X-RAY STUDY ON THE ELECTROLYTIC Fe-Ni ALLOYS.

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Received August 15th, 1932. Published September 28th, 1932.

Synopsis.

Iron and nickel were co-deposited in various proportions electrolytically from their mixed sulphate solutions, and X-ray diffraction patterns were photographed by the Debye-Scherrer and Seemann-Bohlin methods, and the lattice constants were measured by choosing lines of copper as a standard which was mixed with the alloys in the form of powder. The results obtained were as follows. (1) Iron and nickel in the deposit appears as solid solution. The homogeneity of the solid solution thus formed seems not so good as that of the alloy solidified from the melt. (2) The co-existence of α and γ solid solutions is also observed in the deposits the concentration of which ranged from 14% Ni to 58% Ni. In the alloys solidified from the melt this ranges from 25% Ni to 33% Ni. (3) Lattice constant of α or γ solid solution increases slightly at first, reaches maximum and then decreases as the constant of Ni or Fe increases respectively. From these results it has been concluded that when the total or local concentration of the one metal in the deposit is small, two cases may arrise either the metal is forced to deposit among the crystal of the other metal without forming its proper crystal lattice forming

pseudo solid solution as a result or the unit mass of the deposited crystal of that metal is small and consequently it easily diffuses into the other after the deposition. This is the reason why the lattice constant-concentration curve runs upward. But when the concentration is fairly large, the unit mass of that crystal also becomes larger and its diffusion into the other takes place not so easily as before leaving some of that crystal undiffused. This tendency becomes greater as the concentration of that metal increases. The existence of the maximum point on the curve above mentioned and the coexistence of α and γ solid solutions in a wider range of the composition of the deposited alloy are explained sufficiently by the process of deposition above supposed.

Introduction.

There is a few study on the crystal structure of the alloy[1] electrolytically co-deposited from the aqueous solution of the salts of two kinds of metal. Nakamura[2] observed by the X-ray study that the crystal of the electrolytic brass containing 17.52% of Zn co-deposited from the cyanide solution well coincides with the alloy of the same composition obtained from the melt in its form and in its lattice constant. G. Fuseya and K. Sasaki[3] also concluded by the X-ray study that the electrolytic Fe-Cr alloy containing 30% of Cr forms solid solution. As to the mechanism of these phenomena the following cases may be considered.

(1) The discharge of the two kinds of metal ion occurs at the position of each inherent crystal lattice, and not at the position of the crystal lattice of their solid solution. But as the state of mixing of the two metals in the deposit is very intimate, two metals easily diffuse with each other and form solid solution.[4]

(2) The discharge of the two kinds of metal ion occurs at the position of the crystal lattice of their solid solution, and not at the position of each inherent crystal latice when the condition of electrolysis is suitable.

(3) The two kinds of metal ion are forced to discharge at random without being allowed to choose the mode of discharge (1) or (2), and consequently the pseudo solid solution are formed the predominated metal being the solvent. In this case diffusion naturally occurs after the deposition.

By the case of brass or Fe-Cr alloy mentioned above, it is not convenient to decide which is the chief mechanism of deposition among the above three processes, because though Cu and Zn have different crystal forms they diffuse very easily with each other,[5] and though Fe and Cr do

(1) Electrolytic alloy means a mixture of two or more metals co-deposited by electrolysis.
(2) M. Nakamura, *Bul.Inst. Phys. Chem. Research, Japan, (Riken-Ihô)*, **4** (1925), 71.
(3) G. Fuseya and K. Sasaki, *J. Soc. Chem. Ind., Japan, (Kôgyô-Kagaku-kaishi)*, **33** (1930), 1337.
(4), (5) Tammann, Lehrbuch der Metallographie, 3 Auflage (1923), 233.

not diffuse so easily as the case of Cu and Zn, they have the same crystal form and the difference between the lattice constants is very small being 0.017 Å. So we have chosen the alloys of Fe and Ni to study the mechanism of deposition, and we have prepared a series of the alloy whose composition varies from 0~100% of Ni and studied their structure by the X-ray analysis. In the alloy of this system obtained from the melt up to 25% of Ni, the alloy consists of α solid solution only (body centred cubic lattice) and from 33% of Ni to 100% of Ni only of γ solid solution (face centred cubic lattice) and between 25% and 33% of Ni it consists of α and γ solid solutions (both body centred and face centred).[1]

Experimental.

Preparation of Electrolytic Fe-Ni Alloys. Co-deposition of iron and nickel by electrolysis was studied by S. Glasstone and T. E. Symes.[2] Using the chemical analysis, the composition of the alloys, prepared by the electrolysis from the mixed sulphate solution of various concentration, were determined. But whether this so called alloy was the true alloy having a definite crystal structure or not was not studied. L. E. Stout and J. Carol[3] studied the co-deposition of iron and nickel from their mixed cyanide solution, but they also did not touch the problem of the crystal structure of the deposit. For the present study, the sulphate solution was taken as the electrolyte, the total concentration of which was two normal, and to prevent the formation of ferric hydroxide in consequence of the anodic oxidation during electrolysis the electrolyte was acidified to two normal with sulphuric acid. Glasstone observed that when electrolyte is dilute in its concentration and not stirred during electrolysis for a long time, the iron contents in the deposit more or less decreases though the hydrogen ion concentration does not affect the composition of the deposit. In our experiment, electrolyte was sufficiently concentrated and stirred and in addition to these, our deposit was little in quantity compared with the total metal content in the electrolyte (total metal content 28 gr., deposit about 0.2 gr.), and so the inequality of concentration in deposit may be negligible. As the cathode thin plate of copper, 0.17 mm. in thickness and 20 cm^2. in effective area, was used and as the anode two thin plates of platinum, 3.5 cm. long and 1.5 cm. wide, were put on either side of the cathode. Electrolysis was carried out at room temperature, and C.D. was always kept at 0.02 amp/cm^2.,

(1) A. Osawa, *Kinzoku-no-Kenkyu*, **2** (1925), 809; T. Kasé, *ibid.*, **1** (1924), 1215.
(2) S. Glasstone and T. E. Symes, *Trans. Faraday Soc.*, **23** (1927), 213; **24** (1928), 370.
(3) L. E. Stout and J. Carol, *J. Am. Electrochem. Soc.*, 1930, Sept. Meeting; *Stahl .u Eisen*, **50** (1930), 1533.

electrolyte being stirred during it. Before electrolysis cathodes were well polished, washed with concentrated KOH solution, dipped in concentrated nitric acid for a few seconds, washed well with water, dipped in dilute sulphuric acid, washed with water again and then used. The volume of electrolyte was 500 c.c., the time of electrolysis 4 hours. After the electrolysis the deposit was separated from the cathode, powdered, and the one half of it was used for X-ray analysis, the other for chemical analysis and the results obtained were as follows.

Table 1.

No.	Concentration of Nickel in	
	Solution (%)	Deposit (%)
1	0	0
2	33	9
3	51	11
4	61	14
5	67	20
6	84	31
7	89	37
8	98	58
9	99	80
10	100	100

X-ray Analysis. The X-ray analysis of the above 10 specimens has been carried out by Debye-Scherrer and Seemann-Bohlin methods. The results are tabulated in Table 2, and graphically represented in Fig. 1. Some of the diffraction patterns taken by the method of Debye-Scherrer are shown in Photo. 1 as examples.

Table 2. Results of X-ray Analysis.

(a) Body-centred Lattice.

No.	% Ni	R	$h_1h_2h_3$	r	$2b$	θ (Radian)	$\sin\theta$	d	Å
1	0	27.754	211	0.263	108.629	0.977036	0.82884	1.166932	2.858_4
1′	0	27.705	,,	0.288	108.522	0.977640	0.82918	1.166456	2.857_2
2	9	27.754	,,	0.275	108.739	0.976320	0.82844	1.167496	2.859_7
3	11	27.800	,,	0.288	108.456	0.975234	0.82783	1.168354	2.861_8
4	14	27.660	,,	0.385	108.130	0.975137	0.82776	1.168454	2.862_1
5	20	27.727	,,	0.238	108.345	0.977554	0.82801	1.168101	2.861_2
6	31	27.736	,,	0.310	108.620	0.977312	0.82899	1.166720	2.857_8
7	37	27.660	,,	0.325	108.600	0.979745	0.83033	1.164838	2.853_3
8	58	27.721	,,	0.280	108.789	0.979540	0.83023	1.164972	2.853_6

(b) Face-centred Lattice.

No.	% Ni	R	$h_1h_2h_3$	r	$2b$	θ (Radian)	$\sin\theta$	d	Å
4	14	27.735	220	0.385	98.478	0.887666	0.77560	1.24703	3.527_1
5	20	27.744	,,	0.238	98.702	0.887690	0.77562	1.24701	3.527_3
6	31	27.742	,,	0.310	98.530	0.885688	0.77436	1.24903	3.532_8
7	37	27.652	,,	0.325	98.420	0.887470	0.77549	1.24721	3.527_6
8	58	27.698	,,	0.280	98.140	0.883782	0.77315	1.25099	3.538_2
9	80	27.679	,,	0.295	97.632	0.880756	0.77122	1.25411	3.545_1
10	100	27.743	,,	0.280	98.912	0.889344	0.77666	1.24534	3.522_3
10′	100	27.707	,,	0.283	98.834	0.889740	0.77691	1.24499	5.521_2

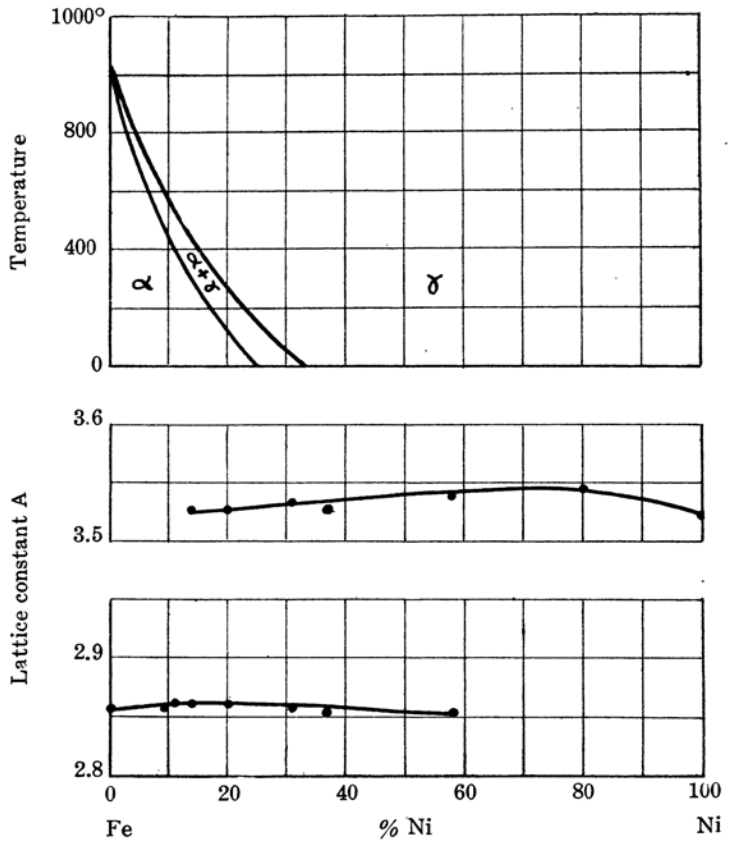

Fig. 1.

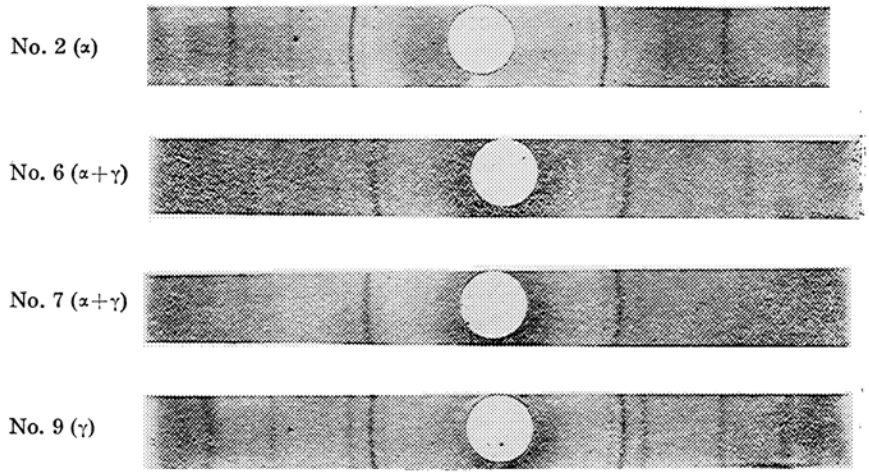

Photo. 1.

Lines in No. 2 consist of those which belong to body centred cubic lattice, lines in No. 9 consist of those which belong to face centred cubic, and in Nos. 6 and 7 we find the mixture of lines of both crystals. Lines of body centred cubic are deeper than those of face centred cubic in No. 6 and opposite in No. 7. This is due to the relative quantity of both crystals. In No. 6 and No. 7 K_α lines diffracted from the crystal plane 110 overwrap with those from the plane 111 and seem very thick and deep. To calculate the lattice constants we photographed the lines from pure Cu crystal at the same time on the same film by mixing the fine powder of Cu with the samples. As the lattice constant of Cu is known, effective radius of camera is calculated from the lines of Cu thus photographed and the lattice constants of the samples were calculated therefrom, thus avoiding the errors caused by camera, film etc. On calculating lattice constants we chose 211 K_α in the case of body centred cubic lattice and 220 K_α in the case of face centred cubic as these lines were relatively thick and not so diffused as others and their reflecting angles are large. For the former line, i.e. 211 K_α of body centred lattice, 220 K_α and 311 K_α lines of Cu are taken as a standard and for the latter line, i.e. 220 K_α of face centred lattice, 220 K_α line of Cu as a standard adopting for the lattice constant of Cu 3.603 Å.[1] The wave-length of X-ray was calculated as 1.9344 Å from two K_α lines by proportion of their intensity. The formula $-r(1+2\cos\theta)$ was used for the correction of the radius of the samples, where r meant the radius of the sample, θ

(1) Int. Crit. Tab., I, 340.

the reflecting angle, because this formula had been used in calculation of the effective radius of the camera from the lines of copper. Care was taken to measure $2b$ because the diffusion of lines caused by electrolysis was great. The lattice constants of the samples are shown in the above table in which R shows the effective radius calculated from the line of copper, the wave-length of X-ray was enacted as 1.9344 Å. In this table samples No. 1′ and No. 10′ were heated in vacuum at 600°C for 30 minutes, and others not heated.

Fig. 1 shows these results graphically. The lower part of it shows the lattice constant-concentration curve, and the upper part the equilibrium diagram of the alloy cooled from the melt.[1]

Interpretation of the Results.

1. Lattice Constants of the Electrolytic Metals and Alloys. The values of lattice constant for iron and nickel found in literature (Table 3) coincide well with ours.

Table 3.

Metal	Fe	Ni
A	2.855 ~ 2.859[2]	3.540[4]
		3.514[5]
	2.855 ~ 2.856[3]	3.514[6]

As iron and nickel electrolyzed contain much hydrogen their lattices expand about 0.001 Å as shown in the previous table. For the iron our result agrees well with other, while for the nickel our value is intermediate one among theirs. As for the lattice constants of the alloys made from the melt, we can find several studies by X-ray analysis[7] but their results don't

(1) A. Ôsawa, T. Kasé, see before.
(2) W. H. Day, *Phys. Rev.*, **25** (1925), 755. Fe_2O_3 was reduced with hydrogen.
(3) A. O. Jung, *Z. Krist.*, **65** (1927), 311. Iron was used which was prepared at Bureau of Standard, the purity of which was 99.937%.
(4) A. W. Hull, *Phys. Rev.*, **17** (1921), 579. Electrolytic nickel was used.
(5) The same with (2).
(6) L. W. McKeehan, *Phys. Rev.*, **21** (1923), 402. Mond nickel the purity of which was 99.7% was used.
(7) M. R. Andrews, *Phys. Rev.*, **17** (1921), 261; **18** (1921), 245; A. Ôsawa, *Kinzoku-no-Kenkyu*, **2** (1925), 809; A. O. Jung, see before; L. W. McKeehan, see before.

coincide with. However all of these studies coincide well with the point that their lattice constants increase in α or γ solid solution as nickel or iron content increases respectively. Contrary to this in our results lattice constants increase at first as the solute increases in its concentration, reach maximum values, and then decrease in both α and γ solid solutions. This is a remarkable difference between their cases and ours. In our preliminary experiment the same phenomena was observed with the two samples containing 42% Ni and containing 58% Ni respectively, which is shown in Fig. 2 (C, D). In this figure the intensity curves are taken with

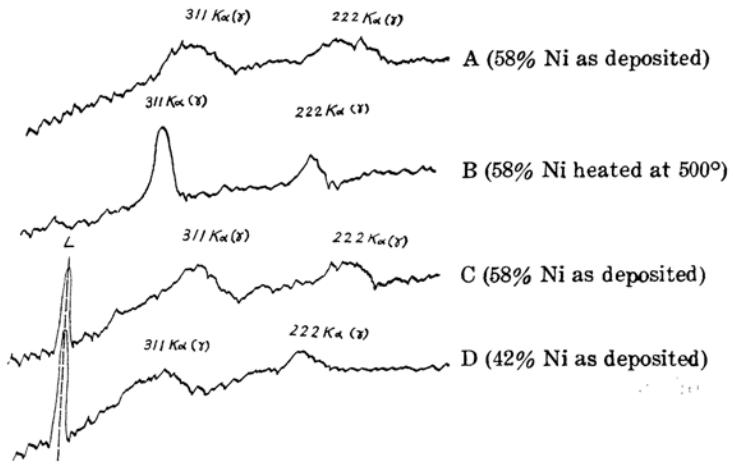

Fig. 2.

the spectral lines corresponding to the two kinds of samples above mentioned, taken on the same film. L means a line marked on the film for taking the intensity curve.

2. **Diffusion of Spectral Lines of Electrolytic Alloys.** It is observed that though lattice of electrolytic iron and nickel expand owing to the hydrogen, their spectral lines are not diffused so much. But in the case of Fe-Ni alloys deposited they are diffused remarkably, which seems to be due to the smallness, internal stress, and inequality of the composition etc.[1] Fig. 2 (A, B) represents the intensity curves of such lines as examples photographed by Seemann-Bohlin method. In the figure A corresponds to the sample No. 8 as electrolyzed while B corresponds to the same sample heated at 500°C. for 5 hours. As seen in the figure spectral line of B is

(1) R. Brill, *Z. Metalk.*, **75** (1930), 217.

remarkably sharper than that of A. The diffusion of the spectral lines of electrolytic alloys is also seen in Fig. 2 (C, D.).

3. Coexistence of α and γ Phases in a Wide Range. As seen in Fig. 1 the range in which α and γ solid solutions of usual alloy coexist lies between 25 and 33% of Ni, but in the electrolytic alloy this ranges from 14% to 58% of Ni. This is a second difference between the two kinds of alloys one of them deposited electrolytically and others solidified from the melt throwing a certain clue to the interpretation of the mechanism of deposition of the two metal ions.

4. Mechamism of Deposition of the Alloy. From the results of experiment explained above it may be concluded that the mechanism (2) that is, the deposition of two kinds of ions takes place at the position corresponding to their solid solution can not be supported in the case of iron and nickel deposited from sulphate solution. The results of our experiment can satisfactorily be explained by assuming that principally the mechanism (1) governs the deposition and in some cases may the mechanism (3) will also play some part, i.e. ions possibly be compelled to discharge without chance to choose the definite position. By these mechanism the results of experiment are satisfactorily explained as follows, taking the α solid solution for example. Though Fe and Ni crystallize individually, when the concentration of nickel in the deposit is small, the number of nickel atoms contained in the single nickel crystal is small, so that the diffusion of this nickel crystal into the surrounding iron crystal after the deposition can easily take place making α solid solution.

When the concentration of nickel in the deposit increases, number of atoms of nickel in single crystal and the concentration of such crystal in the deposit also increases, so the concentration of nickel in the α solid solution formed by the diffusion of nickel atoms may increase and the lattice constant increases as a result. At the same time it becomes more and more difficult to diffuse all of the Ni crystal as the latter becomes large, and thus some of nickel atoms remain undiffused. In the next step as the concentration of nickel increases, this undiffused nickel crystals may become large. Into these crystals iron atoms will be mixed by the mechanism (3). Thus γ solid solution forms.

When the concentration of nickel increases again diffusion of nickel atom into the lattice of iron decreases on the contrary, but the crystal of nickel undiffused increases, and the concentration of nickel in the body centred cubic lattice decreases. At the same time, the concentration of iron in γ solid solution increases, and the lattice constant of it also increases.

Thus lattice constant-concentration curve has maxima and the heterogeneous region of α and γ solid solution appears to be very wide having no connection with the diagram of the alloy formed from melt. And thus that one of the causes of the enormous diffusion of spectral lines of these electrolytic alloy is based upon the inhomogeneity of concentration in the solid solution seems to be possible when such a mechanism is considered.

In conclusion present writers express their hearty thanks to Dr. S. Sekito and Mr. Z. Nishiyama who kindly photographed X-ray spectral lines.

Summary.

1. Iron and nickel were co-deposited from their acidic mixed sulphate solution, and the diffraction patterns were photographed by various samples containing from 0 to 100% of nickel.

2. α and γ solid solution were observed in each sample and neither pure iron nor nickel could be found.

3. The heterogeneous region of α and γ was enormously wide compared with the alloy formed from the melt.

4. The lattice constant-concentration curve has maxima in α and γ solid solution.

5. The spectral lines of the solid solution was remarkably diffused. From these results it has been concluded that these two metals principally discharge at the position of each individual crystal lattice and in some cases discharge having no chance to choose such positions may occur, but they don't discharge at the position of the crystal lattice of solid solution of these two metals in the case experimented.

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