

# The Oxidation of Aluminium Foils

By Kenzo Tanaka and Hisatugu Kano

(Received December 10, 1937)

## Abstract

Electron-diffraction examination of the  $\gamma$ - $\text{Al}_2\text{O}_3$  film, formed by the gradual heating of Al foil—either in air or in a vacuum camera—reveals, that some grains of the cubic crystals of  $\gamma$ - $\text{Al}_2\text{O}_3$  arrange themselves in an orientation similar to that taken by the cubic crystals of Al in the original foil. It is found that this effect does not follow sudden and prolonged heating of the foil at 900°C.

When aluminium is heated in air or oxygen, or otherwise melted, it is covered by a thin film of oxide. Other investigators<sup>1</sup> have found the film to consist of cubic  $\gamma$ - $\text{Al}_2\text{O}_3$ . The writers examined this oxide film by the electron-diffraction method, using electrons of about 74 KV., a homogeneous beam being obtained by magnetic deflection.

The exact wave-length of the beam was calculated from the known spacings of ZnO; the standard specimen was obtained by condensing the smoke, produced by burning pure zinc, upon a thin film of acetylcellulose. Lattice constants of ZnO were taken as  $a=3.25$  Å and  $c=5.23$  Å. The calculated value for wave-length then being 0.04355 Å.

Using this value, the lattice constant of aluminium powder and foil was found to be 4.084 Å, a value somewhat larger than that obtained by the X-ray method.

$\gamma$ - $\text{Al}_2\text{O}_3$  ( $\gamma$ -alumina) formed by heating commercial aluminium foil in air gave the results tabulated in Table I. Brill<sup>2</sup> from X-ray measurement gives the value of  $a$  as 7.91 Å, while the value of  $a$  for  $\gamma$ -alumina formed on molten aluminium was found<sup>3</sup> by electron-diffraction to be 7.780 Å. Our value (7.864 Å) is very near the mean of these two.

The atomic positions for  $\gamma$ -alumina have not yet been fully established.

Commercial beaten aluminium foil thinned by caustic potash always gives the pattern shown in Figs. 1 and 7, Plate I. All of the spots are reflected from atomic planes parallel to one of the cube edges of

1. J. A. Darbyshire and E. R. Cooper: Trans. Faraday Soc., **30**, 1038 (1934). E. Belwe: Z. f. Phys., **100**, 192 (1936). G. D. Preston and L. L. Bircumshaw: Phil. Mag., **22**, 654 (1936).

2. R. Brill: Z. f. Krist., **85**, 323 (1932). 3. J. A. Darbyshire and E. R. Cooper: loc. cit.

the aluminium crystals. The crystals in these foils have their (100) planes nearly parallel to the surface of the foil, and are approximately oriented in the same manner, so the mass of crystals may be regarded as an imperfect single crystal.

Table I.

Indices	Intensity	d (obs.)	$\alpha$ (calc.)
111	m	4.530	7.855
220	s	2.738	7.735
311	ss	2.390	7.925
222	w	2.302	7.975
400	ss	1.978	7.905
511	m	1.511	7.855
440	ss	1.395	7.900
533	m	1.185	7.760
444	m	1.136	7.880
553	w	1.014	7.790
800	m	0.9845	7.870
733	m	0.9795	7.905
844	m	0.8026	7.870
		Mean	7.864

the  $\gamma$ -alumina rings side by side with the weak aluminium spots. (Fig. 3, Plate I. 615°C.)

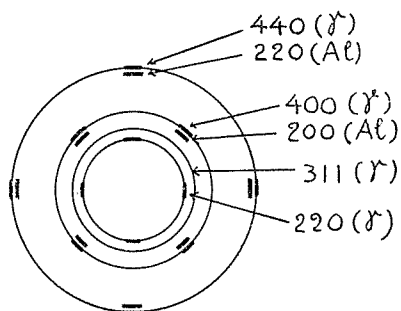
Fig. 1 explains the case more explicitly. As the value of  $\alpha$  for  $\gamma$ -alumina is a little less than twice for that of aluminium, corresponding rings of  $\gamma$ -alumina of the order twice that of the spots of aluminium appear just outside the latter—400 ( $\gamma$ ) outside of 200 (Al) etc.—, and the distribution of the spots due to the  $\gamma$ -alumina is found to be similar to that of the spots of aluminium.

From this one may conclude that some crystals of  $\gamma$ -alumina are oriented in approximately the same orientation as the original aluminium crystals. The presence of the continuous rings indicates that the remaining  $\gamma$ -alumina crystals are in general arranged fortuitously. However, the relative intensities of these rings show that the crystals have their (100) planes nearly parallel to the foil's surface.

When one of these foils is mounted in the diffraction-camera, and the temperature of the foil is gradually raised; the changing diffraction patterns may be continuously observed on the fluorescent screen. Photographs taken at suitable instants are shown in Figs. 1, 2, 3 and 4, Plate I.

The original aluminium pattern gradually weakens with the rise in temperature and the rings due to  $\gamma$ -alumina formed by the residual oxygen in the camera appear. Fig. 2, Plate I, shows the pattern at 580°C. A further rise in temperature is followed by a corresponding weakening of the spots due to aluminium, and the appearance of spots on

Fig. 1



On still further heating, the spots due to aluminium crystals disappear and the pattern is found to be totally due to  $\gamma$ -alumina. (Fig. 4, Plate I.) The oxidation having been completed, further heating or the returning of the specimen to room temperature produces no appreciable change in the pattern.

The orientation effect is also observed when the aluminium foil is heated in air. Fig. 5, Plate I. is a pattern due to two groups of grains, each of which is in (100) orientation and mutually inclined nearly  $45^\circ$  around their common [100] axis. When this foil is heated gradually in air for 4 hours till a final temperature of  $610^\circ\text{C}$  is attained,  $\gamma$ -alumina is formed, the orientation of a part of the crystals in the latter being identical to that found in the original aluminium foil. (Fig. 6, Plate I.)

When the foil (Fig. 7, Plate I.) is suddenly heated by placing in a furnace already heated to  $900^\circ\text{C}$  and is kept there for 20 minutes, the  $\gamma$ -alumina thus formed shows no signs of particular orientation. The pattern being identical to that of Fig. 6, Plate I. minus the spots, and with the intensity distribution of the rings completely changed. (Fig. 8, Plate I.)

From these observations, it may be considered that the "Orientation Effect" appears when the oxidation takes place previous to the melting of aluminium, and that the oxidation of aluminium in the molten state fails to produce this effect.

Some different relations between the orientation of the metal and of its oxide have already been found in the case of sputtered iron<sup>1</sup> and barium<sup>2</sup>. As the atomic positions of  $\gamma$ -alumina have not yet been fully determined, the mechanism of this effect cannot be confirmed. But, it may be said to be due to the entrance of some oxygen atoms into the crystal lattice of aluminium without fully destroying the latter.

The writers wish to express their sincere gratitude to Prof. U. Yosida for his invaluable suggestions.

---

1. H. R. Nelson: *J. Chem. Phys.*, **5**, 252 (1937).

2. W. G. Burgers and J. J. A. P. van Amstel: *Physica*, **3**, 1057 (1936).

Plate I

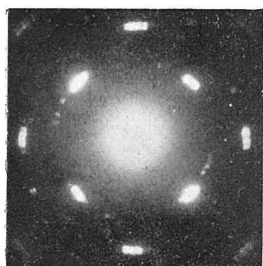


Fig. 1

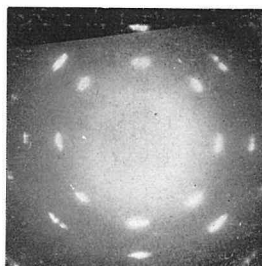


Fig. 5

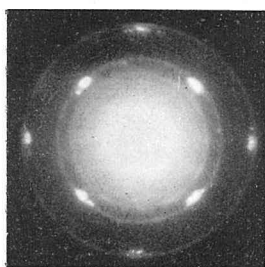


Fig. 2 (580°C)

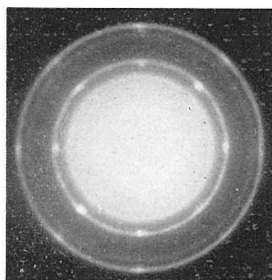


Fig. 6

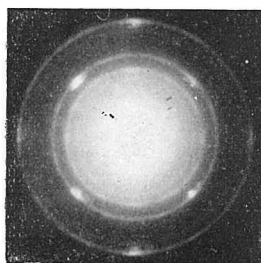


Fig. 3 (615°C)

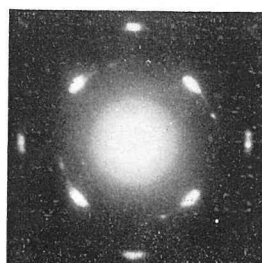


Fig. 7

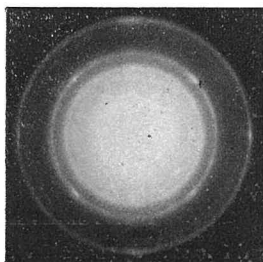


Fig. 4 (720°C)

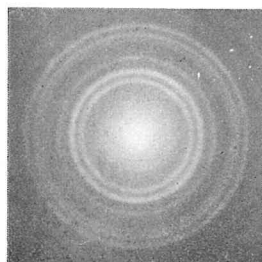


Fig. 8