Estimation of the Thickness of the Contamination on the Surface of Metallic Lead

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By

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Abstract

Powder photographs were obtained by sending K radiations of iron to the surface of lead contaminated by oxidation, and it was found that the contamination was composed mostly of the micro-crystals of tetragonal lead oxide. By comparing the intensity of the diffraction lines due to the contamination and that of the lines of the lead underlying, the thickness of the contamination was estimated to lie between $50\mu\mu$ and $200\mu\mu$.

As the absorption coefficient of lead for soft X-rays is very large, the diffraction photograph which is obtained by the soft characteristic X-rays from the surface of lead must be due to the very thin layer on the surface. When a piece of lead is exposed for a long time in the air, its surface becomes covered with a thin layer of oxide. Thus if we can obtain Debye-Scherrer rings of lead and the oxide at the same time by sending characteristic X-rays of suitable wave length to such a contaminated lead surface, then it will be possible to estimate the thickness of the oxide layer on the surface of the lead by comparing the intensities of the rings.

The camera employed in this experiment is cylindrical in shape, as shown in Fig. 1. Its inner diameter is 8cms., and a photographic film is laid along its inner surface. In this figure, S is the slit, Pb the sample of lead plate to be examined and O is the position of the central line of the cylinder. The lead plate is so placed that the surface which is to be examined just occupies the position of the central line of the cylindrical camera. As the crystal grain of lead is considerable, the lead plate is made to rotate about the central line in an angular range of about 20 degrees by a clockwork mechanism so as to obtain well-defined continuous diffraction rings. The X-rays used in the present experiments were the K radiations starting from an iron target. The Debye-Scherrer rings obtained by this method chiefly belong to lead. This fact indicates that the oxide layer covering the surface of the lead plate is very thin. When the weak rings which do not belong to lead are compared with those of the powder photograph of tetragonal lead oxide, taken with the same camera and the K radiations of iron, the former rings are found to coincide exactly with the strong rings due to tetragonal lead oxide. Hence the contamination on the surface of the lead is proved to be tetragonal lead oxide. In Fig. 2 is shown schematically the distribution in position and in intensity of the diffraction rings due to lead and tetragonal lead oxide separately. In this figure the length of the lines represents rather qualitatively the intensities of the rings. (*a*) in Fig. 2 represents the rings due to tetragonal lead oxide, and (*b*) in the same figure, the rings due to the contaminated lead. The full lines in (*b*) represent the rings caused by lead, and the dotted lines those caused by the tetragonal lead oxide. The numbers under the full lines are the indices of the atomic planes of lead crystals which produce these rings. The lines marked (β) are the rings produced by the K_β line of iron and the other lines marked (α) are those produced by the K_α line of iron. In Fig. 2. only the indices of the atomic planes which are necessary in our case are given and the others are omitted. The tetragonal lead oxide rings which are conspicuous in our case are those produced by the K_α line of iron reflected from the atomic planes (112) and (202) respectively, and these indices are given in the figure.

Fig. 1

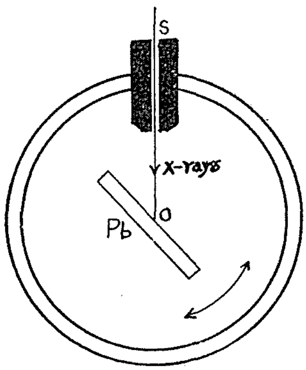
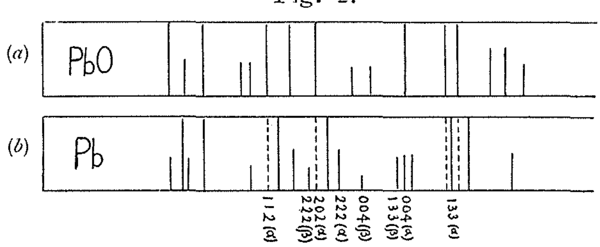


Fig. 2.



The intensity of the X-rays reflected by a thin sample thickness of which is z cms. is given by

$$KI_0F^2\lambda^3\frac{N^2}{\mu}j\frac{1+\cos^2 2\theta}{\sin^2\theta\ \cos\theta}\left[1-e^{-2\mu z\frac{1}{\sin\theta}}\right]^{1}, \qquad (1)$$

where K is a constant which includes the mass and the charge of an electron, I_0 the intensity of the primary X-rays, N the number of atoms in 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, and θ is the glancing angle which satisfies Bragg's equation

$$2\,d\sin\theta = n\,\lambda,$$

where d is the spacing of the atomic plane and n is the order of reflection. F in (1) is the structure factor, and the values for lead and tetragonal lead oxide are given as follows when the indices of the atomic plane are (hkl):

Pb :	$h,\ k,\ l$ are all even or all odd	$F=4\overline{Pb}$
	the other cases	$F=0$
PbO :	$h+k=\text{even}^2$	$F=2(-1)^h\overline{Pb}\cos 2\pi lu+2\overline{O}$
	$h+k=\text{odd}^2$	$F=2\overline{Pb}\sin 2\pi lu$

where $u=0.24$, and $\overline{Pb}$ and $\overline{O}$ indicate the scattering power of lead and oxygen atoms respectively. In the present case the writer took $\overline{Pb}$ and $\overline{O}$ as proportional approximately to the atomic numbers of lead and oxygen respectively.

Exactly speaking, the temperature factor ought to be multiplied into expression (1), but it is abridged in our case since no accurate calculation is required.

When z tends to infinity, expression (1) becomes the expression of the intensity of an ordinary powder photograph, that is,

$$KI_0F^2\lambda^3\frac{N^2}{\mu}j\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}. \qquad (2)$$

The writer assumed that the absorption coefficient of the lead oxide is roughly the same as that of lead, for the absorption of one

1. R. W. G. Wyckoff: The Structure of Crystals, p. 90 and p. 178 (1931)
2. R. G. Dickinson and J. B. Friauf, J. Am. Chem. Soc., **46**, 2457 (1924)

atom of oxyigen is negligible compared with that of one atom of lead, and there is no wide difference between the densisties of lead and lead oxide. The absorption coefficient of lead for the K_α and K_β lines of iron are shown in the following table.

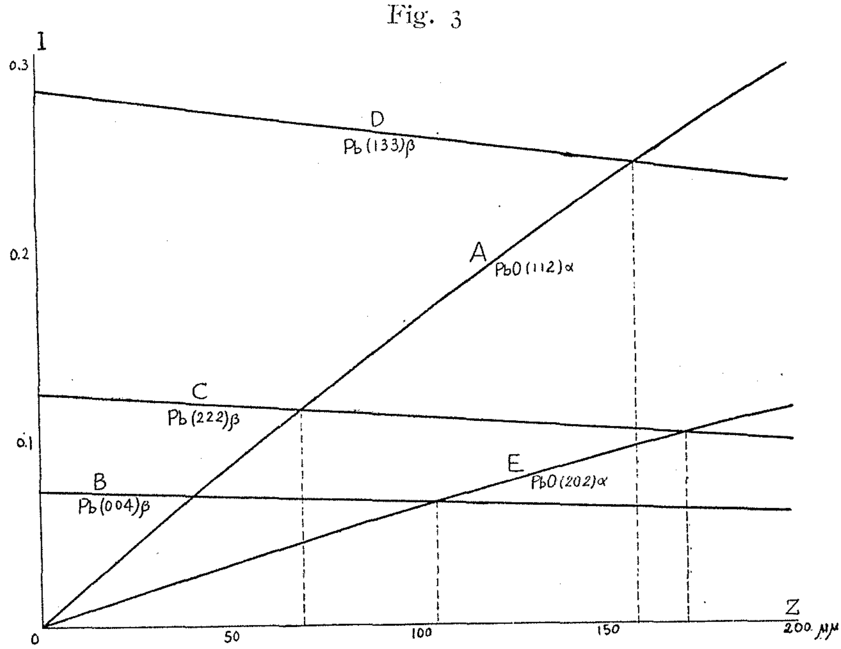
Table I

	λ in A	μ/ρ [1]	μ
K_α	1.935	420	4720
K_β	1.753	335	3770

If the intensity of the X-rays reflected from the atomic plane (112) of tetragonal lead oxide having a sufficient thickness to give maximum intensity is taken as unity, then the relation between the thickness of the layer of the lead oxide (z) and the intensity (I) is given by

$$I = 1 - e^{-2\mu z \frac{1}{\sin\theta}}. \qquad (3)$$

Fig. 3



This relation is graphically shown by the curve A in Fig. 3.

Next, in order to compare the intensities of the rings due to the

1 S. J. M. Allen, Phys. Rev., **28**, 912 (1926)

atomic plane (112) of tetragonal lead oxide and the weak rings due to lead on the photographic film, the three weakest rings of lead are chosen. They are the K_β rings of iron, reflected from the atomic planes (004), (222) and (133) respectively of lead crystal.

By taking the intensity of the K_α radiation reflected from the atomic plane (112) of tetragonal lead oxide of sufficient thickness as unity, the intensities of the above rings of lead can be calculated by means of expression (2) and the ratio of the intensities of the K_α and K_β radiations of iron.[1] This ratio becomes 7.8, taking into consideration the absorption of the X-rays in the aluminium[2] window, 0.015 mm. in thickness, and the air[3] in the camera (about 11 cms.).

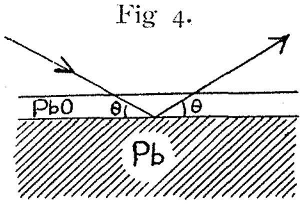
In the above way the following values for the proportions are obtained.

Table II.

	PbO	Pb		
	(121)α	(004)β	(222)β	(133)β
intensity	1	0.073	0.125	0.286

These values for the β radiation are not the proportion of the intensities on the photographic film, but those that have suffered no absorption in the layer of lead oxide. The distance which the X-rays have to go in passing through the layer is varying always as the sample is rotated, but the writer takes it as roughly $2z/\sin\theta$ for each atomic plane, as shown in Fig. 4. Then, if we take I and I_0 as the intensities of the X-rays which have suffered absorption by passing through the layer of lead oxide on the surface of the lead and those which suffered no absorption respectively, they will be connected by the following relation

Fig 4.



$$I = I_0 e^{-2\mu\frac{z}{\sin\theta}}.$$

Applying this equation to the K_β line reflected by the atomic planes of lead before mentioned, we obtain the curves B, C and D in

1 J. H. Williams, Phys. Rev., **44**, 146 (1933)

2 S. J. M. Allen, Phys. Rev., **28**, 912 (1926)

3. H. T. Meyer, Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern, **7**, 108 (1929)

Fig. 3 which represent the relation between z and I for each atomic plane. Generally speaking the intensity of the diffraction rings due to the lead oxide will increase with the thickness of the layer, and the intensity of those due to the lead will decrease with the thickness of the layer; and the thickness of the oxide film which will give the same intensity to those two kinds of diffraction rings will be given by the points at which the curve A intersects the curves B, C and D in Fig. 3. In fact the intensity of the diffraction ring due to the (112) plane of tetragonal lead oxide lies between those of the K_β line reflected by the (222) and the (133) planes of lead on the photographic film. From this fact the thickness of the layer of tetragonal lead oxide is estimated to lie between $70\mu\mu$ and $159\mu\mu$, from the abscissae of the points at which the curve A intersects the curves C and D in Fig. 3.

The intensity of the K_α line reflected by the (202) plane of tetragonal lead oxide lies between those of the K_β lines reflected by the (004) and the (222) planes of lead. Curve E in Fig. 3 indicates the relation between the intensity of the K_α line reflected by the (202) plane of the layer of lead oxide and its thickness. By examining the abscissae of the points of intersection of the curve E with the curves B and C in Fig. 3, we can estimate that the thickness of the layer of the lead oxide lies between $106\mu\mu$ and $172\mu\mu$, which coinsides with the former estimation.

In short, it may be said that the thickness of the thin layer of tetragonal lead oxide on the surface of the metallic lead lies between $50\mu\mu$ and $200\mu\mu$, at least for the specimen examined in the present experiment.

In conclusion, the writer wishes to express his sincere gratitude to Prof. U. Yoshida and Mr. K. Tanaka for their valuable suggestion.