CHAPTER 4

ELECTRODEPOSITION OF ALLOYS

: Electro deposition of Alloys :

4.1 Introduction :

Although metals are highly valued in the pure state, they are usually not strong enough to satisfy the present exacting demands of structural and mechanical engineering. However if the metals are judiciously alloyed, we get materials with requisite properties to withstand the stresses and strands of the present day needs. Also, codeposition of metals results in an appreciable reduction in metal cost. Furthermore, alloys can be used for decorative purposes, in view of their special and variable colour effects.

The problems arising in the deposition of alloys are the composition of the solution, the choice of electrodes (anodes in particular) and the conditions of operation in order to secure the required composition in the deposited alloy. The chemical equivalent of the two constituents influences their proportion in the deposit, so the solution will not necessarily contain the alloy constituents in the same proportion as that of the required alloy deposit. Further anode and cathode efficiencies are not likely to balance and this leads to variation in the composition of the solution. To avoid this insoluble anodes are used wherever possible.

4.2 Co-deposition of Metals : Simultaneous Discharge of Cations:

If a solution contains two cations, there is a possibility that simultaneous discharge may occur, this problem is very interesting in the electrodeposition of alloy. But this problem is also very important in the deposition of single metals, since the aqueous solutions always contain hydrogen ions. Were it not for a variety of complicating factors, such as the influence of one metal on the deposition potential of the other, the situation would in principle be reltively simple. Provided the dicharge potentials of the two ions were the same, simultaneous deposition would occur.

For example the reversible potential of a metal A in a solution of its ions of activity a_{A^+} i.e. of the electrode A, E would be given by

$$E = E^0_A - \frac{RT}{Z_A F} \ln a_A^+ \qquad .. (1)$$

and the theoretical discharge potential E_{dis} is equal to $-E$ i.e.

$$E_{dis} = -E^0_A + \frac{RT}{Z_A F} \ln a_A^+ \qquad .. (2)$$

In order to obtain the actual discharge potential, it is necessary to include the over voltage W_A, and so it follows that

$$E_{dis} = -E^0_A - W_A + \frac{RT}{Z_A F} \ln a_A^+ \;.. (3)$$

If the solution contains two cations, one of which may be the hydrogen ion, provided there is no interaction in solution or in the deposit, simultaneous deposition will occur when the two discharge potentials, e.g. of A and B, become equal, that is, when

$$-E^0_A - \eta_A + \frac{RT}{z_A F} \ln a_{A^+} = -E^0_B - \eta_B + \frac{RT}{z_B F} \ln a_{B^+} \quad ..(4)$$

The subject of simultaneous discharge may be divided into two aspects, first, when it is desired to deposit two metals simultaneously, e.g. in alloy deposition, and second, when simultaneous deposition is to be avoided, e.g. in electroanalytical work. We are concerned with the former.

An examination of equation (4) shows that there are in general, three ways in which the discharge potentials of two cations may be brought together : (i) if the standard potentials are different, but the overvoltages vary sufficiently to compensate for this difference, and (ii) if the differences in reversible potentials and overvoltages are compensated for by differences in activities (concentrations) of the ions.
(iii) of E° of the two are equal and overvoltages are small.

4.3 Influence of Plating Parameters in Alloy Deposition :

Independent parameters in alloy deposition, as in all deposition, processes are current density, temperature, agitation, pH and concentrations of bath constituents. Normally, these must be more tightly controlled in alloy plating than in single metal plating, because it is likely that a change in any one will affect one metal more than the other and thus changes the composition of the alloy. Exact effects can be determined only by experiment. Current efficiency, addition agents, basis metal, throwing power and anodes have a prominent role in alloy deposition (71,72).

Many alloy deposition baths (viz. simple and complex, organic solvent baths) are possible, so that failure with one type in no way proves that the deposition of a given alloy is impractical (73).

4.4. Electrodeposition of Nickel Chromium Alloys

The Aim and Scope of the Present work and Earlier Work:

The studies under consideration deal with the electrodeposition of nickel chromium alloys. It is of interest to note that most of the work done in the past, is largely of qualitative nature and quantitative information available on the subject is very little. The number of combinations of the platable metals in the form of alloys is very large. The alloy deposits, obtained electrolytically are not always sound, coherent, thick, lustrous and smooth so that they can have any practical value. Very few alloy systems have made their way from laboratory to plant and fewer still have evolved into fairly wide spread practical applications. However, there are immense possibilities of novel nature in the studies, if seriously thought from technological as well as theoretical stand point. Cast and wrought nickel chromium alloys give excellent wear resistance, corrosion resistance, electrical resistance, and high hot strength. Electrodeposited alloy coatings probably have similar properties and would allow a cheap substrate to be used, thus eliminating the need for more expensive cast or wrought alloyes. Hence numerous attempts have been made to develop a suitable commercial plating process. Reviews by Arrowsmith ( ) and Chisholm (75) indicate that no such process has yet been perfected. However good quality deposits were reported from a bath containing potassium chromium sulfate, nickel formate, trisodium citrate, boric acid, sodium fluoride, and glycine (75). The current efficiency of the process is not high. A patent on a bath containing dipolar organic compounds claims that chromium nickel coatings can be electrodeposited over a wide range of current densities with adequate current efficiencies (–). Studies on the outdoor corrosion resistance (76) and the behaviour of Ni-Cr electrodeposits in industrial, marine and urban environments indicate the value of such plates when used for decorative purposes (77,78). Attempts have also been made to obtain an alloy deposit of Ni-Cr-Fe, having an appearance and properties of stainless steel (79).

The aim of the present work is to make an attempt for systematic, exhaustive and quantitative study on electrodeposition of binary alloy of nickel and chromium and to establish optimum conditions to obtain the best quality deposit. The influence of the following parameters is studied in greater details to establish the optimum conditions under each system.

1) Composition of the Bath (Electrolyte concentrations),
2) Temperature,
3) Current Density,
4) Duration of Electrolysis,

5) Electrode Distance.

6) Addition Agents.

With the help of certain addition agents, we have succeeded in obtaining an alloy deposit of high quality and properties which may bring about a radical change in the plating industry. Considering increasing cost of nobel metals, inclusion of silver or gold in traces in the solution has evolved a new method of obtaining an alloy deposit with hither to unknown properties.

TABLE NO.17 :- The effect of concentration of nickel sulphate on the metal content and the percentage cathode current efficiency (CCE %) of the nickel chromium alloy deposit.

Potassium chromic sulphate : 15 gms. per 100 ml.
Glycine : 4 gms. per 100 ml.
Temperature : 25°C
Electrode distance : 4 cms.

Potassium thiocyanate : 6 gms. per 100 ml.
Current density : 2.4 amps. per Sq.dm.
Duration of electrolysis : 20 minutes
Voltage : 2.9 to 3 Volts.

Obs. No.	Conc. of Nickel Sulphate per 100 ml. gms.	Wt. of copper deposited in coulometer gms.	Wt. of deposit gms.	Metal content in alloy deposit %		CCE %		Total CCE	Nature of the Deposit
				Ni.	Cr.	Ni.	Cr.		
1	5	0.060	0.021	66.67	29.57	25.04	12.11	37.15	Dirty black nonadherent.
		0.060	0.020	70.00	30.00	25.04	12.11	37.15	
2	15	0.071	0.026	69.23	26.92	27.20	11.90	39.10	Dull white, adherent.
		0.072	0.027	70.37	25.92	28.32	11.78	40.10	
3	* 25	0.086	0.034	73.53	23.53	31.20	11.27	42.47	Uniform, dull white and adherent, slightly blue tinge at edges.
		0.089	0.036	66.67	23.22	28.94	10.89	39.83	
4	30	0.104	0.043	74.42	20.90	31.99	10.48	43.50	Dull white.
		0.106	0.047	72.34	10.15	32.39	10.28	44.70	
5	35	0.105	0.044	72.72	20.45	32.70	10.38	43.08	-do-
		0.105	0.044	72.72	20.45	32.70	10.38	43.08	

* Optimum condition.

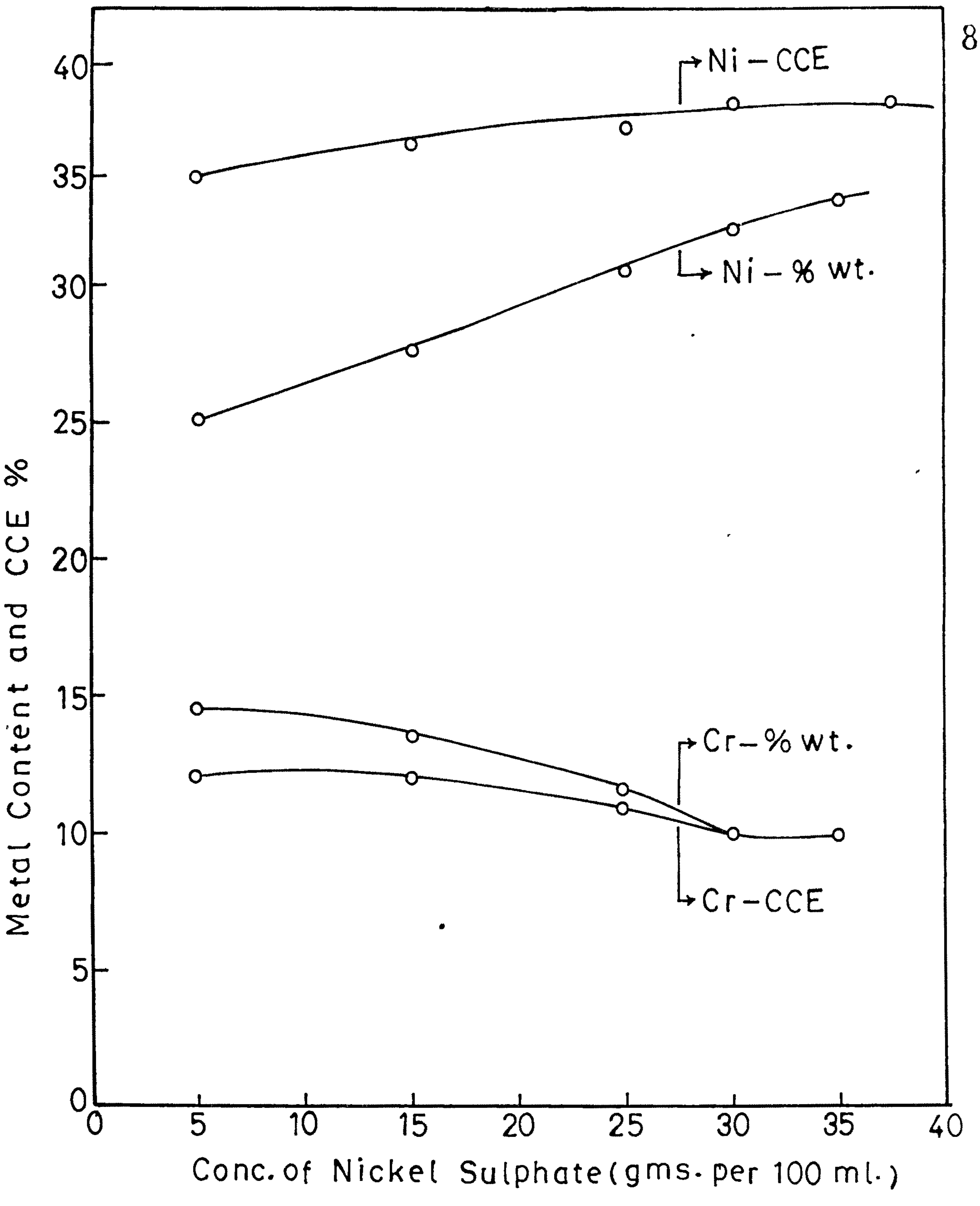


Fig. 17 — Effect of conc. of Nickel Sulphate on CCE % of the Nickel Chromium alloy deposit.

TABLE NO.18:- The effect of concentration of potassium chromic sulphate on the metal content and the percentage cathode current efficiency (CCE %) of nickel chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.
Glycine : 4 gms. per 100 ml.
Temperature : 25° C.
Electrode distance : 4 cms.

Potassium thiocyanate : 6 gms. per 100 ml.
Current density : 2.4 amps. per sq.dm.
Duration of electrolysis : 20 minutes.
Voltage : 2.9 to 3 volts.

Obs. No.	Conc.of potassium chromic sulphate per 100 ml gms.	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni.	Cr.	CCE % Ni.	Cr.	Total CCE	Nature of deposit.
1	5	0.144	0.050	70.00	24.00	26.08	10.11	36.19	Slightly nonadherent. Dark black at edges.
		0.145	0.050	70.59	25.49	26.46	10.79	37.25	
2	10	0.086	0.034	73.53	26.47	31.20	12.70	43.90	Slight improvement.
		0.084	0.033	72.73	27.27	30.66	12.98	43.64	
3	15	0.125	0.044	65.91	31.81	24.90	13.57	38.47	Dull white, adherent.
		0.125	0.045	64.44	31.11	24.90	13.57	38.47	
4	* 20	0.125	0.046	63.04	31.11	24.86	13.57	38.43	White with slight black shade, adherent.
		0.125	0.047	63.83	31.11	25.76	13.57	36.42	
5	25	0.125	0.046	63.04	31.11	24.86	13.57	36.49	Black, slightly nonadherent.
		0.125	0.046	63.04	31.11	24.86	13.57	36.49	
6	35	-	-	-	-	-	-	-	-do -

* Optimum condition.

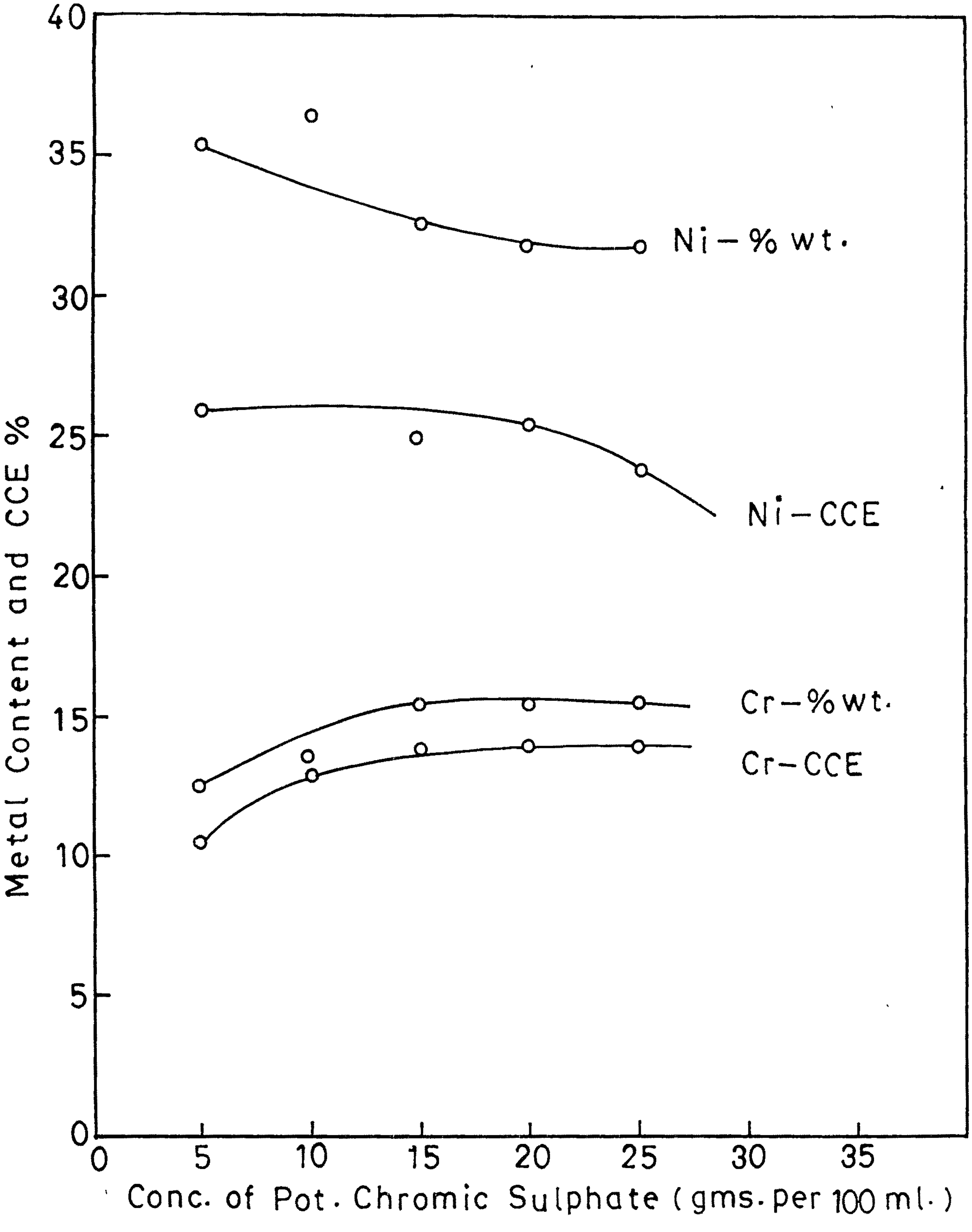


Fig. 18 — Effect of conc. of Potassium Chromic Sulphate on the metal content and CCE % of the Nickel Chromium alloy deposit.

TABLE NO.19 :- The effect of concentration of potassium thiocyanate on the metal content and the percentage cathode current efficiency (CCE %) of Nickel-Chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.
Glycine : 4 gms. per 100 ml.
Temperature : 25°C.
Duration of electrolysis : 20 mins.

Potassium chromic sulphate : 20 gms. per 100 ml.
Current density : 2.4 amps. per Sq.dm.
Electrode distance : 4 cms.
Voltage : 2.9 volts.

Obs. No.	Conc.of Pot.thiocyanate per 100 ml gms.	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni.	Metal content in alloy deposit % Cr.	CCE % Ni.	CCE % Cr.	Total CCE	Nature of deposit.
1	2	0.110	0.032	62.50	37.50	19.51	13.22	32.73	Slight nonadherent, dull white.
		0.110	0.032	65.63	34.30	18.94	10.90	29.84	
2	4	0.110	0.034	58.82	38.23	18.19	13.35	31.54	Slight improvement
		0.119	0.035	60.90	40.90	18.94	14.25	33.19	
3	* 6	0.120	0.037	56.76	35.14	18.78	13.13	31.91	Adherent, dull white.
		0.119	0.036	58.33	33.33	18.94	12.23	31.17	
4	8	0.120	0.040	57.50	35.0	19.28	13.25	32.53	-do-
		0.127	0.040	57.50	35.0	19.44	13.36	32.80	
5	10	0.135	0.041	58.54	34.15	19.08	12.56	31.64	-do-
		0.135	0.040	60.00	35.00	19.08	12.56	31.64	-do-

* Optimum condition.

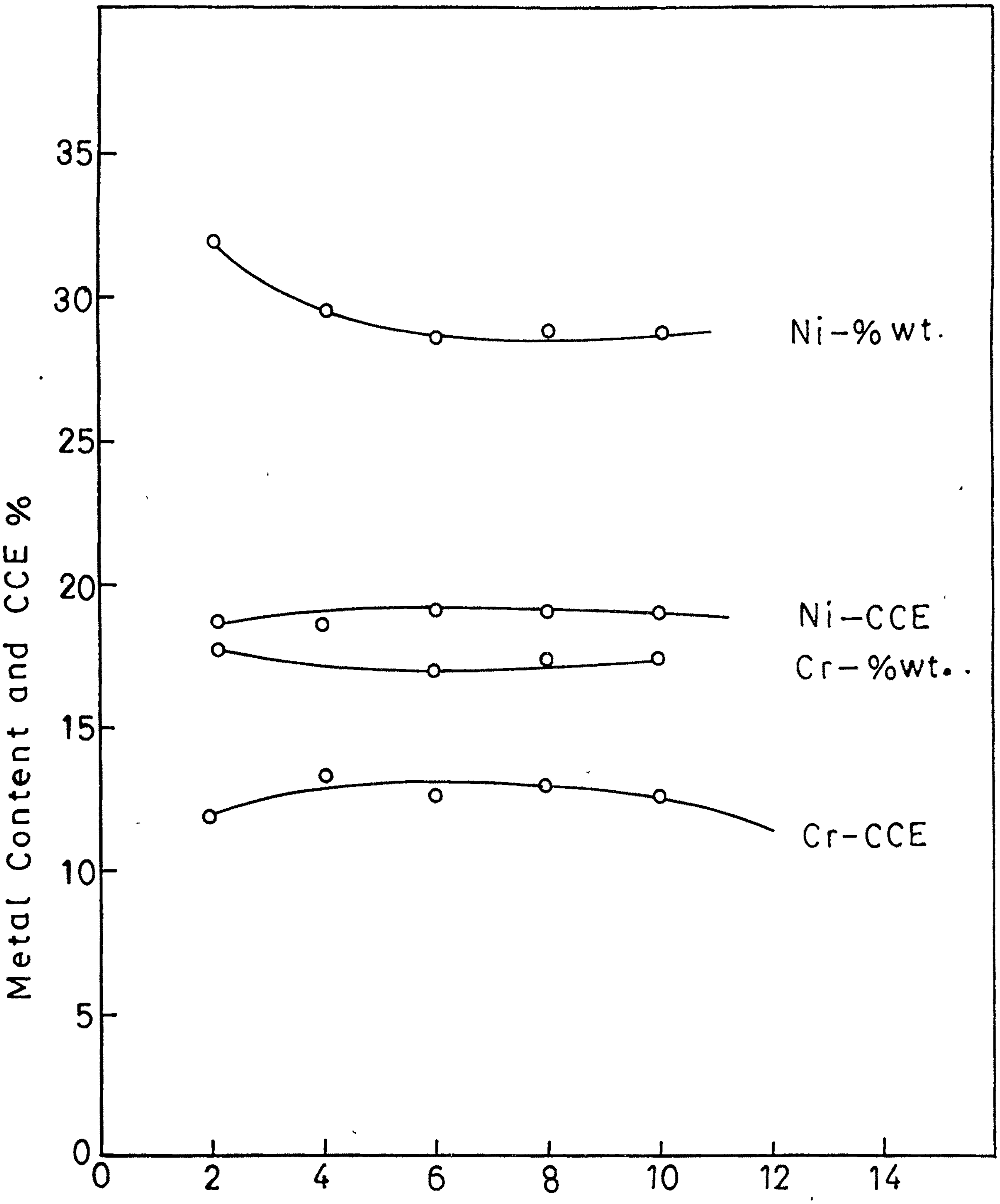


Fig. 19 – Effect of conc. of Potassium Thiocynate on the metal content and CCE % of the Nickel – Chromium alloy deposit.

TABLE NO.20 :- The effect of concentration of Glycine on the metal content and the percentage cathode current efficiency (CCE %) of Nickel-chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.
Potassium thiocyanate :6 gms.per 100 ml.
Temperature : 25°C.
Electrode distance : 4 cms.

Potassium chromic sulphate 20 gms.per 100 ml.
Current density : 2.4 amps.per Sq.dm.
Duration of electrolysis : 30 minutes
Voltage : 3 Volts.

Obs. No.	Cons.of Glycine per 100 ml. gms.	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni.	Cr.	CCE% Ni.	Cr.	Total CCE	Nature of deposit
1	0	0.110	0.030	60.00	33.33	17.56	12.12	29.68	Nonadherent, black
		0.111	0.030	60.00	33.33	17.40	12.01	29.41	
2	+ 2	0.115	0.033	57.50	39.40	17.73	13.70	31.43	Adherent, black
		0.114	0.033	57.50	39.40	17.89	13.81	31.70	
3	* 4	0.120	0.038	57.89	39.47	18.92	15.14	34.06	Adherent, blackish-white.
		0.120	0.038	57.89	39.47	18.92	15.14	34.06	
4	6	0.122	0.040	57.50	37.50	20.23	14.54	34.77	Black, adherent
		0.125	0.040	57.50	40.00	19.75	15.51	35.26	
5	8	0.123	0.042	59.52	40.48	21.81	16.74	39.55	- do -
		0.123	0.041	58.54	41.46	20.94	16.74	37.68	

* Optimum condition.   + cf. Plate II.

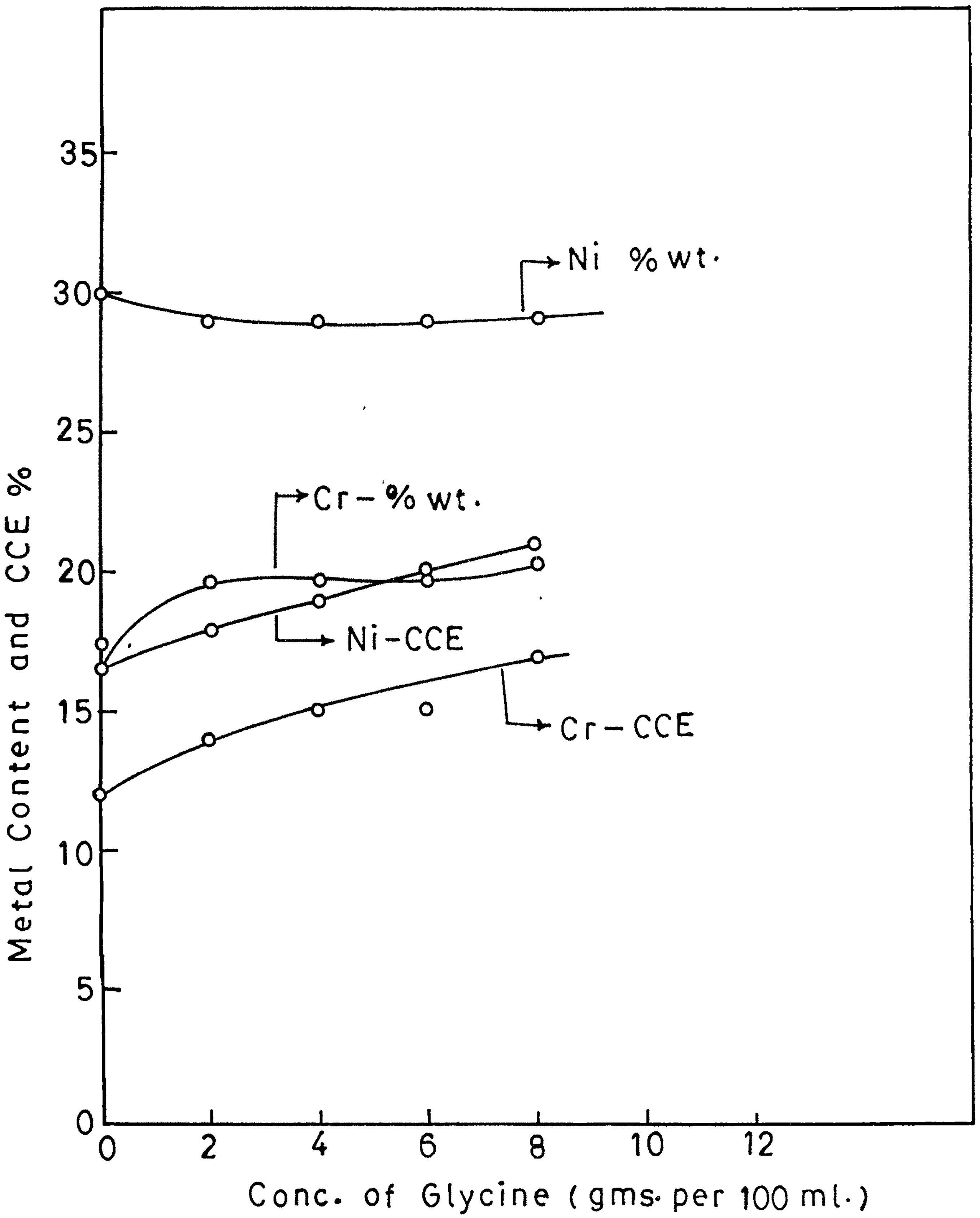


Fig. 20—Effect of conc. of Glycine on the metal content and CCE % of the Nickel Chromium alloy deposit.

TABLE NO.21 :- The effect of current density on the metal content and the percentage cathode current efficiency (CCE %) of nickel-chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.
Potassium chromic sulphate : 20 gms.per 100 ml.
Potassium thiocyanate : 6 gms. per 100ml.
Glycine : 4 gms. per 100 ml.
Temperature : 25°C.
Duration of electrolysis : 20 minutes.
Electrode distance : 4 cms.
Voltage : 2.4 to 3.00 volts.

Obs. No.	Current density amps.per Sq. dm.	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni	Metal content in alloy deposit % Cr.	CCE % Ni.	CCE % Cr.	Total CCE	Nature of deposit.
1	0.8	0.080	0.020	75.00	20.00	20.12	6.06	26.18	Nonadherent black
		0.080	0.020	75.00	20.00	20.12	6.06	26.18	
2	1.6	0.120	0.035	71.42	25.71	22.35	9.09	31.44	Adherent slight black with bluish tinge at edges.
		0.121	0.036	72.22	28.57	22.17	10.01	32.27	
3	* 2.4	0.148	0.052	71.15	26.92	26.83	11.46	38.29	Adherent white.
		0.149	0.052	71.15	26.92	26.65	11.38	38.03	
4	+ 3.2	0.160	0.069	71.01	24.63	31.30	12.26	43.56	Adherent white, black patches.
		0.166	0.065	73.85	26.15	31.30	12.41	43.71	
5	4.0	0.210	0.037	74.71	25.29	33.22	12.75	45.97	Black, treeing effect is observed.
		0.209	0.037	74.71	25.29	33.38	12.75	46.13	

* Optimum condition. + cf. Plate 12

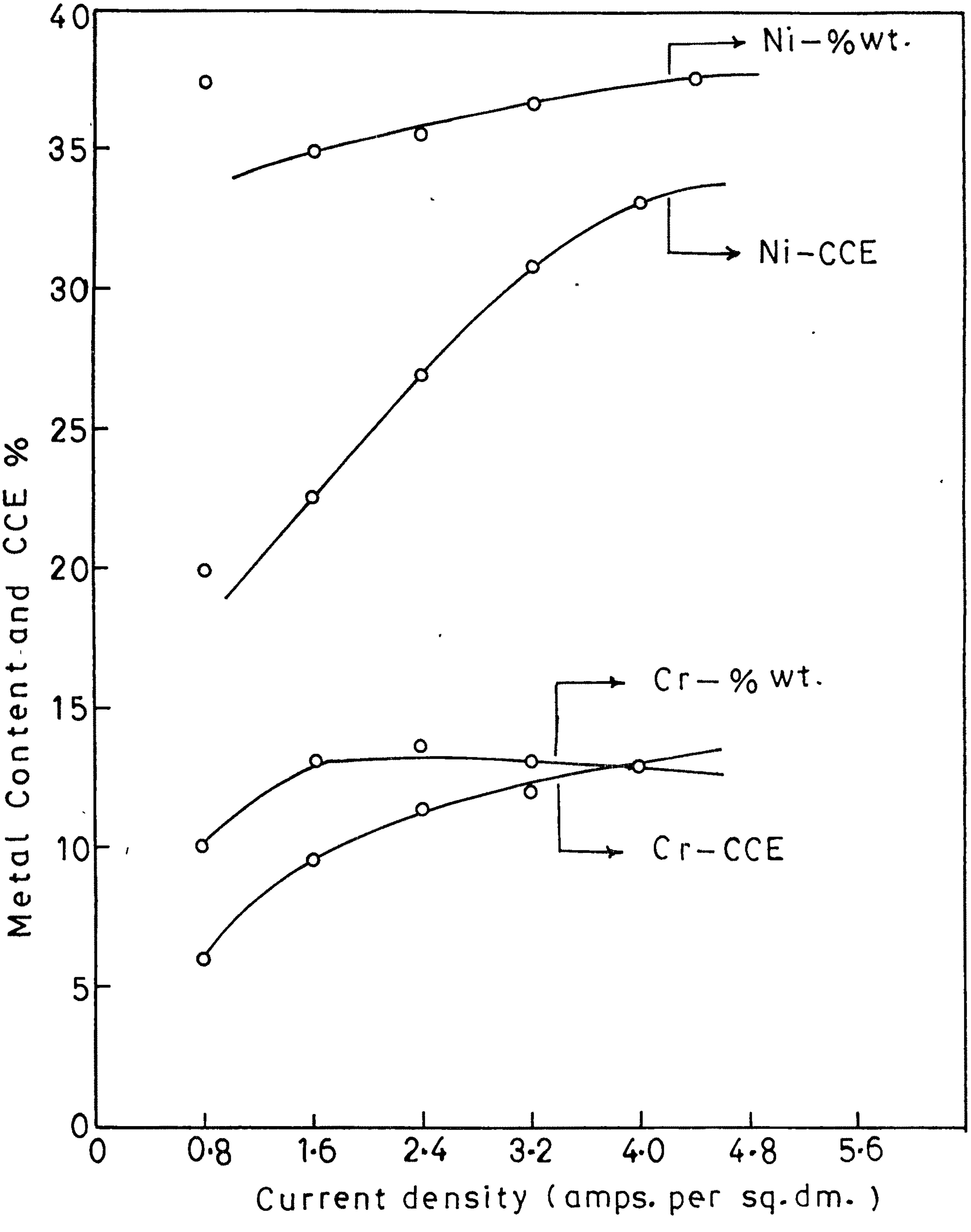


Fig.21 — Effect of current density on the metal content and CCE % of the Nickel Chromium alloy deposit.

TABLE NO.22 :- The effect of temperature on the metal content and the percentage cathode current efficiency (CCE %) of nickel-chromium alloy deposit.

Nickel Sulphate : 25 gms.per 100 ml.
Potassium thiocyanate :6 gms.per 100 ml.
Current density :2.4 amps.per Sq.dm.
Electrode distance : 4 cms.
Potassium chromic sulphate :20 gms.per 100 ml.
Glycine : 4 gms.per 100 ml.
Duration of electrolysis : 20 minutes
Voltage : 2 to 2.3 volts.

Obs. No.	Temperature °C	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal contents in alloy deposit % Ni.	Cr.	CCE % Ni.	Cr.	Total CCE	Nature of deposit.
1	15	0.130	0.035	62.86	34.29	18.16	11.18	29.34	Nonadherent, dull white.
		0.131	0.037	59.46	37.84	18.02	12.95	30.97	
2	25	0.145	0.042	64.29	35.71	19.98	11.10	31.08	Adherent,white.
		0.140	0.038	55.26	39.47	17.63	12.98	30.61	
3	*+ 35	0.160	0.050	66.00	34.00	22.13	12.87	37.01	Adherent,white,good.
		0.163	0.052	59.62	36.53	20.49	14.12	37.02	
4	45	0.146	0.040	62.50	37.50	18.38	12.45	30.83	-do-Slight black tinge.
		0.143	0.040	62.50	37.50	18.38	12.45	30.83	
5	55	0.145	0.041	63.41	34.15	19.24	11.70	30.94	Blackspatchy unsatisfactory.
		0.141	0.039	61.54	41.03	18.27	13.75	32.02	

* Optimum condition. + Cf. Plate 13

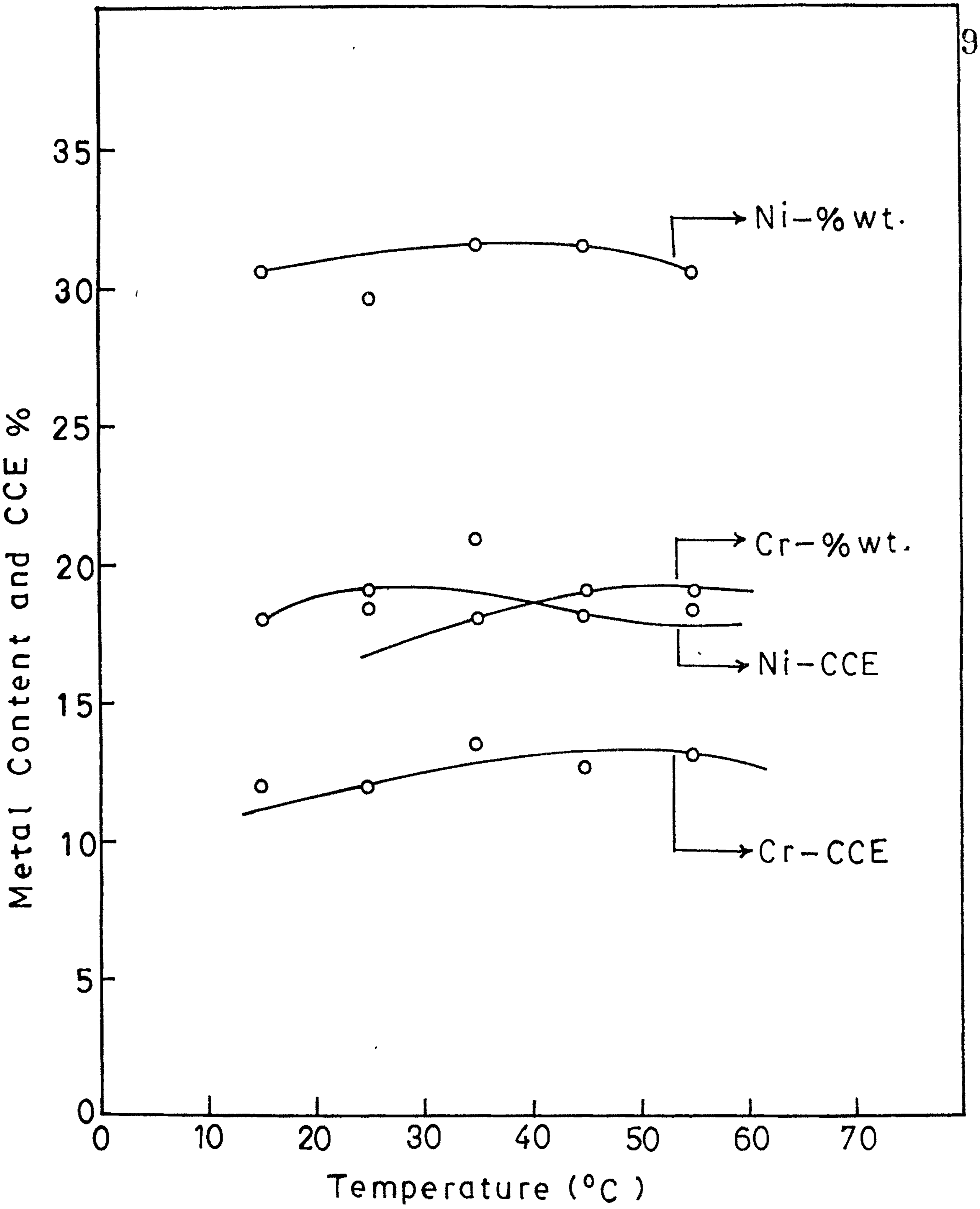


Fig. 22—Effect of temperature on the metal content and CCE % of the Nickel Chromium alloy deposit.

TABLE NO.23 :- The effect of duration of electrolysis on the metal content and the percentage cathode current efficiency (CCE %) of nickel-chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.
Potassium chromium sulphate:20 gms.per 100 ml.
Potassium thiocyanate : 6 gms. per 100 ml.
Glycine : 4 gms. per 100 ml.
Current density : 2.4 amps. per Sq.dm.
Temperature : 35°C.
Electrode distance : 4 cms.
Voltage : 2 volts.

Obs. No.	Duration of electrolysis minutes	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni.	Cr.	CCE % Ni.	Cr.	Total CCE	Nature of deposit.
1	5	0.055	0.016	62.50	31.25	19.51	11.01	30.52	Nonadherent black
		0.055	0.017	64.70	29.41	21.08	10.81	31.89	
2	10	0.095	0.030	63.33	33.33	21.46	12.75	34.21	Adherent,slight improvement
		0.096	0.031	64.52	35.48	22.36	13.88	36.24	
3	15	0.159	0.050	72.00	36.00	24.30	13.71	38.01	Adherent, white with blue tinge at edges.
		0.160	0.052	69.23	36.54	24.15	14.38	38.53	
4	* 20	0.200	0.075	64.00	33.00	25.76	14.53	40.06	Slight improvement.
		0.200	0.074	66.22	32.90	26.29	14.53	40.82	
5	30	-	-	-	-	-	-	-	Dull white adherent.

* Optimum condition. cf. Plate 14.

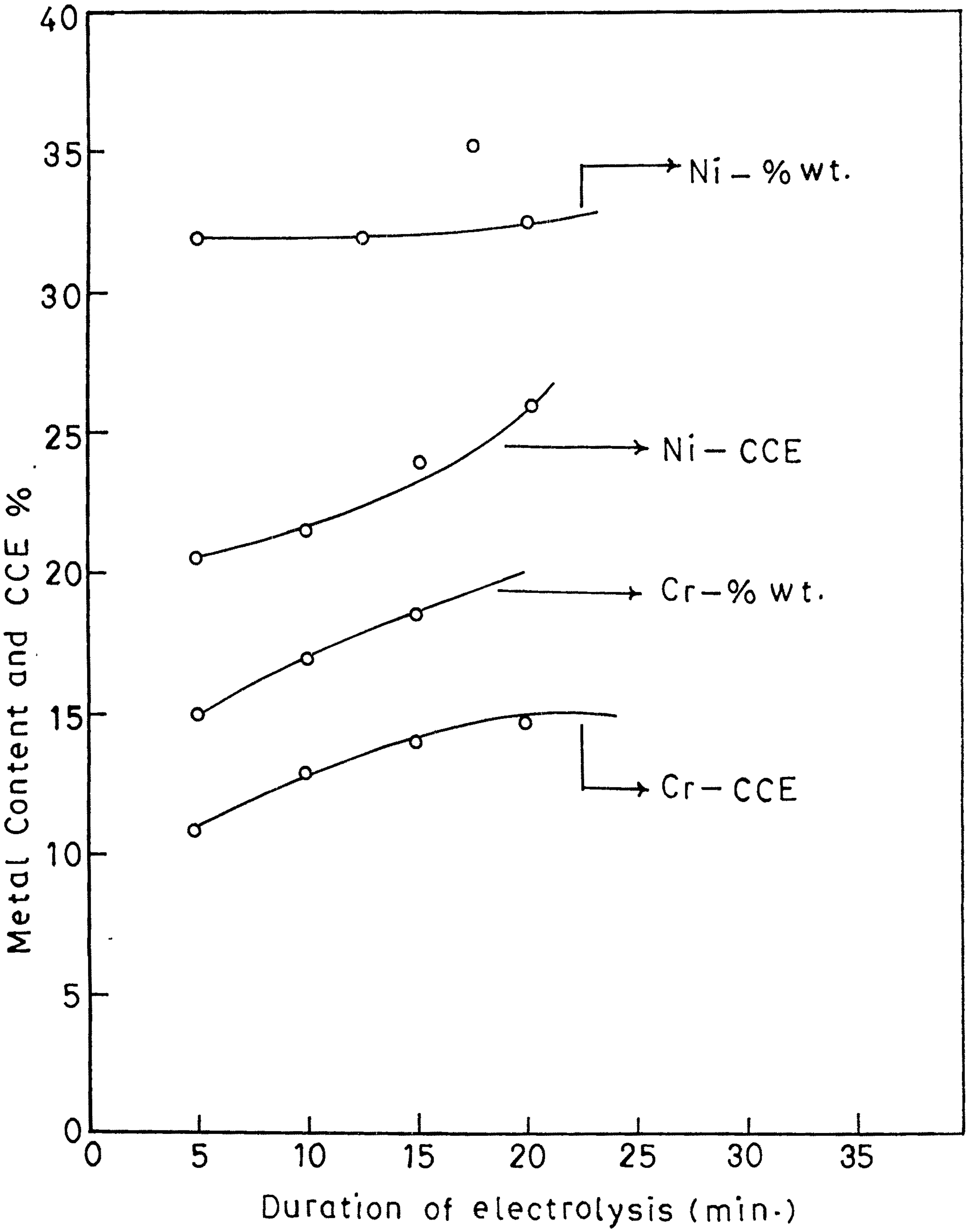


Fig.23 – Effect of duration of electrolysis on the metal content and CCE % of the Nickel Chromium alloy deposit.

TABLE NO.24 :- The effect of Electrode distance on the metal content and the percentage cathode current efficiency (CCE %) of Nickel-chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.
Potassium thiocyanate : 6 gms.per 100 ml.
Current density : 2.4 amps. per Sq.dm.
Duration of electrolysis : 20 minutes

Potassium chromic sulphate :20 gms.per 100 ml.
Glycine : 4 gms. per 100 ml.
Temperature : 35°C
Voltage : 2 to 2.5 volts.

Obs. No.	Electrode distance cms.	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni.	Cr.	CCE % Ni.	Cr.	Total CCE	Nature of deposit
1	1	0.130	0.037	50.46	37.84	18.62	13.04	31.66	White,adherent
		0.130	0.037	50.46	37.84	18.62	13.04	31.66	
2	*+2	0.132	0.039	50.97	33.33	18.70	11.93	30.63	-do- (Slight improvement)
		0.130	0.038	55.26	34.21	17.34	12.11	29.45	
3	3	0.129	0.036	61.11	30.56	10.30	10.33	20.63	-do-
		0.130	0.036	59.55	30.56	10.16	10.33	20.49	
4	4	0.130	0.036	58.34	27.78	17.31	9.32	26.63	-do-
		0.131	0.036	58.34	27.78	17.20	9.25	26.45	-do-
5	5	-	-	-	-	-	-	-	White adherent with some black patches.

* Optimum condition. cf. Plate. 14.

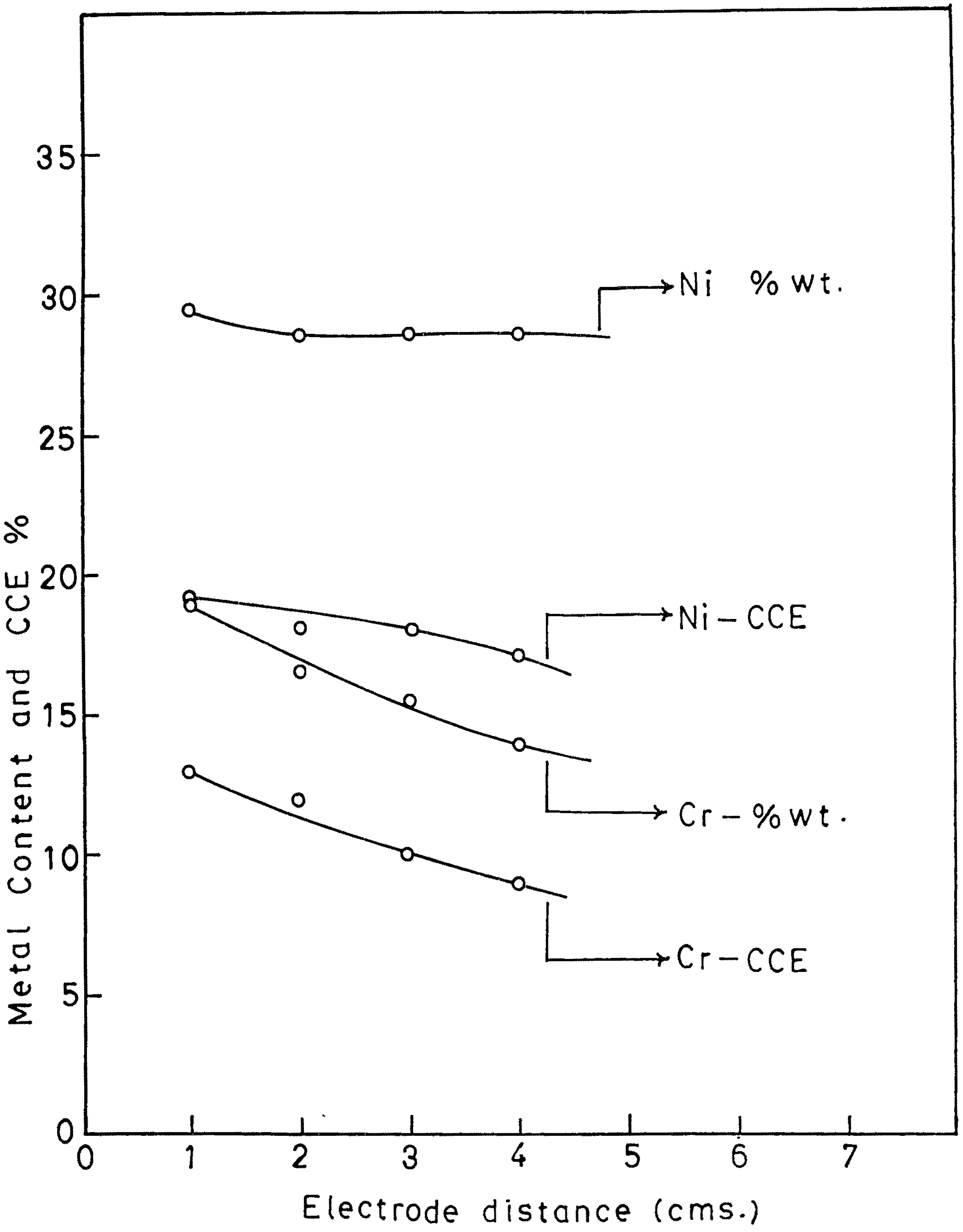


Fig. 24 – Effect of electrode distance on the metal content and CCE % of the Nickel Chromium alloy deposit.

TABLE NO.25 :- The effect of addition agents on the metal content and the percentage cathode current efficiency (CCE %) of the nickel - chromium alloy deposit.

Nickel sulphate : 25 gms. per 100 ml.   Potassium chromic sulphate:20 gms.per 100 ml.
Potassium thiocyanate : 6 gms. per 100 ml.Glycine : 4 gms. per 100 ml.
Current density : 2.4 amps. per Sq.dm.   Temperature : 35°C
Duration of electrolysis : 20 minutes   Electrode distance : 2 cms.
Voltage : 2 to 2.3 volts.

Obs. No.	Addition agent	Amount in gms.per 100 ml.	Wt.of copper deposited in coulometer gms.	Wt.of deposit gms.	Metal content in alloy deposit % Ni.	Cr.	CCE % Ni.	Cr.	Total CCE	Nature of deposit
1	Urea	0.3 gms.	0.125	0.034	61.76	32.35	18.03	10.66	28.69	No improvement in quality
			0.126	0.034	58.82	35.29	17.03	11.54	28.57	
2	Thiourea	-do-	0.125	0.038	60.53	36.84	19.75	13.57	33.32	Brightness enhanced
			0.125	0.037	60.53	35.14	19.75	12.60	32.35	
3	Gum	-do-	-	-	-	-	-	-	-	
4	Dextrose	-do-	0.140	0.040	72.50	25.00	22.23	8.65	30.88	Bright white adherent
			0.139	0.040	72.50	25.00	22.39	8.72	31.11	
5	Boric acid	-do-	0.130	0.034	67.64	26.47	18.99	8.39	27.39	Smooth,bright slight nonadherent
			0.123	0.033	66.67	33.30	18.44	9.46	27.90	
6	*+ Silver nitrate	-do-	0.123	0.036	63.89	33.33	19.25	11.36	30.61	Bright uniform, lustrous,adherent
			0.129	0.037	67.57	33.33	20.80	11.27	32.07	
7	Sulpho salicylic acid	-do-	-	-	-	-	-	-	-	Bright but slight nonadherent.

+ cf. Plate 15   * silver not detected.

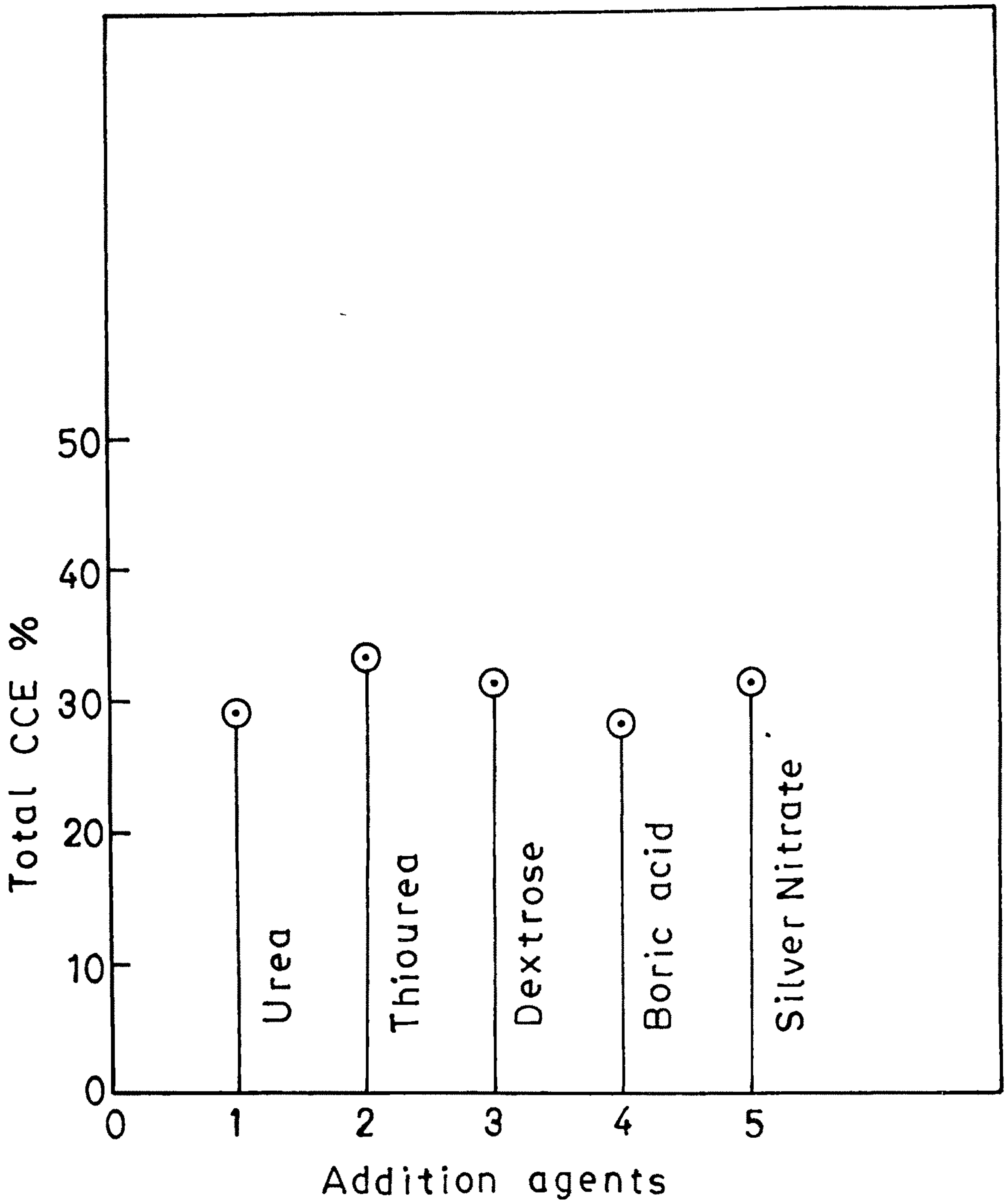


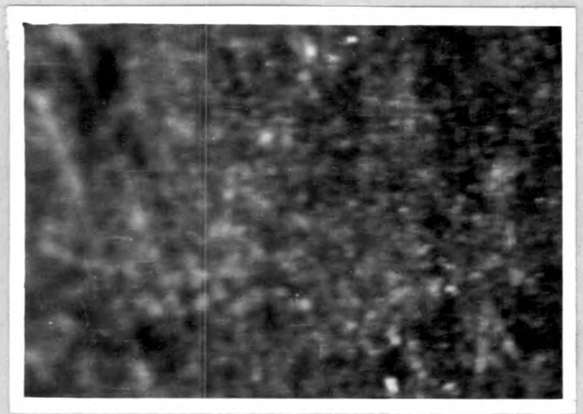
Fig. 25 — Effect of addition agents on the total CCE % of Nickel—Chromium alloy deposit.

SUMMARY

NICKEL-CHROMIUM SYSTEM (OPTIMUM CONDITIONS).

Table 25A: The influence of the Physico-chemical factors upon the nature and magnitude of the Ni-Cr alloy deposit has been shown in the previous Table Nos. 17 to 25 and graphically in Figs. 17-25. The ranges over which parameters were studied and optimum conditions arrived at by experiments are summerised belo

Parameters studied and Range	Optimum condition
1) Composition of the bath	-
a) Concn. of Nickel sulphate 5-35 gms per 100 ml of the solution.	25 gms. per 100 ml. of the solution.
b) Concn. of potassium chromic sulphate 5-35 gms per 100 ml of the solution.	20 gms. per 100 ml of the solution.
c) Concn. of potassium thiocyanate 2-10 gms per 100 ml. of the solution.	6 gms. per 100 ml. of the solution.
d) Glycine 0-8 gms. per 100 ml. of the solution.	4 gms . per 100 ml. of the solution.
2) Current density. 0.8 - 4.00 amps. per Sq. dm.	2.4 amps per sq. dm.
3) Temperature 15°-55°C.	35° C.
4) Duration of Electrolysis 5-30 minutes	20 minutes.
5) Electrode distance 1-5 cms.	2 cms.
6) Silver Nitrate was used as an addition agent which remarkably improves the brightness and adherency of the deposits.	



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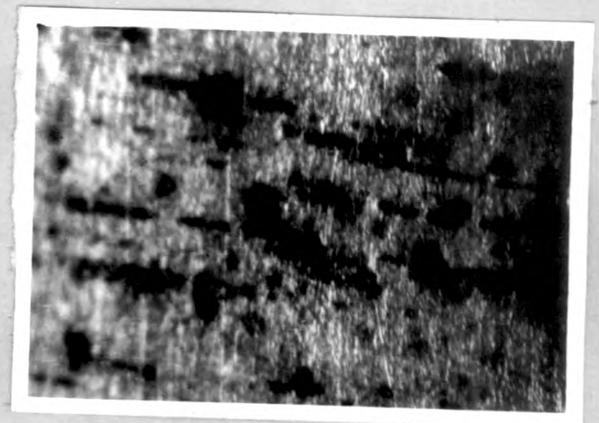

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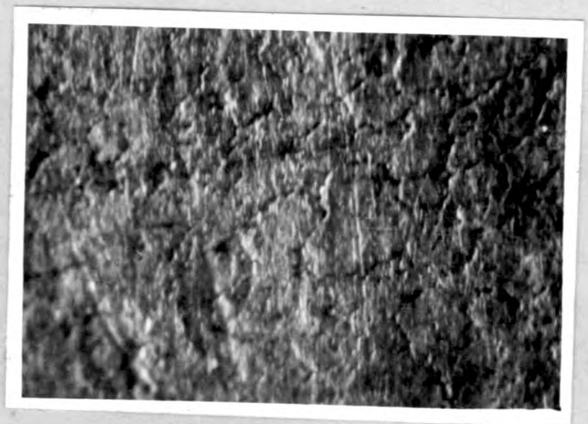

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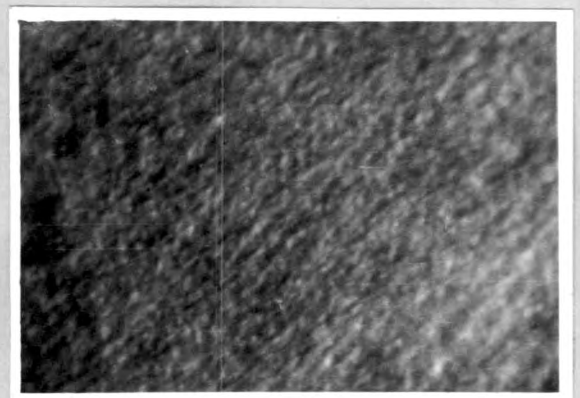

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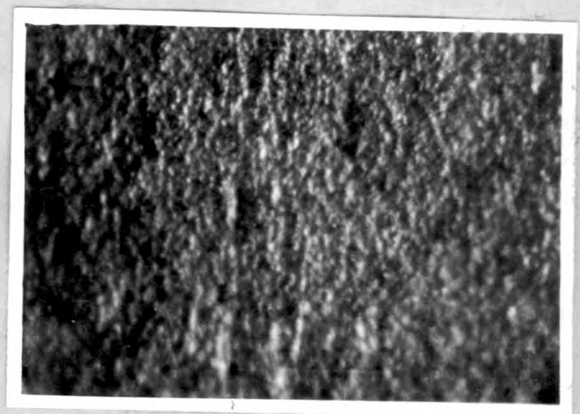

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cf.plate 15 (Nickel-chromium)

4.5 Results and Discussion (Table 17-25, Figs-17-25) Nickel Chromium alloy:

The effect of different variables on the composition of the deposit, cathode current efficiency (CCE) and the nature of the deposits is described below :

Electrolyte Concentration :

1) Effect of Nickel sulphate concentration (Cf Table-17 Fig-17):

Nickel sulphate concentration was varied from 5 gms. to 35 gms per 100 ml. of the solution. When the concentration of Nickel in the bath was increased, its content in the deposits also increased to some extent. Increase of electrolytic concentration furnishes more metallic ions and consequently increases the rate of nuclei formation and reduces the evolution of hydrogen at the cathode. This results in a uniform, fine grained and smooth deposit with greater efficiency. Higher nickel content in the bath produced dull white, unsatisfactory deposit. Similarly at low concentration of the nickel, the deposits obtained were nonadherent. Chromium content in the deposit decreased with increase in the concentration of nickel sulphate. CCE of nickel increased from 25 % to 30 % while that for chromium decreased proportionately. The optimum condition for nickel sulphate concentration was 25 gms per 100 ml. when the deposits obtained were adherent and uniform.

2) Effect of potassium chromic sulphate concentration (Cf Table -18, Fig - 18) :

The concentration of potassium chromic sulphate was changed from 5 gms. to 35 gms. per 100 ml. of the solution. The chromium content in the alloy deposit was increased from 24 % to 31 %. This increase in the chromium content was followed by a consequent increase in the efficiency upto 15 gms. of potassium chromic sulphate, after which the efficiency practically remained constant. The nickel content in the alloy deposit as well as the C.D., in general, decreased with increase in the concentration of potassium chromic sulphate. The deposits obtained at lower as well higher concentrations of potassium chromic sulphate, were nonadherent and black. The optimum condition selected was 20 gms per 100 ml. of potassium chromic sulphate.

3) Effect of concentration of potassium thiocyanate (Cf Table-19, Fig-19) :

Potassium thiocyanate mainly acts as the solvent. Its concentration in the bath was varied from 2 gms. to 10 gms. per 100 ml. of the solution. For low concentration range, the deposits obtained were nonadherent. The quality of the deposit improves as there is increase in the concentration. However at high concentrations dull deposits were obtained.

4) Effect of concentration of Glycine (Cf Table - 20, Fig - 20) :

Glycine has a marked effect on the nature of the deposit and especially on CCD. As concentration of Glycine was increased the total CCD was also increased. Hence the effect of Glycine was studied using concentrations between 0 to 8 gms. per 100 ml of the solution. Partly shining, uniform and satisfactory deposits were obtained at 4 gms. per 100 ml. The deposits become dull when the concentration was further increased. The metal content as well as CCE increased with increase in the concentration of glycine. Thus, the presence of glycine improved the condition of bath as well as the CCE.

5) Effect of current density (Cf Table -21, Fig - 21):

Increase in current density normally tends to increase the proportion of the less noble metal in the alloy deposit. Some addition agents may reverse this generalisation, by having more effect on the polarisation behaviour of one metal than on the other. The extent of the change is normally greater in simple salt solutions than in complex solutions, and greatest when the codepositing metals are in complex ions with a common ligand than when the anions of the complexes are different.

Using a bath of optimum composition, current densities varying from 0.[illegible] to 4.[illegible] amps per sq. dm. were studied. In the lower region of current density (0.[illegible] amps per sq. dm.) the deposits were nonadherent and [illegible], but with an increase in current density upto 2.4 amps per sq.dm. more shining, uniform and adherent deposits were obtained. Above this current density, the deposits turned black and showed burning effect. At higher C.D. the deposit became loose, especially at the edge, being partly due to the decrease in metal ion concentration near the cathode and evolution of hydrogen. The treeing effect was also observed at high C.D. (4.5 amps. per sq.dm.) in general the weight of deposit and total CCE increased with increase in current density.

d) Effect of Temperature (Cf Table - 22, Fig - 22) :

Increase in temperature usually increases the proportion of the more noble metal in the deposit. However, the effect is complicated, since the temperature change may also alter the degree of dissociation of complexes and have various effects on polarization factors. The temperature range studied was 15 - 55°C under optimum conditions of bath composition and C.D. It was seen that, the quality of deposit improved on raising the temperature to 35°C and then decreased with further rise of temperature. Increase of temperature on one hand favours diffusion and tends to produce a fine grained uniform deposit, but on the other it increases the rate of crystal growth, decreases the hydrogen overvoltage, favouring evolution of the gas and causes the precipitation of basic salts, resulting in a coarse, poorly adherent and dark deposit. At moderate temperatures the influence of the former factor is predominating while at higher temperatures latter ones are increasingly operative. Chromium content in the alloy deposit and CCE increased slightly, while the Nikel content in the alloy deposit and its CCE decreased proportionally with an increase in the temperature. This is some what unusual because an increase in the temperature, usually tends to increase the proportion of more nobel metal in the alloy plate. However, the variation being very small the point need not be stressed further.

7) Effect of duration of electrolysis (Cf Table -23, Fig-23):

At the optimum concentrations, current density and temperature, the duration of electrolysis was varied from 5 minutes to 30 minutes. The total cathode current efficiency of the deposit was found to increase from 31 % to 41 % over the whole range of duration studied. The metal contents both nickel and chromium increased in general with increase in the duration of electrolysis. The nature of the deposits, were found unaffected for different periods, except at 5 minutes nonadherent deposits were obtained.

8) Effect of distance between electrodes (Cf Table -24, Fig-24):

The distance between cathode and anode was changed between 1-5 cms. It was noticed that the character of the deposit was not affected to any appreciable extent, either qualitatively or quantitatively, excepting that the cathode current efficiency tends to decrease with increase in the distance between cathode and anode.

9) Effect of addition agents (Cf Table 25, Fig- 25) :

The addition agents listed in Table 25 were introduced singly to the bath under the optimum conditions and the effect was studied. In presence of gum, thiourea and dextrose the quality of the deposit was considerably improved and bright white, adherent deposits were obtained. The deposits obtained in presence of silver nitrate was lustrous, bright, and uniform. The silver was not detected during the quantitative analysis in the deposit. The composition and pH remained more or less the same for all observations.

It is well known that even small quantities of certain substances added to a depositing solution markedly influence, the structure of the resulting deposit. These are called as addition agents. Most of them are colloidal in nature and they form disperse system with the electrolyte. They produce beneficial change in the character and structure of the deposit. Small quantities of the colloidal addition agents may cause the metal to collect as very small crystals and produce a smooth, uniform and adherent deposit. Also, current density on the cathod surface is never perfectly uniform. There may be a few points on the surface which being nearer to the cathode receive more of the current. The crystal growth at these points will be faster. But when colloidal particles are present, due to higher current density, they preferentially collect at these points constituting a non conducting layer around them, until the general level of the metal builds upto them, thus producing a smoother deposit.

At this background, the influence of addition agents listed in Table - 25 could be explained in relation to observations stated earlier.

4.5.2 The Role of Silver as an addition agent in alloy-deposition:

Lustrous, white shining deposit of silver can be obtained on a base metal from well known silver baths. Silver or any nobel metal can easily be plated out from a plating solution in preference to any other metal preceding the same in EM series. Due to hydrogen-over voltage and uniform, stirring of the plating solution (polarisation effects being minimised), Co-deposition of the metals can be achieved. In a solution containing sufficient amounts of a nobel metal and anyother base metal, the latter can be co-deposited with silver, depend on metal contents of the two metals in the alloy and their relative proportions in the plating solutions, differences in reversible potentials and overvoltages of the depositing ions (Cf equation - 4) govern the codeposition.

However, in presence of silver added to the plating solution, in traces, there appears to be no possibility of silver depositing simultaneously with nickel and chromium which are in much larger quantities in the bath solution as demanded by the equation - 4. This is confirmed by analysing the deposit in which silver was not detected. However, the remarkable improvement in the nature of the deposit suggests, the possibility of silver acting as an addition agent in the alloy deposition. The experimental conditions would tend to exclude any silver to be detected in the alloy deposit. However, it can be argued that silver entering into the Ni-Cr alloy structure by substitution, leading to a solid solution could not be up to the limit of detection by our analytical methods. It is this silver present in traces in the alloy deposit, which renders its shining propeties to the alloy, giving it an appearance of silver deposit.

Alternatively, silver added in traces may get transformed into colloidal silver hydroxide acting as an addition agent which may cause the other two metals to collect as very small crystals and produce the observed effects, or it may be that the colloidal silver hydroxide constitutes a non-conducting layer around the points of higher current density at the cathode, thus producing a silvery shining deposit of the alloy.

The resulting alloy has much superior qualities of nobel metals as compared to the stainless steel coatings obtained by Rama Char etal (79) for nickel, chromium and iron alloy system.

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