CCCLXXXVI.—*Studies of Electrolytic Polarisation. Part V. The Electro-deposition Potentials of Alloys of Iron, Cobalt, and Nickel.*

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As a consequence of experiments on the electro-deposition potentials of iron, cobalt, and nickel (preceding paper), it was decided to extend the observations to the initial potentials at which alloys of

these metals are deposited from mixed solutions of their salts. Some general observations have been made by Küster (*Z. Elektrochem.*, 1901, **7**, 688) and by the author (*Trans. Faraday Soc.*, 1924, **19**, 574), but the results are not trustworthy, since they include the errors inherent in the direct method of measuring polarisation potentials, and, moreover, no attempt was made to regulate the hydrogen-ion concentration of the electrolyte. In the work now described, acetate buffer solutions were used in order to maintain a fairly definite hydrogen-ion concentration, and the polarisation potentials were measured by the author's commutator–extrapolation method.

EXPERIMENTAL.

The materials and procedure were as described in the preceding paper, Walpole's acetate–acetic acid solutions again being used as the basis for almost all of the electrolytic baths. The solutions contained varying amounts of the sulphates of two or three of the iron-group metals, the total concentration of these metals being one g.-equiv. per litre. The cathodes were of copper covered with a complete layer of alloy deposited at fairly low *C.D.* from the solution under examination; the exposed part was generally 7·5 sq. cm. in area. When the solutions contained iron salts, the anode and cathode compartments were separated.

Nickel–Iron Alloys.—The potentials recorded in Table I were obtained with a solution containing equivalent amounts of iron and nickel in solutions of varying hydrogen-ion concentration at 15°. (Throughout this paper current densities are expressed in terms of amps. $\times 10^{-4}$ per sq. cm.)

TABLE I.

Cathode potentials in 1Fe : 1Ni solution.

C.D.	$N/10$-H_2SO_4.	p_H 2·8.	p_H 4·0.	p_H 5·0.
0·42	— 0·33	— 0·36	— 0·38	— 0·44
1·40	— 0·36	— 0·38	— 0·46	— 0·52
2·80	— 0·39	— 0·41	— 0·53	— 0·55
5·60	— 0·43	— 0·50	— 0·56	— 0·59
8·40	— 0·48	— 0·55	— 0·58	— 0·66 *
12·0	— 0·52	— 0·58	— 0·67 *	— 0·68
20·0	— 0·54	— 0·65 *	— 0·69	— 0·70
40·0	— 0·58	— 0·67	— 0·71	— 0·71
80·0	— 0·66 *	— 0·69	— 0·72	— 0·72
160·0	— 0·68	— 0·71	— 0·73	— 0·73

* Break-point.

In each case, with increasing *C.D.* the potential increases at first slowly, then jumps suddenly to a value that is always very near to − 0·66 volt, after which it changes comparatively slightly. Observations with a polished copper cathode (see preceding paper)

indicate that the potential noted as " break-point " in Table I is that at which deposition of metal commences; this is in agreement with the results obtained in the deposition of the single metals. It appears, therefore, that from a solution containing equivalent amounts of nickel and iron an alloy commences to be deposited at a potential of -0.66 volt independently of the hydrogen-ion concentration of the solution; the $C.D.$ at which deposition commences will, of course, be lower the smaller the hydrogen-ion concentration of the solution.

The measurements were repeated with solutions containing other ratios of iron and nickel, and the results were of exactly the same type as those given in Table I. A summary is contained in Table II. The temperature was approximately 15° throughout.

TABLE II.

Solution : 1Fe : 9Ni.

	p_H 2.8.	p_H 4.0.	p_H 5.0.	p_H 6.0.
Initial deposition potential	-0.59	-0.60	-0.60	-0.59
Current density	8.4	8.4	5.6	4.2

Solution : 3Fe : 7Ni.

	p_H 2.8.	p_H 4.0.	p_H 5.0.
Initial deposition potential	-0.64	-0.63	-0.63
Current density	20.0	12.0	5.6

Solution : 7Fe : 3Ni.

	p_H 2.8.	p_H 4.0.	p_H 5.0.	$N/50\text{-}$ H_2SO_4.
Initial deposition potential	-0.68	-0.68	-0.68	-0.67
Current density	40.0	20.0	8.4	40.0

The experiments were repeated at 55° and at 95° and the initial deposition potentials of the alloys from electrolytes of varying composition were determined. The results are summarised in Table III.

TABLE III.				TABLE IV.			
Ratio Fe : Ni in solution.	Deposition potential at			Ratio Fe : Co in solution.	Deposition potential at		
	15°.	55°.	95°.		15°.	55°.	95°.
Ni only.	-0.57	-0.43	-0.29	Co only.	-0.56	-0.46	-0.36
1 : 9	-0.595	-0.44	-0.29	1 : 9	-0.60	-0.46	-0.36
3 : 7	-0.63	-0.45	-0.30	3 : 7	-0.62	-0.46	-0.36
1 : 1	-0.66	-0.46	-0.31	1 : 1	-0.64	-0.47	-0.38
7 : 3	-0.68	-0.49	-0.35	7 : 3	-0.67	-0.49	-0.40
Fe only.	-0.68	-0.50	-0.46	Fe only.	-0.68	-0.50	-0.46

Tables IV, V, and VI, respectively, give the deposition potentials found for alloys from solutions containing the sulphates of iron and cobalt, nickel and cobalt, and iron, cobalt, and nickel. Except in the last case, data are given for 15°, 55°, and 95°.

TABLE V.				TABLE VI.			
Ratio Ni : Co in solution.	Deposition potential at			Ratio in solution.			Deposition potential at 15°.
	15°.	55°.	95°.	Fe :	Co :	Ni	
Ni only.	−0·57	−0·43	−0·29	1	4·5	4·5	−0·57
3 : 1	−0·57	−0·44	−0·32	1	2	1	−0·58
1 : 1	−0·57	−0·44	−0·32	1	1	2	−0·60
1 : 3	−0·57	−0·45	−0·34	1	1	1	−0·63
Co only.	−0·56	−0·46	−0·36	2	1	1	−0·68

Discussion.

An examination of Table III shows that at 15° the deposition potential increases rapidly at first with increasing iron ratio in the electrolyte; thus, when only half of the dissolved salt is ferrous sulphate, the deposition potential (− 0·66) is very close to that of pure iron (− 0·68). If we adopt the view that the metal which is primarily deposited is a metastable form with an electronic arrangement which differs from that of the ordinary metal and subsequently changes into it (see preceding paper), then the results obtained in this work indicate that the rate of change of metastable to stable form is hindered by the simultaneous deposition of a small amount of iron. Thus the initial deposition occurs at a potential which is more negative than that at which pure nickel is deposited; since the former potential approaches that at which pure iron is deposited from a ferrous sulphate solution, it is probable that even the initial deposit will contain a fairly large proportion of this metal. If the C.D. is raised, the polarisation potential also rises, and so the amount of iron in the deposit will tend to increase; this increased proportion of iron will exert an additional retarding effect on the change of metastable to stable nickel, with the result that the deposition of nickel requires a still more negative potential. The deposit will thus tend to contain even less nickel, and so with increasing C.D. the proportion of iron should increase very rapidly. This increase is soon counteracted, since the deposit will contain a much larger proportion of iron than does the electrolyte, and the solution will become relatively richer in nickel ions in the vicinity of the electrode; thus an alloy somewhat poorer in iron will be deposited and eventually a point of balance will be reached at which the composition of the alloy remains constant even if the C.D. is increased. A further *large* increase of C.D., especially in dilute solution, may result in an actual decrease in the proportion of iron in the deposited alloy owing to the impoverishment of the electrolyte. At higher temperatures, it is clear from the results that iron has very much less influence on the rate of the nickel transformation, since the deposition potentials are much nearer

those at which pure nickel can be deposited. We should thus expect the deposits from a given solution to contain much less iron than at ordinary temperatures (compare Kremann, *et al.*, *Monatsh.*, 1913, **34**, 1757; 1914, **35**, 731) and the increase of the proportion of iron with increasing *C.D.* to be much more gradual. When the amount of iron in the electrolyte is increased, the behaviour should approach more closely that found at ordinary temperatures. In order to test these predictions, a comprehensive series of investigations has been commenced on the variation of the composition of alloys deposited from solutions containing two of the iron-group metals at different concentrations and at a number of *C.D.*'s. An examination of Table I shows that at a given *C.D.* the potential may depend on the hydrogen-ion concentration of the solution, and hence the composition of the alloy may also depend on this. It is thus essential that the hydrogen-ion concentration of the electrolyte be kept as constant as possible during the course of the experiment in which the alloy is being deposited; failure to observe this precaution may account for the results of Toeppfer (*Diss.*, Breslau, 1899; *Z. Elektrochem.*, 1899, **6**, 342) and also for the apparent variation of the composition of the alloy with time found by Foerster ("Elektrochemie Wässeriger Lösungen," 1922, p. 376). The preliminary observations at ordinary temperatures which have been made so far in connexion with the deposition of nickel–iron alloys indicate that the initial deposit often contains relatively less iron than does the electrolyte, but the proportion increases at first rapidly with increasing *C.D.*, then more slowly, and finally reaches an almost constant value.

The results obtained in the deposition of iron–cobalt alloys (Table IV) are similar to those for the iron–nickel alloys. The retarding effect of iron on the change of metastable cobalt to the stable form appears to be less than in the case of nickel. We should expect, therefore, that the alloys would not be so rich in iron and that the increase of iron concentration in the deposit with increasing *C.D.* should be somewhat less rapid than is the case with nickel–iron alloys deposited under similar conditions. The experiments now in hand will give further information on these points.

The case of the nickel–cobalt alloys (Table V) is interesting but inconclusive : it indicates the necessity for an investigation, which is being undertaken, on the variation in composition of the alloys with changes in the conditions of deposition.

Table VI affords but little information regarding the iron–cobalt–nickel alloys; it appears, however, that the effect of iron in retarding the change of metastable to stable atoms is less in the presence

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of a mixture of cobalt and nickel than in that of either of these metals alone.

It is considered very unlikely that cobalt or nickel can appreciably retard the conversion of metastable iron into the stable form; if this retardation were possible, then alloys rich in iron, but containing a small proportion of nickel or cobalt, should commence to be deposited only at potentials more negative than that at which pure iron may be deposited.   This has, however, not been observed.

Summary.

(1) The initial deposition potentials of alloys of iron, nickel, and cobalt, in pairs or all together, from solutions of various metallic and hydrogen-ion concentrations have been measured at 15°, 55°, and 95°.

(2) The deposition potential varies with the ratio of the metals in solution and with the temperature, but is independent of the hydrogen-ion concentration.

(3) The results are discussed in the light of a theory previously proposed to account for the overvoltage of deposition of the iron-group metals.   It appears that in the deposition of alloys of iron with nickel and with cobalt the concentration of iron in the alloy should increase at first rapidly with increasing current density and then reach an almost constant value.