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NICKEL PLATING

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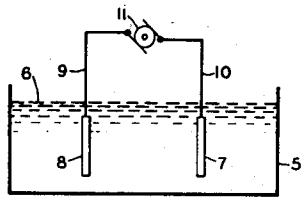


FIG. 1

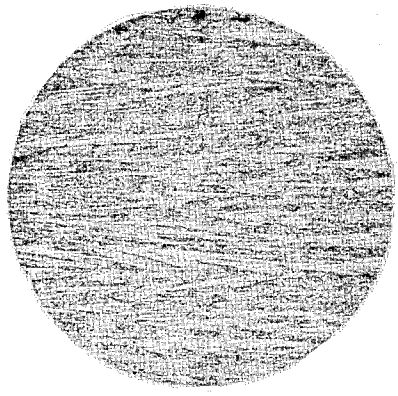


FIG. 2

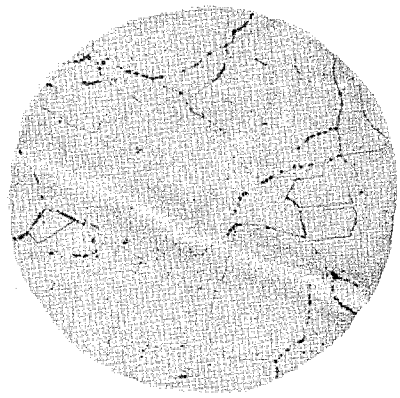


FIG. 3

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NICKEL PLATING

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9 Claims. (Cl. 204—49)

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This invention relates to the electrodeposition of nickel, commonly called "plating," and particularly to an improved nickel anode, a method of preparing the anodes and a method of plating adapted to effect the more satisfactory deposition of nickel in plating operations.

This application is a continuation in part of my application Serial No. 749,731 filed May 22, 1947, now abandoned.

In the customary plating operation, nickel anodes are suspended in a solution of nickel salts called the "electrolyte." Upon the application of a suitable electric current, nickel is deposited at the cathode (the work-piece to be plated) and is dissolved simultaneously from the anode to replenish the nickel content of the electrolyte. The anodes commonly used are of rolled or cast nickel which dissolve uniformly as the operation proceeds. Such anodes are relatively costly as compared with commercial electrolytic nickel.

Electrolytic nickel is the product of the well known process for the electrolytic refining of nickel. It comes from the refinery usually in large sheets about a quarter of an inch thick, and substantially square. The nickel is of high purity (about 99.95% including cobalt) and is in this respect entirely suitable for use in an electrolytic plating operation. Nickel produced by electrolytic refining can be distinguished from cast nickel by the fact that it shows a columnar structure with the column axis perpendicular to the face of the cathode; and the term "electrolytic nickel" is used herein and in the appended claims to refer to such nickel.

Unfortunately, electrolytic nickel is not adaptable (except as hereinafter explained) for use as the anode of a plating operation. Instead of dissolving uniformly over the surface as rolled or cast anodes do, electrolytic nickel begins to dissolve under usual plating conditions by showing a deeply pitted structure. As the application of the current continues, electrolytic nickel may separate into layers having a lacework structure. The inside of the anode becomes very porous. Flakes of the metal drop off and fall into the bottom of the anode bag. Occasionally a large piece of solid nickel drops because the metal surrounding it has been eaten away.

Another reason why it has not been found practicable to operate plating baths with electrolytic nickel anodes is the fact that when a number of such anodes are suspended from a common bar, as they are in commercial practice, individual anodes show marked variations in behavior. It is not uncommon to find differences in potential between individual anodes on the same bar as high as 100 to 200 millivolts. Since the anode bar acts as a common source of current for the anodes hung from it, some anodes draw more current than others; some therefore dissolve more rapidly than others and some do not dissolve at all. Moreover, unequal distribution of current among the anodes results in unequal distribution over the cathodes with unfavorable results there too.

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In U. S. Patent No. 2,358,995, Pinner has approached the problem of using electrolytic nickel anodes by modifying the electrolyte so as to provide conditions favorable for smooth corrosion of the electrolytic nickel. This is accomplished by correlating the chloride content and pH value of the electrolyte within well defined limits. The results obtained following the optimum conditions laid down by Pinner are excellent. However, the modifications required in the electrolyte considerably restrict performance at the cathode and influence the resulting nickel deposit in a manner which is not always desirable. Moreover, the procedure does not permit the use of standard electrolytes which do not conform to the conditions necessary for operation of the patented procedure.

The primary object of the present invention is to provide an anode of electrolytic nickel modified so that it may be used generally in nickel plating electrolytes to produce the desired results.

Another object of the invention is the provision of a method of treating electrolytic nickel to modify its characteristics so that it may be used successfully in the deposition of nickel in connection with the usual electrolytes.

A further object of the invention is the provision of a method of electrodepositing nickel in a more economical and commercially advantageous manner.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specifications and the accompanying drawing, in which

Fig. 1 is a diagrammatic illustration of a plating operation;

Fig. 2 is a photomicrograph showing the columnar structure in a piece of commercial electrolytic nickel; and

Fig. 3 is a similar photomicrograph showing an equi-axed grain structure with coarse but fairly uniform grains developed in the same piece of nickel by the procedure hereinafter described.

I have discovered that electrolytic nickel which normally has the columnar metallographic structure as shown in Fig. 2 may be modified by suitable heat treatment to provide throughout the metal an equi-axed grain structure with coarse, uniform grains as shown in Fig. 3, and that such modified electrolytic nickel, when used as the anode in a plating operation, dissolves smoothly

and uniformly in the electrolyte, essentially as a cast nickel anode does. Thus the difficulties heretofore experienced in attempting to use electrolytic nickel as the anode in a plating operation are avoided. The electrolytes used may be any of those commonly employed in electrolytic plating operations, and the other normal conditions of such operations may be unchanged. Hence it becomes possible to employ commercial electrolytic nickel without the necessity for remelting, casting or rolling. The heat treatment is a relatively simple operation which can be carried out under the conditions hereinafter described.

The sheets of electrolytic nickel as received from the refinery always have the characteristic columnar structure shown in Fig. 2. The grain size, however, may vary according to the conditions under which the nickel has been deposited. When heat treated so as to produce recrystallization of the nickel, the columnar structure changes to an equi-axed structure. I have found that when recrystallization is carried out at lower temperatures, the grain size of the recrystallized nickel may vary considerably, depending not only on the temperature and the time of heating but also on the conditions under which the electrolytic nickel was deposited. On the other hand, if recrystallization is carried out at a high enough temperature, the time of heating and the conditions of deposition no longer seem to be significant factors: coarse grains of fairly uniform size are produced irrespective of the time of heating and of the previous history of the nickel undergoing this heat treatment.

The melting point of pure nickel is approximately 2645 degrees Fahrenheit. I prefer to carry out the heat treatment of electrolytic nickel at a temperature not far below the melting point, preferably between 2200 and 2500 degrees Fahrenheit and in any case above 2100 degrees. There is no reason why the temperature should not go above 2500 degrees except the risk of melting the nickel if the melting point is approached too closely. Within this temperature range, namely above 2100 degrees and below the melting point, essentially the same results are obtained irrespective of the time of heating: for example, by induction heating for 30 seconds or by soaking in a Globar furnace for 30 minutes. Likewise, annealing for an hour or more at a lower temperature before pushing up to the higher temperature has been found to have no appreciable effect.

The structure obtained by recrystallizing electrolytic nickel in this manner is always of the equi-axed type. The range of grain size and the average grain size produced by annealing at varying temperatures are shown in the following table. These grain size measurements were made by projecting the image of suitably polished specimens on the ground glass plate of a metallurgical microscope at a magnification of 100 diameters and comparing with standard nonferrous metal grain size charts of the American Society for Testing Materials.

Temperature, Degrees Fahrenheit	Grain Size (mm.)		Average
	Small	Large	
2,000	0.035–0.045	0.120	0.050.
2,100	0.035–0.045	0.150	0.090.
2,200	0.035	below 0.200	0.090.
2,300	0.035	0.200	
2,400	0.070	over 0.200	over 0.200.
2,500	0.070	do	Do.

The average grain size in the above table corresponds closely to the size of grain found with greatest frequency.

As stated above, the preferred temperature for heat treating electrolytic nickel in accordance with my invention is from 2200 degrees to about 2500 degrees Fahrenheit and in no case under 2100 degrees. The corresponding average grain size would be approximately 0.090 millimeter or larger.

When there has been an interruption in current while the electrolytic nickel is being deposited, the effect is to show an interruption "line" which can be seen under the microscope and sometimes even with the naked eye. Wherever a discontinuity of this kind occurs, the grain size immediately adjacent thereto tends to remain smaller after heat treatment than in the main body of the electrolytic nickel. But the use of annealing temperatures in the range specified above insures that, even in these areas, grain growth is adequate. Hence current interruption lines are not a significant factor in the overall performance of such heat treated electrolytic nickel when used as an anode for nickel plating.

The treatment described brings about a corresponding change in respect to the hardness. Electrolytic nickel after this heat treatment becomes "dead soft."

The heating may be carried out by any suitable means, such, for example, as induction heating or heating in a muffle furnace or a salt bath. It is desirable to avoid oxidizing the nickel, which may be done by using a neutral or reducing atmosphere. The particular type of furnace or fuel employed forms no part of the invention, since many furnaces and fuels suitable for the purpose are readily available.

Individual pieces of electrolytic nickel heat treated in accordance with this invention behave uniformly when suspended from a common anode bar, as is the practice in commercial plating. The difference in potential among such individual anodes is usually under a millivolt. They dissolve smoothly and uniformly in any of the common electrolytes used for nickel plating without leaving an objectionable amount of insoluble scrap.

In carrying out the plating operation with heat-treated electrolytic anodes according to my invention, any conventional plating arrangement may be used, for example, a tank 5 containing the electrolyte 6. The anode 7 may be a sheet of electrolytic nickel modified as hereinbefore described. The cathode 8 may be the work-piece to be plated. The anode and cathode are connected by conductors 9 and 10 to a source of electric current 11.

As an electrolyte, practically any of those now in commercial use may be employed. The most common type of electrolyte is a modification of the well-known Watts solution, of which the following is a typical example:

	Grams per liter
Nickel sulphate	240
Nickel chloride	45
Boric acid	30

The proportions as above stated may be varied, and addition agents may be included. Since the foregoing example is merely illustrative, it is to be understood that the invention is not restricted to any particular electrolyte. The modified electrolytic nickel described herein has been found to

be operative as the anode in electrolytes including nickel salts of various kinds and in various proportions. Thus, the anode may be used in an electrolyte containing only nickel chloride and free from sulphate.

The operating conditions such as pH and temperature of the electrolyte, the anode current density and the cathode current density may also be varied over the usual range common in commercial practice. As a typical example, the following conditions are suitable:

pH	3.
Temperature	130° F.
Cathode current density	40 amp. per square foot.
Anode current density	40 amp. per square foot.

None of these conditions is critical in respect to the uniform solution of the electrolytic nickel anode modified in accordance with the present invention.

The invention as described affords a marked improvement in the technic of nickel plating, in as much as entirely satisfactory results are obtainable with a variety of electrolytes and the usual operating conditions. The expense incident to the preparation of nickel anodes as heretofore practiced is avoided, since the heat treatment of electrolytic nickel can be conducted at relatively slight expense and the modified electrolytic nickel produced by that treatment dissolves uniformly in the electrolyte under normal plating conditions and permits the disposition of satisfactory nickel coatings.

The term "cathode sheet" as used in the appended claims is to be understood as including tubes, bars or rods deposited as a cathode in the electrolytic refining of nickel and modified in accordance with the present invention.

The above detailed description has been given by way of explanation and illustration only, and not by way of limitation. Various changes may be made in the procedure as described without departing from the invention or sacrificing the advantages thereof.

I claim:

1. An anode for use in the electrodeposition of nickel consisting of a cathode sheet of electrolytic nickel having the normal columnar grain structure modified by heating to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to an equi-axed grain structure with an average grain size not less than about 0.090 millimeter throughout the body thereof.

2. An anode for use in the electrodedeposition of nickel consisting of a cathode sheet of electrolytic nickel having the normal columnar grain structure modified by heating to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to an equi-axed grain structure with an average grain size not less than about 0.090 millimeter throughout the body thereof, the grain size varying from 0.035 to over 0.200 millimeter.

3. An anode for use in the electrodeposition of nickel consisting of a cathode sheet of electrolytic nickel having the normal columnar grain structure modified by heating to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to an equi-axed grain structure with a grain size exceeding 0.035 millimeter throughout the body thereof, the grain size averaging approximately 0.090 millimeter.

4. The method of preparing an anode for use in the electrodeposition of nickel which consists of subjecting a cathode sheet of electrolytic nickel to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to modify the normal columnar metallographic structure of the metal to an equi-axed grain structure with an average grain size not less than about 0.090 millimeter.

5. The method of preparing an anode for use in the electrodeposition of nickel which consists of subjecting a cathode sheet of electrolytic nickel to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to modify the normal columnar metallographic structure of the metal to an equi-axed grain structure with a grain size not less than about 0.035 millimeter and ranging to over 0.200 millimeter and averaging not less than about 0.090 millimeter.

6. The method of preparing an anode for use in the electrodeposition of nickel which consists of subjecting a cathode sheet of electrolytic nickel to a temperature of from about 2200 degrees F. to 2500 degrees F. to modify the normal columnar metallographic structure of the metal to an equi-axed grain structure with a grain size averaging approximately 0.090 millimeter.

7. The method of electrodepositing nickel which comprises suspending the work-piece to be plated in an electrolyte containing a nickel salt in solution with an anode consisting of a cathode sheet of electrolytic nickel in which the normal columnar metallographic grain structure has been modified by heating to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to an equi-axed grain structure with a grain size not less than about 0.035 millimeter and ranging to over 0.200 millimeter and averaging not less than about 0.090 millimeter, and connecting a source of current to the work-piece and anode.

8. The method of electrodepositing nickel which comprises suspending the work-piece to be plated in an electrolyte containing a nickel salt in solution with an anode consisting of a cathode sheet of electrolytic nickel in which the normal columnar metallographic grain structure has been modified by heating to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to an equi-axed grain structure with a grain size exceeding about 0.035 millimeter and averaging approximately 0.090 millimeter, and connecting a source of current to the work-piece and anode.

9. The method of electrodepositing nickel which comprises suspending the work-piece to be plated in an electrolyte containing a nickel salt in solution with an anode consisting of a cathode sheet of electrolytic nickel in which the normal columnar metallographic grain structure has been modified by heating to a temperature of from about 2200 degrees F. to slightly less than the melting point of nickel to an equi-axed grain structure with an average grain size not less than about 0.090 millimeter, and connecting a source of current to the work-piece and anode.

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