The Effect of Nickel Salts on Electroless Nickel Plating

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Abstract

Nickel chloride, fluoride, bromide, iodide, formate, acetate, sulfamate, fluoborate, borate and sulfate were compared in an acid lactate-acetate electroless nickel plating solution formulation for plating rate and bath stability, as well as deposit nitric acid resistance and hardness.

Introduction

In previous experiments, the effect of monovalent anions (NH_4^+, Li^+, Na^+, K^+) on electroless nickel (EN) plating was investigated[1]. The effects of various chelating agents in EN baths has been extensively studied[2,3,4]. However, no systematic comparison of different nickel salts in EN plating has been published except for internal stress measurements of EN plated strips by the author[5]. He found that in 25 μm EN deposits containing 8-10% phosphorus, the nickel chloride produced higher stress than the sulfamate, while the nickel sulfate coatings had the lowest stress. A recent article[6] reported that the substitution of bromide ions for chloride ions in a Watts electroplating bath reduced the tensile stress in the nickel deposit.

The first EN plating solutions used by Brenner and Riddell in 1944 were prepared with nickel chloride[7]. Later, the Kanigen® process and proprietary EN plating solutions employed nickel sulfate almost exclusively in acid EN plating formulations[8].

A number of patents have been granted for EN plating solutions containing fluoride ions based on either faster plating rate[9,10] or higher deposit hardness[11]. The use of nickel ammonium fluoride[12] and nickel fluoborate[13] has also been patented.

At present, commercial acid EN plating solutions are made up with nickel sulfate, however, most alkaline baths contain nickel chloride. The experiments reported here were designed to evaluate and compare various non-complexing nickel salts in a generic EN plating formulation.

Experimental Procedure

The EN plating was performed on clean, mild steel coupons (20 cm^2 surface area) in 200 mL solutions in a constant temperature bath at 90±1° C. Similar to the one used in previous work, the following formulation was used in all experiments:

Nickel salt	0.1 M
Lactic acid	0.3 M
Sodium acetate	0.25 M
Sodium hypophosphite	0.3 M
Sodium hydroxide	0.2 M
Lead ion	0.5ppm

All solutions were initially adjusted to pH 4.8-4.9. Most of the chemicals were obtained from commercial sources: the nickel salts as purified, liquid concentrates except for the borate, formate and fluoride, which were prepared in situ from nickel carbonate and the appropriate dilute acid.

The plating rates were calculated from the weight gain of the plated coupons. The EN bath stabilities were determined by measuring the elapsed time to decomposition (black solution) after the addition of 2.0mL 100ppm palladium solution to 100mL plating bath aliquot at 60° C on a magnetic stirrer-hot plate. The nitric acid resistance was evaluated by a 30 sec partial immersion of the plated coupons in the concentrated acid. The buffering capacity of the nickel salts was found out by pH measurements of the solutions after plating. The hardness of some EN deposits was measured on a Micromet II Digital Micro Hardness Tester using a Knoop indentor with a 100g load. Plated EN foils were analyzed for phosphorus content by the vanadate-molybdate photometric method.

Discussion of Results

All of the experimental results are shown in the Table. The nickel sulfate, chloride and ammonium sulfate solutions had essentially the same plating rates. The only nickel salt producing a faster rate was the borate probably due to its buffering effect.

Comparing the nickel halides, the plating rates decreased in the following order: Cl^-, F^-, Br^-, I^-, whereas the bath stabilities increased in the same order. Thus, the nickel iodide solution had by far the best palladium stability, but also the slowest plating rate. The nickel fluoride bath deposited a coating with excellent nitric acid resistance and hardness.

The plating rates of the other nickel salts evaluated decreased as follows: sulfate, acetate, formate, sulfamate, fluoborate. All the deposits were bright except for the nickel formate coating, which was dull. The nickel acetate deposit had the least nitric acid resistance.

It is noteworthy that the plating rates of the various nickel salt EN solutions decrease in the opposite order of their solubilities. Thus, nickel iodide is the most soluble, but the slowest plating; the opposite is true for nickel borate.

Conclusions

Since for most EN applications the plating rate and cost are the most important considerations, the nickel sulfate salt is the best choice for the formulator and plater. If needed, boric acid or sodium borate could be added to maintain the bath pH and possibly increase the plating rate. When increased as-plated hardness is desired, the use of nickel fluoride or the addition of a fluoride salt to the EN bath should be considered. This should also improve the nitric acid resistance of the deposit.

Summary

The performance of various non-complexing nickel salts was compared in an acid EN plating solution formulated with lactic acid as the complexing agent and sodium hypophosphite as the nickel reducing agent. The plating rates of the nickel sulfate, nickel ammonium sulfate and nickel chloride plating baths were about equal. The nickel halide solution rates decreased as follows: Cl^-, F^-, Br^-, I^-, whereas their bath stabilities increased in the same order. The nickel sulfamate, acetate, formate and fluoborate induced slower plating rates, while the nickel borate plated appreciably faster than the nickel sulfate solution. Evaluation of the EN deposits found the nickel fluoride to yield the highest hardness and best nitric acid resistance.

References

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Nickel Salt	Plating Rate μm/h	Palladium Stability sec	pH Change	Nitric a. Resistance	Hardness HK 100	%P
Sulfate	19	12	-0.3	OK	580	8.2
Chloride	19	12	-0.3	shadow	550	
Fluoride	16	12	-0.1	exc.	650	
Bromide	15	150	-0.2	shadow		
Iodide	3	600+	0	shadow		
Formate	16	12	0	OK		
Acetate	16	12	-0.1	black		
Ammonium Sulfate	18	12	-0.2	OK		
Sulfamate	16	20	-0.3	shadow		
Fluoborate	15	15	-0.3	OK		
Borate	23	12	0	OK		