



TITLE:

The Thickness of Silver Chloride Film Produced on the Surface of Silver Plate

AUTHOR(S):

Shimadzu, Shinichi

CITATION:

Shimadzu, Shinichi. The Thickness of Silver Chloride Film Produced on the Surface of Silver Plate. *Memoirs of the College of Science, Kyoto Imperial University*. Series A 1936, 19(5): 229-236

ISSUE DATE:

1936-09-30

URL:

<http://hdl.handle.net/2433/257153>

RIGHT:

The Thickness of Silver Chloride Film Produced on the Surface of Silver Plate

By Shin'ichi Shimadzu

(Received Sept. 18, 1936)

Abstract

A powder X-ray photograph taken of a silver plate coated with silver chloride film which is produced by dipping the plate into chlorine water, contains Debye-Scherrer rings of silver and silver chloride. The thickness of the film can be measured by comparing the intensities of the rings of both substances. The present experiment was made to learn how the thickness changes with the concentration of the chlorine water, its temperature, and the duration of the time of dipping the plate.

(1) Measurement of the thickness of silver chloride film

In the present experiment the writer used the same method as in the case of the contamination on the surface of lead plate, which results have already been published.¹ The intensity of the X-rays reflected by a thin sample of x cms. thickness is given by the equation

$$I_1 = KI_0 F^2 \lambda^3 \frac{N^2}{\mu} j \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \left(1 - e^{-2\mu x \frac{1}{\sin \theta}} \right) \quad (1)$$

when its surface makes an angle θ with the incident beam. Here λ is the wave length of the X-rays, K a constant, I_0 the intensity of the primary X-rays, N the number of the unit cells in a unit volume, μ the absorption coefficient of the sample for the X-rays, j the number of the like faces of the crystal which contribute to a single reflection, θ the glancing angle which satisfies Bragg's equation, and F is the structure amplitude. The value of F for silver and silver chloride are given as follows when the indices of the atomic plane are (hkl) :

Ag: h, k, l are all even or all odd	$F = 4\overline{Ag}$
the other cases	$F = 0$
AgCl: h, k, l are all even	$F = 4(\overline{Ag} + \overline{Cl})$
h, k, l are all odd	$F = 4(\overline{Ag} - \overline{Cl})$
the other cases	$F = 0$

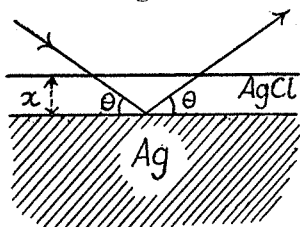
\overline{Ag} and \overline{Cl} indicate the scattering powers of silver and chlorine atoms respectively.

1. These Memoirs, 17, 79 (1934)

When the thickness x tends to infinity, expression (1) becomes identical with that of an ordinary powder photograph, that is

$$I = KI_0 F^2 \lambda^3 \frac{N^2}{\mu} j \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}. \quad (2)$$

Fig. 1



If we apply expression (2) to the case of silver plate, I gives the intensity of X-rays reflected by the silver plate when there is no film on its surface. When there is a silver chloride film on the surface of the plate and the thickness of the film which X-rays have to pass through is $2x/\sin\theta$ as shown in Fig. 1, then the

intensity of X-rays reflected by the silver plate is given by

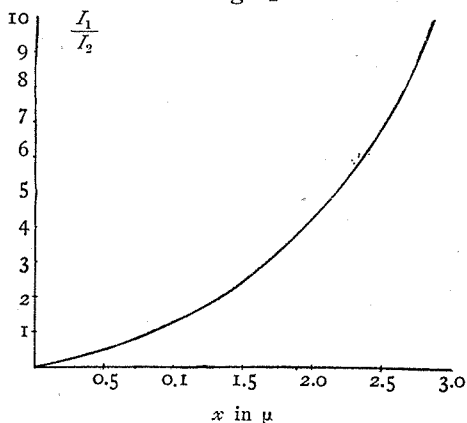
$$I_2 = I e^{-2\mu x \frac{1}{\sin\theta}} \\ = KI_0 F^2 \lambda^3 \frac{N^2}{\mu} j \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} e^{-2\mu x \frac{1}{\sin\theta}}. \quad (3)$$

If we apply expression (1) to an atomic plane of silver chloride and expression (3) to an atomic plane of silver plate for the same value of x , then I_1 and I_2 give respectively the intensities of X-rays reflected by these atomic planes of the silver chloride film and of the silver plate. Therefore if we find the ratio of these intensities, we can ascertain the value of the thickness of the silver chloride layer.

The writer chose the atomic planes (200) for silver and (220) for silver chloride respectively, because the X-rays reflected by these planes were very intense and their spectral lines were situated close to each other. The ratio I_1/I_2 for various values of x is calculated with the expressions (1) and (3) by giving known values for the constants.

The relation between I_1/I_2 and x is plotted in the curve shown in Fig. 2. By means of this curve the value of x is obtained when the value of I_1/I_2 is found experimentally. This value of I_1/I_2 was obtained in the

Fig. 2



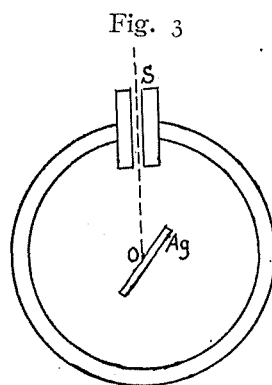
present experiment by measuring the relative intensities of the spectral lines on the photographic film with a standard optical wedge.

(2) Experiment

The camera employed in the present experiment was cylindrical in shape as shown in Fig. 3, and a photographic film was laid along its inner surface. In the figure, S is the slit, Ag the sample of silver plate and O is the position of the axis of the cylinder. The silver plate was so placed that its surface which was to be examined occupied exactly the position of the axis of the cylinder; and the thickness of the chloride layer through which the X-rays reflected by the atomic plane (200) of silver had to pass was just $2x/\sin\theta$ as shown in Fig. 1. The X-rays used in the present experiment were *K* radiations starting from an iron target.

To prepare the samples the writer dipped the silver plates into a three litre flask of chlorine water, the neck of which was narrow and long. The flask was filled with chlorine water up to its neck; thus by making the contacting surface of the chlorine water and air very small, the escaping of the chlorine gas and consequently the change of its concentration was greatly minimized. The temperature of the chlorine water was kept constant by immersing the flask in a water bath of large volume.

As soon as the silver plate was coated with a thin silver chloride film, its surface became violet coloured instead of white, which colour is peculiar to silver chloride. This was probably due to the separation of metallic silver from silver chloride upon exposure to light. In order to estimate the influence of the presence of such metallic silver, the writer examined by *K* radiations of iron a free thin film of the silver chloride which was obtained from the surface of a silver anode, on which it was formed by electrolysis in a hydrochloric acid solution. In spite of the separation of the metallic silver on both sides of the film in this case by the action of light, there were no rings of silver in the photograph. Thus it may be concluded that the quantity of silver separated by light is so small that it has no influence upon the measurement of the thickness of the film.



The values of the thickness gained by the above method was compared with those determined by weighing. For this purpose a silver plate of 32 mm. in length, 25 mm. in width and 0.5 mm. in thickness was weighed. Next, this plate was coated with silver chloride film by dipping it into chlorine water, and an X-ray diffraction photograph of it was taken. Lastly, it was weighed to find the weight of the chlorine combined with silver. From this weight and the chemical equation $\text{Ag}_2 + \text{Cl}_2 = 2\text{AgCl}$, the weight of silver chloride produced in this case was calculated. Moreover, by weighing the silver plate after dissolving the silver chloride in ammonia water, the weight of silver chloride was directly measured. As the values of the weight of the silver chloride obtained by these two methods closely coincided, the writer took the mean value as the value of the silver chloride. From this value, the specific gravity of silver chloride and the surface area of the silver plate, the thickness of the silver chloride film was calculated; and it was ascertained that the value of the thickness of the film thus obtained coincided well with that found by the X-ray method. This showed that the method of measuring the thickness of silver chloride film by comparing the intensities of the rings in the X-ray diffraction photograph was correct.

(3) Results

Pieces of silver plate 25 mm. long and 3 mm. wide were cut out from a large silver plate 0.5 mm. thick. These pieces were dipped into chlorine water of various temperatures and concentrations for various durations of time after their surfaces were cleaned. In the present experiment different chlorine waters, each containing 2.49 gr, 1.12 gr, 0.39 gr, 0.11 gr, and 0.06 gr of chlorine in one litre of water, were kept at the temperatures of 43°C, 25°C and 6°C. The specimens were dipped in all of these chlorine waters for various durations of time. The X-ray diffraction photographs were taken with each of these specimens. One series of such photographs are shown in Fig. 1 in Plate I, which were obtained with the samples prepared in chlorine water containing 1.12 gr of chlorine at 25°C.

By the method mentioned above the thickness of the silver chloride film was measured for each of the photographs thus obtained; and the relation between the thickness of the film and the time of the dipping of the silver plate are shown in Figs. 4a and 4b for various concentrations and temperatures of the chlorine water. The curves

drawn in these figures reveal that the rate of increase in the thickness of the silver chloride film is very rapid upon first dipping, then after a while suddenly lowers, scarcely rises for a certain interval, and at last rises again rather linearly with the time.

Judging from these curves, when the thickness of the silver chloride film attains a certain value, cracks arise here and there in the film, permitting the chlorine water to invade and touch the silver plate directly. This seems very clear from the fact that the size of the unit cell of silver chloride (cubic, lattice constant: 5.54 \AA) is larger than that of silver (cubic, lattice constant: 4.077 \AA), and that the

Fig. 4a

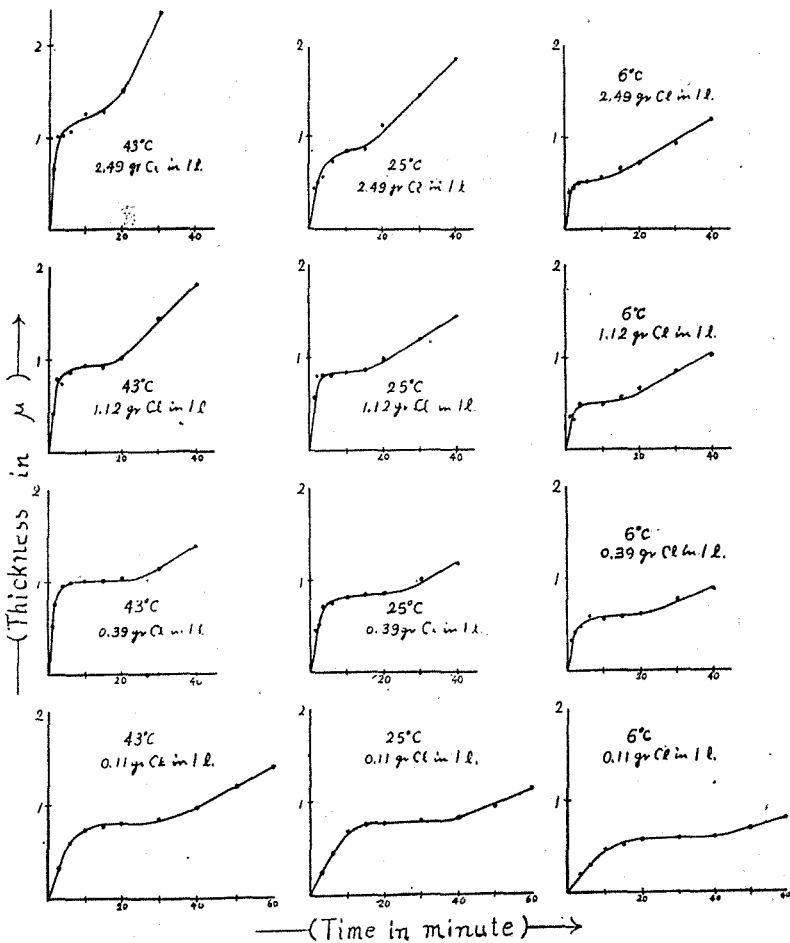
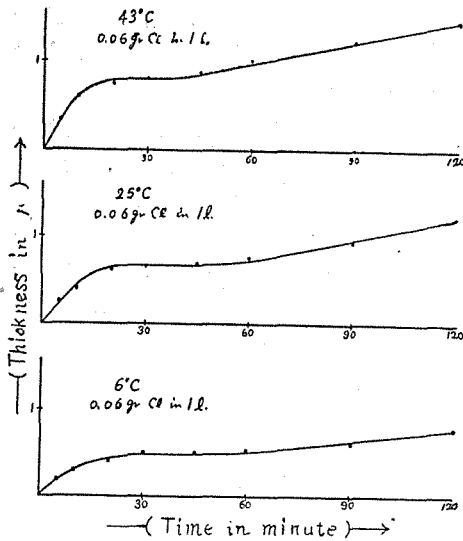


Fig. 4b



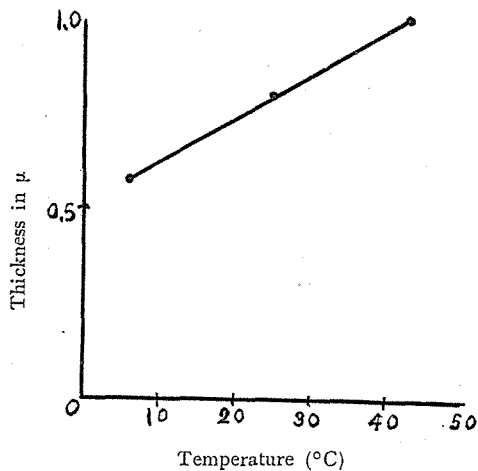
specific gravity of the former (5.56) is smaller than that of the latter (10.50).

Next, the thickness of the film at the part in the curves where it scarcely increases with the time, hardly depends upon the concentration of the chlorine water, but upon increases in the temperature, i. e., about 1μ at 43°C , 0.8μ at 25°C and 0.6μ at 6°C . This relation of the thickness with the temperature is shown in Fig. 5. In the part of the curves where the thickness increases linearly with time, the inclination of the line

showing this linear relation becomes steeper with increase of the concentration and the temperature. If the inclination of such a straight line is indicated by $\tan\alpha$, where α is the angle between the line and the abscissa, then $\tan\alpha$ increases almost linearly with the concentration for a given temperature, and also increases similarly with the temperature for a given concentration, as is shown in Figs. 6 and 7.

The writer examined the effect of the size of the crystal grains of silver upon the rate of increase in the thickness of silver chloride film. For this purpose the writer selected two silver plates consisting of crystal grains of different size: one fine-grained and the other coarse-grained. These silver plates were dipped separately in chlorine water containing 1.03 gr of

Fig. 5



chlorine in one litre at 17°C for various durations of time. The size of the crystal grains of the silver plates were examined by X-rays: the fine-grained one was revealed by continuous diffraction rings on the photograph and the coarse-grained one by an

Fig. 6

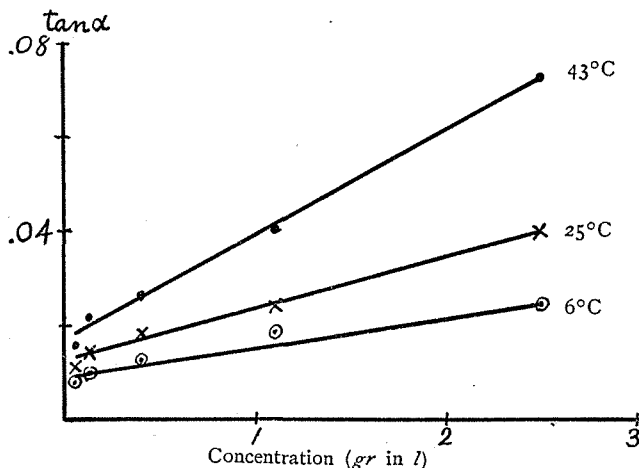
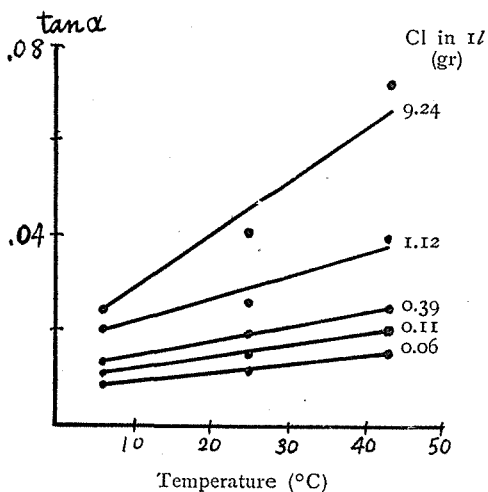


Fig. 7

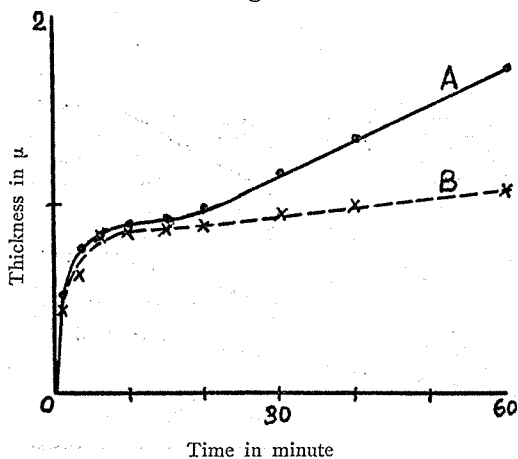


assemblage of many distinct spots as shown in Figs. 2 and 3 in Plate I. The results of the experiment on these two samples are shown in Fig. 8; where curve A corresponds to the fine-grained one and curve B to the large-grained one. The general aspect of these two curves is entirely the same as those in Figs. 4a and 4b. The two curves A and B coincide almost entirely until the state is reached where the thickness of the chloride film increases

linearly with time, but in this state the thickness of the film increases more rapidly with the fine-grained sample than with the large-grained one. This indicates that the larger the crystal grains of silver, the harder it is for the cracks to be formed in the chloride film.

As to the thickness of the chloride film formed when the silver plate is dipped in the chlorine water for a very long time, very probably

Fig. 8



gestions in preparing the samples.

it nearly attains a maximum value. But this is not clear yet, a further study on this point being now in progress.

In conclusion the writer wishes to express his sincere thanks to Prof. U. Yoshida for his kind guidance in the present research; and also to Prof. N. Sasaki of the Chemical Institute for his helpful sug-

Plate I

Fig. 1

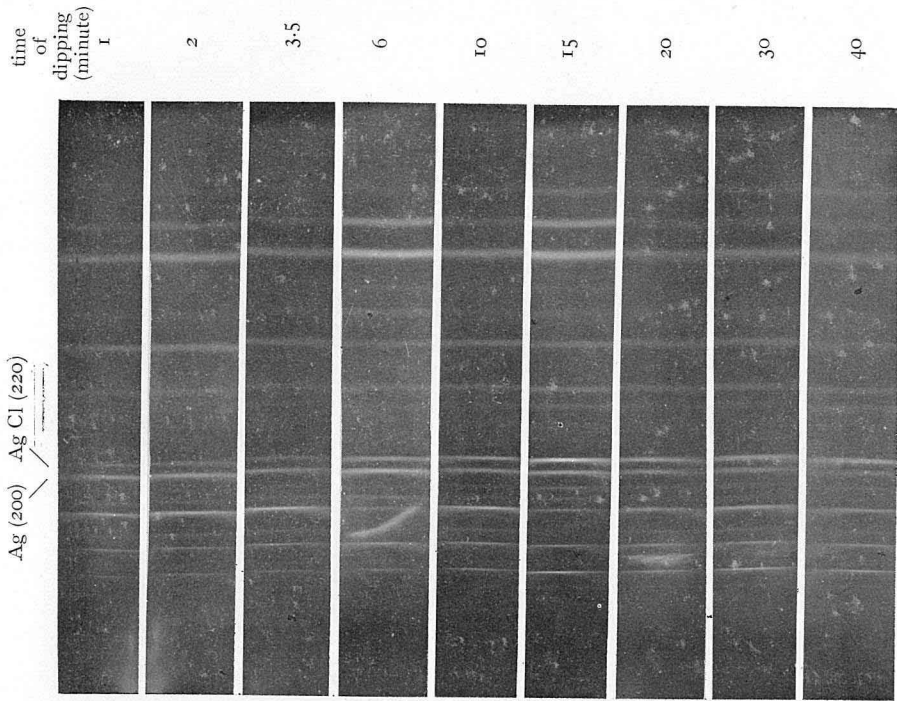


Fig. 2

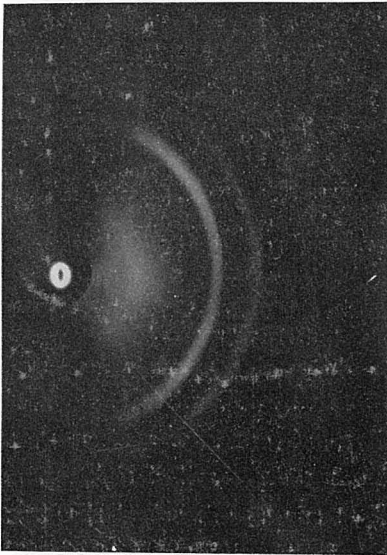


Fig. 3

