

The electrical properties and quality factor of nickel electrodeposits

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The quality factor Q , of the nickel electrodeposits prepared under different conditions (bath pH, current density, etc.), was measured by a Q -meter and the in-series method was utilized. The inductance (L) and ohmic resistance (R) were obtained through the resonance frequency (F) by use of appropriate equations. The measurements can be shown on C , L , R and Q against F plots. The above electrical properties of nickel electrodeposits are affected by the electrodeposition conditions and slightly by the deposits' thickness.

1. Introduction

For Ni electrodeposition the nature of the electrolyte, pH, bath temperature, current density, stirring and the addition of organic compounds (additives) strongly affects the selective orientation or the texture axis of the nickel electrodeposits [1–4], the secondary structure and the morphology of deposits [4–6]. The dependence of the texture axis on pH and current density for nickel deposits prepared in pure 1.22 M NiSO₄ and NiCl₂ baths at a bath temperature of 50 °C and a stirring rate of 1200 rpm is given in Fig. 1(a and b) [4].

All deposits prepared in the NiSO₄ bath are compacted materials with a structure which is characterized as a non-porous spheroidized/pyramidic structure with a columnar growth in the [100] texture axis region [4]. All deposits prepared in the NiCl₂ bath have a pyramidic, porous, spongy and dendritic structure which varies largely with pH and current density [4]. It has also been shown that, generally, the above electrodeposition conditions and the obtained structures significantly affect physicochemical properties such as (i) their behaviour in a corrosive environment such as 3.5% NaCl aqueous solution [7] and in a strong oxidizing aqueous H₂O₂ solution [8], (ii) sorptive properties of their surfaces [9, 10] and (iii) hardness [11]. Such influences are also expected to be exerted on the electrical properties of the nickel electrodeposits [12]. A preliminary investigation of these properties is performed in the present study.

2. Experimental procedure

The experimental configuration, the materials, the procedure and the conditions (pH values, current densities (j) and a charge density of 146.3 C cm⁻²) employed for the Ni deposits prepared on brass circu-

lar plates in 1.22 M NiSO₄ and NiCl₂ baths were the same as those previously described [4]. With an electrochemical efficiency of 100% the above charge density produces a 50 μm thick compact Ni deposit. Since this efficiency is variable [4] the deposited thickness is also variable. In Table 1 are listed the real thickness of the NiSO₄ deposits (compact material) and the equivalent to compact material thickness of the NiCl₂ bath deposits (porous material). In the NiCl₂ bath deposits the real Ni thickness can exceed 50 μm. The conditions for the Ni depositions employed in the present study were such that the real thickness (NiSO₄ bath) and the equivalent thickness (NiCl₂ bath) do not differ significantly from 50 μm except for one case in the NiCl₂ bath deposits.

The quality factor (Q) of the nickel electrodeposits on a circular brass substrate of 27 mm diameter [4] was measured by a Q -meter (Hewlett Packard 4342 A). Because the Ni deposits have a low ohmic resistance the in-series method in which the unknown sample is connected in series with a reference coil (Hewlett Packard 16472 A – 16489 A) was utilized. At each desired a.c. frequency (varying between 8–22 MHz) the resonance capacities were determined by means of a variable capacitor in the instrument in both the cases of short-circuited and non-short-circuited terminals on the Ni deposits (C_1 and C_2 respectively). In addition the corresponding Q_1 and Q_2 values were also measured. Then, the Q value of the Ni deposit was determined from the equation

$$Q = Q_1 Q_2 (C_1 - C_2) (C_1 Q_1 - C_2 Q_2)^{-1} \quad (1)$$

The capacitance (C), inductance (L) and ohmic resistance (R) of the Ni samples were obtained through the resonance frequency (F) by use of the equations

$$C = C_1 C_2 (C_2 - C_1)^{-1} \quad (2)$$

$$L = (C_1 - C_2) (2\pi F)^{-2} (C_1 C_2)^{-1} \quad (3)$$

$$R = (C_1 C_2^{-1} Q_1 - Q_2) (2\pi F C_1 Q_1 Q_2)^{-1} \quad (4)$$

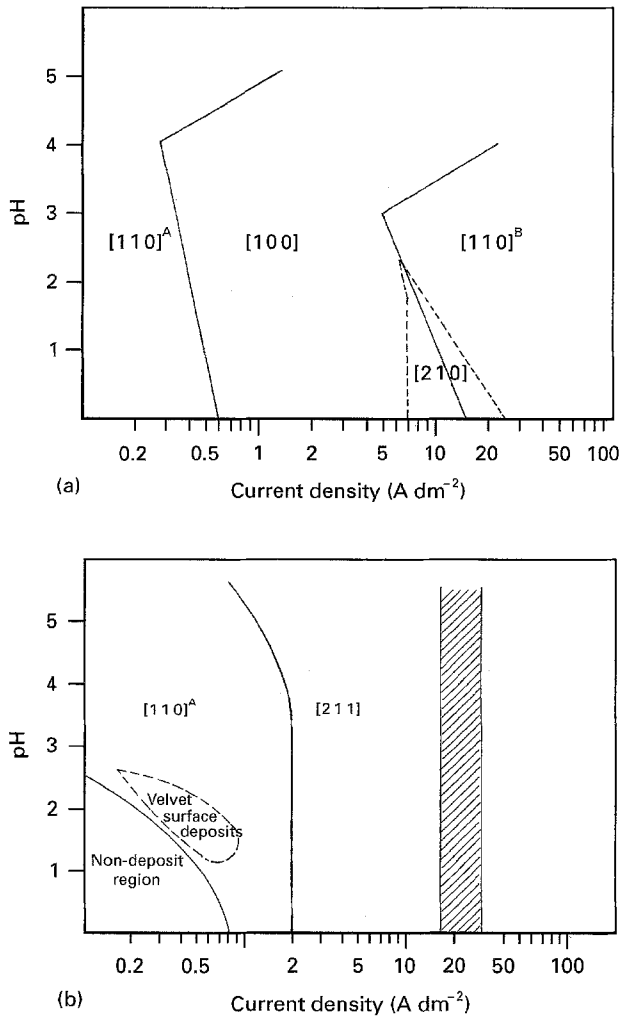


Figure 1 Dependence of the selective texture axis of Ni electrodeposits on current density and pH in (a) a NiSO_4 1.22 M bath and (b) a NiCl_2 1.22 M bath at a bath temperature of 50°C and a stirring rate of 1200 rpm. The superscript A or B means that the corresponding texture axis is met at the lower or the higher current densities. Broken lines in (a) mean that the boundaries between the corresponding texture axes are unclear. The dashed region in (b) is the boundary between the region where satisfactory deposits and no deposits is observed.

3. Results and discussion

The C , L , R and Q versus F plots at different pH and j values for the Ni deposits prepared in the NiSO_4 bath ($\text{NiSO}_4\text{-Ni}$) and NiCl_2 bath ($\text{NiCl}_2\text{-Ni}$) are shown in Fig. 2(a-d) and Fig. 3(a-d) respectively.

For both the $\text{NiSO}_4\text{-Ni}$ and $\text{NiCl}_2\text{-Ni}$ deposits C shows a sharp minimum and a sharp maximum at 9–10 and 11 MHz and then it strongly decreases with F . The influence of pH and j and probably of the film thickness on C is noticeable mainly at low F values and especially around $F = 11$ MHz but not at high F values. No clear relationship between the variation of C with pH and j at each F value is apparent. In addition a noticeable effect of the bath electrolyte on C is only exerted around $F = 11$ MHz where the maximum in C occurs. This average maximum and the scatter in the C values, are higher for the $\text{NiSO}_4\text{-Ni}$ deposits. At $F > 11$ MHz the average C versus F plots for both the $\text{NiSO}_4\text{-Ni}$ and $\text{NiCl}_2\text{-Ni}$ deposits essentially coincide.

The L value has a sharp minimum at $F = 11$ MHz for Ni deposits from both baths. Then, for the $\text{NiSO}_4\text{-Ni}$ deposits L generally increases with the appearance of a slight minimum, a slight maximum and a slight minimum at about 17, 18 and 21 MHz respectively being observed. For the $\text{NiCl}_2\text{-Ni}$ deposits a rather constant L value for $F \geq 12$ MHz is observed with the exception of a maximum that appears at about 18 MHz. The L values of the Ni deposits from both baths are comparable on average at each F value while a significant scatter of L values is observed. In addition no general relationship between the variation of L with pH and j is apparent.

In contrast to the more or less regular variations of C and L with F , the variation of R as a function of F is very complicated. For the $\text{NiSO}_4\text{-Ni}$ deposits,

TABLE I Values of F_m , Q_m , C_m , L_m and R_m for the Ni electrodeposits prepared in the NiSO_4 and NiCl_2 baths and at different pH and j values. The real thickness of the compact $\text{NiSO}_4\text{-Ni}$ deposits, the equivalent compact thickness for the $\text{NiCl}_2\text{-Ni}$ deposits and the relevant texture axes are also given

Electrolyte	pH	j (A dm^{-2})	Ni thickness (μm)	Texture axis	F_m (MHz)	Q_m	$10^9 C_m$ F	$10^8 L_m$ H	$10^9 R_m$ (Ohm)
NiSO_4	4.0	0.2	45.8	$[110]^A$	15	390	3.05	3.64	8.80
NiSO_4	4.0	0.3	41.5	$[110]^A + [100]$	15	460	2.95	3.80	11.10
NiSO_4	4.0	1.2	49.4	$[100]$	19	660	2.04	3.34	6.05
NiSO_4	4.0	3.5	44.1	$[100]$	17	380	2.92	3.00	10.20
NiSO_4	4.0	4.0	43.0	$[100]$	16	345	2.40	4.13	12.10
NiSO_4	4.5	5.0	48.0	$[100]$	18	240	1.60	4.87	25.00
NiSO_4	5.0	9.0	41.7	$[100]$	19	265	1.97	3.56	15.70
NiCl_2	2.0	0.9	16.0	$[110]^A$	18	344	2.89	3.42	5.09
NiCl_2	2.5	3.0	45.0	$[211]$	19	290	2.23	3.13	9.30
NiCl_2	2.5	1.5	46.0	$[110]^A$	17	320	2.91	3.00	3.07
NiCl_2	2.5	1.0	43.1	$[110]^A$	18	360	1.81	4.31	5.86
NiCl_2	3.0	1.5	50.0	$[110]^A$	16	750	3.01	3.28	4.35
NiCl_2	3.0	2.5	47.5	$[110]^A$	17	465	2.92	3.00	6.93
NiCl_2	4.0	2.5	47.0	$[211]$	18	310	1.80	4.36	16.40
NiCl_2	4.5	1.2	45.8	$[211]$	18	340	1.60	4.87	14.10

^A Appears first at small values of current density.

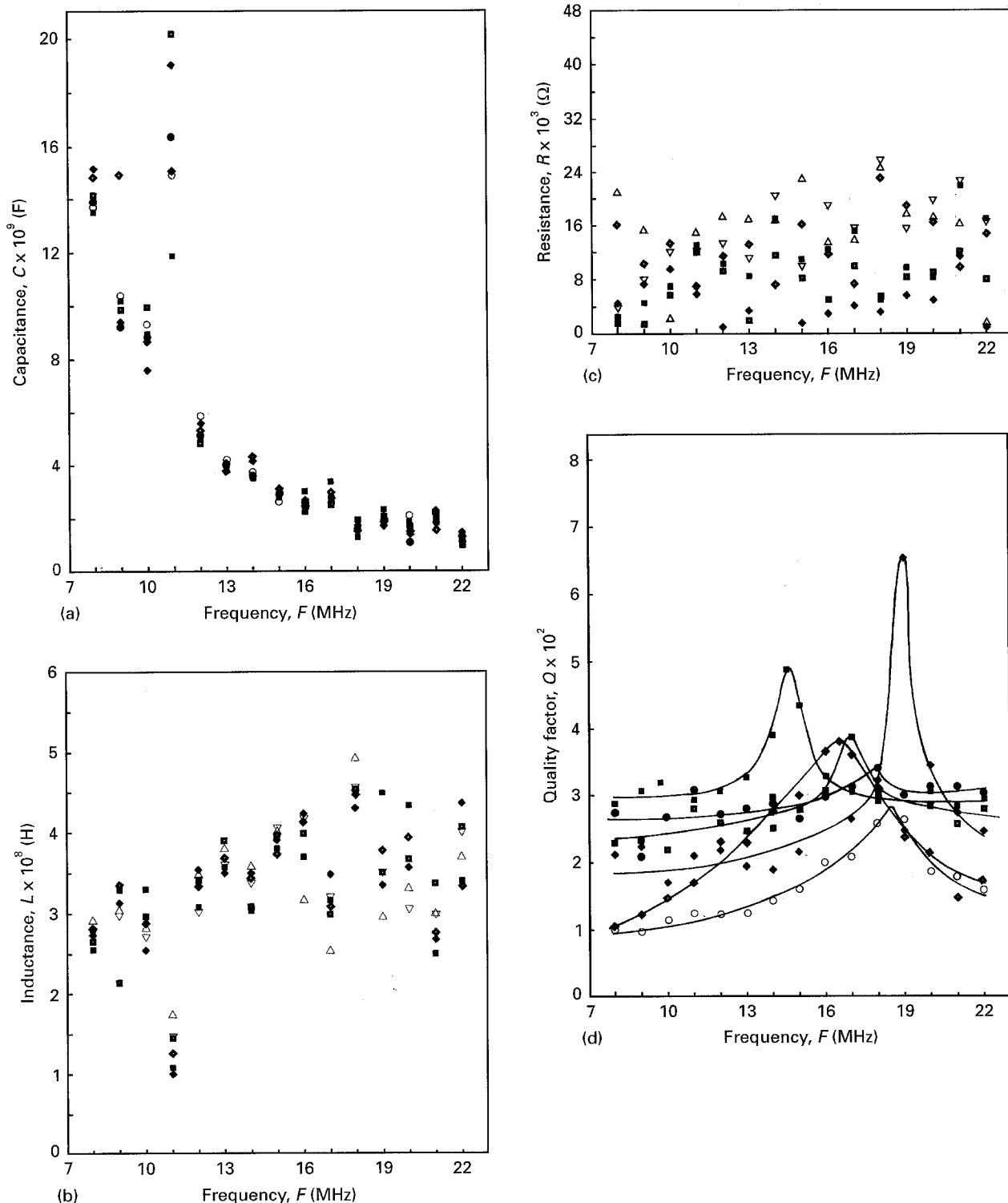


Figure 2 For the $\text{NiSO}_4\text{-Ni}$ electrodeposits (a) capacitance, (c), as a function of frequency, (F), for pH and j values of; (■) 2, 10 A dm^{-2} ; (◆) 4, 0.3 A dm^{-2} ; (□) 4, 1.2 A dm^{-2} ; (◇) 4, 3.5 A dm^{-2} ; (●) 4, 4 A dm^{-2} and (○) 5, 9 A dm^{-2} , (b) Inductance, (L), as a function of frequency (F), for pH and j values of; (■) 4, 0.3 A dm^{-2} ; (◆) 4, 1.2 A dm^{-2} ; (□) 4, 3.5 A dm^{-2} ; (◇) 4, 4 A dm^{-2} ; (△) 4.5, 5 A dm^{-2} and (▽) 5, 9 A dm^{-2} , (c) ohmic resistance, (R), as a function of frequency (F), for pH and j values of; (■) 4, 0.3 A dm^{-2} ; (◆) 4, 1.2 A dm^{-2} ; (□) 4, 3.5 A dm^{-2} ; (◇) 4, 4 A dm^{-2} ; (△) 4.5, 5 A dm^{-2} and (▽) 5, 9 A dm^{-2} , (d) the quality factor, (Q), as a function of frequency (F), for pH and j values of; (■) 4, 0.3 A dm^{-2} ; (◆) 4, 1.2 A dm^{-2} ; (□) 4, 3.5 A dm^{-2} ; (◇) 4, 4 A dm^{-2} ; (●) 4.5, 5 A dm^{-2} and (○) 5, 9 A dm^{-2} . SO_4

minima and maxima at different F values tend to appear. For the $\text{NiCl}_2\text{-Ni}$ deposits, R is roughly constant, with only slight minima or maxima appearing at intermediate F values. In all cases scatter in R values for each F value is observed with the effect being considerably significant for the $\text{NiCl}_2\text{-Ni}$ deposits. The R values vary largely within the range of $0\text{-}32 \times 10^{-3}$ ohm. No general relationship between

the R variation and the pH and j value at different F values is apparent. Although the variation in the above R values can be partially attributed to experimental errors, the effect of the structure and morphology of the Ni deposits, which are strongly affected by pH and j [4], should also be considered.

The Q value significantly varies with F according to a bell shaped curve and reaches a maximum value

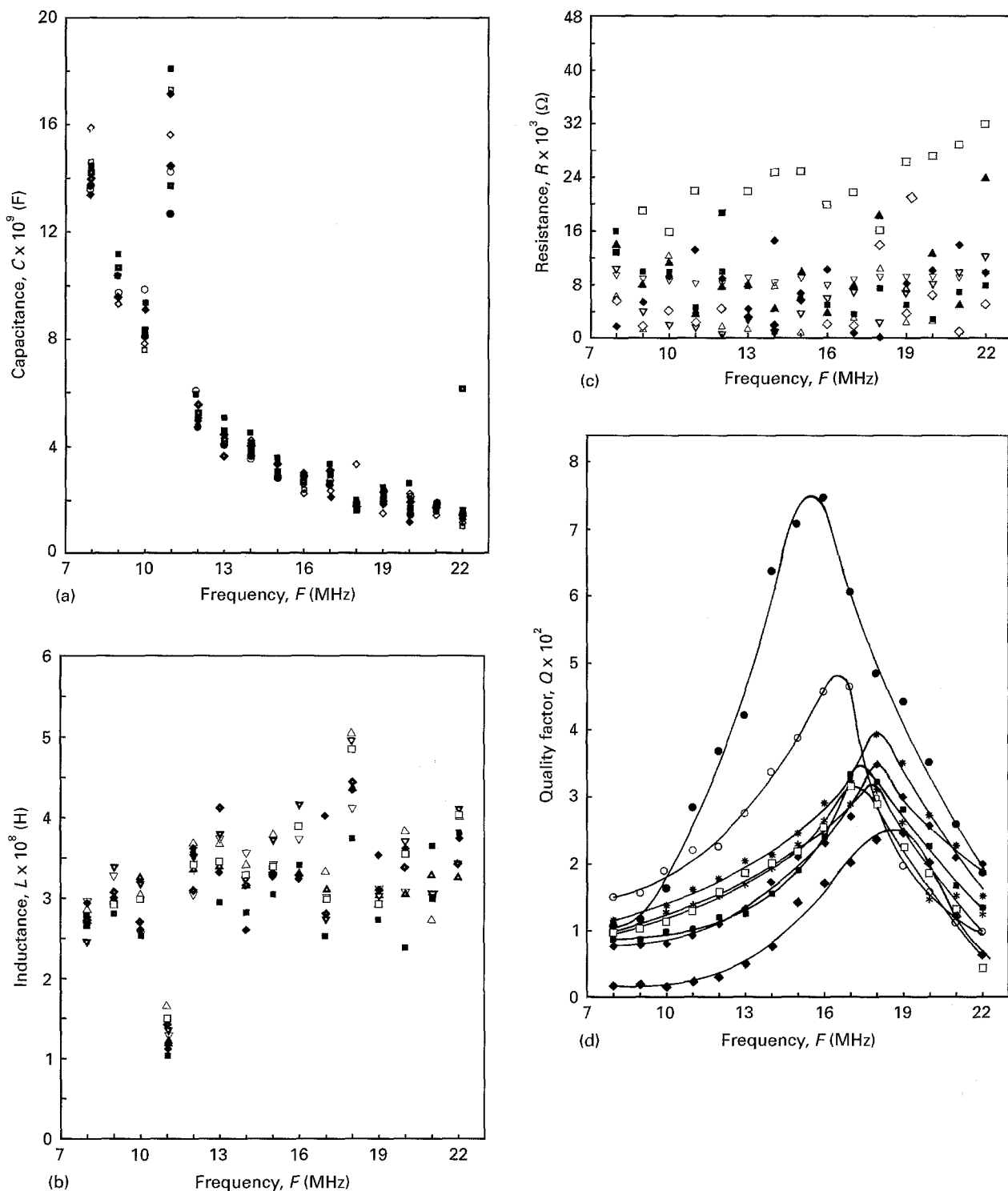


Figure 3 For the NiCl₂-Ni electrodeposits (a) Capacitance, (c), as a function of frequency, (F), for pH and *j* values of; (■) 2, 0.9 A dm⁻²; (◆) 2.5, 1 A dm⁻²; (●) 2.5, 1.5 A dm⁻²; (◆) 2.5, 3 A dm⁻²; (●) 3, 1.5 A dm⁻², (○) 3, 2.5 A dm⁻²; (□) 4, 2.5 A dm⁻² and (◇) 4.5, 1.2 A dm⁻²; (b) Inductance, (L), as a function of frequency (F), for pH and *j* values of; (■) 2, 0.9 A dm⁻²; (◆) 2.5, 1.0 A dm⁻²; (□) 2.5, 1.5 A dm⁻²; (◆) 2.5, 3 A dm⁻²; (△) 3, 1.5 A dm⁻²; (▽) 3, 2.5 A dm⁻²; (▲) 4, 2.5 A dm⁻² and (▼) 4.5, 1.2 A dm⁻²; (c) ohmic resistance, (R), as a function of frequency, (F), for pH and *j* values of; (■) 2, 0.9 A dm⁻²; (◆) 2.5, 1.0 A dm⁻²; (△) 2.5, 1.5 A dm⁻²; (▽) 2.5, 3 A dm⁻²; (▲) 3, 1.5 A dm⁻²; (▼) 3, 2.5 A dm⁻²; (▽) 3, 2.5 A dm⁻²; (□) 4, 2.5 A dm⁻² and (◇) 4.5, 1.2 A dm⁻²; (d) the quality factor, (Q), as a function of frequency, (F), for pH and *j* values of; (■) 2, 0.9 A dm⁻²; (◆) 2.5, 1.0 A dm⁻²; (□) 2.5, 1.5 A dm⁻²; (◆) 2.5, 3 A dm⁻²; (●) 3, 1.5 A dm⁻²; (○) 3, 2.5 A dm⁻²; (×) 4, 2.5 A dm⁻² and (*) 4.5, 1.2 A dm⁻².

(Q_m) at a specific (F_m) value for each Ni deposit from both baths. It is reasonable to examine the effect of pH and *j* on the F_m , and Q_m values as well as on the corresponding C_m , L_m and R_m values. The dependence of their values on pH and *j* and on the corresponding texture axis type is listed in Table 1. Large variations in F_m and Q_m are observed for Ni deposits produced in

both baths. The F_m value varies in the ranges 15–19 MHz and 16–19 MHz and the Q_m value varies in the ranges 240–660 MHz and 290–750 MHz for the NiSO₄-Ni and NiCl₂-Ni deposits respectively. These ranges seem to significantly depend on the bath electrolyte. For the NiSO₄-Ni deposits, although the variations of F_m and Q_m with *j* and pH seems to be

complicated, at a constant pH, maxima in the F_m and Q_m values appear at a specific j . Such a variation of F_m and Q_m with j is not apparent for the NiCl_2 -Ni deposits for which the variation of these parameters with j and pH seems to be much more complicated. In both cases the effect of j on the F_m and Q_m values is much more significant than that of pH. The variation in C_m , L_m and R_m parameters with j and pH is consistent with the variation of these parameters on F as previously discussed.

For Ni deposits from both baths, no break or discontinuity is observed in the variation of C , L , R and Q with F at different j and pH values or the variation of F_m , C_m , L_m , R_m and Q_m with j and pH on passing from the one texture axis region to a successive one. Also, the effect of the Ni deposit thickness on all of the above parameters seems to be very slight in the regions of the Ni deposit thickness employed 41.5–49.4 and 43.1–50 μm for the NiSO_4 -Ni and NiCl_2 -Ni deposits respectively. However quite unexpectedly, this point remains valid even when the much lower NiCl_2 -Ni deposit thickness of 16 μm is considered. Therefore, the effect of the texture axis type and the thickness of the Ni deposit on the above parameters is not significant. The strong effect of j and pH values on the above parameters can only be partially ascribed to the texture axis type. Therefore it must be mainly attributed to the structure [4] together with the variation in grain size and the incorporation of different inclusions for each bath which are strongly affected by j and pH. This later effect is much more significant for the NiCl_2 -Ni deposits [4] and explains the more extensive and complicated variations of the electrical property values with j and pH that were observed for the NiCl_2 -Ni deposits in comparison to those of the NiSO_4 -Ni deposits.

4. Conclusion

It is inferred for the Ni electrodepositions, that the nature of the bath electrolyte, the current density, the

pH, the relevant kind of texture axis, the nature and the structure of the epitaxial Ni grown on the brass substrate significantly affect the electrical properties of the deposits. The results of the present study suggest that further investigation on the electrical properties of Ni deposits should be undertaken. In particular further detailed work must be performed to determine the electrical properties of the Ni deposits and to fully elucidate the effects of the deposition conditions and the deposit composition and structure on the electrical properties of the Ni deposits.

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