THE EFFECT OF THE SUPERPOSITION OF AN ALTERNATING CURRENT ON A DIRECT CURRENT ON THE ELECTRODEPOSITION OF Ni–Fe ALLOYS

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Summary

Electrodeposited Ni–Fe alloys show a variable composition when they are electroplated in the presence of a superimposed alternating current. The alloy composition depends on the ratio of the alternating to the direct current, the frequency, the amplitude and the waveform. By a suitable choice of conditions the electrodeposited Ni–Fe alloy can be prepared with a specified composition throughout. A mechanism for the action of the alternating current on the direct current which produces the specified composition is proposed.

1. Introduction

Alternating currents have a significant effect on many electrode processes and are widely used in electrochemical investigations, such as double-layer studies [1 - 3], determination of the kinetics of the formation and dissolution of oxide films [4] and the examination of fast electrode reactions [5, 6], and in the electrodeposition and dissolution of metals [7 - 10]. Alternating currents have been shown to affect the grain size, the brightness and the porosity of electrodeposited metals [11]. The superposition of alternating on direct currents has been shown to reduce the internal stress in electrodeposited nickel [12]. The magnetic properties of electrodeposited alloys have been improved by superimposing alternating on direct currents during their codeposition.

In this paper we report the effect of the superimposition of alternating currents of variable frequency, amplitude and waveform on the composition and uniformity of electrodeposited Ni–Fe alloys.

2. Experimental details

The experiments were performed in two-compartment cells. The cathode was a platinum foil of area 1 cm^2. The auxiliary electrode used was also

made of platinum but its area was a factor of 40 larger than the cathode. A 90 V battery in series with a resistor was used as a source of constant direct current. A Systronics signal generator (type 1012) was used to deliver a constant alternating current as well as variable a.c. amplitudes and waveforms. The electrical circuit employed to superimpose alternating on direct currents was similar to the one used in our earlier studies [13]. The a.c. densities were calculated using the absolute values of the strength of the current passing through the cell and were expressed in r.m.s. values. In all our experiments the a.c. densities I_{AC} for various frequencies and waveforms were always greater than the d.c. densities I_{DC} because there was no effect on alloy composition when I_{AC} was equal to or less than I_{DC}. The Ni–Fe alloy was deposited at a constant thickness at various d.c. densities as well as in the presence of superimposed alternating currents.

A bath containing 0.024 M $NiSO_4$, 0.006 M $FeSO_4$ and 0.035 M $NaKC_4H_4O_6$ (pH 4.6) was used to electrodeposit the Ni–Fe alloy. The molar ratio of iron to nickel in the solution was 20:80. The reagents used were of AnalaR grade and were dissolved in freshly prepared triple-distilled water. Fresh solutions were used for each experiment. After electroplating, the Ni–Fe alloy was dissolved in distilled HCl which was free from iron and nickel and was analysed spectrophotometrically [14].

3. Results

Experiments were carried out with low d.c. densities in the range 0.25 - 1 mA cm^{-2} and the deposition rate in milligrams per hour of iron and nickel was determined. Figure 1 shows the deposition rate of the alloy. It was found that nickel always had a higher deposition rate than iron at any given d.c. density.

In the first series of experiments we examined the effect of different a.c. frequencies at a fixed $I_{AC}:I_{DC}$ ratio on the deposition rate of iron and nickel in the alloy. The effective frequency range for altering the composition of the alloy was found to be 10 - 50 Hz. At a.c. frequencies above 50 Hz the deposition rate was markedly reduced. It was also found that when I_{AC} was equal to or less than I_{DC} there was no effect on the alloy composition. Therefore in the experiments reported here I_{AC} was always higher than I_{DC}. These preliminary experiments enabled us to determine the appropriate a.c. frequency range and a.c. density for superposition.

In the second series of experiments different a.c. waveforms, *i.e.* sine, square and triangular, were superimposed in order to study the changes in the composition of the alloy deposited in the current density and frequency ranges determined earlier. A variation in the alloy composition with different waveforms was observed at a fixed a.c. frequency and various d.c. densities. Figure 2 shows the variation in the iron content in the alloy at different d.c. densities and an alternating current of frequency 10 Hz and density 5 mA cm^{-2} for square, sine and triangular waveforms. Figure 2
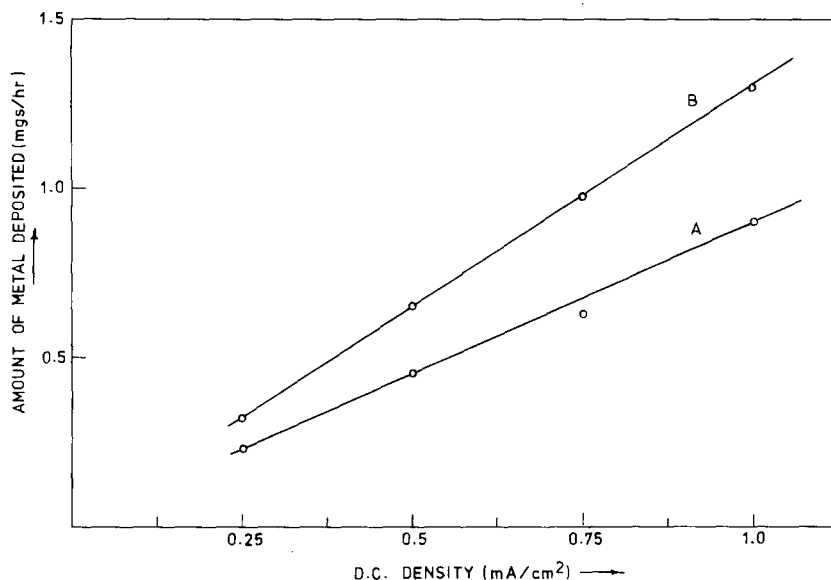
Fig. 1. Rates of deposition of iron (line A) and nickel (line B) at various d.c. densities.

shows that the iron content varies markedly for different waveforms at different d.c. densities. The effect increased in the order square, sine, triangular. The ratios of nickel to iron in the alloy were calculated and are given in Table 1.
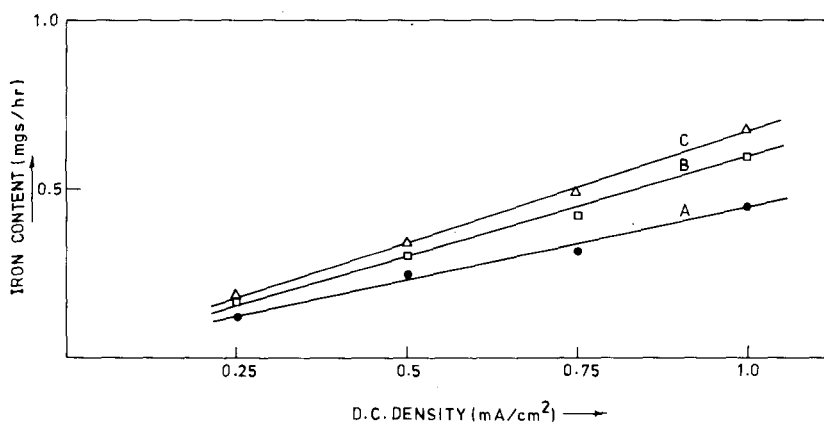

Fig. 2. The effect of the superposition of an alternating current of density 5 mA cm^{-2} and frequency 10 Hz with various waveforms on the rate of iron deposition at various d.c. densities: line A, square wave; line B, sine wave; line C, triangular wave.

The effect of the a.c. frequency on the composition of alloys for different waveforms was observed at a fixed $I_{AC}:I_{DC}$ ratio. The variation in the iron content in the alloy as a function of the frequency at $I_{AC}:I_{DC} = 5:1$

TABLE 1

Ratio of nickel to iron in alloys electrodeposited at different d.c. densities with superimposed alternating currents of various waveforms

D.c. density (mA cm^{-2})	Waveform	Ni:Fe ratio
0.25	Square	2.90
0.25	Sine	2.13
0.25	Triangular	1.88
0.5	Square	2.60
0.5	Sine	2.16
0.5	Triangular	1.91
0.75	Square	3.00
0.75	Sine	2.26
0.75	Triangular	1.90
1.00	Square	2.88
1.00	Sine	2.16
1.00	Triangular	1.91

A.c. frequency, 10 Hz; a.c. density, 5 mA cm^{-2}.

is shown in Fig. 3 for square, sine and triangular waves. The ratios of nickel to iron obtained under these conditions are given in Table 2. The iron content in the alloy was found to decrease with decreasing frequency for all the waveforms investigated. The polarizing effect of the different a.c. waveforms on the iron content in the alloy was found to increase in the order square, sine, triangular.
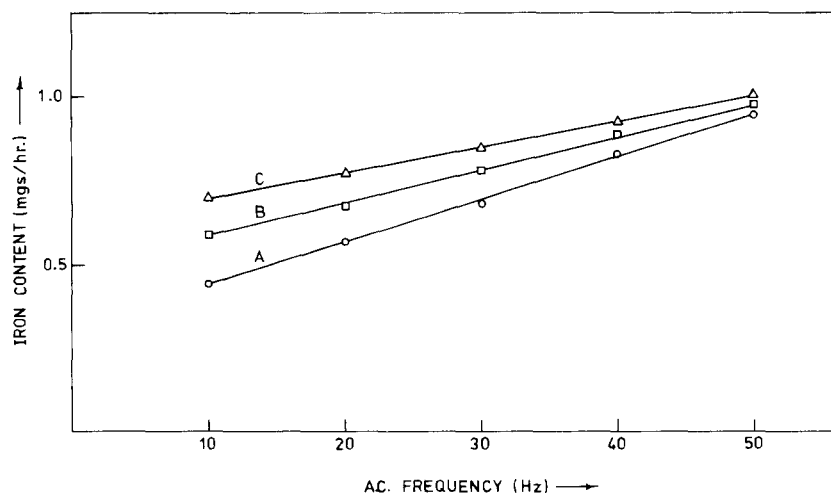

Fig. 3. Rate of iron deposition as a function of a.c. frequency at $I_{AC}:I_{DC} = 5:1$ for different waveforms: line A, square wave; line B, sine wave; line C, triangular wave.

TABLE 2

Ratio of nickel to iron in alloys electrodeposited at a d.c. density of 1 mA cm^{-2} with a superimposed alternating current of density 5 mA cm^{-2} and different frequencies

A.c. frequency (Hz)	Ni:Fe ratio		
	Square wave	Sine wave	Triangular wave
10	2.88	1.96	1.85
20	2.32	1.91	1.73
30	1.91	1.66	1.52
40	1.60	1.44	1.44
50	1.36	1.40	1.30

In another series of experiments the variation in the alloy composition at different superimposed a.c. densities was observed for different waveforms at a fixed a.c. frequency and d.c. density. It was found that the higher the a.c. density, the greater was the effect on the alloy composition. Figure 4 shows the effect of the a.c. density on the iron content in the alloy at an a.c. frequency of 10 Hz and a d.c. density of 1 mA cm^{-2}. It was found that the square wave had a much greater effect on the alloy composition than the sine and triangular waves at all a.c. densities investigated.
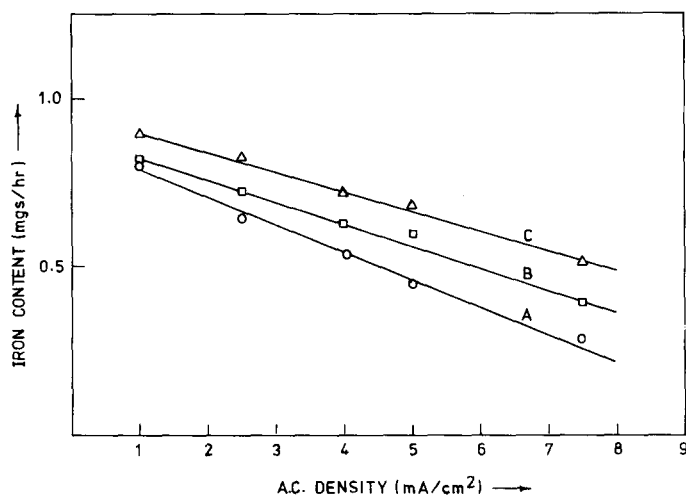

Fig. 4. Rate of iron deposition as a function of different a.c. densities for different waveforms at a frequency of 10 Hz and a d.c. density of 1 mA cm^{-2}: line A, square wave; line B, sine wave; line C, triangular wave.

Little effect on the nickel content of the alloy was found in the above series of experiments. Figure 5 shows the effect of superimposing an alternating current of frequency 10 Hz and various densities. Although the effect on the rate of nickel deposition was not marked, the molar ratio of nickel to iron was strongly affected as a result of the significant change in the iron deposition rate.
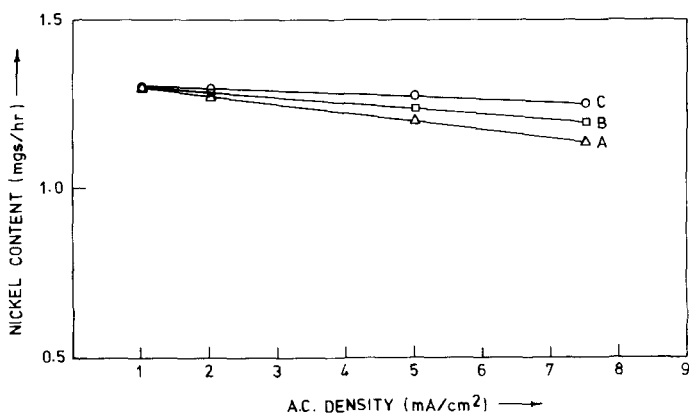
Fig. 5. Rate of nickel deposition as a function of different a.c. densities and waveforms at a frequency of 10 Hz and a d.c. density of 1 mA cm^{-2}: line A, square wave; line B, sine wave; line C, triangular wave.

4. Discussion

In analysing the effect of superimposing an alternating current on a direct current, we should take into account the anodic current which flows in the reverse direction. The periodic combination of the anodic component of the current and the ordinary d.c. process of electrodeposition may account for the changes in the composition of the Fe–Ni alloy.

The decreased rate of alloy deposition is lower for combined alternating and direct currents than for direct currents alone. This indicates that some dissolution of the alloy is taking place [15]. We can argue that according to the electrochemical series iron dissolves faster than nickel and hence there should be less iron present in the deposit. This argument is supported by the fact that when the a.c. density is increased for any given waveform the anodic cycle will be large and hence more iron will dissolve in the anodic cycle. During the cathodic cycle deposition of the alloy occurs as for normal electrodeposition.

Figure 3 shows that the iron deposition rate at high frequencies is almost double that at low frequencies, e.g. compare the rate at 10 Hz with that at 50 Hz. This is due to the fact that the electrode potential varies slowly under superimposed alternating currents with low frequencies and thus the electrode remains in the anodic region for long enough to allow the metal to dissolve. Iron dissolves preferentially to nickel owing to its position in the electrochemical series. However, Fig. 5 shows that the nickel deposition rate is not suppressed at all. Figure 3 also shows that the deposition rate for a superimposed alternating current of frequency 50 Hz is almost the same as that for a pure direct current which indicates its negligible effect at this frequency. At frequencies higher than 50 Hz the electrode spends less and less time in the anodic region and hence there is no effect on the alloy composition.

Figures 2 - 4 show that the square waveform is the most effective and the triangular waveform is the least effective in changing the alloy composition. This may be due to the fact that the duration of the peak potential is larger for the square waveform than for either the sine or the triangular waveforms. At a given a.c. frequency the duration of the peak potential in each square wave cycle is greater than that in each sine wave cycle which is greater than that in each triangular wave cycle. In other words, the polarization time at the peak maximum is longest for the square wave.

The variation in the alloy composition is therefore significant at low a.c. frequencies, high a.c. densities (amplitudes) and for a square waveform. The structure and magnetic properties of the electrodeposited alloy are under examination.

5. Conclusions

The composition of an alloy deposited from the same solution can be varied over a rather wide range (5% - 60%) merely by varying the a.c. frequency. This method could be usefully applied in studies of grain size, morphology of deposits and internal stress as a function of constant direct current. Deposits of uniform composition can be obtained.

Acknowledgments

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