Studies on the Diffusion of Metals in the Solid State, Part II

By

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Abstract

The diffusion phenomena of various metals were studied at several temperatures by observing the change in the electrical resistance of metal foils which were made by alternate electro-plating. It was concluded that the phenomena with metals which form the solid solution in all proportions not only show a similar appearance but also have nearly equal values of D, which is about 10^{-9} cm^2/day at 500°C. The phenomena, however, occur in a quite different manner when the component metals do not form the solid solution.

Method of Experiment

The object of this investigation was to study the diffusion of metals in the solid state by measuring the change in the electrical resistance of strips consisting of many thin layers of two kinds of metals. The foils were made by the electro-plating of the one metal on the other, or alternately, upon wax covered with graphite, and after a suitable thickness was obtained, the foils were peeled off. Many strips of nearly 1 mm. in breadth and 15 cm. in length were cut off from them and the electrical resistance between 13.3 cm. was measured at various temperatures as in the previous experiment.[1] The electro-plating solutions had the following compositions:

100 c.c. of water containing

for silver, 1.7 gms. of silver nitrate and 0.8 gms. of potassium cyanide,

for gold, 0.17 gms. of gold chloride and 0.75 gms. of potassium cyanide,

1. S. Tanaka and C. Matano; Kyoto Coll. Sci. Mem., Vol. XIII (1930) p. 343.

for copper, 2.6 gms. of copper sulphate, 4.4 gms. of caustic soda and 13.0 gms. of Rochelle salt, and

for nickel, 5.2 gms. of nickel ammonium sulphate and 2.6 gms. of ammonium chloride, (1)

or 2.9 gms. of nickel ammonium sulphate and 1.4 gms. of boric acid. (2)

The various data of the foils are summarized in Table I.

Table I

Material	Foil	Electro-plating solution	Current density m.a./cm².	Time of each plating, min.	Number of layers	Total thickness, cm. × 10^{-3}
Ag-Au	I	Ag	3.3	10	8	2.5
		Au	1.2	30	7	
Au-Cu	II	Au	0.75	3	36	2.0
		Cu	2.15	5	37	
	III	Au	2.0	1	90	1.7
		Cu	4.0	1	90	
Cu-Ni	IV	Cu	3.7	3	50	3.4
		Ni (1)	4.5	1	50	
	V	Cu	3.7	1/2	150	3.0
		Ni (1)	5.5	1/3	150	
Ag-Ni	VI	Ag	3.5	20	6	4.6
		Ni (1)	4.5	20	6	
	VII	Ag	3.7	1	75	5.1
		Ni (1)	4.5	1	75	
	VIII	Ag	3.7	1	75	3.0
		Ni (2)	4.5	1	75	
Ag-Cu	IX	Ag	3.8	1/2	100	4.2
		Cu	3.8	5/6	100	

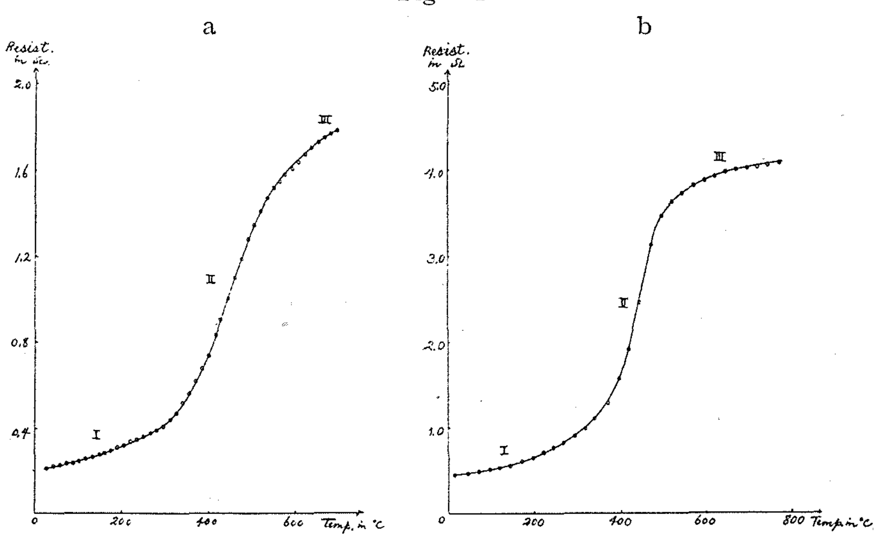
Results of Experiments

The first experiment: The samples were examined by taking X-ray photographs of them before and after heating, and the formation of the alloy confirmed. The Debye-Scherrer camera of a Müller spectrograph was used and the X-rays were obtained from a Shearer metal tube with copper anticathode excited by a transformer; about 40—50 K.V. and 3—4 m.a. output. The exposure was about 5 hours. The photographs obtained from Foil IV are reproduced in Fig. I, Plate I, for illustration, Ia being the one taken before heating, and Ib that after heating. (In the case of Foil I the examination was not carried out, since the lattice constants of gold and silver are nearly the same.) The distributions of the spectral lines clearly show the formation of an alloy on heating the sample.

In the case of Foil IX scarcely any difference was observed between the photographs taken before and after heating.

The second experiment: The electrical resistances of all the samples were measured by raising the temperature at a suitable rate in order to study the relation between the diffusion and temperature. The

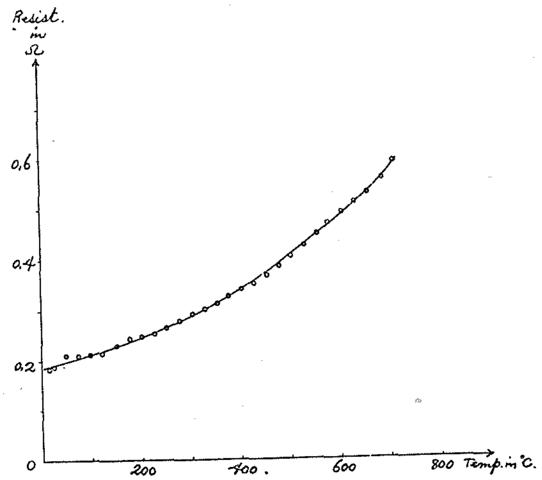
Fig. 2



curves in Fig. 2 showed the results given by the samples (mass of 32.5 mgms. or 15.7 mgms.) which were obtained from Foils I and IV. In the former case the temperature was raised 3 degrees per minute and in the latter 5 degrees per minute. There are three stages I, II and III as in the case of the Au-Cu system of the previous experiments[1] and they can be explained in the same way, i. e. the first stage indicated the temperature effect on the pure metals, the second stage the effect of temperature and diffusion, and the third stage the effect of temperature on the alloy. These systems always form the solid solution and all the samples showed the same nature.

Next a quite different form in the change of the electrical resistance was observed when the samples obtained from Foils VII, VIII and IX were examined. In these cases there could not be found any rapid change in the resistance. The result of the sample (mass of 30.0 mgms.) obtained from Foil IX is, for instance, represented by the curve shown in Fig. 3, from which the general features will be recognized. These systems do not form the solid solution with all portions of the component metals, and this seems to be the cause of the above difference.

Fig. 3

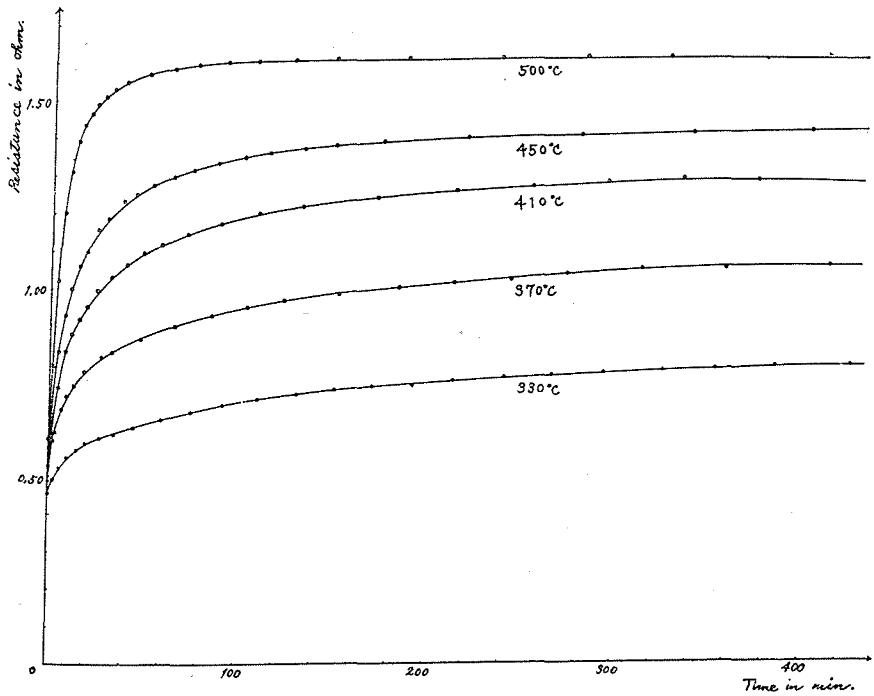


The third experiment: The change in the electrical resistance at various constant temperatures was observed in order to study how the diffusion is related to time. The results for samples (mass of 30.0 mgms.) obtained from Foil I and samples (mass of 15.0 mgms.) from Foil IV are shown by the curves in Fig. 4a and Fig. 4b respectively.

1. S. Tanaka and C. Matano. loc. cit.

There will also be found a similarity with the case of the Au-Cu system in the previous experiment.

Fig. 4 a



When, however, samples obtained from Foils VI, VII and IX are taken, the results seem to be somewhat different from the above ones. In the case of the Ag-Ni system no change in the electrical resistance due to diffusion could be observed, as is shown in Fig. V, which was given by the samples (mass of 30.0 mgms.) from the Foil VI. This difference must be due to the mechanism of making the alloy or to diffusion, and further investigation will be needed for these points.

Determination of Diffusion-Coefficient

The coefficient of diffusion for the Ag-Au system given by Fick's law has already been determined at 500°C by these authors.[2] A similar

2. Phys. Math. Soc. Japan. Proc., Vol. 12, (1930) p. 279.

Fig. 4 b

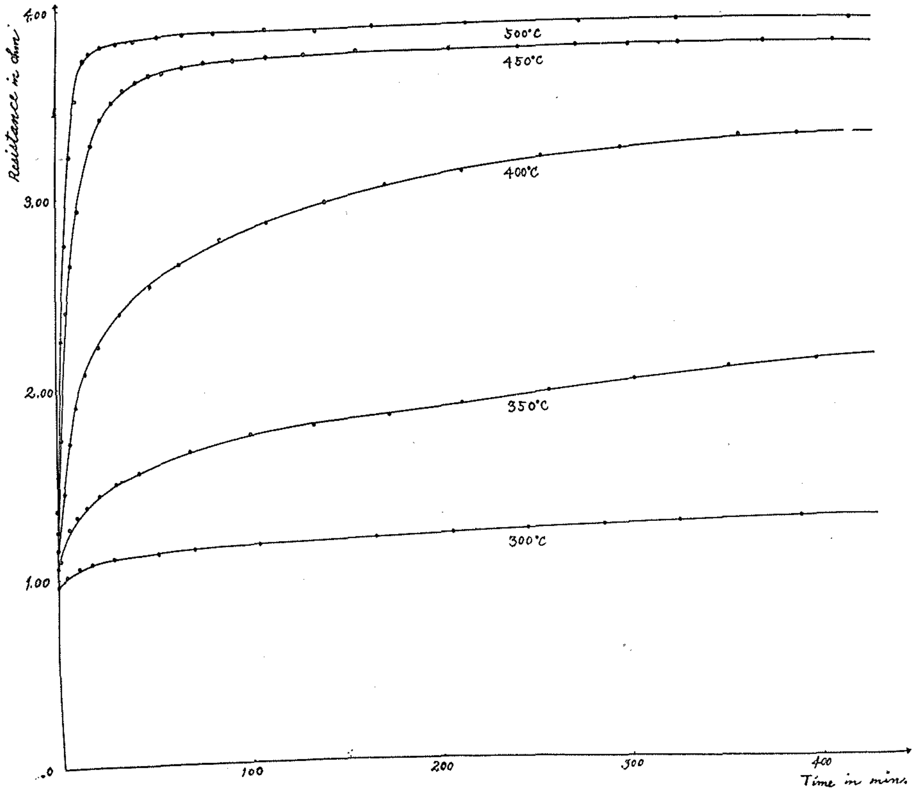
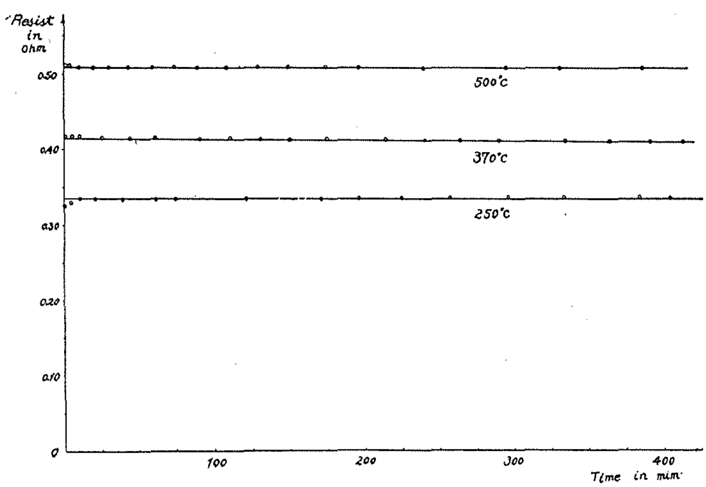

Resistance in ohm
4.00
3.00
2.00
1.00
0
500°C
450°C
400°C
350°C
300°C
100
200
300
400
Time in mins.

Fig. 5

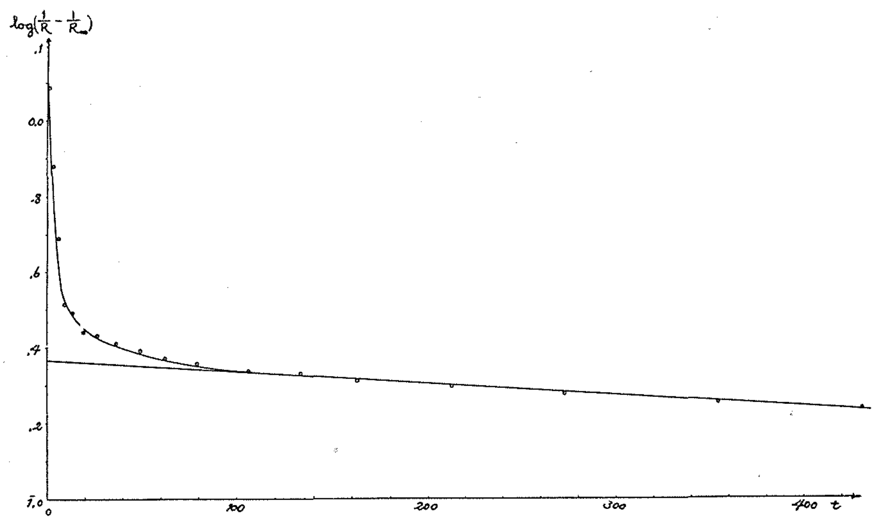

Resist in ohm
0.50
0.40
0.30
0.20
0.10
0
500°C
370°C
250°C
100
200
300
400
Time in min.

consideration was utilised to determine those of the Au-Cu and Cu-Ni systems. In the third experiment, in the above section, let the resistance at time t be R and that at $t \rightarrow \infty$ (in practice, it is sufficient if we take t sufficiently great) R_∞, then there exists the following relation in the proper range of time,

$$\log(1/R - 1/R_\infty) = \text{const.} - 2D(\pi/d)^2 \log e \cdot t,$$ [1]

where D is the coefficient of diffusion, d the mean thickness of each layer, π the modulus of circumference, e the base of natural logarithms, and consequently $2\pi^2 \log e = 8.56$. The above equation shows a straight line and D can be determined from its slope.

Fig. 6



The authors show, as an example, the curve for the sample (mass of 16.5 mgms.) from Foil IV in Fig. 6, from which D can be obtained at once.

The values of D for other samples were determined at 500°C in this way and are tabulated in Table II.

1. The factor 2 in this expression must be multiplied because the value of E_1 is generally equal to zero and E_2 is not zero in the expression $K = \Sigma E_n e^{-n\beta t}$ of the previous paper cited in (2).

Table II

Material	Foil	Thickness of each layer d, cm.	Coefficient of diffusion D, cm^2./min.	D mean cm^2./min.
Au-Cu	II	2.8×10^{-5}	1.0×10^{-12}	0.6×10^{-12}
	III	9.5×10^{-6}	0.3×10^{-12}	
Cu-Ni	IV	3.4×10^{-5}	0.4×10^{-12}	0.7×10^{-12}
	V	1.0×10^{-6}	1.0×10^{-12}	

Since the value of D for the Au-Ag system which was obtained in the previous experiment is about $0.8 \times 10^{-12} cm^2$./min., the conclusion seems to be that all the coefficients of diffusion have nearly equal values for metals which make the solid solution in all proportions.

In conclusion the authers wish to express their sincere thanks to Prof. U. Yoshida for his cordial advice and to Mr. S. Hirose for his kind assistance in this work.

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December 25, 1930.

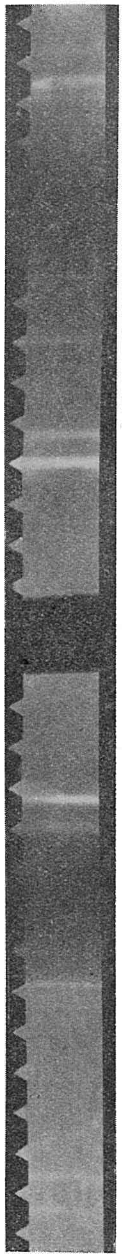

Fig. 1 a

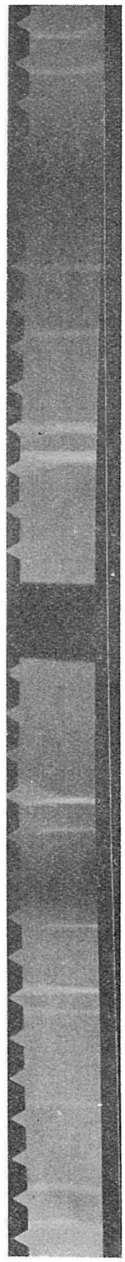

Fig. 1 b