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Effect of nickel on the electrodeposition of copper

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The mechanism of copper electrocrystallization from various solutions has been investigated to determine the influence of foreign cations and, particularly, of nickel. The study was performed by cyclic voltammetry and scanning electron microscopy. In sulphate solutions the Na^+ and NH^{4+} cations affect the copper deposition by changing the nucleation overpotential and the presence of nickel cations makes the copper deposition easier by decreasing the nucleation overpotentials of both copper and nickel. In chloride solutions, the strong adsorption of the chloride species prevents all other influences by blocking the active sites of nucleation and growth and, therefore, Na^+ or NH^{4+} addition does not modify the copper deposition. Consequently, the nickel does not modify the nucleation overpotential of copper. Whatever the solution, sulphate or chloride, the anodic behaviour of the copper–nickel codeposits are similar to the anodic behaviour of bulk Cu–Ni alloys.

1. Introduction

The codeposition of copper and nickel has been thoroughly studied with two principal intensions. First, that of obtaining Cu–Ni alloys with high corrosion resistance. In this case the deposition was performed from a complexing bath, which makes it possible to reduce the large potential difference between the equilibrium electrode potential of the two metals. Several complexing agents have been tested, but the most interesting seems to be the citrate bath [1, 2]. Secondly, that of obtaining laminar deposits, and in this case the large potential difference between the equilibrium potentials of the metals must be preserved. The baths were sulphamate [3] or sulphate [4–6].

The aim of the present study was not to prepare Cu–Ni alloys or laminar deposits, but to determine the reciprocal influence of the components of the plating bath. It is well known that anions of the supporting electrolyte can be adsorbed on the electrode surface and, therefore, influence the nucleation mechanism by blocking the growth sites on the substrate. A correlation between the anion size and the morphology of the deposit was observed, the basic action of an anion being similar to that of an additive [7]. Therefore, before studying the reciprocal influence of copper and nickel, the anions have to be taken into account, and comparisons were performed with the deposition of pure copper from two solutions containing sulphate or chloride ions. This study was conducted by cyclic voltammetry (CV), and scanning electron microscopy (SEM) to observe the morphology of the initial stage of the deposit.

2. Experimental details

A classic three-electrode cell was used. The glassy carbon electrode (Tokaï) was the cross section of a 3 mm diameter rod embedded in resin. Particular care was taken with the polishing of the carbon. After polishing with diamond paste, it was ultrasonically cleaned for 1 min and then immersed in the plating bath without drying. The reproducibility of the results depended greatly on the quality of the polishing. The least speck of dust changed the electrochemical curves recorded because impurities adsorbed on the surface act as active centres for crystallization. The counter electrode was a carbon disc, and all the potentials were recorded with respect to a saturated calomel electrode (SCE). In the voltammograms, the currents were referred to the carbon glass area, that is $0.07\,cm^{-2}$.

The sulphate solutions were copper sulphate in 0.5 M sulphuric acid or in 0.5 M sodium or ammonium sulphate. The chloride solutions were copper chloride in 1 M hydrochloric acid or in 0.5 M hydrochloric acid plus 0.5 M sodium or ammonium chloride. The codeposition was performed from copper and nickel sulphate in 0.5 M sodium sulphate, and copper and nickel chloride in 0.5 M sodium chloride. All the solutions were prepared with water treated by a Millipore system. The solution was deaerated by bubbling pure argon gas before the experiments, and then an argon blanket was maintained over the surface of the quiescent solution.

The equipment consisted of a PAR model 273 potentiostat, using a microcomputer system (IBM-AT) capable of both controlling the experiments, and collecting and plotting the data. All the curves were corrected for ohmic drop by compensation. The potential sweeps started from a potential where the carbon was considered to be free of adsorbed species, going in the cathodic direction. The reproducibility of the voltammograms was excellent.

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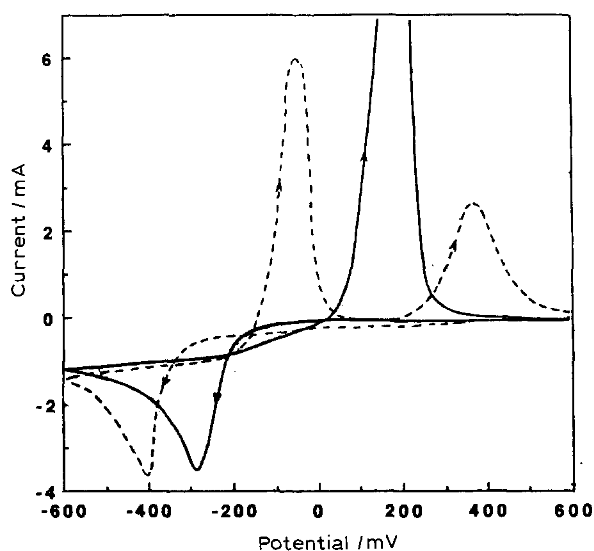


Fig. 1. Cyclic voltammograms for copper deposition from: (——) 0.1 M $CuSO_4$ in 0.5 M H_2SO_4; (– – –) 0.1 M CuCl in 0.5 M HCl.

Deposits were prepared by sweeping or stepping the potential from an anodic value to a cathodic value in the potential range of formation of the deposit and then taking out the electrodes immediately to prevent full covering of the carbon surface. Several potential arrests were chosen in the cathodic potential region. The morphological study was performed using SEM.

3. Results and discussion

3.1. *Electrodeposition of copper from sulphate and chloride solutions*

Figure 1 compares the voltammograms corresponding to copper deposition from sulphate and chloride solutions. Both the voltammograms present, in the cathodic sweep, typical features of a nucleation process which are: a steep increase in current after an induction time, and a current loop between the forward and the reverse direction. The cathodic nucleation peak for chloride solution shifts by about 100 mV negative from the peak for sulphate solution and this indicates retardation of the nucleation. In sulphate solution there is no significant cathodic background current until nucleation commences. In chloride solution, a significant background current exists. In the anodic part, the copper dissolution in sulphate solution is indicated by one peak, the copper dissolution in chloride solution occurs in two steps as observed for bulk copper [8].

Figure 2 presents the effect of added cations (Na^+ and NH_4^+) on the voltammograms. In sulphate solution (Fig. 2(a)), Na^+ addition does not change the nucleation potential defined as the intersection of the ascending part of the nucleation peak with the zero current line, but decreases the slope of the ascending part of the peak. The effect of NH_4^+ is more significant, it catalyses the nucleation by decreasing the nucleation overpotential by roughly 100 mV and by increasing the limiting current. In chloride solution (Fig. 2(b)) the presence of Na^+ or NH_4^+ has little effect on the nucleation overpotential, slightly decreasing the peak current. It is likely that the adsorption of chloride ions prevents any other influence.

The effect of sulphate or chloride content is also an interesting feature. In sulphate solution, the voltammogram does not change with increasing amount of sulphate. In chloride solutions the chloride content is a parameter of paramount importance. Figure 3 presents the voltammograms obtained for 0.01 M copper chloride in 0.05–1.5 M hydrochloric acid. The chloride concentration has a significant effect on the current, the peak current increases with chloride content to a maximum for 0.5 M chloride concentration, and then decreases. The peak potential increases with chloride content, and it is likely that this effect is due to the formation of copper complexes $CuCl_2^-$ and $CuCl_3^{2-}$ depending on the chloride content [9]. The same experiment, performed by adding 0.4 M perchlorate to 0.01 M copper chloride in 0.1 M chlorhydric acid solution, shows that perchlorate addition does not change the voltammogram.

3.2. *Codeposition of copper and nickel from sulphate solutions*

Nickel deposits in the same potential region as hydrogen and it is impossible to observe a significant nucleation peak in acid solution, the nickel peak

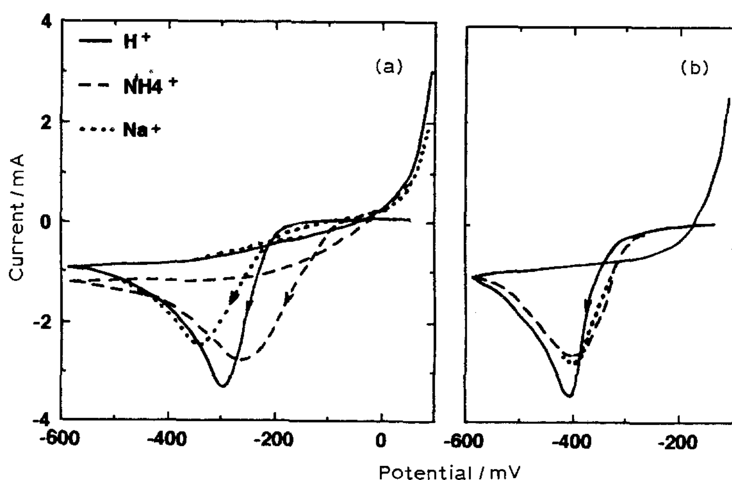


Fig. 2(a) Effect of Na^+ and NH_4^+ on the voltammogram for copper deposition from sulphate solution. (——) 0.5 M H_2SO_4; (– – –) 0.01 M H_2SO_4 + 0.49M $(NH_4)SO_4$; (····) 0.01 M H_2SO_4 + 0.49 M Na_2SO_4. (b) Effect of Na^+ and NH_4^+ on the voltammogram for copper deposition from chloride solution. (——) 1 M HCl; (– – –) 0.5 M HCl + 0.5 M $(NH_4)Cl$; (····) 0.5 M HCl + 0.5 M NaCl.

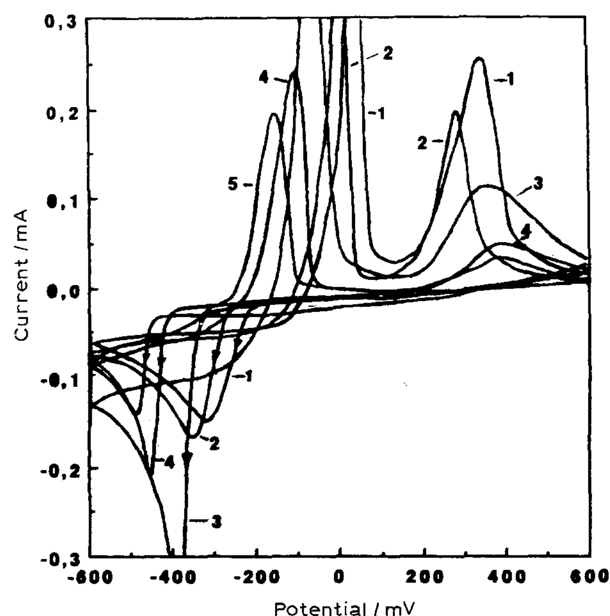


Fig. 3. Effect of Cl^- concentration for deposition of copper from 0.01 M CuCl in x M HCl. Scan rate $20\,mV\,s^{-1}$. x/M: (1) 0.05, (2) 0.1, (3) 0.5, (4) 1, and (5) 1.5.

being hidden by the strong current for hydrogen evolution. Therefore the codeposition of copper and nickel was studied in acidified (pH 3.5) sodium sulphate and sodium chloride, because neutral sodium sulphate solutions are unstable.

Figure 4 presents the voltammograms obtained

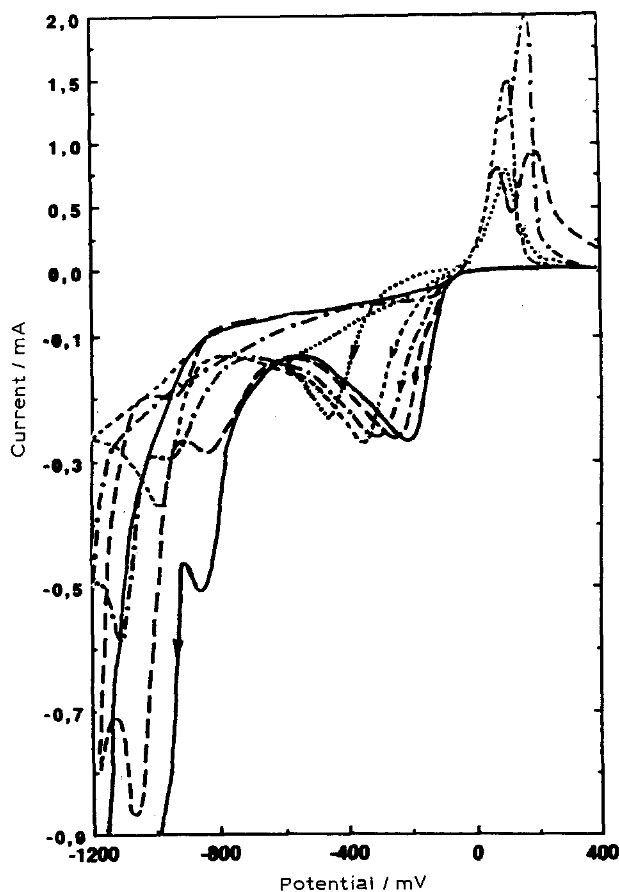


Fig. 4. Cyclic voltammograms for copper and nickel deposition from 0.01 M $CuSO_4$ in 0.5 M Na_2SO_4 plus x M $NiSO_4$ (pH 3.5). x/M: (····) 0, (- - -) 0.001, (– · – ·) 0.01, (– – –) 0.02, and (——) 0.05.

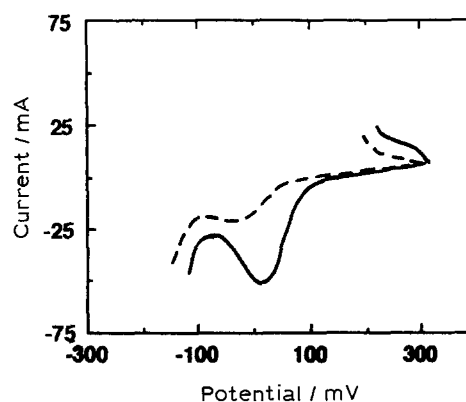


Fig. 5. Magnification of the potential region around 0 mV for curve in Fig. 6. (– – –) Ni/Cu = 0.1, (——) Ni/Cu = 5.

from copper sulphate in sodium sulphate containing various amounts of nickel sulphate. The voltammogram for pure copper deposition from the same solution without the nickel salt is also indicated for comparison. The main feature of these voltammograms is the shift of the cathodic peak of both copper and nickel toward the anodic potentials.

3.2.1. Cathodic peaks.

(a) *Copper peak.* The first peak in the cathodic sweep pertains to copper deposition. As soon as 0.001 M nickel salt is added to the copper solution, the nucleation overpotential no longer exists and the reaction becomes almost reversible. At increasing nickel addition, the copper nucleation potential is identical but the slope of the ascending part of the peak increases and, therefore, the peak potential becomes more anodic. The difference between the copper peak potential from pure copper and copper plus 0.05 M nickel solutions is about 250 mV and, by decreasing the nucleation overpotential, the nickel makes the copper deposition easier. The peak current increases as soon as 0.001 M nickel is added but does not increase with increasing nickel content.

A magnification of the potential region around 0 mV (Fig. 5) makes it possible to see that a small peak exists before the copper peak. This peak increases from a ratio Ni/Cu = 0.1 to Ni/Cu = 5 (i.e. nickel sulphate from 0.001 M to 0.05 M). The charge passed under this peak is roughly $600\,\mu C\,cm^{-2}$ for 0.001 M and $1800\,\mu C\,cm^{-2}$ for 0.05 M nickel (excluding double layer correction). This peak is positive with respect to the reversible Nernst potential of copper and nickel and, therefore, arises in the underpotential deposition (UPD) region of both cations. The electrochemical behaviour is, to a certain extent, in agreement with an adsorption process. Potentiostatic polarization performed in this region shows monotonically decreasing current–time transients. The peak increases with sweep rate but the peak is too large for the relationship between the current and the scan rate to be accurate enough to discriminate between a linear current against scan rate relation, which is related to a UPD process, and a linear current against square root of the scan rate

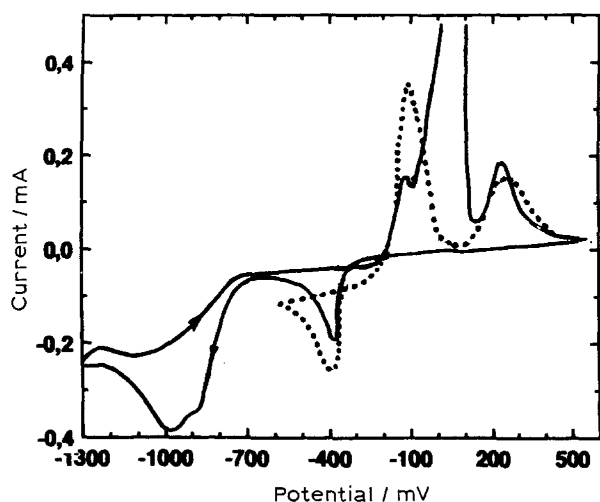


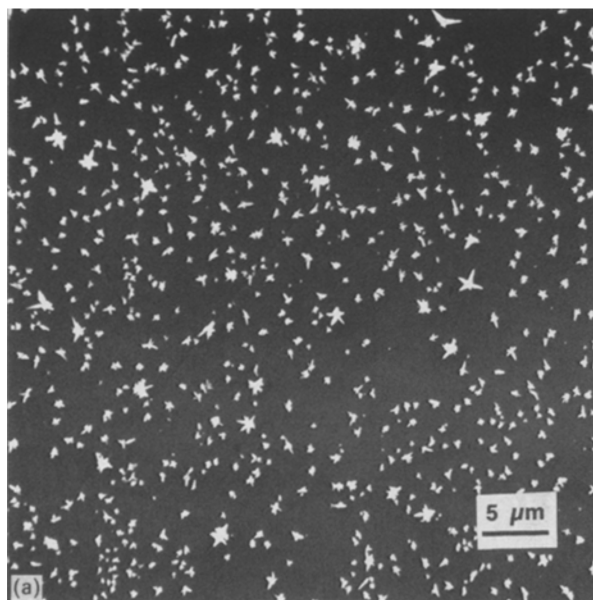
Fig. 6. Cyclic voltammograms for copper and nickel deposition from 0.01 M $CuCl$ + 0.02 M $NiCl_2$ in 0.5 M NaCl (pH 3); (···) 0.01 M CuCl + 0.5 M NaCl (pH 3).

relation. On the other hand, the charge under this peak is higher than the charge expected for a UPD process. This charge increases with the nickel content when, for a UPD process, the charge does not depend on the cation content. This peak does not appear in the voltammogram for solutions containing copper and nickel in chloride solution and, therefore, it seems related to a competitive adsorption between nickel cations and chloride species. This peak is large, which indicates poor interaction with the substrate.

(b) *Nickel peak.* The second cathodic peak results from nickel deposition. This peak, as the copper peak, shifts toward anodic potentials. This shift may be explained by considering that after the copper peak, the carbon substrate is covered by copper crystallites and, therefore, the deposition of nickel takes place more easily on copper crystallites than on amorphous carbon, which would need a higher overpotential. Actually, as seen later, the morphology of the deposit is not in keeping with this explanation. Another explanation may be to consider that after the copper peak, copper goes on to deposit under diffusion control and hence nickel is swept along by the copper and deposits easily, but does not deposit on the copper crystallites already formed. The morphology of the deposit is in agreement with this hypothesis.

3.2.2. Anodic peaks. When two metals are deposited from the same solution, a question arises: is the deposit formed as an alloy, i.e. a copper–nickel solid solution, or crystallites of pure copper and nickel appearing separately? The anodic sweep corresponding to the dissolution of the new phase deposited during the cathodic scan can give information on the phase structure of the deposit.

The voltammogram from copper sulphate solution presents only one anodic peak. By adding 0.001 M nickel sulphate to the solution, there is always one anodic peak at the same potential but of higher intensity. For nickel sulphate addition $\geq$ 0.01 M, a second, more anodic, peak arises. When nickel is deposited from 0.01 M nickel sulphate in the same supporting electrolyte, but without the copper salt, the potential at zero current in the anodic going scan is about 0.4 V/SCE which corresponds approximately to the value of the equilibrium potential of nickel in nickel sulphate solution, and a small and wide anodic peak occurs from −0.4 to 0.2 V, which is far from the second anodic peak obtained in Fig. 4 for the copper–nickel solution. Therefore the second anodic peak obtained by dissolution of the Cu–Ni deposit is due to a Cu–Ni solid solution.



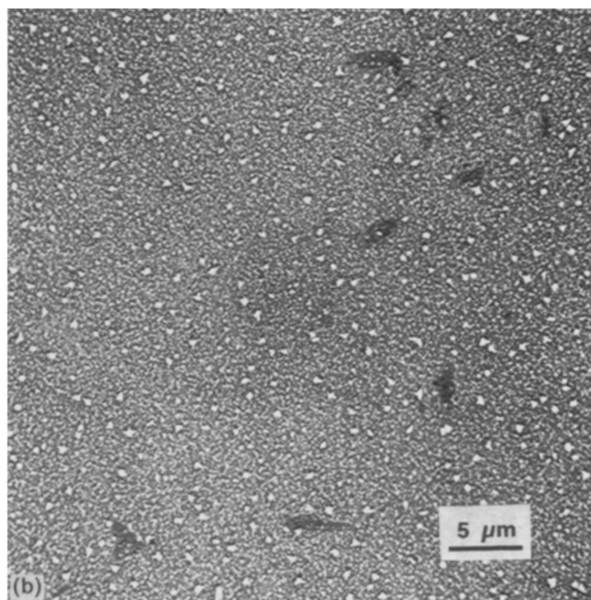


Fig. 7. Scanning electron micrographs of the deposit from 0.01 M $CuSO_4$ + 0.001 M $NiSO_4$ in 0.5 M Na_2SO_4 solution. (a) Scanning down to −300 mV; (b) scanning down to −1000 mV.

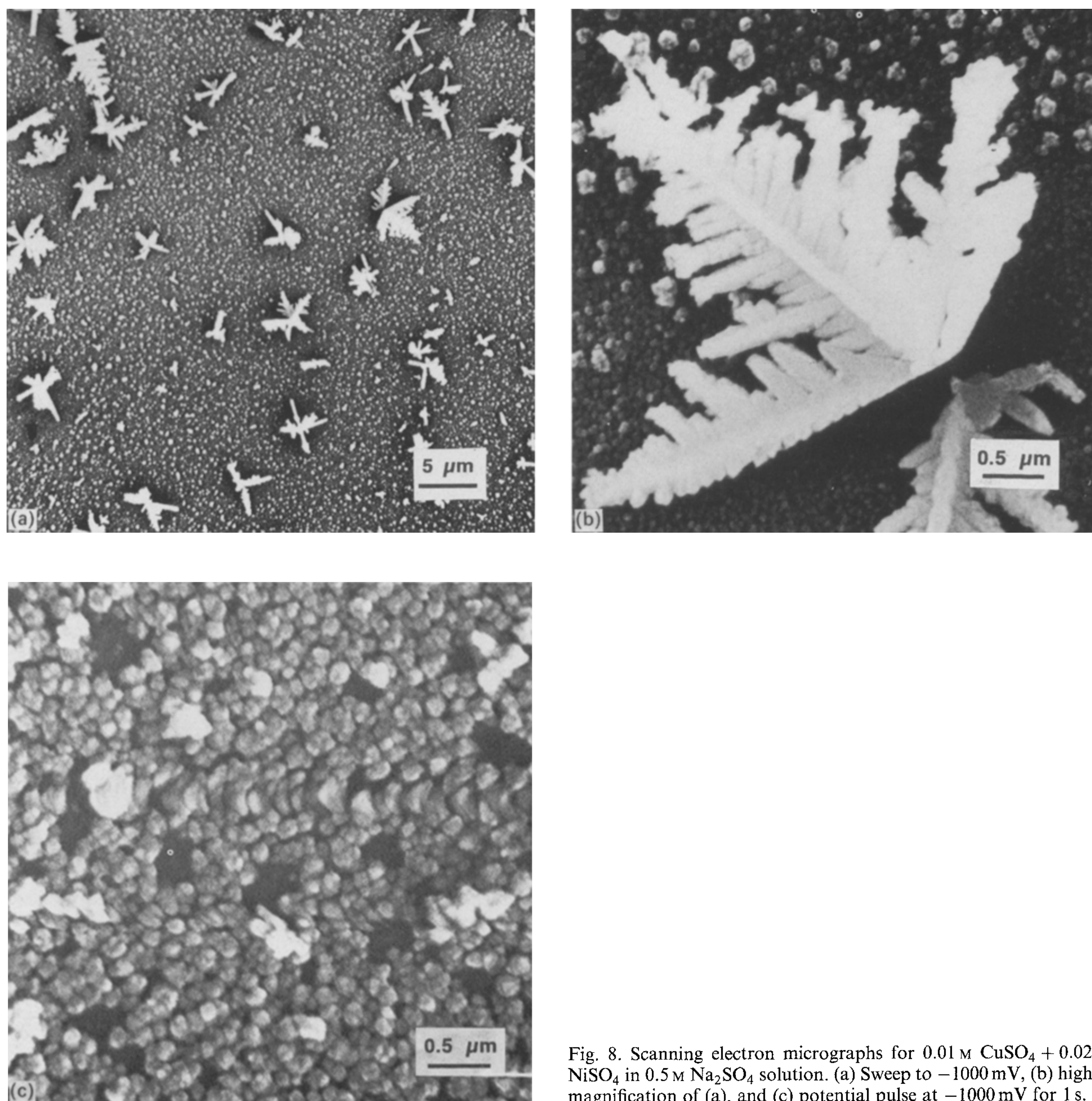


Fig. 8. Scanning electron micrographs for 0.01 M $CuSO_4$ + 0.02 M $NiSO_4$ in 0.5 M Na_2SO_4 solution. (a) Sweep to −1000 mV, (b) higher magnification of (a), and (c) potential pulse at −1000 mV for 1 s.

3.3. *Codeposition of copper and nickel from chloride solutions*

Figure 6 presents the voltammogram obtained from copper and nickel chlorides in sodium chloride. The voltammogram from the same solution without the nickel salt is indicated in the figure. The cathodic peak due to copper deposition appears at the same potential in both curves, but it is smaller when nickel ions are present in the solution. Neither shift of the peak potential nor change in the nucleation overpotential is observed. The peak corresponding to nickel deposition is larger and hydrogen evolution is shifted toward cathodic potentials. On the anodic scan, the crossover at zero current takes place at the same potential for copper and copper–nickel solutions. The first and third anodic peaks appear at the same potential as for pure copper solution. The second anodic peak cannot be due to pure nickel dissolution owing to the fact that, in chloride solution, bulk nickel passivates and no dissolution peak occurs. A study of the anodic behaviour of a series of Cu–Ni alloys in sodium chloride solution [10] allows for the second anodic peak to be related to the dissolution of a Cu–Ni alloy.

3.4. *Deposit morphology*

3.4.1. Sulphate solutions. The potential was scanned down to three potential values chosen in the cathodic voltammogram, then after one second at this potential the electrodes were taken out of the solution and observed by SEM.

Figure 7 presents the micrographs obtained from 0.01 M copper sulphate plus 0.001 M nickel sulphate in 0.5 M sodium sulphate (pH 3.5). Micrograph (a) (obtained by scanning to −300 mV) shows numerous pure copper fern-shaped crystallites. Micrograph (b) (obtained by scanning to −1000 mV) corresponds to Cu–Ni deposition. The Cu–Ni deposit consists of small nodules but some pure copper crystallites of larger size are observed owing to the fact that the

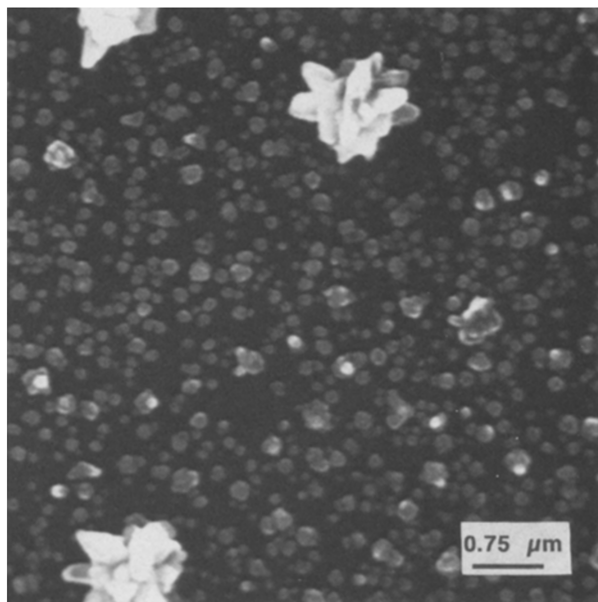


Fig. 9. Scanning electron micrograph for 0.01 M CuCl + 0.02 M $NiCl_2$ in 0.5 M NaCl solution.

deposit was not obtained by potentiostatic polarization but by scanning the potential. A deposit obtained by stepping down the potential at −1000 mV does not present such crystallites. Micrograph (a), in Fig. 8, shows the deposit obtained by scanning to −1000 mV in 0.01 M copper sulphate plus 0.02 M nickel sulphate in 0.5 M sodium sulphate. The comparison with micrograph (b) in Fig. 7 shows that the same fine grain deposit covers the electrode but the pure copper crystallites are larger and have the shape of secondary two-dimensional dendrites [11]. The magnification (micrograph (b) in Fig. 8) emphasizes the perfect shape of the dendrites and the zones around them in which no new nucleation can occur [12]. Micrograph (c) in Fig. 8 shows the deposit achieved from the same solution by a potential pulse of 1 s to the same cathodic potential as above. In this case, owing to the fast increase in potential, the dendrites cannot grow and a Cu–Ni deposit is obtained with a fairly uniform grain size.

The most interesting feature is the comparison between Figs 7(b) and 8(a). These were obtained under identical experimental conditions from two solutions which are different only by the nickel concentration, 0.001 M for Fig. 7(b) and 0.02 M for Fig. 8(a). It is evident that the presence of nickel makes the copper deposition easier and that it is responsible for the dendrite formation, because such dendrites were never found for experiments performed from pure copper solutions [13].

3.4.2. Chloride solution. The deposit was obtained from 0.01 M copper chloride plus 0.02 M nickel chloride in 0.5 M sodium chloride by scanning to −1000 mV. The micrograph in Fig. 9 shows the hemispherical crystallites of Cu–Ni and some large pure copper crystallites presenting the same fern shape as the crystallites obtained for pure copper chloride solution.

4. Conclusion

This study has shown that the strong inhibiting effect of chloride ions on the electrodeposition of copper prevents any other influence. The NH_4^+ cations, which decrease the nucleation overpotential of copper when the deposition is performed from sulphate solutions, play no role when the plating bath contains chloride ions.

In the case of copper plus nickel solutions, by polarizing in the copper deposition potential region, i.e. at potentials much more anodic than the nickel deposition potential, the presence of nickel in sulphate plating baths permits the formation of copper dendrites. If the plating bath contains chloride ions, this dendritic growth does not occur. Here again, the chloride ions block the active sites, and prevent the influence of nickel.

The anodic dissolution of the deposits obtained from sulphate or chloride solutions is in accordance with the dissolution of bulk Cu–Ni alloys.

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