'S' NICKEL IN THE PLATING INDUSTRY*

INTRODUCTION

Technical and economic advantages of the use of primary nickel in titanium baskets have been claimed by the plating industry, but further comment on these advantages is not intended in this paper. A number of different forms of primary nickel, including commercially pure electrolytic squares, carbonyl pellets, compacted and sintered nickel powder have been used by platers with varying degrees of success. A special type of electrolytic nickel, called 'S' Nickel, has been found to meet the needs of platers using titanium baskets as well as those who, for reasons of greater economy, prefer the material in strip form.

'S' Nickel, containing sulphur but otherwise similar in composition and appearance to ordinary electrolytic nickel, has a number of advantages over commercially pure nickel when used in titanium baskets or in strip form.

Under normal plating conditions pure electrolytic or pellet nickel dissolves at 100 per cent efficiency. Complete passivity resulting in anode insolubility and oxygen evolution only occurs when the chloride content of the solution is zero or very low or when very high current densities (in excess of 300 amps/sq. ft. (32.4 amps/dm^2)) are used. In chloride-free solution pure nickel is immediately polarised and the potential rises to +1.5v (hydrogen scale), at which level oxygen is evolved. Intermediate chloride contents cause pure nickel to dissolve at potential around +0.4v. Under this condition pitting corrosion occurs and the metal dissolves as the pits widen and deepen, leaving areas of the surface unattacked. In time, the number of pits multiplies until the surface layers become completely honeycombed to form a spongy, loosely attached skin.

Electrolyte pH has an effect on dissolution characteristics; a low pH (around 1.5 to 2.0) and current densities around 10-20 amps/sq. ft (1.08-2.16 amps/dm^2) gives smooth dissolution of commercially pure nickel in Watts type solutions. Pitting corrosion, with the eventual formation of sponge and skin, occurs when the pH and current density is increased above these values.

Activation of Nickel

Although smooth dissolution may be obtained in high chloride, low pH solutions and at low current density, it is additionally possible to activate nickel by the incorporation during manufacture of other elements into the nickel matrix. Sulphur is the best known of these activators, although selenium, tellurium and possibly others are known to have similar, though less marked, effects.

Pure nickel may also be activated by adsorption of sulphur compounds present in the plating electrolyte. The type of compounds (such as thiosulphate) which do this most effectively, usually have deleterious effects on the deposit. Many of the commonly used organic sulphur-containing brighteners do not appear to be effective activators although Depolarised nickel already containing a controlled amount of sulphur, generally suffers local preferential attack and high grain losses in "bright" electrolytes, due to locally increased activity.

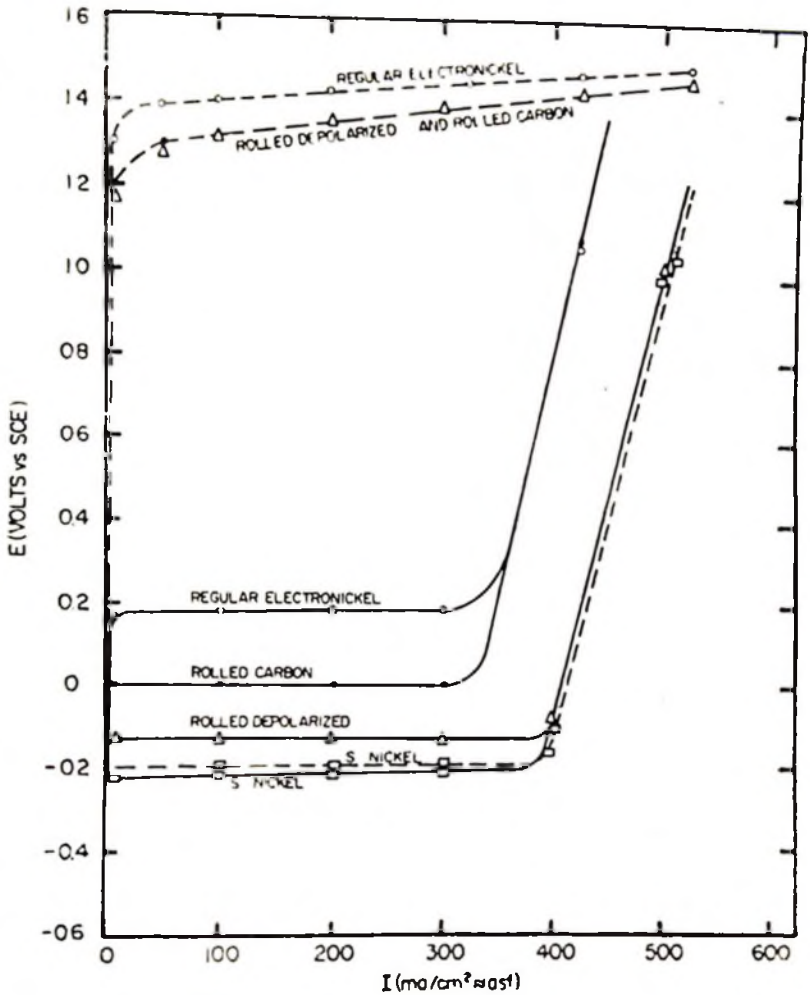
Experimental and practical trials have shown that electrolytic nickel activated by the presence of a small amount of sulphur ('S' Nickel) is a very satisfactory plating material. Losses by metallic residue are practically nil in all proprietary solutions tested, while the dissolution voltage is lower than for other primary nickel forms. 'S' Nickel is active over a wide range of pH, current density, and even when the electrolyte contains no chloride.

Electrochemical Aspects of 'S' Nickel

In work carried out in the Inco Bayonne laboratories, polarisation curves were obtained of various materials in Watts type and chloride-free plating solutions. The conclusions drawn from this work are illustrated in the Figure, and may be summarised as follows:

(*a*) 'S' Nickel is the most electronegative of all materials tested in both Watts type and chloride-free electrolytes. 'S' Nickel is active up to between 400 and 500 amps/sq. ft. (43.2 to 54 amps/dm^2) and up to pH 5.5.

* Developed by the International Nickel Co. (Mond) Ltd, London.



DISSOLUTION-POTENTIAL CURVES FOR 'S' NICKEL AND OTHER MATERIALS IN NICKEL-PLATING SOLUTIONS

——— WATTS-TYPE BATH, pH 4.5, 140°F.
------ SULFATE BATH (CHLORIDE-FREE), pH 3.0 AND pH 4.0, 140°F.

TABLE I: Residues from various materials

Solution	*Electrolytic Nickel*		*Pellet*		*'S' Nickel*	
	Metallic Residue(%)	Non-Met. Residue(%)	Metallic Residue(%)	Non-Met. Residue(%)	Metallic Residue(%)	Non-Met. Residue(%)
Watts	0.24	0.24	0.96	0.08	0.002	0.007
Perflow	0.27	0.04	0.80	0.03	0.0033	0.139
Airglow	0.16	0.01	1.0	0.07	0.028	0.15
B.Q. Super	0.09	0.06	1.3	0.14	0.0024	0.12
Gleamol	0.27	0.08	0.88	0.13	0.020	0.11
Super Gleamax	0.5	0.10	0.5	0.1	0.04	—
Udylite 66	0.17	0.02	1.0	0.03	0.02	0.16
Udylite 66 H	0.40	0.50	1.1	0.09	0.0058	0.19
Plusbrite	0.33	0.20	1.4	0.35	0.028	0.15
Nivolit	—	—	1.47	0.75	0.038	0.17
Jewel Extra	—	—	0.63	0.1	0.003	0.08

(*b*) Rolled Depolarised and carbon-containing nickel is active (at slightly higher potentials) in chloride-containing electrolytes.

(*c*) Pellet and pure electrolytic nickel (other than 'S' Nickel) are the most electropositive materials tested and will dissolve only in chloride-containing electrolytes.

Apart from the greater flexibility of 'S' Nickel, its lower potential offers another worthwhile advantage to the plater in that lower cell voltages mean that a greater proportion of current is available, from a given supply, for actual plating. Thus, if a plating vat requires a cell voltage of 10 volts, the reduction of dissolution voltage by 0.5 volt by using 'S' Nickel can result in a 5 per cent saving in current or alternatively a 5 per cent increase in plating capacity in the plant.

Residues

A feature which has always been of great importance to the plater is the amount of metal loss (as skin sponge and grain) suffered by any particular form of material. Clearly, the less the amount of nickel lost in this way the greater is the economy. For this reason Depolarised nickel has always been recommended for regular Watts type solutions and carbon-containing Durvanic nickel is generally recommended for organic "bright" solutions since in both cases metal losses in the form of undissolved grain or skin are practically nil.

For the same reason 'S' Nickel is now recommended for use in titanium baskets although, because of mechanical consideration, metallic residues from pure nickel may be kept in electrical contact with the titanium and will continue to dissolve to some extent. However, in spite of this latter feature, results of dissolution trials in a number of different proprietary solutions have shown that both electrolytic and pellet nickel produce more metallic residue than does 'S' Nickel. The metallic residue varies slightly from solution to solution but the average value, expressed as a percentage of the amount of nickel dissolved, is roughly 0.9 per cent for pellet, 0.3 per cent for electrolytic nickel and 0.02 per cent for 'S' Nickel.

Table 1 compares metallic and non-metallic residues from electrolytic nickel, pellet and 'S' Nickel in a number of different proprietary solutions. These and other similar trials were carried out for varying periods of time, some lasting nearly 2 years. Non-metallic residue occurs with all forms of primary nickel and, like metallic residue, it can cause roughness at the cathode, if allowed to discharge into the solution. Bags on strip and baskets are therefore always required, and should be of satisfactory durability so that the opportunity for reduced maintenance can be exploited.

Rise in Cell Voltage

More residue collects as the time of the trial increases, and eventually the titanium baskets may become clogged with undissolved and insoluble residue. This effect is indicated by a rise in cell voltage.

Trials with 'S' Nickel in a 2" (5.08 cm) dia-

meter titanium basket in a proprietary bright nickel solution produced an increase in cell voltage of just over 0.4 volts after a test lasting for 6000 Ah. Under similar conditions with a compacted and sintered nickel, which in the same solution produces a hundred times more metallic residue (5.3 per cent as against 0.05 per cent for 'S' Nickel), the cell voltage rose by about 4.5 volts. In larger cross section rectangular baskets, however, the rise in voltage with sintered nickel was only 1 volt, while the rise in voltage with 'S' Nickel in the same baskets was correspondingly less.

A rise in cell voltage is clearly brought about by the production of insoluble residue. The larger the cross section of the basket the more residue can be accommodated before voltage increase becomes significant and the basket needs to be cleaned out.

Conclusions and Summary

1. Pellet and regular electrolytic nickel dissolves under normal plating conditions by pitting corrosion with the formation of skin or sponge. Practically 100 per cent efficiency is, however, maintained with these two forms, except when chloride is absent from plating solutions and at high current densities and high pH when passivity can occur.
2. 'S' Nickel in titanium baskets or in strip form is active and dissolves smoothly at a potential about 0.4v less than any other primary form. 'S' Nickel is active over a wide range of current density and over a pH range within which most modern plating solutions are operated.
3. 'S' Nickel is active and dissolves smoothly over a similar ranges of current density and pH in chloride-free solutions.
4. The metallic residue from 'S' Nickel is on the average (depending on the type of plating solution) only one thirteenth to one fiftieth of that from electrolytic or pellet nickel.
5. A rise in dissolution voltage occurs with all basket anodes as time goes on. This rise is associated with the formation of residues and is greater with baskets of small cross sectional area. With 'S' Nickel the rise in dissolution voltage is less than with other forms, and maintenance costs may be lowered by reducing the frequency with which baskets must be cleaned out.