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Nickel Deposition from a Watts Bath Containing Monosodium Glutamate

by
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ABSTRACT

Nickel electrodeposition onto copper substrates was carried out from a Watts bath in the presence of monosodium glutamate (MSG) as a complexing agent. The study dealt with the influence of MSG concentrations on the cathodic current efficiency, cathodic polarization curves, anodic linear stripping voltammetry and the throwing power as well as the throwing index of the bath. The presence of MSG resulted in a marked shift in the polarization curves towards more negative potential values, indicating an inhibition of Ni^{+2} ion deposition. On the other hand, the extent of the inhibition increased with increasing MSG concentration. The addition of MSG improved the appearance of nickel deposited from the Watts bath. Moreover, the throwing power increased by a factor of more than three in the presence of MSG. The surface morphology of the nickel plated with and without MSG was examined using scanning electron microscopy (SEM), while the microstructure was examined using x-ray diffraction (XRD).

Keywords: nickel electrodeposition, Watts bath, monosodium glutamate, potentiodynamic polarization, throwing power.

Introduction

Nickel electrodeposition is one of the most widely used surface finishing processes for decorative, engineering and electroforming applications.[1] Decorative applications account for about 80% of nickel consumption in plating while 20% is consumed for engineering and electroforming aims.[2] In electrodeposition processes, it is not enough just to produce deposits having the desired appearance and properties. The deposit must also be applied in such a way as to completely cover the substrate with a deposit as near uniform in thickness as practicable.[3]

It is well known that the structural and the mechanical properties are strongly influenced by the electrolyte parameters: composition, temperature, pH and agitation of the electrolytic bath, presence and concentration of additives in the bath, mode of imposed current and current density values. Among these factors, one of the most effective in controlling the nickel crystal growth and the resultant properties of the deposits is the use of complexing agents in the bath. Nickel electrodeposition has been studied extensively by several investigators and deposition has been carried out from different baths including, sulfamate, chloride, sulfate, citrate or acetate baths, in addition to the well-known mixed chloride-sulfate Watts bath, with or without additives.[4-16] The current work aims to develop new baths for producing good quality nickel deposits, which have the advantages of being more environmentally friendly.

Experimental details

The electrodeposition of nickel was carried out using a bath containing: 0.63M $NiSO_4 \cdot 6H_2O$, 0.09M $NiCl_2 \cdot 6H_2O$ and 0.3M H_3BO_3, commonly known as the Watts bath. All of the plating baths and reagents were made from analytical grade chemicals without further purification and doubly distilled water. Monosodium glutamate (MSG) was added to the Watts bath as a complexing agent. MSG is the sodium salt of glutamic acid ($C_5H_8NNaO_4$), one of the most abundant naturally occurring non-essential amino acids.[17] It has the following chemical structure:

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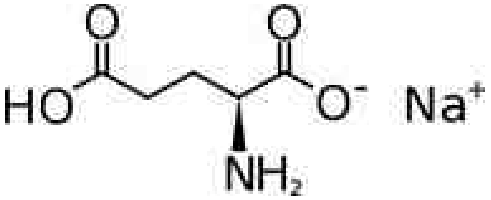

Monosodium glutamate

For electrodeposition, a copper cathode and platinum sheet anode, both of dimensions 2.0 × 2.0 cm, were used. The plating cell used was a rectangular Perspex trough (8 × 2 cm) provided with vertical grooves, on each of the side walls, to fix the electrodes. Before each run, the copper cathode was cleaned using a pickling solution and then washed with distilled water, rinsed with ethanol and weighed. Direct current was supplied by a DC power supply unit. The cathodic current efficiencies (%*F*) were determined with the help of a copper coulometer.

$$F = \frac{W_{exp}}{W_{th}}, \tag{1}$$

where W_{exp} is the weight of the deposit obtained experimentally and W_{th} is the weight of the deposit calculated theoretically according to Faraday's Law. Electrodeposition was carried out for 10 min in each case.

The percentage throwing power (%*TP*) of the solution was measured using a Haring-Blum rectangular Perspex cell (2.0 cm wide, 13.0 cm long, with 2.5 cm solution depth) fitted with one anode between two parallel copper cathodes where the ratio of the far to the near distance was 3:1. This was calculated from Field's formula:[18]

$$\%TP = \frac{L-M}{L+M-2} \times 100\ , \tag{2}$$

where *L* is the ratio of the cathode distance to the anode distance (far to near) and *M* is the ratio of the weight of the deposited metal on the near to the weight of the metal deposited on the far cathode. The values of *M* were measured as a function of *L* over a wide range of linear ratios varying between 1:1 and 5:1. The throwing index (*TI*) of each bath was considered as the reciprocal of the slope of the *M* versus *L* plot.[19]

Potentiodynamic cathodic polarization curves were recorded using copper substrates by sweeping the potential from the rest potential in the negative direction at a scan rate of 10 mV/sec. A potentiostat/galvanostat controlled by a computer was used for all electrochemical measurements. All potentials were measured relative to a saturated calomel electrode (SCE). To avoid contamination, the reference electrode was connected to the working cathode via a bridge provided with a Luggin-Haber tip and filled with the solution under test.

Anodic linear stripping voltammetry (ALSV) measurements were carried out in a conventional electrolytic cell containing a glassy carbon electrode (GCE) as a working electrode, a saturated calomel reference electrode and a platinum wire as a counter electrode. The carbon electrode was polished before each run with diamond paste (0.25 µm) until a mirror surface was obtained, then washed several times. Deposition of nickel from the plating bath was carried out on the GCE at a constant deposition potential of -1.0 V_{SCE} for 100 sec. At the end of this deposition time, stripping analysis was performed immediately in the same plating bath (*in situ*) by sweeping the potential to more anodic values at a potential sweep rate of 10 mV/sec.

The surface morphology of the nickel electrodeposited on copper in the absence and presence of MSG was examined using scanning electron microscopy. The crystalline structure of the nickel thin film deposited on copper from the Watts bath in the absence and presence of MSG was examined by x-ray diffraction using a diffractometer (40 kV, 20 mA) with a nickel filter and CuKa radiation.

Results and discussion:

Cathodic current efficiency

In the electrodeposition process, the cathodic current efficiency, %*F* is important for economic reasons, as it is a measure of the effective utilization of the electrical energy. The addition of MSG (25 to 100 g/L) to the Watts bath significantly enhanced the surface brightness over that produced without MSG. Moreover, the nickel appearance becomes a bright dark grey. The effect of applied current density (0.6 to 1.9 A/dm^2) on the %*F* during nickel electrodeposition in the absence of MSG was studied (Fig. 1). The results show that the %*F* increased with increasing current density and then leveled off at about 100% in the current range between 0.7 and 1.4 A/dm^2. However, further increase in the current density decreased the %*F*. This could be attributed to the simultaneous hydrogen evolution. Visual investigation of the samples electrodeposited at different current densities showed that 1.0 A/dm^2 was found to be a suitable current density for further investigation, since it produced a bright, smooth nickel deposit. Generally, the %*F* value for a Watts bath is always around 100%, over a wide range of current density.[8]

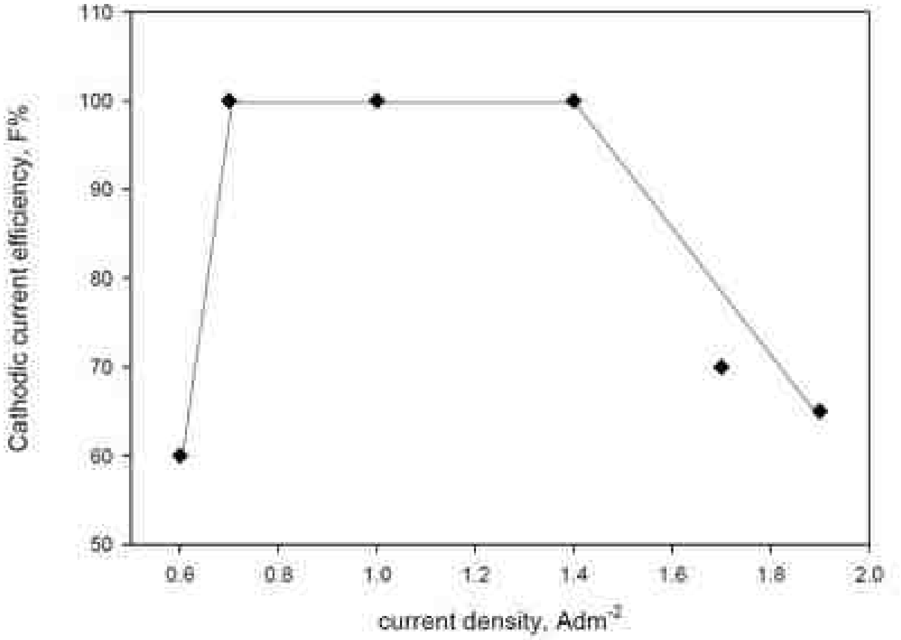

Figure 1 - The effect of current density on the cathodic current efficiency, %*F* for nickel electrodeposition from a Watts bath in the absence of MSG.

Figure 2 shows the effect of adding different concentrations of MSG (25 to 100 g/L) on the %*F* at 1.0 A/dm^2. The results showed an obvious decrease in the %*F* with increasing MSG concentration.   This could be attributed to the fact that Ni^{+2} ions form a soluble complex with MSG molecules and the stability of this complex increased with increasing MSG concentration:

$$2L + Ni^{+2} \longrightarrow NiL_2 \qquad (3)$$

where L is the MSG molecule and NiL$_2$ is the soluble complex formed.

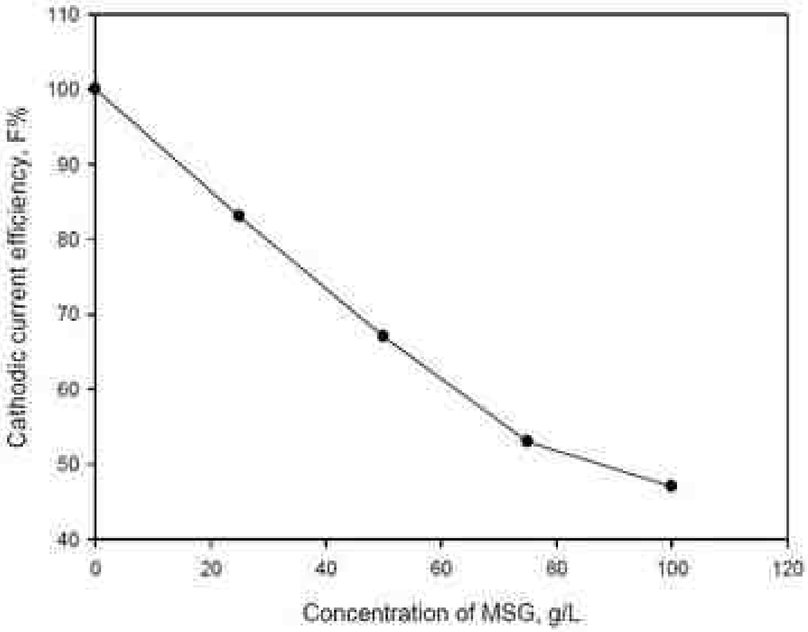

Figure 2 - The effect of MSG concentration on %*F* for nickel electrodeposition from a Watts bath.

In addition, increasing MSG concentrations in the bath, leads to decrease the concentrations of free Ni^{+2} ions in the electrolytic bath and consequently decrease the %*F*.

In general, nickel deposition from nickel ions can be described by the following reaction:

$$Ni^{+2} + 2e^- \rightarrow Ni \quad (4)$$

However, in presence of MSG, a soluble nickel glutamate complex is formed. The following electro-reduction reaction is possible with hydrogen evolution from independent side reactions:

$$NiL_2 + 2e^- \rightarrow Ni + 2L^- \quad (5)$$

Therefore, the reduction of the nickel complex is not as easy as the reduction of the free Ni^{+2} ions. This is the reason for decreasing %*F* during nickel electrodeposition from the baths containing MSG.

Potentiodynamic cathodic polarization curves

The potentiodynamic polarization curves (*i*/*E* curves) are of special interest because they involve the nature of the whole deposition process. Therefore, the potentiodynamic cathodic polarization curves during the electrodeposition of nickel on copper substrates from a Watts bath in the presence and absence of MSG were measured and the results are given in Fig. 3.

The data show the influence of adding different concentrations of MSG (25 to 75 g/L) to the Watts bath. The presence of MSG resulted in a marked shift in the polarization curves towards more negative potential values, indicating an inhibition of Ni^{+2} ion deposition. The extent of the inhibition increased with increasing MSG concentration. The inhibitory effect of MSG could be related to its complex formation with Ni^{+2} ions in the electrolytic solutions and the decrease in the free Ni^{+2} ions in the bath as mentioned earlier.

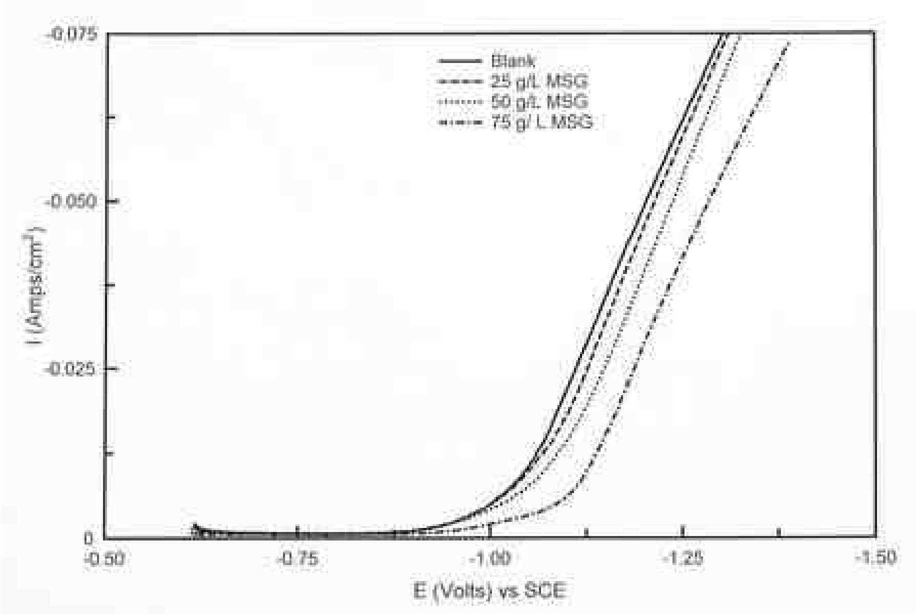

Figure 3 - Cathodic polarization curves in the absence and presence of different concentrations of MSG.

Anodic linear stripping voltammetry (ALSV)

A series of voltammetric experiments was carried out by the deposition of nickel on a glassy carbon electrode (GCE) in the presence and absence of MSG at a given constant cathodic potential (-1.0 V_{SCE}) for a given time (100 sec). Immediately after nickel deposition, the potential was swept linearly in the positive direction at a scan rate of 10 mV/sec and an anodic stripping voltammogram was recorded without removing the electrode from the solution or changing the prevailing conditions. Some representative data is given in Fig. 4.

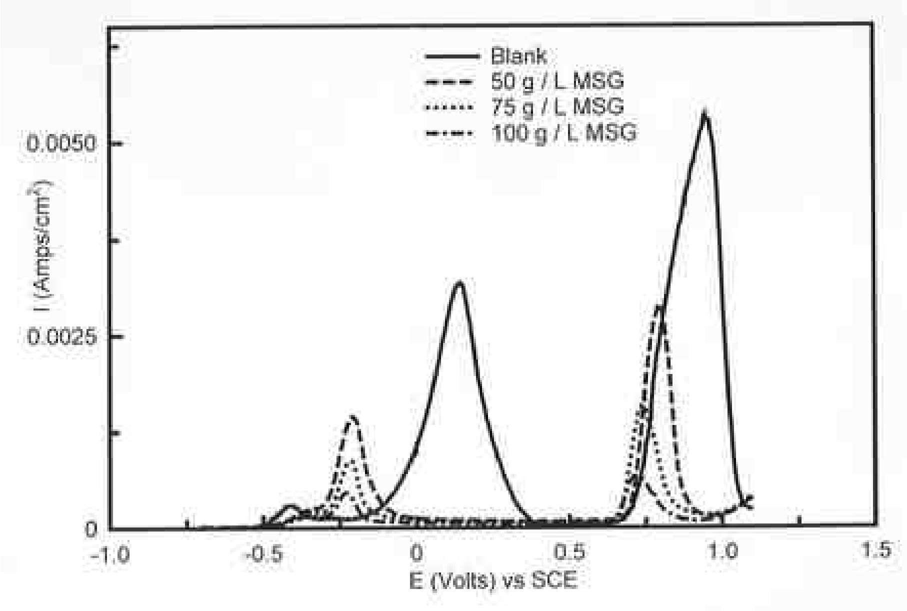

Figure 4 - Anodic linear stripping voltammetry for nickel electrodeposited from a Watts bath in the presence and absence of different concentrations of MSG.

The ALSV curve for the nickel deposited from the Watts bath showed two high peaks at 0.14 V_{SCE} and at 0.95 V_{SCE} respectively and one small peak at -0.4 V_{SCE}, corresponding to three different phases of nickel deposited. These anodic peaks were related to the anodic dissolution (anodic stripping) of the nickel potentiostatically deposited on the GCE. No residual nickel or nickel oxide was visible on the GCE beyond the anodic peak. Therefore, the charge consumed through anodic stripping could be taken as a quantitative measure of the current efficiency of nickel deposition, *i.e.*, the area under the peak is equivalent to the amount of nickel deposited. Addition of MSG to the Watts bath (50 to 100 g/L) sharply decreased the height and the area under the stripping peaks, and consequently the cathodic efficiency decreased with increasing concentration of MSG. The decrease in the height of the peaks is attributed to the decrease in the amount of nickel deposited in the presence of MSG, indicating strong inhibition of the Ni^{+2} reduction. This result agrees with the results previously obtained from the polarization curves and cathodic current efficiency values from those studies.

X-ray diffraction analysis

The microstructure of the as-electrodeposited nickel obtained from Watts bath in the presence and absence of MSG was examined by x-ray diffraction analysis as shown in Fig. 5. The results indicate that the nickel deposited from the Watts bath without MSG, exhibited a face centered cubic structure, with a strong (200) diffraction peak (preferred growth orientation) in addition to (220) and (111) peaks. The intensities of all these peaks decreased in the presence of MSG. These results obviously agree well with results obtained by ALSV, which showed a decrease in the peaks in presence of MSG (see Fig. 4). Moreover, these results are in good agreement with the results of Tripathy, *et al*.[11] They observed that the (200) plane was the most preferred plane during nickel electrodeposition.

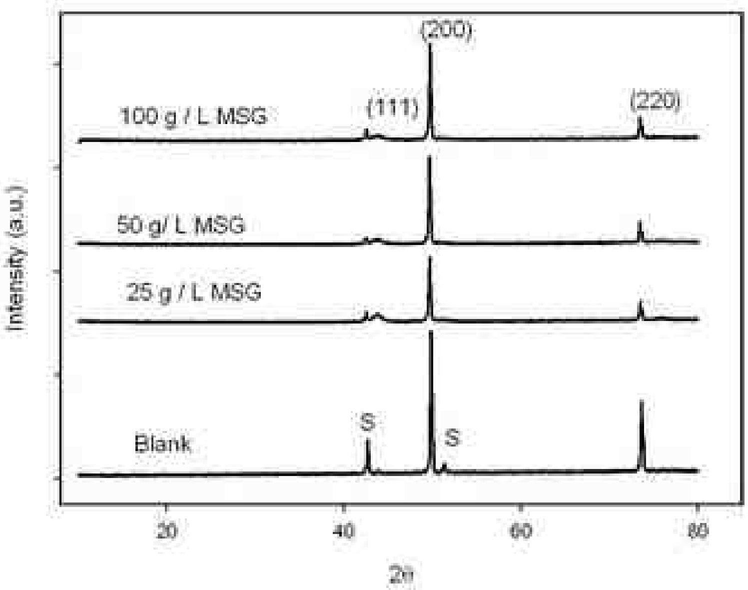

Figure 5 - X-ray diffraction analysis data of nickel electrodeposited from a Watts bath in the presence and absence of MSG.

Surface morphology

An SEM morphological examination of the nickel electrodeposited was carried out to better understand the electrochemical results. The SEM results showed that the nickel deposited from the Watts bath produced a non-homogeneous surface containing some surface defects in the form of pits resulting from hydrogen evolution (Fig. 6). However, in the presence of MSG, the surface became homogeneous consisting of very fine and compact grains of a circular shape.

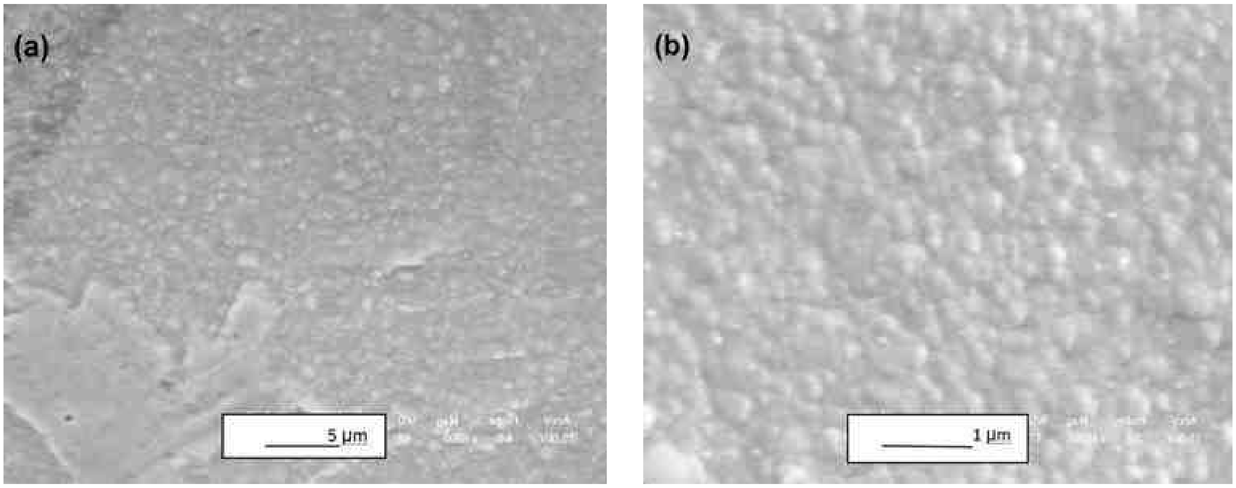

Figure 6 - Photomicrograph of nickel electrodeposited from a Watts bath in (a) the presence and (b) absence of MSG.

Throwing power and throwing index

The throwing power of the acidic sulfate baths was measured using a Haring-Blum cell under variable plating conditions. According to the cell geometry, the total cell current i is divided into two partial currents, i_n and i_f, corresponding to the respective cathodes. In the absence of polarization, the primary current ratio (i_n/i_f) depends on the electrical resistance of the electrolyte between the anode and the respective cathodes, *i.e.* it is inversely proportional to the ratio of their distances from the anode. Thus the primary current ratio should be equal to the distance ratio, *L*. Once the current passes, polarization takes place and it is assumed that it will be higher at the nearer cathode than at the farther one. Because polarization resistance may be considered as being in series with the ohmic resistance, the current at the nearer cathode is decreased, giving rise to a more uniform secondary current distribution ratio. More equalization of the current ratio could be achieved by increasing the conductivity of the bath.

The throwing power of the Watts baths was measured using a Haring- Blum cell in the presence and absence of MSG. The throwing power values of the Watts nickel plating baths calculated by Field's empirical formula at a distance ratio of 1:3 in the presence and absence of MSG are shown in Table 1. Inspection of the data shows that the percentage throwing power, %*TP*, of the Watts bath is low, 6.6%. Addition of MSG greatly increases the %*TP* to 20.1% at an MSG concentration of 75 g/L.

Table 1 - The %*TP* and the *TI* values for the Watts bath in the presence and absence of MSG.

TI	*TP%*	MSG Concentration, g/L
0.67	6.6	0
0.74	9.6	25
0.83	14.3	50
0.97	20.1	75

Another way of expressing the throwing power of the plating bath is the throwing index (*TI*). There are several advantages associated with expressing %*TP* in the form of *TI*. For example, a single number is obtained, characteristic of a range of linear ratios. In addition, *TI* is obtained from several experimental points and thus minimizes errors in measurement of any one point.[20] The throwing index (*TI*) was determined by plotting the metal distribution ratio *M*, and the linear ratio *L* (1:1 to 1:5) as shown in Fig. 7. The reciprocal of the slopes of these lines is called the throwing index (*TI*) and represents a measure of bath throwing power. It should be noted that a solution with excellent characteristics would produce a horizontal line at $M = 1$, whereas, a bath with a poor %*TP* would exhibit a very steep line in this plot.

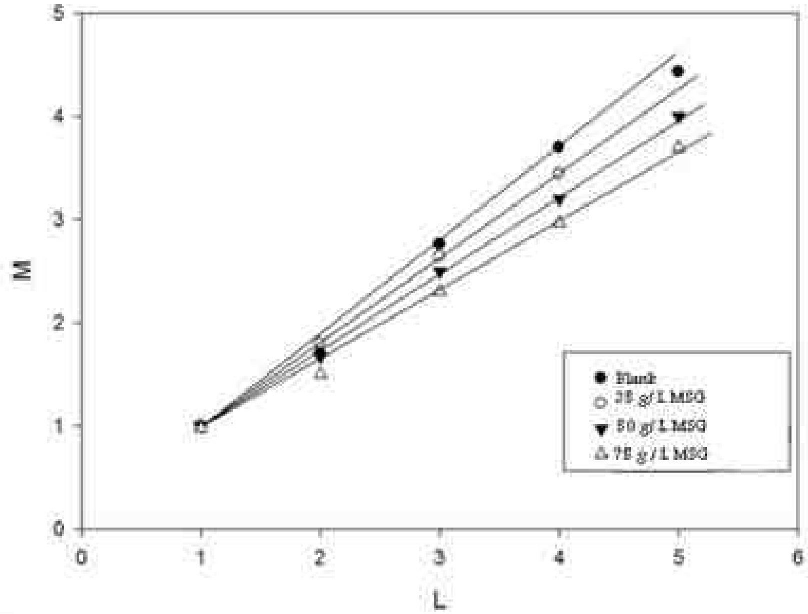

Figure 7 - Metal distribution ratio *M* versus linear ratio *L* for nickel electrodeposited in the presence and absence of different concentration of MSG.

The Watts bath was characterized by a *TI* value of 0.67. The addition of MSG to the Watts bath improved the *TI* to 0.97 (Table 1). The improvement in %*TP* could be ascribed to the complex formation between MSG and Ni^{+2} ions, leading to high polarization as shown in Fig. 3. Increasing the cathodic polarization enhanced the equalization of the secondary current distribution between the two cathodes.

Conclusions

Analysis of the results led us to the following conclusions:

1. The electrodeposition of nickel onto copper substrates from a Watts bath containing MSG was successfully obtained for the first time.
2. The throwing power increases by a factor of more than three in the presence of MSG.
3. The %*F* decreased in presence of MSG as a result of complex formation between Ni^{+2} ions and the MSG molecule.
4. The addition of MSG to the Watts bath resulted in a marked shift in the polarization curves towards more negative potential values, indicating an inhibition of Ni^{+2} ion deposition.
5. The nickel electrodeposited exhibited a face centered cubic structure, with a strong (200) diffraction peak (preferred growth orientation) in addition to (220) and (111) peaks.
6. Results of SEM investigations showed that, in the presence of MSG, the surface became homogeneous, containing very fine and compact grains of circular shape.

References

1. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating*, Portcullis Press Ltd., Redhill, Surrey, UK, 1979; p. 12.
2. G.A. Di Bari, "Electrodeposition of Nickel," in *Modern Electroplating*, M. Schlesinger & M. Paunovic, (Eds.), Wiley & Sons, New Jersey, 2000; pp. 139-201.
3. W. Blum & G.B. Hogaboom, *Principles of Electroplating and Electroforming*, McGraw-Hill, New York (1949).
4. T. Mimani, S.M. Mayanna & N. Munichandraiah, *J. Appl. Electrochem.*, 23 (4), 339 (1993).
5. U.S. Mohanty, *et al*., *J. Appl. Electrochem.*, 31 (9), 969 (2001).
6. E.A. Pavlatou, M. Raptakis & N. Spyrellis, *Surf. & Coat. Technol.*, 201 (8), 4571 (2007).
7. F. Ebrahimi & Z. Ahmed, *J. Appl. Electrochem.*, 33 (8), 733 (2003).

8. M.A.M. Ibrahim, *et al*., *Plating & Surface Finishing*, 86 (4), 69 (1999).
9. G.H. Kelsall & A. Kovaleva, *ECS Transactions*, 28 (6), 317 (2010).
10. X. Zhang, *et al*., *Appl. Surf. Sci*., 252 (23), 8067 (2006).
11. B.C. Tripathy, *et al*., *J. Appl. Electrochem*., 31 (3), 301 (2001).
12. Y. Tsuru, M. Nomura & F.R. Foulkes, *J. Appl. Electrochem*., 30 (2), 231 (2001).
13. U.S. Mohanty, *et al*., *Metallurgical & Materials Trans. B*, 36 (6), 737 (2005).
14. K.R. Marikkannu & G.P. Kalaignan, *J. Appl. Surf. Finish.*, 1 (4), 282 (2006).
15. M.A.M. Ibrahim, *J. Appl. Electrochem*., 36 (3), 295 (2006).
16. M.A.M. Ibrahim & S.N. Alamri, *J. Appl. Surf. Finish*., 2 (4), 332 (2007).
17. K. Ninomiya, *Food Reviews International*, 14 (2-3), 177 (1998).
18. S. Field, *Met. Ind. (London)*, 44, 614 (1934).
19. M.A.M. Ibrahim, *J. Appl. Surf. Finish*., 3 (2), 89 (2008).

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