness of the alloys increases with increase in phosphorus content. Through heating and exposure for 15-30 minutes at a temperature of 500-600°C the hardness of the deposits may be increased as much as 2-2.5 times. A nickel-phosphorus alloy may be obtained both electrochemically and chemically.

When the chemical method is used, the phosphorus content in the deposit amounts to 6-7%.

In electrochemical deposition of a coating the percentage of phosphorus in the alloy may vary within wide limits (from 0 to 20%). The chemical method is already being widely used in industry.

A description of the chemical method of depositing a nickel-phosphorus alloy (better known as the process of chemical nickel plating) is given in No. 5 of the "Bibliotechka".

A Ni-P alloy may be deposited electrochemically from several electrolytes.

Electrolytes prepared on a base of phosphoric and phosphorous acid have been mentioned in scientific reports (2).

However, in view of the cost and the scarcity of phosphorous acid, it is difficult to anticipate wide-spread use of these electrolytes in industry.

To deposit the alloy, an ordinary nickel electrolyte with an addition of sodium hypophosphite NaH_2PO_2 was proposed (10).

In this electrolyte the strongest effect on the phosphorus content in the deposit and, consequently, on the hardness of the coating is due to: the concentration of sodium hypophosphite, the acidity of the electrolyte, and the density of the current.

The phosphorus content in the deposit decreases with increase in acidity and current density, and also when the concentration of sodium hypophosphite in the electrolyte falls below 10 g/l.

Increase of the concentration of sodium hyposulfite above 10 g/l is not advisable, since the phosphorus content, and, consequently, the hardness practically do not change. Furthermore, concentrated solutions of sodium hypophosphite have a tendency to spontaneous decomposition at high temperatures.

Deposits obtained at low temperatures start to crack and peel even during the process of electrolysis. Therefore, it is recommended that the deposition take place at a temperature not less than 70° C.

To deposit an alloy containing 10-11% phosphorus, the following electrolyte composition and conditions of operation may be recommended:

Nickel sulfate $NiSO_4 \cdot 7H_2O$ .... 140 g/l

Sodium sulfate $Na_2SO_4 \cdot 10H_2O$ .... 60 g/l

Sodium chloride NaCl .... 20 g/l

Boric acid H_3BO_3 .... 20 g/1

Sodium hypophosphite $NaH_2PO_2 \cdot H_2O$ 8-10 g/1

Cathode current density D_k .... 1-2 amp/dm^2

Temperature .... 70° C

pH of the electrolyte 4-5.5

The microhardness of a coating obtained under these conditions amounts to 500-550 kg/mm^2. Heat treatment at a temperature of 600°C for 30 minutes increases the microhardness to 1200-1300 kg/mm^2.

A nickel-phosphorus coating, subjected to heat treatment, practically does not change its hardness during operation at high temperatures, in contradistinction to a chromium coating, the hardness of which decreases noticeably at temperatures greater than 400°C.

It has been shown (15) that the addition of phosphoric acid to the electrolyte noticeably stabilizes its sodium hypophosphite content. In this case there is a possibility of operating with great current densities without stirring.

The author recommends the following electrolyte composition and conditions of operation for high-speed solid nickel plating:

Nickel sulfate $NiSO_4 \cdot 7H_2O$ 200 g/1

Nickel chloride $NiCl_2 \cdot 6H_2O$ 30 g/1

Sodium hypophosphite $NaH_2PO_2 \cdot H_2O$ 30 g/1

Phosphoric acid H_3PO_4 .... 40 g/1

Cathode current density D_k .... 10-15 amp/dm^2

Temperature .... 80-90°C

pH of the electrolyte 2.0-2.5

Output efficiency 60-80%

After the electricity passes through at a rate of 25 amp-hr/l, the concentration of sodium hypophosphite in the electrolyte decreases from 30 to 3 g/l. The phosphorus content in the deposit decreases correspondingly from 17 to 5%.

Coatings containing 9% phosphorus and more have a brilliant, stable luster and a smooth surface, even when they are 0.2-0.3 mm thick. When the phosphorus content is less than 5%, the coating loses its luster and becomes dull.

Comparison of the process of deposition of a nickel-phosphorus alloy and the process of chromium plating shows the following:

1) The hardness of nickel-phosphorus coatings is not inferior to the hardness of chromium coatings and does not change with increase in temperature (after heat treatment);

2) The rate of deposition of nickel-phosphorus coatings is 0.07-0.1 mm/hr, while for chromium coatings it is 0.02-0.03 mm/hr, and in the case of chemical nickel plating it is 0.015 mm/hr;

3) The dispersing ability of the electrolyte for solid nickel plating is considerably higher than the dispersing ability of a chromium electrolyte;

4) The cathode output efficiency in an electrolyte in the case of solid nickel plating is 60-80%, while in the case of chromium plating it varies from 12 to 15%.

Thus, nickel-phosphorus coatings may be successfully used instead of chromium coatings, especially for coating components which operate at high temperatures.

In like manner alloys of cobalt with phosphorus may be obtained. However, the latter are not yet being used in industry.