Some Peculiar Observations in the Electrodeposition of Nickle-Zinc Alloys from the Sulphamate Bath

By S. VENKATACHALAM

Electrochemistry Laboratory, Dept. of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore.

ABSTRACT

Studies on the electrodeposition of nickel-zinc alloys from the sulphamate bath have shown that a deposit with a high nickel content can be obtained only by electrolysis at controlled cathode potential. The cathode potential-time curves have been discussed, and the structure of the plates examined by photomicrography.

INTRODUCTION

Alloys of nickel with zinc are of importance in decorative and protective finishing of metals. They have been deposited from sulphate[1-4], chloride[5], sulphate-chloride[6], sulphamate[7] and pyrophosphate[8] baths. Schoch and Hirsch[1,2], were able to obtain a deposit containing 42 per cent nickel only with a nickel to zinc ratio of 26 in the solution. Potential jumps of 0.2—0. 3 volt have been noticed during deposition of this alloy from sulphate[1,3,4] and chloride[5] solutions. Glasstone[3] has attributed the sudden change in the cathode potential to a decrease in the nickel ion concentration in the vicinity of the cathode, with the result that an alloy richer in zinc and with a high hydrogen overvoltage is deposited. Lustman[4] found that the potential arrests corresponded to the change in structure of the deposit from alpha solid solution to the gamma phase, and then from gamma to delta or eta phase. During electrodeposition from the pyrophosphate bath[8], the sudden changes in plate composition and cathode potential were found to correspond more or less to the deposition of alloys of different phases from high nickel to high zinc: alpha, gamma, gamma plus delta, delta plus eta. Preliminary work on plating of this alloy from the sulphamate bath[7] indicated that it was not possible to obtain deposits with a nickel content greater than 14 per cent. This paper gives a digest of further investigations carried out in relation to this aspect of the problem.

EXPERIMENTAL AND RESULTS

The plating solutions contained nickel (as sulphamate) 30 g/l, zinc (as sulphamate) 10 g/l (solution I) and 20 g/l (solution II), sodium acetate (for buffering) 27 g/l, and sulphamic acid to adjust the pH at 4. The temperature was 35°C, and the bath was worked under still conditions. Except in one case solution I was used throughout. In the beginning electrolysis was carried out at a low current density of 0.2 amp/dm^2 with a view to obtain a nickel rich alloy. It was, however, found that the zinc content of the deposit varied with the time of plating, the values being 84, 83, 56, and 50 per cent at 25, 30, 75 and 120 minutes respectively. It was then considered worthwhile to run the potential-time curves at a particular current density. The results are presented in Figures 1 and 2. The potential values have a negative sign and refer to the hydrogen scale.

SUMMARY OF RESULTS AND DISCUSSION

The cathode potential-time curves show that at low current densities the potential suddenly drops to a less negative value after a certain time, and thereafter it remains constant over an appreciable period. At higher current densities, however, the potential is practically independent of time (Fig. 1). In the case of solution II the potential drops occurred even at higher current densities (Fig. 2). Previous reports have attributed these variations to changes in the phase of the deposited alloy. Analysis of the alloy deposit was therefore carried out at controlled cathode potential, since it was not possible to obtain an appreciable quantity of the alloy under constant current conditions. The zinc content of the deposit at a potential of 0.57 and 0.79 volt was 28.0 and 75.5 per cent respectively. A high—zinc alloy could be obtained under constant cur-

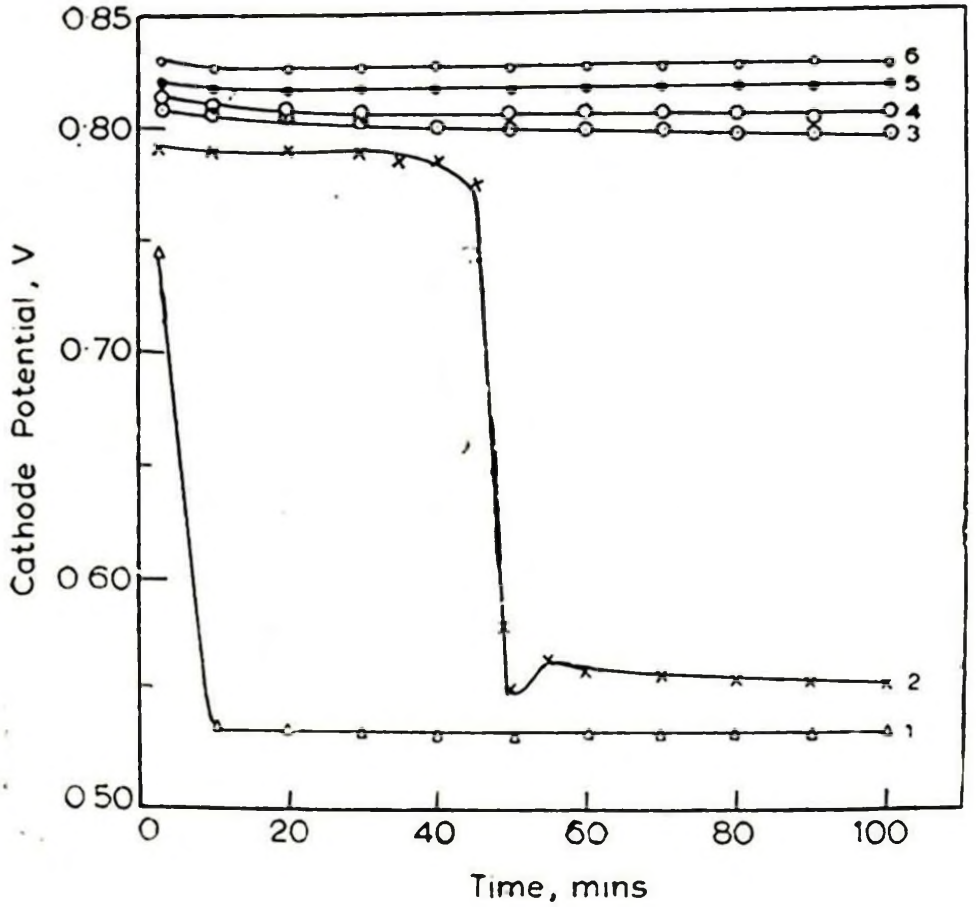


Fig. 1.

Effect of Time on Cathode Potential

SOLUTION I.

Current density : (1) 0·15, (2) 0·20, (3) 0·25, (4) 0·50, (5) 1·0, (6) 2·0 amp/dm².

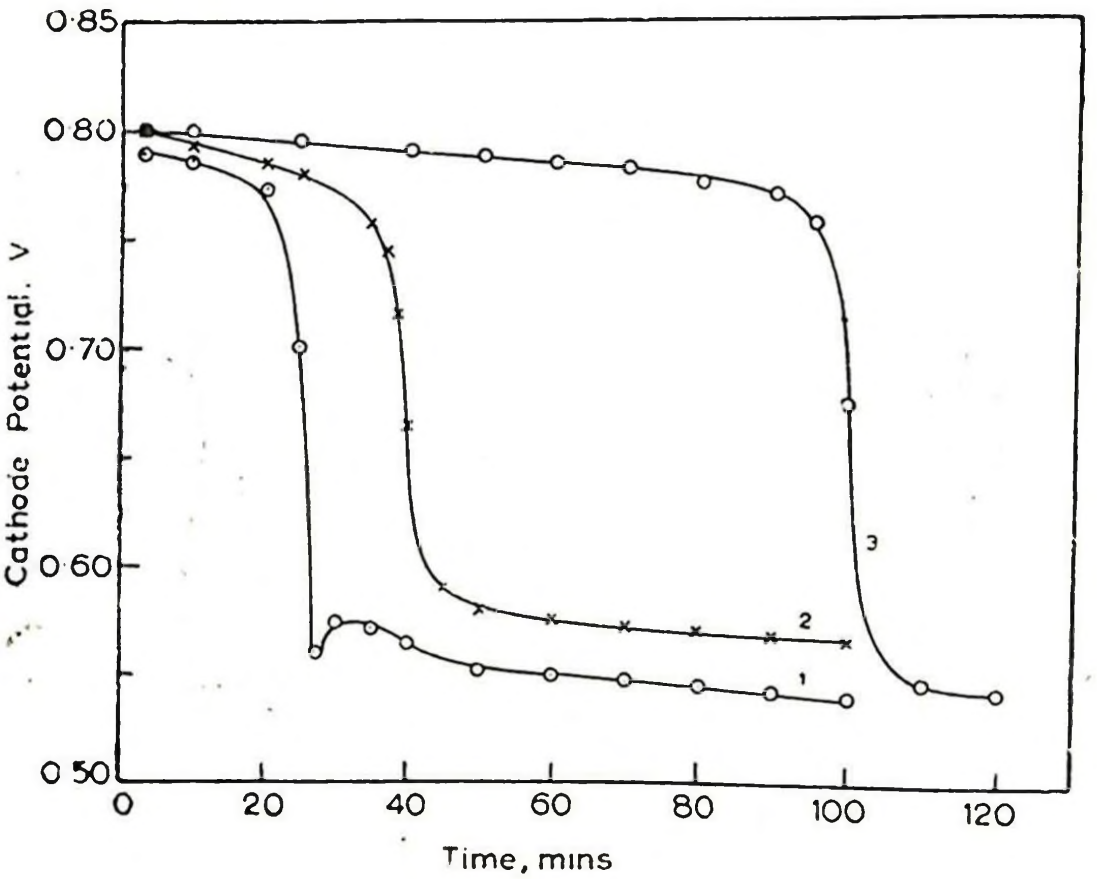


Fig. 2.

Effect of Time on Cathode Potential

SOLUTION II.

Current density :

(1) 0·15, (2) 0·25, (3) 0·50 amp/dm².

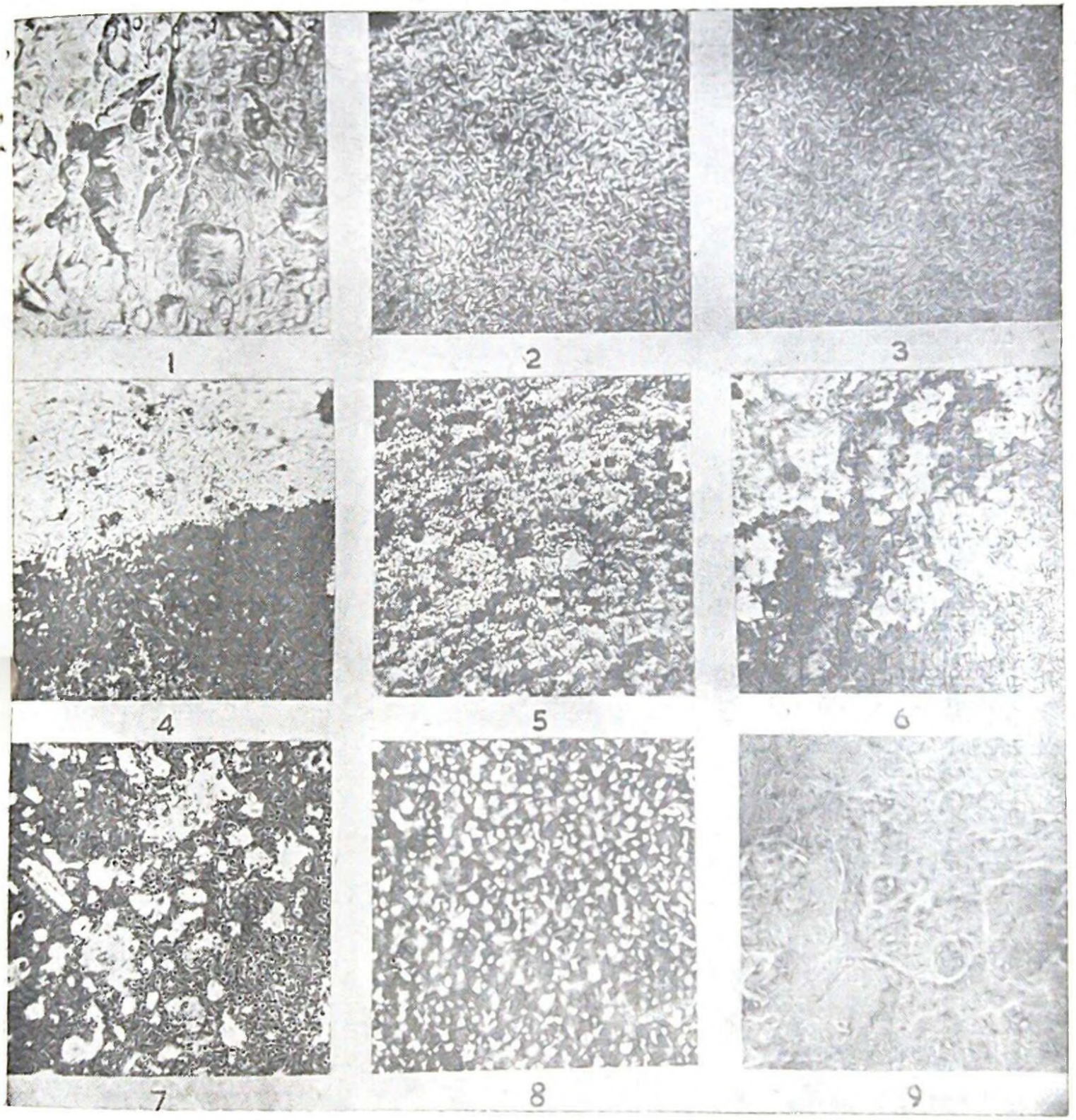


Fig. 3. Photomicrographs of Deposits

Copper base, magnification 1 × 800. Plate 1, copper base; Plate 2, zinc only; Plate 3, 30th minute, 75·5 per cent zinc; Plate 4, 40th minute; plate 5, 42nd minute; Plate 6, 44th minute; Plate 7, 45th minute; Plate 8, 70th minute, 28 per cent zinc; Plate 9, nickel only.

rent electrolysis, the values being 76, 80, 84 and 85 per cent at 0.25, 0.5, 1 and 2 amp/dm^2 respectively.

An increase in the current was observed at the time when the potential suddenly changed to a lower value. The ammeter reading came back to the original value after about thirty minutes. The critical period during which the potential changes occurred was also associated with the formation of a small black patch together with profuse evolution of hydrogen on the surface. As stated by other workers, the hydrogen ion discharges more easily at a high-nickel alloy surface, that is, corresponding to the horizontal portion of the potential-time curves at the lower potential, due to a lower hydrogen overvoltage as compared with that of zinc. It appears that the sudden change in potential is possibly due to dezincification which starts after a certain time under a given set of conditions. In the case of curve 2 of Fig 1 the change takes place at about the 48th minute This can be visualized as being due to the deposition of a small quantity of an unknown phase with a higher nickel content as compared with the gamma phase. If this is the case, galvanic corrosion can easily take place between the gamma and gamma plus unknown phase resulting in dissolution of the zinc-rich phase, that is, dezincification. Thereafter galvanic action increases due to the formation of a nickel-rich component with time. Immersion deposition of nickel on the cathode is also possible, as in the case of copper in brass[9]. This process continues till the potential approaches that of nickel, resulting in the deposition of a high-nickel alpha phase. The last step refers to the horizontal portion of the potential curve mentioned above. The galvanic current can also explain the rise in the ammeter reading.

Fig. 3 presents the photomicrographs of deposits of nickel, zinc, and the alloy at various stages during electrolysis. The zinc and high-zinc plates (2 and 3) have a fine-grained structure, whereas the nickel plate reveals an orientation of the base due to a very thin layer (plate 9). Plates 4-7 show the formation and development of the black patch, and plate 8 is hat of a high-nickel bright deposit.

It is necessary to carry out detailed investigations on the above lines in order to provide a fairly definite answer to the peculiarities observed during the deposition of this alloy.

ACKNOWLEDGEMENT

My thanks are due to Dr. T. L. Rama Char, Assistant Professor, for suggestions and guidance, and Prof. M. R. A. Rao for his keen interest in the work.

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