

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

By

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Abstract

The diffusion between gold and copper in the solid state was studied by using foils composed of many layers of the two metals, made by alternate electro-plating. The change in the electrical resistance caused by diffusion on heating a sample in a vacuum furnace was measured and the formation of an alloy was confirmed by X-ray analysis. It was first ascertained that there did not exist any portion of the alloy in the transition layers between the electro-deposited metals at the room temperature. The diffusion takes place very slowly at 140°C and becomes very strong at temperatures of over 250°C. The increase in the resistance caused by the diffusion at a certain constant temperature is expressed by the formula $R = Ae^{-\frac{\alpha}{t}}$, and the velocity with which the alloy layers will expand from the contact planes of each metal is expressed by the formula.

$$v = \frac{L}{lN(b-a)} \frac{A\alpha e^{-\frac{\alpha}{t}} t^{-2}}{(R_0 + Ae^{-\frac{\alpha}{t}})^2}$$

Introduction

It is a well-known fact that when two metals are in contact with each other, the atoms move away from one to the other when their temperature is raised, and diffusion will occur. This problem, however, has been very little investigated, and little seems to be known about it. The main object of the present investigation was to study how the phenomena are connected with temperature and time.

The electrical resistance of an alloy is generally greater than that of the component metals, consequently if two metals in contact with each other diffuse from one to the other, the electrical resistance will

increase owing to the formation of an alloy. In the present experiment this change in the resistance was observed by the method described in the next paragraph and the formation of the alloy was ascertained by X-ray analysis.

The metals now examined are gold and copper owing to the following advantages; 1) the crystal forms are both face-centered cubic, the lattice constants of which differ very much, 2) the equilibrium diagram of this binary system is very simple and the physical properties and the lattice constant of this whole system have been thoroughly observed by many authors, 3) electro-plating with these metals is very easy and samples can be made without any difficulty, as is shown in the next paragraph, 4) the melting points are equally high and no considerable diffusion occurs at the room temperature.

Method of Experiment

Production of Samples: Many thin foils of the metals piled up on each other or a compressed mixture of the powdered metals should be used to increase the effects of diffusion, but the results will be much affected by the pressure. To avoid this defect the authors made foils composed of many layers of the two metals by alternate electro-plating. Gold was first plated on the surface of wax specially prepared and covered uniformly with graphite, and then copper and gold were plated alternately until a suitable thickness was obtained. The plating always ended with gold and the foil could be easily taken off. The electro-plating solutions had the following compositions:

for gold, 600 c.c. of water containing 1 gm. of gold chloride,
and 4.5 gms. of potassium cyanide,

for copper, 600 c.c. of water containing 30 gms. of potassium
hydroxide, 18 gms. of copper sulphate and 90 gms.
of Rochelle salt.

Apparatus and method of measurement: A small strip 1 mm. in breadth, and 15 cms. in length was cut off from the foil and the resistance was measured by the null method with a Wheatstone bridge made by Hartmann & Brawn. The strip was supported by a device which was designed to avert many ill effects and which is represented diagrammatically in Fig. 1. A and B are blocks of copper having a knife-edge N, and become the terminals when the measurement is being made. A is inserted and fixed to C which is insulated from

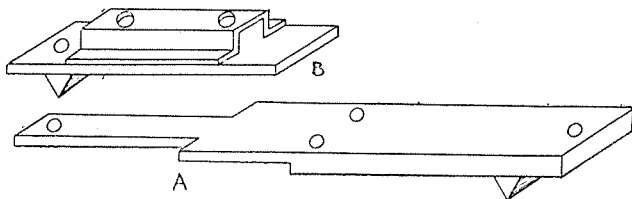
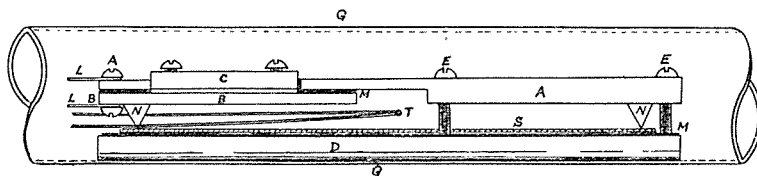


Fig. 1



B with mica plates M. The sample S is laid on the mica plate M which is placed on the thick copper plate D. The terminals A and B touch the sample S with the knife edges N by their own pressure, and the resistance of the sample between these knife edges is measured. The whole device is put inside the glass tube G. The screw-pins E serve only to prevent the terminals on the base plate D from slipping when it is inserted into the glass tube. L L represent the lead wires and T one junction of the thermo-couple with which the temperature is observed by a pyrometer. The glass tube is placed horizontally in an electrical resistance furnace and evacuated by a Cenco hyvac pump during the whole time of measurement.

By using the above apparatus the ill effects which must be averted are minimized, viz. 1) uniformity of the temperature in the sample is obtained by the good conductivity of copper, 2) small fluctuations in temperature are averted by the comparatively large mass of the apparatus, 3) change in the resistance at the contact position is minimized by the constant pressure of the knife edges, 4) the sample is protected from oxidation by the good evacuation. Moreover, two readings were taken for each observation by changing the direction of the current in order to eliminate the effect of thermoelectricity. (In fact this effect was nearly negligible).

The resistance of the lead wires and the terminals was first measured and it was found that it is not very great compared with that of the sample. The heating current in the electric furnace was supplied from secondary batteries when constant temperature was needed.

Results of Experiments

The first experiment: The first question to settle is whether there is any alloy in the transition layers of the electro-deposited metals. X-ray powder photographs were taken with many samples prepared by the method above described. The total number of layers in every sample was between 20 and 300 and the thickness of each layer calculated from the data of the electro-plating was between 10^{-4} and 10^{-7} cms. All the photographs gave the superposition of gold and copper lines similar to that reproduced in Fig. 6. The only difference is the diffuseness of the lines due to the thinness of each layer. The X-rays were obtained from a Shearer metal tube with copper anti-cathode excited by a transformer; about 40—50 K.V., and 3—4 m.a. output. The Debye-Scherrer camera of a Müller X-ray spectrograph with a slit instead of a pin-hole was employed and the time of exposure was about 5 hours. It will be clearly concluded that there does not exist any portion of alloy in the transition layers between these electro-deposited metals. From the above results, the samples can be used in studying the phenomena of diffusion without any trouble.

The second experiment: The object of this experiment was to study the relation between the diffusion and temperature. The samples examined in this and the next experiment were obtained from the same foil prepared as described below. The currents and the times of every plating were 115 m.a. and 5 minutes for copper, and 40 m.a. and 3 minutes for gold. The total number of layers was 73 and the thickness of the foil 0.002 cm.

A strip 15 cms. in length and 0.14 cm. in breadth was cut off from this foil, the weight of which was 22.2 mgms. The distance between the two knife edges was 13.5 cms. and the total resistance including that of the lead wire was 0.35 ohms at the room temperature while that of the sample alone was 0.269 ohms. The temperature was raised 3 or 4 degrees a minute and the resistance was observed every 5 minutes. The results are represented by the curve in Fig. 2 and can be divided into three stages I, II and III. In the first stage, the increase in the resistance is mainly caused by the effect of the temperature upon the resistance of the pure metals. In the second stage, the increase in the resistance is caused by the superposition of the temperature effect and the formation of the alloy. In the last stage, the increase in the resistance is mainly caused by the temperature

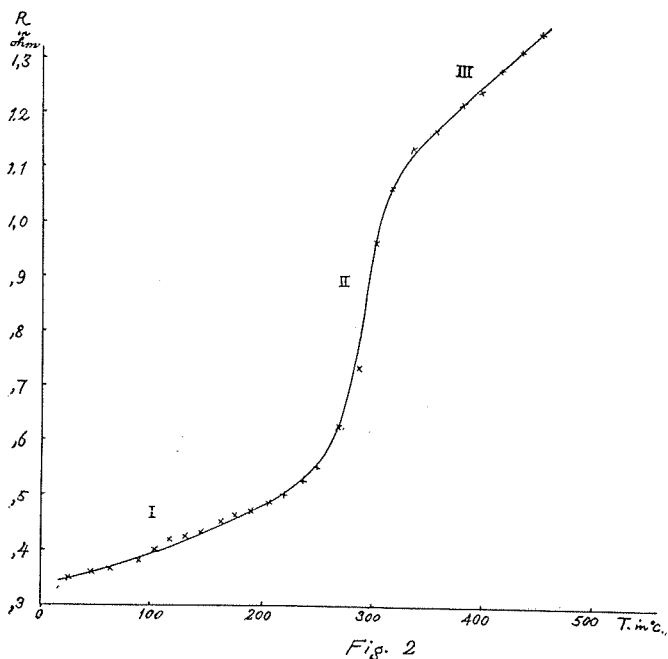


Fig. 2

effect of the alloy. The first stage continues until about 230°C and the third stage begins about 400°C as is seen in the curve. Vigorous diffusion, however, occurs at a temperature of from 250°C to 350°C. The results agreed perfectly with those obtained in the next experiment. In spite of the fact that the temperature coefficient of the solid solution is smaller than that of the pure metals, the inclination of the curve in stage III is greater than that in stage I. This indicates that considerable diffusion still occurs in the third stage and this point was actually confirmed with the sample after long heating.

The final resistance was also measured at the room temperature and the value of 1.06 ohms was obtained as the total resistance and 1.00 ohm as that of the sample alone. Moreover X-ray powder photographs were taken with the sample in the initial and the final state, and are reproduced in Fig. 6 and Fig. 7. Fig. 6 shows merely the superposition of lines corresponding to the two metals and Fig. 7 shows those of the solid solution. This is a good confirmation for the above conclusions.

The third experiment: It is interesting to study how the diffusion is related to the time at a certain definite temperature, because in this case the effect of temperature will be eliminated. Several strips were

cut off from the same foil as was used in the former experiment. The length and the thickness of all strips were 15 cms. and 0.002 cm. respectively and the distance of the knife edges was always 13.5 cms. The breadths, however, differed more or less. The furnace was heated to the required temperature before the sample was placed in it, and consequently it reached the constant temperature in a few minutes. The temperature was then kept constant by the supply of the heating current from the secondary batteries. The resistances were measured at a certain interval and those of the initial and the final state were always measured at the room temperature.

The sample A of mass 14.5 mgms. was first examined at the temperature of 480°C ; the resistance increased rapidly and reached the maximum point in several minutes after the constant temperature was obtained. The initial and the final resistance at the room temperature were 0.394 and 1.40 ohms. The sample B of mass 15 mgms. was next examined at the temperature of 140°C . The increase in the resistance was constant but very slow, and accordingly the temperature was raised to 200°C after several hours. The increase in the resistance was still slow though it became somewhat greater.

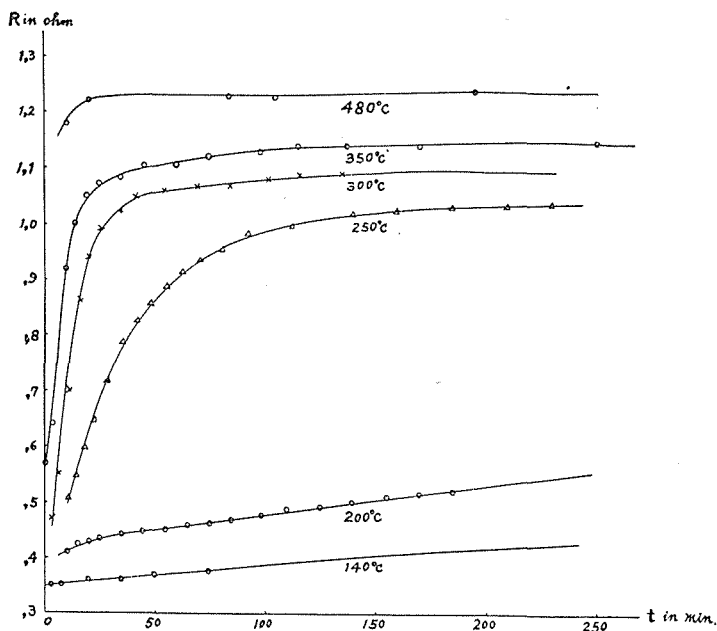


Fig. 3

After measurements had been made in a few hours, the sample was cooled to the room temperature and the resistance was again measured and then the temperature was raised to 350°C. The resistance now increased rapidly and soon arrived at the saturation value. The initial and the final resistance of this sample were 0.384 and 1.41 ohms. The samples C and D were then examined at 300°C and 250°C. The increase in the resistance was this time moderate. The mass of the samples was 22.5 mgms. and 17.0 mgms, the initial resistances 0.264 ohms. and 0.344 ohms, and the final resistances 0.81 ohms and 1.03 ohms.

All the results are represented by the curves in Fig. 3, in which the observed values of the resistances are reduced to those that would be obtained if all the specimens had the same mass as specimen C. The reduction is made on the consideration that the product of the resistance and the mass is constant at a certain temperature and represented by the formula $RM = LI' \delta \rho$, where L is the total length of the specimen, L' the distance between the knife edges, δ the density and ρ the specific resistance. There is some interval of time until the specimen acquires the constant temperature and the diffusion occurs in this interval. The determination of the origin of the time is naturally somewhat uncertain.

The formation of the alloy was also tested by X-ray analysis and photographs similar to those in Fig. 6 and Fig. 7 were obtained.

It is to be noted that the ratios of the initial and final resistances for A, B, C and D are 3.6, 3.7, 3.1 and 3.0 respectively. The smallness for C and D is probably caused by some imperfection in the diffusion.

Discussion of Results

The third experiment shows that the diffusion takes place very slowly at 140°C and becomes very strong at temperatures of over 250°C. One of the writers and G. Shinoda obtained 125°C as the initial temperature of the diffusion between these metals. This gives good coincidence with the result of the present experiment. The authors tried to find the mathematical expression for the diffusion at

constant temperature. It is very difficult to know the initial resistance, because the determination of the time at which the constant temperature is just obtained is quite difficult. These resistances for the samples C and D were taken as 0.53 ohms and 0.51 ohms respectively, and, the increase in the resistance from these values being denoted by R , the relation between $t \log_{10} R$ and t is shown in Fig. 4. where the units of R and t are $\text{ohm} \times 10^{-2}$ and 1 minute. (for sample D the reduced values of the resistances were used as in Fig. 3). As these are fine straight lines, the following expression will be obtained,

$$t \log_e R = t \log_e A - \alpha$$

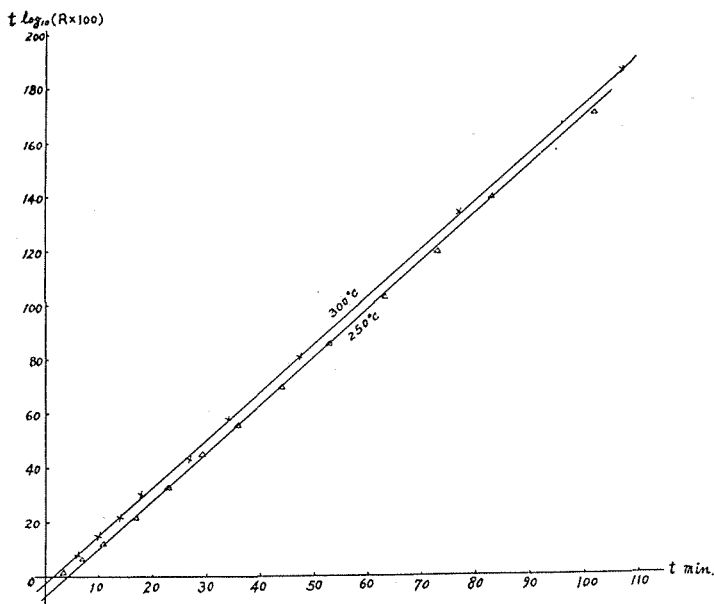


Fig. 4

and the constants A and α can be determined as 0.575 and 13.8 for the sample C, and 0.575 and 4.6 for the sample D. And then

$$R = Ae^{-\frac{\alpha}{t}}$$

When $t=0$ or $t=\infty$, $R=0$ or $R=A$ respectively, and the comparison of the calculated and the observed values is given in Fig. 5. The coincidence seems to be sufficient.

Next, we shall find the velocity with which the layers of alloy will expand from the contact planes of each metal. As the mechanism of the formation of an alloy by diffusion is naturally rather complex,

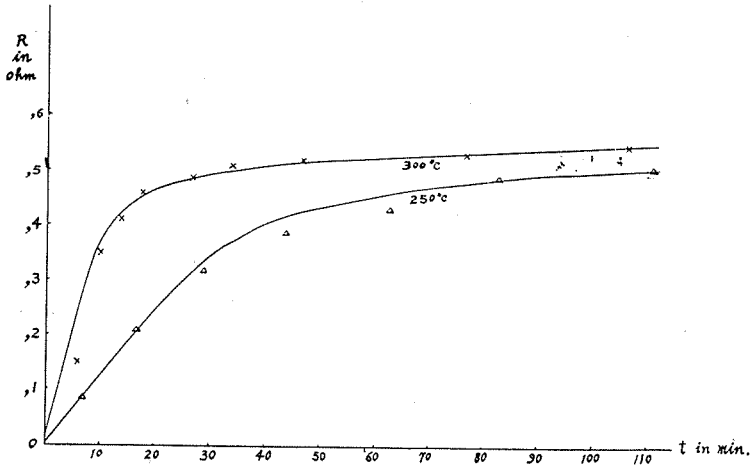


Fig. 5

the following calculation will give only a rough idea. Let the conductivity of the alloy be a , that of the pure metals b , the velocity above mentioned v , and the length and the breadth of the sample L and l , and then the decrease in the total conductivity $-\delta K$ in the small time δt will be given by the formula,

$$-\delta K = N(b-a)\frac{l}{L}v\delta t,$$

where N is the total number of the layers. (In the present experiment $N=73$ $L=13.5$),

therefore,

$$v = -\frac{L}{lN} \frac{1}{b-a} \frac{dK}{dt}$$

but $K = \frac{l}{R}$ and $R = R_0 + Ae^{-\frac{\alpha}{\tau}t}$, where R_0 is the initial resistance,

and thus

$$v = \frac{L}{lN(b-a)} \frac{Aae^{-\frac{\alpha}{\tau}t}}{(R_0 + Ae^{-\frac{\alpha}{\tau}t})^2}$$

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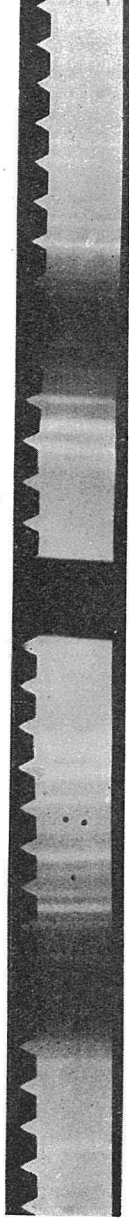


Fig. 6

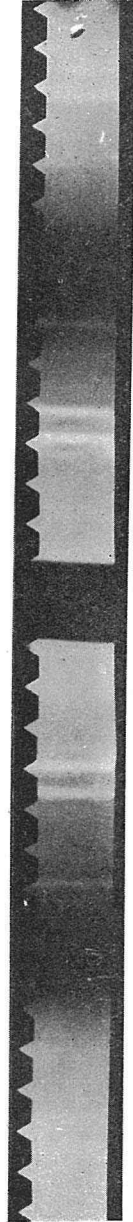


Fig. 7