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Structure and Crystallization of Nearly Amorphous Beryllium Oxide and Aluminium Oxide Films

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Two methods of preparing beryllium oxide films suitable for electron-diffraction examination are described. These films gave a halo diffraction pattern differing appreciably from that corresponding to a broadened ring pattern from normal hexagonal BeO. The crystallization of this form of the oxide was shown to occur at 300° C. by heating in air. Calculation showed that the halo pattern originated from diffraction by BeO crystals of normal structure, but the crystals were only 8 Å in diameter.

The oxide film partially stripped from anodized aluminium was examined by electron diffraction, and haloes were obtained similar to those reported previously. This film was found to crystallize into γ-Al_2O_3 after heating to 700° C. for 7 hr. in air. The possible structure of the nearly amorphous oxide is discussed and the model suggested by Wilsdorf is shown to be likely.

Introduction

In Part I methods of preparing thin beryllium oxide films are described. These films were first thought to consist of beryllium hydroxide, but it was shown in the course of the work that they were composed of nearly amorphous beryllium oxide. There appears to be no previous reference to this form of the oxide.

Part II of this paper is concerned with thin anodized aluminium films. The diffraction patterns from these films are compared with data obtained by earlier workers from both air-formed and anodized oxide films, and shown to be similar. A possible structure of the aluminium oxide is discussed.

In 1936 Preston & Bircumshaw (1936) found that the aluminium surface at room temperature gave an electron-diffraction pattern of two haloes corresponding to $(\sin \theta)/\lambda$ of 0·17 and 0·37 Å^{-1}. Stripped oxide films heated to temperatures over 650° C. recrystallized into γ-Al_2O_3. De Brouckère (1945), in observing atmospheric oxidation, obtained similar halo patterns. After heating at temperatures between 400–700° C. for several minutes it was found that the surface gave a halo pattern, but after longer periods of several hours, crystalline γ-Al_2O_3 was observed. An equilibrium between speed of formation and speed of crystallization of the oxide was suggested.

A structure has been put forward by Wilsdorf (1951) to account for the halo pattern. He formed oxide films by heating aluminium in air at 400° C., and then stripped them from the metal for examination by electron diffraction. Two haloes were found, corresponding to $(\sin \theta)/\lambda$ 0·17 and 0·36 Å^{-1}. Wilsdorf then tried to account for the haloes assuming they were due to diffraction from very small crystals of γ-Al_2O_3, using the Wierl formula. He was not successful until he assumed a configuration not present in face-centred cubic γ-Al_2O_3. This consisted of six closely packed oxygen atoms at the corners of an octahedron and four aluminium atoms tetrahedrally arranged between them, as in the molecule of As_4O_6.

The structure of anodically formed films on aluminium was investigated by Harrington & Nelson (1940), who found that anodized surfaces gave halo patterns that varied slightly according to the electrolyte and its temperature. The crystal diameter estimated from ring breadths was 12 Å. Unexpectedly, they stated that heating to 650° C. did not crystallize the film. Hass (1946) examined both anodically- and air-formed films on aluminium, and found that films adhering to the metal would crystallize (to γ-Al_2O_3) at 500° C. but that stripped films required 680° C., independent of the method of preparation.

PART I. BERYLLIUM OXIDE FILMS

1. Experimental results

(a) Preparation and examination: Method I

A solution of beryllium sulphate was first prepared by dissolving some Brush beryllium in dilute sulphuric acid (1 part in 50). From this the oxide was precipitated by adding a strong solution of either Na_2CO_3 or $(NH_4)_2CO_3$, from which some of the precipitate was scooped out on a nickel gauze and floated off on the cleaned surface of distilled water. Here it remained for 10 min. to remove any unchanged salt, after which the precipitate, which was still intact as a surface film, was lifted back on to nickel gauze and transferred to the electron-diffraction camera, where approximately 60 kV. electrons were used, with a camera length of about 48 cm.

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On scanning the specimen with the electron beam in transmission, the beryllium oxide film was found to contain some relatively thick regions through which the beam could not penetrate; but there were thinner regions yielding halo diffraction patterns, as Fig. 1(*a*). Table 1 gives the measurements of halo diameters together with $(\sin\theta)/\lambda$ values, θ being half the angle of scattering, and λ the wavelength of the electrons.

Table 1. *Halo pattern from beryllium oxide, prepared by Method I*

$2R$ (cm.)	Intensity	$(\sin\theta)/\lambda$ (Å^{-1})
1·184	*s*	0·118
2·294	*vs*	0·228
4·074	*vs*	0·405
6·200	*w*	0·618
7·984	*vw*	0·790

(*b*) *Preparation and examination*: *Method II*

In this method of preparation, the beryllium oxide films were produced as a floating precipitate on the surface of $BeSO_4$ solution. Some $BeSO_4$ solution in a shallow glass dish was placed close to a small beaker of strong ammonia solution, and a glass vessel placed over the two. After 15 min. it was possible to lift off a portion of the amorphous BeO film with a nickel gauze and wash it by floating it on distilled water, as before.

The time that the solution was exposed to ammonia vapour was not critical, as the reaction appeared to go to completion in about 15 min. For electron-diffraction purposes $N/4$ $BeSO_4$ solution produced films of satisfactory thickness, but this probably also depends on the size of the vessels and the quantities used.

Electron diffraction showed the film to be uneven in thickness, with about 50% by area sufficiently thin to give a halo pattern, as in Fig. 2(*a*). Measurements are given in Table 2.

Table 2. *Halo pattern from beryllium oxide, prepared by Method II*

$2R$ (cm.)	Intensity	$(\sin\theta)/\lambda$ (Å^{-1})
1·146	*m*	0·118
2·137	*vs*	0·220
3·949	*vs*	0·405
5·900	*w*	0·607

(*c*) *Crystallization by heating in air, of films prepared by both the above methods*

Films prepared by either Method I or II were first examined in the electron-diffraction camera to ensure that they were of satisfactory thickness and also free from impurities. They were then transferred, still on the nickel gauze, to a pyrex-tube oven for heating in air for half an hour or more. In each case the time necessary to reach the stated temperature and to cool down from it is not included in the stated time, but was of the order 5 and 15 min., respectively.

The films were then re-examined in the diffraction camera, and the results (Table 3) show the extent to which crystallization had taken place. Table 4 gives measurements of the pattern of Fig. 1(*b*), prepared by Method I and heated half an hour in air at 300° C., and shows that the net-plane spacings now correspond to X-ray data for crystalline (hexagonal) BeO.

To analyse the results in greater detail, the crystal size was estimated from ring breadths. The formula used was $t \simeq \lambda L/B'$, where B' is the 'half-breadth' of the hkl ring and t is the effective mean thickness of the crystal in a direction normal to the (hkl) plane. The term half-breadth denotes the radial distance between points on opposite sides of the ring where the intensity is half the maximum intensity. For present purposes a sufficiently accurate correction for the primary beam width was made by subtracting the central-spot diameter from the measured half-breadths.

The rings chosen for the measurement were the 110 ring, giving an estimate of thickness normal to the

Table 3. *Estimated crystal size, after heating in air, for beryllium oxide films*

The central spot diameter varied between 0·018 and 0·028 cm., and λL was of the order of 2·20–2·40 Å cm.

			Corrected breadths		Crystal size	
Fig. No.	Temp. (°C.)	Time of heating (hr.)	102 ring (cm.)	110 ring (cm.)	From 102 ring (Å)	From 110 ring (Å)
			Beryllium oxide films prepared by Method I			
1(*a*)	—	—	—	0·273*	—	8·8
1(*b*)	300	½	0·053	0·024	42·5	94
1(*c*)	400	1	0·027	0·015	85	153
1(*d*)	300	3	0·040	0·024	58	97
			Beryllium oxide films prepared by Method II			
2(*a*)	—	—	—	0·214*	—	11·2
2(*b*)	180	½	—	0·132*	—	16·8
2(*c*)	250	½	—	0·077*	—	31
2(*d*)	280	½	—	0·068	—	35
2(*e*)	300	½	0·062	0·030	37	77
2(*f*)	500	½	0·029	0·017	77	113

* Indicates halo measured in place of 110 ring.

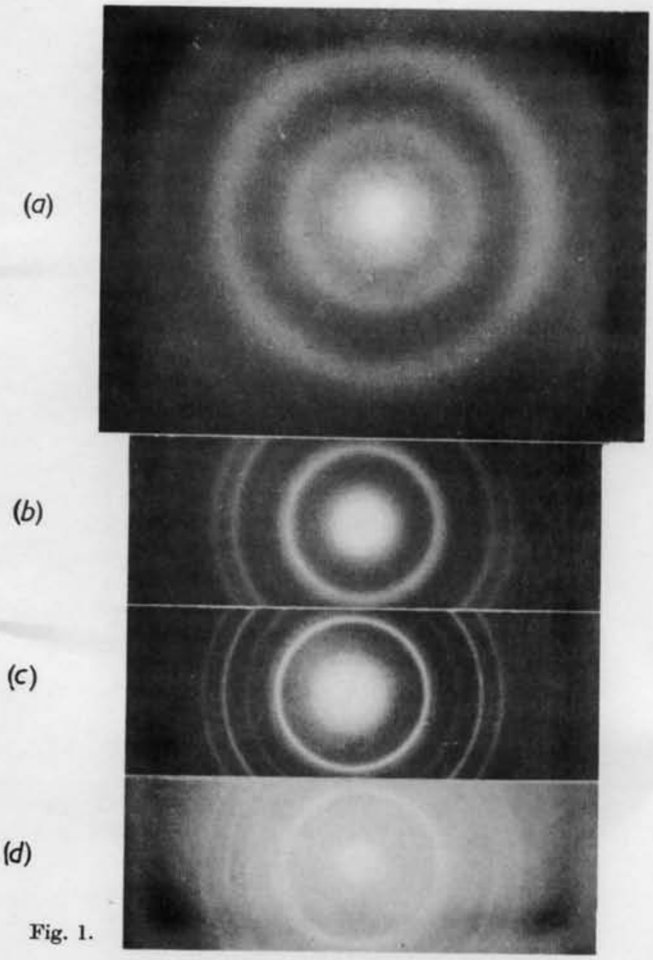

Fig. 1.

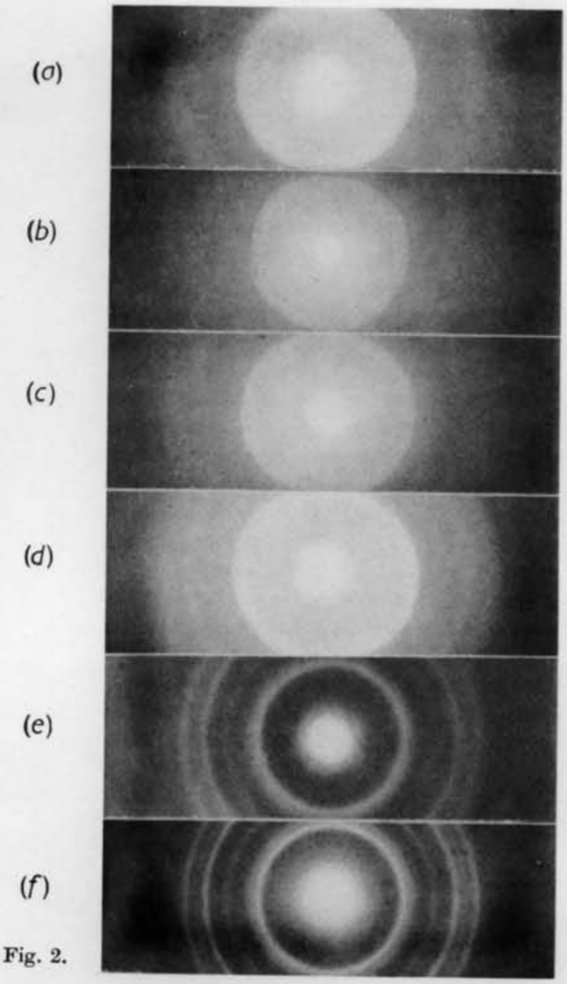

Fig. 2.

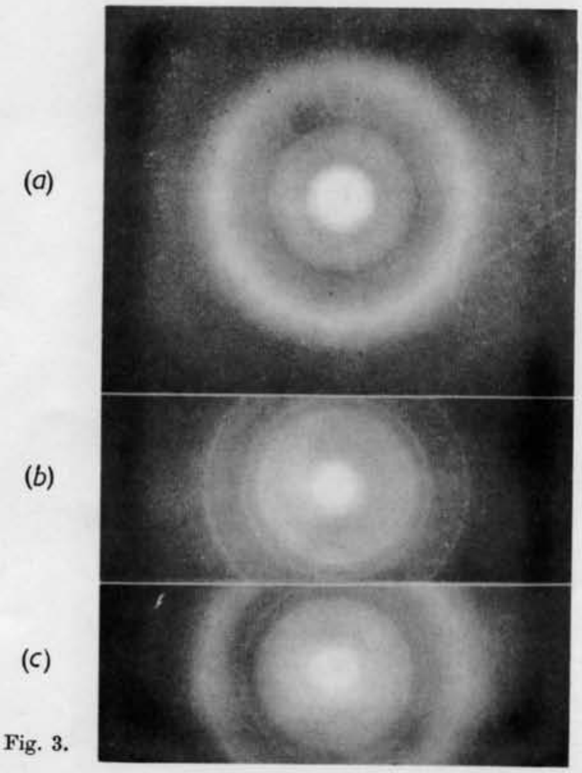

Fig. 3.

Fig. 1. Electron-diffraction patterns from BeO films prepared by Method I and heated in air. The conditions are as below.

(*a*) As prepared.
(*b*) 300° C.; ½ hr.
(*c*) 400° C.; 1 hr.
(*d*) 300° C.; 3 hr.

Fig. 2. Patterns from BeO films prepared by Method II and heated. The conditions are as below.

(*a*) As prepared.
(*b*) 180° C.; ½ hr.
(*c*) 250° C.; ½ hr.
(*d*) 280° C.; ½ hr.
(*e*) 300° C.; ½ hr.
(*f*) 500° C.; ½ hr.

Fig. 3. (*a*) Anodized aluminium film prepared in ammonium borate and stripped with chlorine. (*b*), (*c*) The foil after heating at 700° C. in air for 7 hr. Both patterns are from the same specimen and show complete and partial crystallization respectively.

Table 4. *Beryllium oxide film prepared by Method I and heated to* 300° C. *for* ½ *hr. in air*

The *hkl* indices given are for diffractions from hexagonal BeO

2*R* (cm.)	Intensity	*d* (Å)	*hkl*	X-ray data, *d* (Å)
1·937	*vs*	2·32	100	2·337
2·154	*w*	2·09	101	2·06
2·758	*w*	1·63	102	1·60
3·340	*s*	1·35	110	1·35
3·889	*m*	1·16	200	1·17
			112	1·15
			201	1·13

c axis, and the 102 ring, wherever possible, giving the thickness in a direction roughly 42° from the *c* axis towards the basal plane.

The results are listed in Table 3, giving corrected ring breadths etc. and calculated crystal thickness for ten of the specimens of beryllium oxide. Fig. 4 shows the observed BeO crystal size after heating for half an hour in air, at temperatures up to 500° C. This curve was investigated systematically only for the BeO films prepared by Method II.

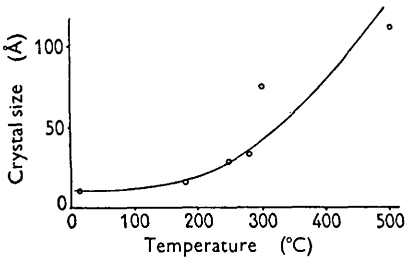

Fig. 4. Estimated crystal diameter of BeO films plotted against temperature of heating, for ½ hr. periods.

(*d*) *Ageing of beryllium oxide films at room temperature*

Beryllium oxide films were prepared by Method II and after a preliminary examination by electron-diffraction were aged by leaving them, still dry, in a tube partially open to atmospheric air, for periods up to 12 days. The final patterns obtained from these specimens did not differ from the original. It was therefore concluded there is no appreciable crystallization at room temperature.

2. Discussion

(*a*) *General*

From the identical halo patterns and similar behaviour when heated, the films prepared by Methods I and II are concluded to be substantially of the same material. Furthermore, reflexion patterns from the oxide layer on the surfaces of electropolished beryllium and also condensed beryllium exposed to air (as described by Kerr & Wilman, 1956), are similar to the halo patterns obtained as above. Agreement of crystallizing temperatures (280–300° C.) again suggests the halo patterns originate from this same nearly amorphous material. These data and the fact that $Be(OH)_2$ is known to lose water and be converted to BeO at temperatures much below 300° C. (Hüttig & Toischer, 1930) indicate that the films examined were BeO, not $Be(OH)_2$.

Crystallization up to a diameter of about 80 Å took place steadily over the range 250–300° C., and the fact that the second and third haloes fell near prominent rings of the sharp beryllium oxide pattern shows that the halo pattern is most probably due to beryllium oxide of crystal diameter about 10 Å. A more detailed discussion of this conclusion is given below.

In every case where measurement was possible, the 102 ring was broader than the 110 ring; thus the small crystals must be shaped as more or less flat flakes normal to the *c* axis. The flake thickness in a freshly prepared film must be of the order of 6 Å. Clearly such minute crystals, having a size little in excess of the unit cell, will give a diffraction pattern considerably different from that of the normal crystalline material, as shown by Germer (1939) and by Germer & White (1941). This may explain the existence of the first halo, which corresponds closely to the 001 diffraction, normally forbidden in close-packed structures.

(*b*) *Calculation of theoretical pattern from small* BeO *crystals*

In order to confirm more closely the above conclusion that the halo patterns produced as above are due to beryllium oxide of very small crystal diameter, and not to some other compound, such as $Be(OH)_2$, the theoretical electron scattering functions were calculated for certain groups of Be and O atoms thought most likely. The Wierl formula for diffraction by a gas was used:

$$\frac{I}{I_0}=\sum_p\sum_q E_pE_q\frac{\sin\{4\pi r_{pq}(\sin\theta)/\lambda\}}{4\pi r_{pq}(\sin\theta)/\lambda},$$

where θ is the half-angle of scattering; λ the wavelength of the electron beam; r_{pq} the distance between the atoms p and q; and E_p and E_q are the respective atomic scattering factors for electrons (functions of θ).

In applying this calculation to the present problem, a number of approximations were made. The first was in applying the formula to the diffraction from a nearly amorphous solid, instead of a gas. This assumes that the structural units (ordered groups of atoms) in the material are randomly distributed with respect to their nearest neighbours. This assumption, although not necessarily always true, is often practically so, as is borne out by the way a number of workers have successfully used this method. Thus Germer & White (1941) used the Wierl formula to give a satisfactory explanation of electron intensity anomalies in patterns from very thin films of copper, and Karle (1946, 1947), on a similar basis, determined the angle of tilt at which the long chains of liquid hydrocarbons orientate themselves with respect to the substrate. Wilsdorf (1951) applied the same method to the halo pattern produced from oxidized aluminium, as mentioned below in Part II.

Other approximations were made in the first calculations, as described by Thomson & Cochrane (1939, p. 249). The E's in the formula were replaced by atomic numbers, Z's. This error was greatest when θ was small. Terms where $p = q$ were not included in the summation, as they account only for the scattering from single atoms, which does not give rise to any maxima or minima. Thus the formula becomes as follows where the summation is over all pairs of atoms in the small crystal:

$$\frac{I}{I_0} = \Sigma Z_p Z_q \frac{\sin \{4\pi r_{pq} (\sin \theta)/\lambda\}}{4\pi r_{pq} (\sin \theta)/\lambda} .$$

It was necessary to tabulate: the lengths of vectors between atoms, i.e. r_{pq}; the number of times each vector occurs in the group of atoms, and the product of the Z's of the atoms at the ends of each vector. The calculation was made for a range of $(\sin \theta)/\lambda$ in intervals of 0·02 Å^{-1} and subdivided in places for increased accuracy. Tables of $(\sin x)/x$ were used (Sherman, 1933).

(*c*) *Calculation of intensity of scattering for tetrahedral groups of atoms*

In crystalline beryllium oxide the atoms of one kind are arranged at the corners of a structure built up from regular tetrahedra, with a length of edge equal to the a axis of the unit cell. Atoms of the other kind are to be found at the centres of the tetrahedra. It was therefore first considered whether these nearly amorphous BeO films were composed of randomly disposed units of such tetrahedra. Tetrahedra with beryllium atoms at the corners were considered to exist in equal numbers to those having oxygen at the corners. In each tetrahedron there are six vectors of length a between like atoms, and four of length $a \times \sqrt{(3/8)}$ between unlike atoms. With atomic numbers 4 and 8, weighting factors respectively 15:8 are obtained.

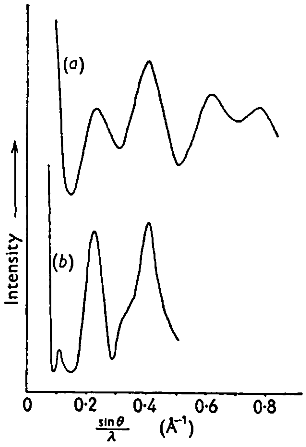

Fig. 5. Theoretical electron scattering functions:
(*a*) for tetrahedra of BeO, (*b*) for the small crystal of BeO shown in Fig. 6.

The result of the calculation is shown in Fig. 5, curve (*a*), and the positions of the outer haloes observed in the electron-diffraction pattern agree well with the maxima of the curve. However, the existence of the innermost halo is not explained.

(*d*) *Calculation of electron scattering function for a larger unit*

For a second calculation the small crystal considered was shaped as a hexagonal prism of diameter $2a$ and height $11c/8$, containing seventeen of both beryllium and oxygen atoms (see Fig. 6). This configuration was chosen as ring-breadth measurements have led to an estimated crystal diameter of about this size. Furthermore, the shape is likely to give rise to a 001 diffraction. This crystal required twenty different vector lengths for the calculation, the result of which is shown in Fig. 5, curve (*b*). The curve, which has maxima corresponding relatively accurately to the 2nd and 3rd haloes, also has a small maximum agreeing closely with the first halo.

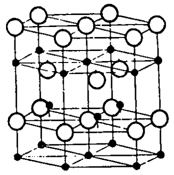

Fig. 6. Small crystal of beryllium oxide.

The positions of these maxima agree satisfactorily with the relative $(\sin \theta)/\lambda$ values given in Tables 1 and 2, and also with the $(\sin \theta)/\lambda$ values obtained from the oxidized bulk metal (Kerr & Wilman, 1956), which are independent of errors in voltage measurement. It thus appears that a random distribution of beryllium oxide of approximately this shape and size will account for the halo diffraction pattern.

(*e*) *The previous electron scattering function with the E's varying with θ*

In order to see if the approximations made above had any appreciable effect on the position and relative heights of the maxima, the calculation was repeated with due allowance made for the E's being functions of θ, and also including the coherent scattering from single atoms. Although the effect of secondary scattering on the form of the final curve must be appreciable, it was not taken into account as the theory is incomplete and it would be necessary to know the thickness of the film in order to estimate the amount of secondary scattering at any point in the pattern.

$$E = \frac{\{4\pi (\sin \theta)/\lambda\}^2}{Z - f} ,$$

where f is the atomic scattering factor for X-rays. In addition a further factor of $1/\tan\theta$ was used as electrons are collected on the plane of a photographic plate.

Beryllium oxide consisting of strongly electropositive and electronegative elements, is most probably fully ionized in the crystalline state, cf. NaCl. Therefore the X-ray atomic factors for the respective ions were used. These were taken from Pirenne (1946), who used an interpolation method. The f's for small values of $(\sin\theta)/\lambda$ are therefore not very reliable, but it is apparent that for $(\sin\theta)/\lambda$ less than 0·1 Å^{-1} the scattering of electrons due to an O^{--} ion is negligibly small compared with that of a Be^{++} ion.

With the above considerations the result of the summation, which now includes terms where $p = q$, is shown by curve (*a*) in Fig. 7. The logarithm of the intensity is plotted in order to be more comparable with curve (*b*), which is a photometer plot. This was obtained by traversing a photometer across one of the halo patterns and plotting the negative of the logarithm of the galvanometer deflection. The two curves should be directly proportional. Although the halo positions of the two curves in Fig. 7 agree, the experimental curve shows considerably less contrast than the theoretical curve. It is therefore concluded that the flattening out is due to incoherent scattering together with secondary or multiple scattering, neither of which has been taken into account in the theoretical calculation, for reasons stated previously.

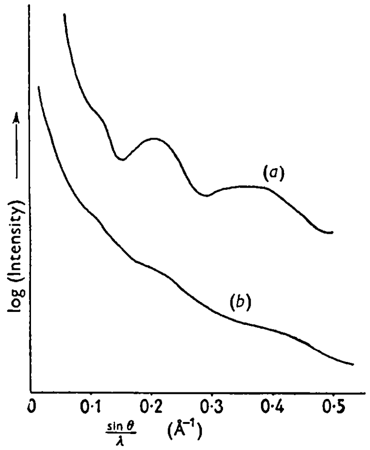

Fig. 7. Curve (*a*): Full theoretical electron scattering function for the small crystal of BeO. Curve (*b*): A photometer trace from a BeO halo pattern.

It thus appears by comparison of Fig. 7 (curve (*a*)) with Fig. 5 (curve (*b*)) that the positions of maxima and their relative heights are not affected greatly by the approximations made in § 2(*d*). It seems, however, advisable to take into account the variation of E with θ when angles with $(\sin\theta)/\lambda < 0{\cdot}2$ Å^{-1} are considered. In conclusion it may be stated that the suggested crystal size given in § 2(*d*) is completely justified.

PART II. ALUMINIUM OXIDE FILMS

1. Experimental results

(*a*) *Anodized aluminium films*

The anodized films used in these experiments were prepared by Dr A. Charlesby in the Metallurgy Division of A.E.R.E., Harwell, and consisted of aluminium foil (about 0·01 cm. thick) anodized at 50 V. in an ammonium borate solution. Most of the aluminium was then stripped from the oxide film with chlorine at 200° C., leaving a metal foil network sufficiently rigid to support the unaffected oxide film across 'windows' where the metal was completely removed. The oxide film thickness was about 700 Å (14 Å per volt) so it was possible to examine the films by transmission electron diffraction. In doing so, patterns such as Fig. 3(*a*) were obtained, giving measurements for two patterns as in Table 5.

Table 5. *Measurements from two aluminium oxide halo patterns from anodized foil*

Intensity	$(\sin\theta)/\lambda$ (Å^{-1})	Intensity	$(\sin\theta)/\lambda$ (Å^{-1})
vs halo	0·167	*vs* halo	0·167
w ring	0·238	*w* ring	0·239
s halo	0·362	*vs* halo	0·367
w halo	0·563	*vw* halo	0·594

The $(\sin\theta)/\lambda$ values obtained from the haloes agree satisfactorily with previous data, but the patterns show the existence of a small percentage of γ-Al_2O_3 of crystal diameter about 20 Å (compare Tables 5 and 6). This is indicated by the sharp outer edge of the innermost halo, due to the 311 ring, and by the broad ring, which corresponds to the 400 diffraction of γ-Al_2O_3. A trace of the 440 γ-Al_2O_3 ring was possibly present on the central region of the second broad halo. In other respects the material of the films seems identical with that used by previous workers.

(*b*) *Crystallization of aluminium oxide films by heating in air*

A piece of the above described aluminium oxide film was placed in a pyrex tube and heated in air at 700° C. for 7 hr. On examination, electron-diffraction patterns such as Figs. 3(*b*) and 3(*c*) were obtained

Table 6. γ-Al_2O_3 *pattern, from an anodized aluminium surface film heated to* 700° C. *for* 7 *hr. in air*

$2R$ (cm.)	Intensity	d (Å)	*hkl*	X-ray data, d (Å)
1·684	*w–m*	2·78	220	2·80
1·951	*s*	2·41	311	2·39
2·370	*vs*	1·98	400	1·98
3·083	*vw*	1·52	$\left\{\begin{matrix}333\\511\end{matrix}\right\}$	1·52
3·353	*vs*	1·40	440	1·40
3·939	*vw*	1·19	622	1·21
4·097	*w*	1·14	444	1·14
4·749	*vw*	0·988	800	0·99
5·315	*w*	0·88	—	—
5·805	*w*	0·81	—	—

from different parts of the same specimen. Fig. 3(*b*) shows only sharp rings, agreeing with the net-plane spacings and intensities of γ-Al_2O_3 (Table 6), while Fig. 3(*c*) shows, in addition, haloes due to the unaltered film.

2. Discussion

Comparison of the present results with previously published data obtained from air-formed films on aluminium, suggests that the two methods of preparation lead to oxides of similar structure, although the anodized oxide films contain a small percentage of γ-Al_2O_3. The structure of this nearly amorphous oxide cannot be totally dissimilar from γ-Al_2O_3, as one of the strong haloes has its maximum practically coinciding with the strong 440 ring of γ-Al_2O_3 (see Fig. 3(*c*)); however, the first halo falls considerably within the innermost of the stronger γ-Al_2O_3 rings.

A calculation has been carried out, similar to that described in § 2(*e*), to find the radial distribution of scattered intensity from the model suggested by Wilsdorf (1951). The result of this calculation is shown in Fig. 8. This shows fairly good agreement with the positions of the two inner strong haloes, and the model therefore seems a justifiable basis for solution of the structure. The contrast in the pattern from the aluminium oxide film (Fig. 3(*a*)) is at least equal to that of the BeO pattern (Fig. 1(*a*)), so it would be expected that the heights of the maxima in the respective theoretical curves would be roughly equal. Secondary scattering and incoherent background will be evident in patterns from both films to about the same extent. In view of the maxima in the theoretical pattern (Fig. 7(*a*)) being greater than the maxima in Fig. 8, it seems possible that the halo diffractions may be due to a group of atoms arranged in a way resembling the model investigated, but of slightly larger extent (in the same way as the peaks of the Laue interference function for diffraction by a crystal increase in magnitude with increase of crystal size).

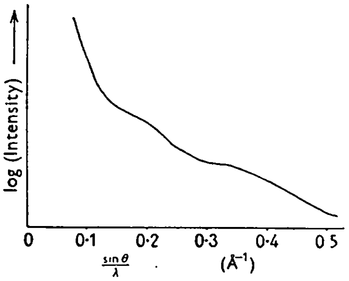

Fig. 8. Theoretical electron scattering function for a small group of Al_2O_3.

GENERAL DISCUSSION

At first sight it may seem possible that the beryllium films, as prepared by Methods I and II, may have been $Be(OH)_2$ when first precipitated, in which case they must have been dehydrated on evacuation in the electron-diffraction camera, thus giving BeO of about 8 Å crystal diameter, whose existence has been shown in this paper. It is, however, unlikely that beryllium oxide would be so unstable, as the hydroxides $Zn(OH)_2$, $Mg(OH)_2$, α- and γ-AlOOH, all of metals situated nearby in the periodic table, are stable when examined in the electron beam in vacuum. By X-ray diffraction, stable and metastable beryllium hydroxides have, however, been shown to exist (Fricke & Humme, 1929) and the structure of an orthorhombic form has been described (Seitz, Rosler & Schubert, 1950). None of these hydroxides has been found in the present work. A further reason for concluding that the diffraction halo patterns correspond to BeO is that the pattern was unchanged by half an hour's heating of the deposit at 250° C. Hüttig & Toischer (1930) showed that beryllium hydroxide gives off most of the removable water at about 170–190° C.

One difference noted in the behaviour of the BeO and Al_2O_3 films is that the BeO films crystallize homogeneously when heated, as shown by the same diffraction pattern being obtained from different areas of each specimen, whereas in the Al_2O_3 films the crystallization was uneven, as if originating from a number of nuclei. This may be due to the slight change in structure required to convert the Wilsdorf group of atoms into the arrangement present in γ-Al_2O_3.

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A Set of Effective Coordination Number (12) Radii for the β-Wolfram Structure Elements

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A set of effective coordination number (12) radii is derived from the known compounds of 'β-wolfram' structure from which the lattice constants of the compounds are reproduced to within ±0·03 Å. In several cases there are significant differences between the CN(12) radii here derived and those given by Pauling and Wells. Crystallographic data are given on all the known compounds with β-W structure, including three not heretofore reported. It is found that Pauling's resonating-valence-bond theory of metals does not apply to this series of compounds.

Introduction

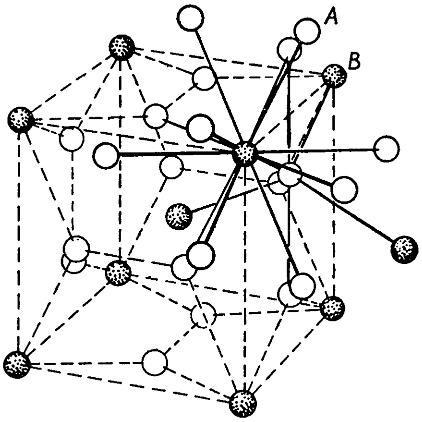

Fig. 1. The β-W structure.

To date,* thirty-two intermetallic compounds with the β-wolfram structure† (Fig. 1) are known. This structure is favorable to superconductivity, a fact established by Hardy & Hulm (1954) and by Matthias, who has discovered eleven of the compounds shown in Table 1 (see references *a*, *b*, *c* of Table 1). In particular Nb_3Sn (Matthias, Geballe, Geller & Corenzwit, 1954) has the highest superconducting transition temperature, 18·05±0·1° K., known to date. An examination of the compounds crystallizing with the β-W structure has produced a list of effective 12-coordination radii for the elements involved from which the lattice constants of these compounds may be reproduced to within ±0·03 Å.

Discussion

The β-W structure belongs to space group O_h^3–$Pm3n$. Two types of sites are occupied by the atoms in the A_3B compounds (Fig. 1): the A atoms occupy positions 6(*c*): $\pm(\frac{1}{4}, \frac{1}{2}, 0; \circlearrowleft)$; the B atoms occupy positions 2(*a*): $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The A atoms have an effective coordination number of 14 whereas that of the B atoms is 12. Each A atom is coordinated to two A atoms at the distance $\frac{1}{2}a_0$, $(A\text{–}A)_1$; to 8 A atoms at distance $\frac{1}{4}a_0\sqrt{6}$, $(A\text{–}A)_2$; and to 4 B atoms at distance $\frac{1}{4}a_0\sqrt{5}$, $(B\text{–}A)$. Each B atom is coordinated to twelve A atoms at the distance $(B\text{–}A)$. These distances are listed in Table 1 together with the measured lattice constants and those derived from the 12-coordination radii given in Table 2. The derived lattice constants are obtained by adding the radii of the two atoms in the compound and multiplying this sum by $4/\sqrt{5}$.

It is seen (Table 1) that only in the case of Cr_3Ir is the difference between the measured and derived lattice constants as large as 0·03 Å. In this case a homogeneity range has been reported by Raub (1954) and the value taken for the 75 atomic % Cr compound has been obtained by interpolation.

Although an exhaustive survey has not been made, such excellent agreement obtained from a specialized set of radii does not appear to be the rule. Except for the Cr_3Ir, the discrepancies are within the rounding-off

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[*] This is the date of the revision. At the time of the first writing 29 compounds were reported. The paper by Greenfield & Beck (1956, see Table 1) appeared after the first writing.

[†] See also Hägg & Schönberg (1954), who show that W_3O has a completely disordered β-W structure and argue that β-W itself does not exist.