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Structure and Growth of Beryllium Oxide on Single Crystals of Beryllium

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The nature of the structure and growth of BeO films formed by heating single crystals of beryllium in air over a wide range of temperatures was studied in detail using electron diffraction, and electron microscopy.

The epitaxial nature of the oxide formed in the temperature range 300 °C. to 400 °C. on a Be (001) cleavage face was established.

In the case of electropolished (001) surfaces of beryllium, it was found that the epitaxial BeO overgrowth was less well-defined. It was suggested that this disorientation was due to the formation, during the electropolishing procedure, of surface elements other than (001) upon which the oxide could grow.

One-degree (103)-oriented BeO was observed on (100) and (110) faces of Be.

The oxidation rate increased with increase in temperature, resulting in a corresponding increase in the proportion of randomly-oriented BeO until, above 600 °C., only random growth was observed in the upper regions of the layer. At about 800 °C., a pronounced (001) habit of the randomly-oriented BeO crystals was developed. The diameter of the oxide crystals was estimated from the diffraction patterns to be some tens of Ångströms below 300 °C., and in the order of thousands of Ångströms at about 800 °C.

The non-protective nature of the oxide layer formed at 600 °C. and above, is evident from the electron micrographs which showed the development of projecting needles of BeO up to 5μ in length and several hundred Ångströms in thickness. The needles possessed a $\langle 110 \rangle$ axis, and possibly grew around screw dislocations. Thin BeO flakes up to several μ in diameter were also observed in this temperature range, the diffraction pattern indicating considerable distortion of the flake.

1. Introduction

The presence of beryllium oxide in hot-extruded polycrystalline beryllium rod has been recently reported (Scott & Wilman, 1958). Such BeO in the metal or on the surface must affect the physical properties of the metal, particularly with regard to corrosion-resistance and fabrication qualities. The experiments described below provide detailed information on the oxidation of single crystals of beryllium, and in particular, establish the epitaxial nature of the protective oxide on the (001) Be surface, and the form of the non-protective high temperature oxide (above 600 °C.).

A definite epitaxial orientation relationship of thin films of the oxide to the metal crystal substrate has been observed, using electron diffraction, on copper, (Leu, 1951; Steiner, 1953; Piggott, 1957; cf. also X-ray observations on thicker films by Mehl, McCandless & Rhines, 1934), antimony (Acharya, 1948), lead (Pash, 1957) and zinc (Acharya, 1948; Raether, 1950; Lucas, 1951, 1952). It is of particular interest to compare the present results on Be with these previous observations on the oxidation of zinc, because these metals, though similar in crystallographic structure, differ much in properties, such as melting point and the rate of diffusion of metal ions through the oxide.

No previous experiments on oxidation of beryllium single crystals appear to have been reported although rather limited studies on the oxidation of polycrystalline beryllium have been made by Yamaguchi (1943), Cubicciotti (1950), Gulbransen & Andrew (1950). Kerr & Wilman (1956) using electron diffraction, found that beryllium oxide grew on a one-degree (001)-oriented beryllium deposit (condensed from the vapour in vacuo), so that the BeO (001) planes were parallel to the Be (001) planes, although the occurrence of epitaxy could only be inferred as likely from their results. They also concluded that (103)-oriented oxide was formed upon (110) faces of beryllium.

2. Experimental details

Materials

Polycrystalline beryllium rod of 1·2 cm. diameter was machined from hot-extruded bar produced from French Flake beryllium. The single crystals were grown from the rod by the zone-melting method.

The main impurities present in normal zone-melted material are 0·14% BeO, 0·014% Fe, 0·005% Al, 0·005% Si, 0·003% Cl, and a trace of Mg, N and F.

Preparation of specimen surfaces

After etching the beryllium single crystal in a

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solution of 50% aqueous H_2SO_4, fine cracks became apparent which were found to be parallel to (001) planes.

Fresh (001) faces were prepared by cleavage of the single-crystal rod along these cracks at liquid-air temperature using a hammer and chisel.

Other single-crystal faces, (001), (100) and (110), were prepared by cutting the crystal in the required direction (with reference to the cracks parallel to (001)), and then smoothing the surface upon successively finer grades of emery paper down to 0000, using propyl alcohol as lubricant. The final mechanical surfacing was performed upon a rotating wheel using a diamond compound abrasive (Hyprez) of a mean particle size of 3μ. The distorted layer produced by this polishing was removed electrolytically in a solution of 100 ml. orthophosphoric acid, 30 ml. ethyl alcohol, 30 ml. concentrated sulphuric acid and 30 ml. glycerol, as recommended by Mott & Haines (1951–2). The surface was then thoroughly washed in distilled water followed by propyl alcohol.

Oxidation experiments

The present work was restricted to oxidation of beryllium in air. The specimen was inserted into the hot furnace, which was maintained at the particular temperature for a duration of, usually, 30 minutes. After removal from the furnace, the specimen was allowed to cool in air. Owing to a scarcity of suitably smooth cleavage surfaces, the same crystal was used throughout the series of experiments upon this face.

Examination of the specimen surface

Optical photographs were recorded after each stage of the heating by means of a Vickers projection microscope using normal back-reflection illumination.

The oxide growth formed at particular temperatures on small single-crystal fragments of Be was studied in the electron microscope.

The electron diffraction camera was of the type described by Finch & Wilman (1937), but evacuated by oil diffusion pumps. An accelerating potential of 50 to 60 kilovolts and a specimen-plate distance of 48 cm. were used. The orientations of the beryllium single crystals, and of the oxide films formed by heating, were determined from the diffraction patterns using the methods described by Wilman (1948, 1952). They were adjusted if necessary by further abrasion and polishing to within one or two degrees of the desired orientation. Surfaces prepared in this way were relatively smooth and perfect as adjudged from the clear electron diffraction patterns, which consisted of spots, often with Kikuchi lines. These spots were usually elongated normal to the shadow edge of the surface (Fig. 9), owing to the refraction of the electron beam at the smooth surface of the crystals.

3. Results

Electron diffraction patterns from the specimen surfaces were obtained with the beam along a main lattice row of the crystal, and in a second main azimuth usually perpendicular to the first.

In all these experiments, an increase of the sharpness of the diffractions with increase in temperature indicated that a corresponding increase in the size of the oxide crystals had occurred. The diffuse spots and broad rings or arcs, obtained in the patterns taken from the specimens after oxidation for 30 minutes at 300 °C. indicated that the crystal size was in the order of a few tens of Ångströms, while the sharp, spotty rings obtained from the surfaces after subjecting them to 800 °C. for 30 minutes, corresponded to a crystal diameter of some thousands of Ångströms.

Measurements of the patterns showed only the presence of normal hexagonal BeO. Calibration of the patterns using graphite powder ($d110 = 1{\cdot}230$ Å) gave $a = 2{\cdot}70$ Å and $c = 4{\cdot}38$ Å, i.e. $c/a = 1{\cdot}62$, closely agreeing with the data given by Swanson & Tatge (1953), $a = 2{\cdot}6979$ Å and $c = 4{\cdot}380$ Å.

(*a*) *Oxidation of a* (001) *cleavage face*

An electron diffraction pattern from the cleaved surface with the beam parallel to $\langle 100 \rangle$, Fig. 1, shows some spots from the beryllium metal but no Kikuchi lines. The presence of only one very strong spot, 002 in the plane of incidence, indicates that the circular Laue zones associated with the lattice row which is parallel to the beam direction are narrow, in fact the zero-order zone is less than 0·5 cm. wide. This is evidence of the large extent (several thousand Ångströms) of most of the diffracting material, in the beam direction. The higher intensity at the upper end of the much fainter remaining spots, shows that they are formed partly by transmission through projecting parts of the surface. The greater extent of the zero-order Laue zones on which these spots lie, show the very much smaller extent in the beam direction, of these projections (a few hundred Å). Thus the cleavage surface approximates relatively closely to a (001) face, and contains stepped regions or plateaux of several thousand Ångströms in extent together with a small proportion of much smaller projecting (001) surfaces.

The optical micrograph, Fig. 2, also shows on a coarser scale, such a surface form. The six-fold symmetry of the system of crystallographic planes bounding (001) faces can be seen in the optical microphotograph. Fig. 1, which was obtained with the beam along one of the sets of parallel lines, (see Fig. 2), shows that these bounding faces are ($10l$) planes.

No beryllium oxide diffractions (either rings or haloes) were observed in the patterns from the cleavage face, even when the specimen was left for several days exposed to air at room temperature. This does not indicate the total absence of oxide, but that the BeO layer on the surface was sufficiently thin (10 Å or less) not to obscure the diffractions from the Be.

Fig. 3, from the cleaved surface after heating at 300 °C. for 30 minutes, shows in addition to the spots from the beryllium, faint diffractions due to growth of a thin crystalline BeO film. Some of this oxide was in the form of randomly oriented crystals, as shown by the continuous rings, but the diffuse vertically-elongated spots which are faintly visible, especially the BeO 002 and 004 spots in the plane of incidence, show the first stages in the growth of an epitaxially oriented layer of oxide with the *a* and *c* axes of the BeO parallel to the *a* and *c* axes of the metal substrate. This example of parallel growth is represented diagrammatically in Fig. 19.

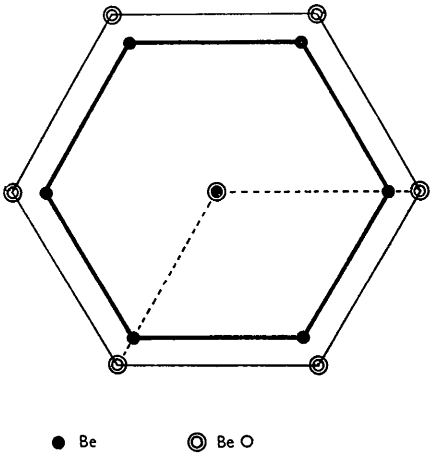

Fig. 19. Parallel growth of Be(001) on BeO(001) with ⟨100⟩ Be parallel to ⟨100⟩ BeO.

Further heating, for 30 min., at 350 °C., showed this parallel growth more clearly, as in Figs. 4(*a*) and 4(*b*), taken with the electron beam along Be ⟨100⟩ and ⟨210⟩ directions, respectively. Some sharp spots due to Be are still seen, due to transmission through the small oxide-covered projections of the Be. The arcing of the BeO diffractions indicates that a small amount of disorientation of the epitaxial BeO has occurred, in this case up to about 3° from the mean. These arcs are elongated normal to the shadow edge, owing to refraction of the electron beam in the relatively smooth (001) surfaces of the small oxide crystals.

In addition to this mode of growth of the oxide there existed some oxide in an orientation with the (101) planes parallel to the (001) beryllium surface. This is most clearly seen in Fig. 4(*a*) as a short arc centred on the plane of incidence and lying on the 101 diffraction position about 1 mm. above the strong 002 BeO diffraction. In order to determine the degree of azimuthal orientation of the (101) planes, Fig. 4(*a*) was compared with the pattern, Fig. 4(*b*), from the surface with the beam in the ⟨210⟩ direction, i.e. 30° from the beam direction of Fig. 4(*a*). If the (101) BeO growth is epitaxial, there will be six equivalent epitaxial orientations at 60° intervals, for the BeO on the Be, arising from the six-fold symmetry of the hexagonal lattice around the ⟨001⟩ direction. The disorientation of the BeO crystals makes it difficult to determine whether, in fact, there is an azimuthal preference for the (101) planes of the oxide with respect to the (001) planes of the Be. Indeed, the positions of the arcs on the (110) diffraction ring seen in Figs. 4(*a*) and 4(*b*) suggest that the proportion of epitaxial (101) oxide is small, and that the (101) BeO is, in effect, of one-degree type, i.e. azimuthally random. The theoretical positions of the diffractions from a (101) one-degree orientation of the hexagonal BeO structure ($c/a = 1{\cdot}62$), are shown for comparison in Fig. 20. The appearance of the surface at this stage of the oxidation shows little, if any, change when compared with Fig. 2.

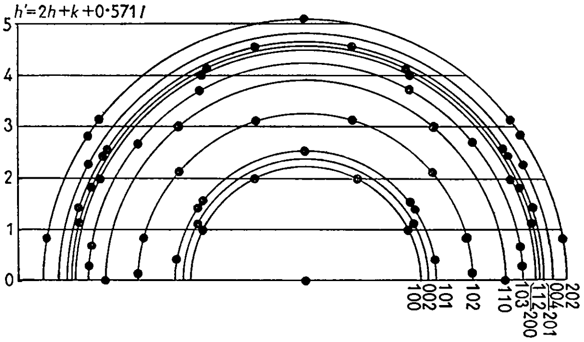

Fig. 20. Theoretical pattern from hexagonal structure ($c/a = 1{\cdot}62$) in one-degree {101} orientation.

The diffraction patterns from the surface, after heating for 2 hours at 350 °C., show little change from Figs. 4(*a*) and 4(*b*), and consequently no attempt was made to remove the BeO film formed after each period of heating before proceeding with the next experiment.

The specimen was further heated for periods of 30 minutes at progressively higher temperatures, 400 °C., 450 °C., 500 °C., etc., and the diffraction patterns from the surface showed an increasing proportion of oxide in a random orientation.

After heating for 30 min. at 600 °C., the oriented growth in the surface regions of the oxide accessible to the beam had nearly disappeared and most of the oxide showed random growth, Fig. 5.

Above this temperature, only random oxide growth at the surface was observed, Fig. 6. The weakness of the 002 diffraction in the patterns from the oxide produced at 800 °C., indicates a pronounced (001) habit of the oxide crystals. This conclusion is further substantiated by the decrease in intensity and increase in breadth of the 10*l* diffraction rings with increase in *l*.

Fig. 7 is a typical microphotograph of the surface at this stage, and shows a marked change of appearance. The surface of the beryllium is now seen to be covered with many dark spots 0·1 mm. diameter,

Fig. 1. Be(001) cleavage face; beam along ⟨100⟩.

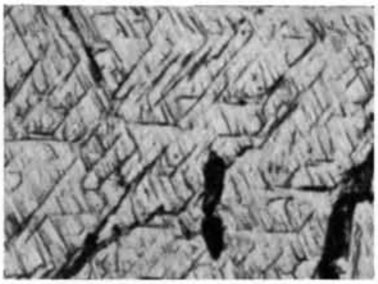

Fig. 2. Be(001) cleavage face (×130).

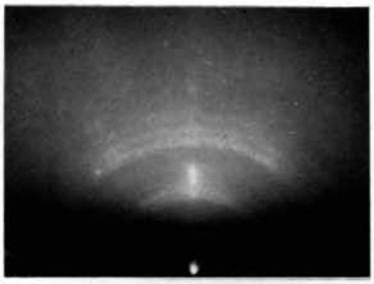

Fig. 3. As Fig. 1, but heated in air at 300 °C. for 30 min.

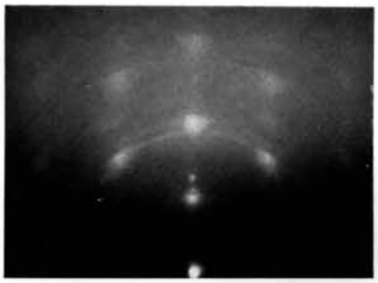

Fig. 4(*a*). As Fig. 3, after heating at 300 °C. and then 350 °C. for 30 min.; beam along ⟨100⟩.

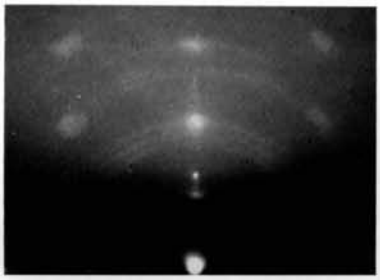

Fig. 4(*b*). As Fig. 3, after heating at 300 °C and then 350 °C. for 30 min.; beam along ⟨210⟩.

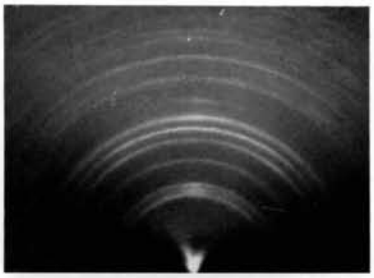

Fig. 5. As Fig. 4, after heating at 600 °C. for 30 min.; beam along ⟨100⟩.

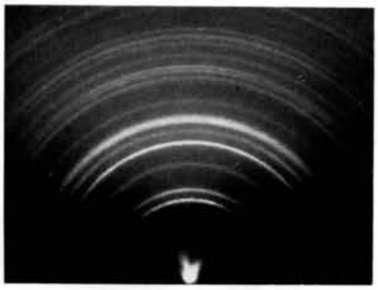

Fig. 6. As Fig. 5, after heating at 800 °C. for 30 min.

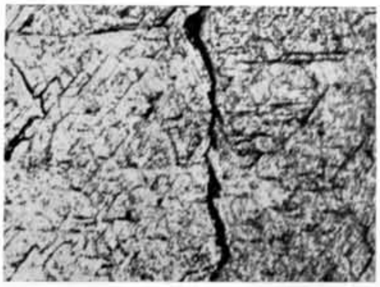

Fig. 7. Be(001) cleavage face, after heating at 800 °C. for 30 min. (×130).

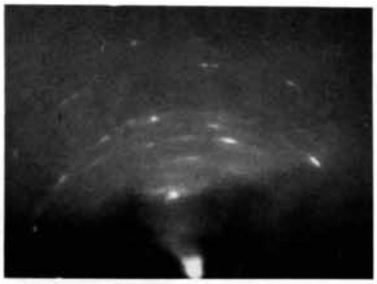

Fig. 8. As Fig. 6, after heating at 1050 °C. for 30 min.

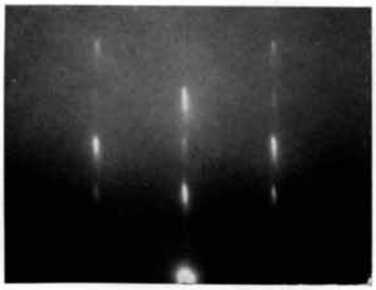

Fig. 9. First electropolished (001) face; beam along ⟨100⟩.

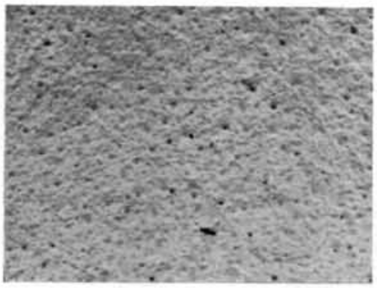

Fig. 10. First electropolished (001) face (×130).

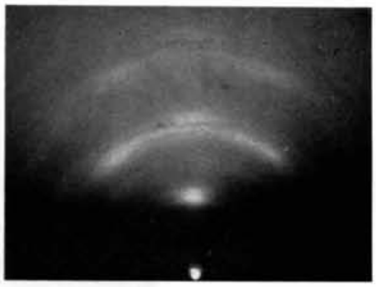

Fig. 11. As Fig. 9, after heating at 350 °C. for 30 min.; beam along ⟨100⟩.

Fig. 12. Second electropolished (001) face, after heating at 350 °C. for 30 min.

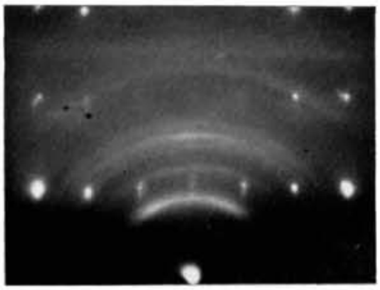

Fig. 13(*a*). Electropolished (100) face after heating at 350 °C. for 30 min.; beam along ⟨100⟩.

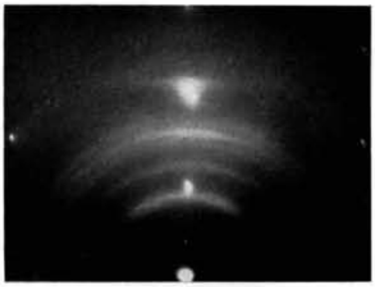

Fig. 13(*b*). Electropolished (100) face after heating at 350 °C. for 30 min.; beam ⊥ ⟨100⟩.

Fig. 14. Electropolished (110) face; beam along ⟨001⟩.

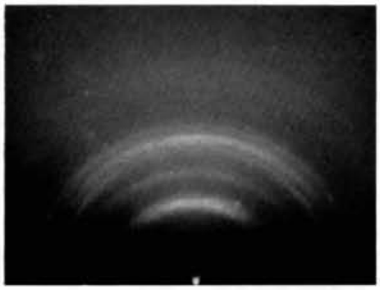

Fig. 15. As Fig. 14, after heating at 350 °C. for 30 min.; beam along ⟨001⟩.

Fig. 16(*a*) Electron micrograph (× 14,000) of Be crystal heated at 800 °C. for 1 hour, showing needle-like growth.

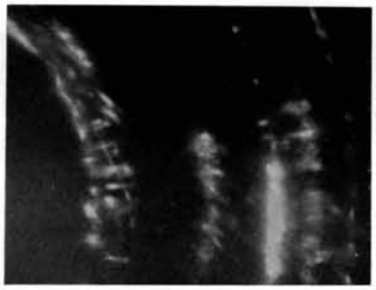

Fig. 16(*b*). As Fig. 16(*a*), but diffraction pattern (enlarged 2½ times).

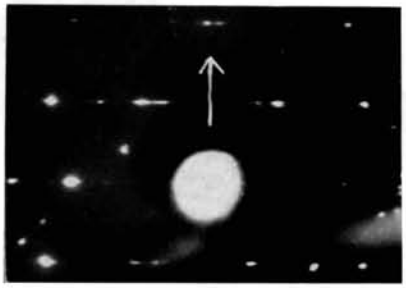

Fig. 17. Diffraction pattern mainly from an individual BeO needle; arrow shows needle axis.

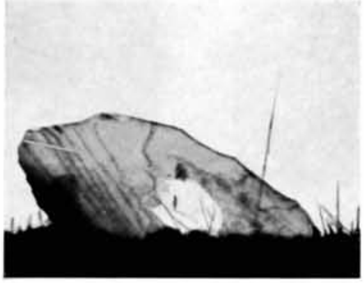

Fig. 18(*a*). Electron micrograph (× 5,000) of BeO flake.

Fig. 18(*b*). Diffraction pattern from a BeO flake.

(about 1 μ actual size), presumably due to the oxide growth, while the metal surface itself is apparently less strongly-stepped.

The uneven shadow edge seen in Fig. 8, obtained after further heating for 30 min. at 1050 °C., indicates that the BeO surface has now become very much rougher. The electron beam is accessible only to the upper regions of a few, relatively large BeO crystals which project from the surface. This results in the limited number of BeO diffractions seen in the spotty diffraction pattern, Fig. 8.

(*b*) *Oxidation of electropolished* (001) *faces*

Two experiments were performed on electropolished (001) faces. Since it was found difficult to remove the thick oxide film formed at the higher temperatures involved in the first experiment, a second crystal had to be prepared for the remaining studies on a (001) face.

After preparation of a (001) surface, as described in § 2, it was seen to possess smoothly-rounded projecting regions, Fig. 10. The relatively high local smoothness of the undulating surface is further indicated from the elongation of the diffraction spots normal to the shadow edge in Fig. 9, recorded from the surface with the beam along ⟨100⟩. The increased number of strong spots as compared with Fig. 1 from the cleavage face, shows the much smaller extent (probably less than 100 Å) of these surface projections in the beam direction.

Fig. 11 was from the surface after heating at 350 °C. for 30 min., and shows that the BeO (001) planes were aligned parallel to the Be (001) planes. Although there was considerable azimuthal spread of the BeO (001) planes around the [001] normal, an azimuthal preference was observed with the [100] BeO direction parallel to [100] Be (as with the cleavage face). The (001) one-degree oriented BeO is indicated most clearly by the 103 and 105 arcs which appear with the beam along [210], as well as in Fig. 11 with the beam along [100]. A disorientation of the epitaxial growth has occurred, in this case of nearly ±10°. The high degree of smoothness of the crystal surface is indicated by the elongation of the BeO diffraction arcs, due to refraction, in a direction normal to the shadow edge.

In addition, some of the beryllium oxide crystals had grown with (100) planes parallel to the substrate, as can be seen in Fig. 11 by the 100 arc in the plane of incidence. The broad BeO diffractions obtained at this stage of the heating makes it difficult to determine with certainty the nature of the azimuthal preference (if any) of this (100) orientation. However, the positions of the 110 arcs (just below the 103 diffractions from the epitaxial (001) BeO), when compared with the theoretical pattern (not illustrated), indicates a (100) one-degree orientation.

Diffraction patterns from the surface after heating at higher temperatures showed a progressively increasing amount of random BeO in the surface regions until, at 700 °C., the oxide was completely random.

The second electropolished (001) face was seen to be slightly rougher after the electropolishing procedure, than that used in the previous experiment. However, the diffraction pattern from the surface was not appreciably different from Fig. 9, indicating a high degree of smoothness of the crystal face.

The specimen was heated at 300 °C. for 30 min., and the pattern showed the presence of a thin film of BeO. After further heating for 30 min. at 350 °C., the patterns taken at the [100] azimuth and 15° and 30° from this, were identical, e.g. Fig. 12, showing no azimuthal preference for the (001) BeO on the (001) Be surface. The BeO thus appeared to be in one-degree (001) orientation, and this was confirmed from the theoretical pattern (not illustrated). The length of the BeO arcs indicates that a disorientation has occurred, such that the (001) planes make an angle of up to 15° with the mean surface. The (100) orientation found in the previous experiment on the electropolished (001) face was not observed.

(*c*) *Oxidation of an electropolished* (100) *face*

During the surfacing and electropolishing of this crystal, deep cracks appeared perpendicular to the (100) face, i.e. parallel to cleavage planes. The electron diffraction patterns from the surfaces showed that these cracks were accompanied by an increasing amount of orientation difference of the crystal lattice on the two sides of the crevice. For instance, in Fig. 13(*a*), each spot of the Be single crystal pattern is replaced by a group of closely neighbouring spots, showing several component blocks of the crystal lattice differing in orientation by several degrees about the electron beam, or ⟨100⟩ direction.

Figs. 13(*a*) and 13(*b*), with the beam parallel and perpendicular to ⟨100⟩ respectively, are from the (100) face after heating at 350 °C. for 30 min. The Be spots referred to in the previous paragraph had evidently been produced by transmission of the electron beam through small projections of the relatively rough Be surface. The arcs and rings are diffractions from the BeO. These BeO arc patterns are the same at different

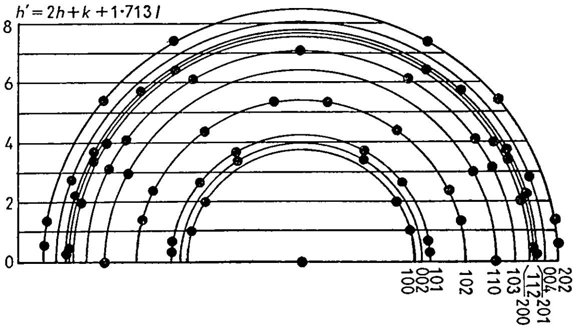

Fig. 21. Theoretical pattern from hexagonal structure (c/a = 1·62) in one-degree {103} orientation.

azimuths, showing a one-degree orientation of the oxide with the (103) planes parallel to the substrate. Fig. 21 shows the theoretical diffraction positions for such a one-degree (103) orientation and this agrees well with the arc positions in Figs. 13(*a*) and 13(*b*) (note particularly the lateral positions of the 002 arcs).

The (103) orientation persisted up to about 600 °C., above which temperature only random BeO growth was observed.

(*d*) *Oxidation of an electropolished* (110) *face*

The disorientation of the crystal lattice caused by the deep cracks developed parallel to cleavage planes, is illustrated in Fig. 14, which was from the electropolished surface with the electron beam in the [001] direction.

The orientation of the BeO growth produced by heating the crystal at 350 °C. for 30 min., appears from the long 103 and 002 arcs in the plane of incidence of Fig. 15 to be a mixture of one-degree (103) and (001) types. Comparison of the 110 diffraction arc positions in Fig. 15 with those in the theoretical patterns shows that the main orientation of the BeO is indeed (103), although some (001) orientation is also present.

The amount of orientated BeO decreased with increase in temperature until, at 600 °C., only random growth was observed.

(*e*) *Electron microscope observations*

Fig. 16(*a*) (at ×14,000), is a typical electron micrograph from the edge of a crystal fragment of beryllium after heating it in air at 800 °C. for one hour, and shows the development of a prominent whisker-like growth. The whiskers are 2 or 3 μ in length and several hundred Ångströms in thickness. The electron diffraction pattern of this growth was closely similar to Fig. 6 (obtained after heating the cleavage face at 800 °C.).

The slightly higher resolution of the electron beam in the electron microscope enables the diffraction rings to be resolved into a large number of single crystal spots, each of which is elongated, see Fig. 16(*b*) (enlarged 2½ times). This effect can be attributed to the shape of the crystals and to refraction of the electron beam in their surface.

Fig. 17 is a diffraction pattern, originating mainly from an individual BeO needle which was vertical with respect to the print. Unfortunately, difficulty was experienced in reproducing a print to show perfectly all the features that were visible on the original negative; nevertheless, these finer features will be referred to. Some diffraction spots are extended in a direction perpendicular to the needle-axis, forming a pattern of parallel, and almost continuous straight lines, of a separation corresponding to twice the (110) plane spacing. The positions of the spots from the single needle, show that the axis is ⟨110⟩ and, furthermore, that a limited range of orientation exists around this direction. The presence of strong 102 and 103 diffractions on the line through the centre spot ($h' = 0$), together with the absence of the corresponding 100, 002 and 101 diffractions on this line indicates that the extent of azimuthal spread about the ⟨110⟩ axis is less than about 20°, (see for comparison the theoretical one-degree (110) orientation pattern, Fig. 22). The remaining spots scattered over the lower part of Fig. 17 are from the numerous shorter BeO crystals on the surface.

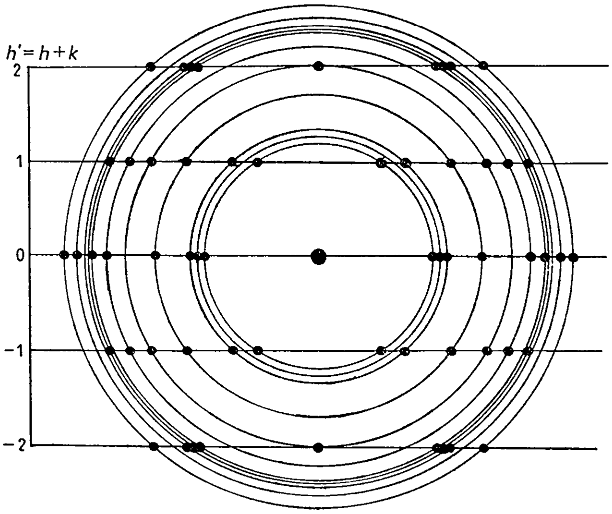

Fig. 22. Theoretical pattern from hexagonal structure (c/a = 1·62) in one-degree {110} orientation.

In addition to the needle-shape growth, thin flakes of BeO, several μ in diameter, were also observed projecting from the surface; (see, for example, Fig. 18(*a*) ×5000 from a Be crystal heated at 600 °C. for 1 hour). A typical diffraction pattern, Fig. 18(*b*), from such a flake shows the superposition of several single crystal spot patterns.

Only very few of these BeO needles and flakes were observed on crystals that had been heated below 600 °C., and none at all on crystals heated at 350 °C. for one hour.

4. Discussion

The present work shows that an epitaxial growth of BeO on a beryllium (001) cleavage face occurs when the crystal is heated in air for 30 min. in the range 300–400 °C. The (001) BeO planes are parallel to the (001) Be planes and the [100] BeO direction is parallel to [100] Be.

The small crystal size and slow rate of crystal growth of the thin BeO films (~ 10 Å) at about 300 °C. are similar to that found by Kerr & Wilman (1956) and Kerr (1956) and indicate a low mobility at this temperature. It is particularly interesting to observe such epitaxial overgrowths under these conditions.

The *a*-axis of the Be unit cell is 2·285 Å (Barrett,

1952) and that of the BeO 2·6979 Å (Swanson & Tatge, 1953). Epitaxial (001) parallel overgrowth thus corresponds to a lattice misfit of about 19%. Many other examples have been observed where the misfit is greater than the theoretical estimate of 10–15% suggested by van der Merwe (1949), e.g. Cu_2O on Cu (100) has a misfit of $18\frac{1}{2}$% (Mehl, McCandless & Rhines, 1934), ZnO on Zn (001) 21% (Acharya, 1948), and Sb_2O_3 on Sb (111) a misfit of 83% (Acharya, 1948). The relative positions of the atoms in such cases of epitaxy have been discussed in some detail by Aminoff & Broomé (1938) and by Seifert (1953).

Although the epitaxial (001) growth of BeO on the Be (001) cleavage face was the main orientation of the oxide at these temperatures (300–400 °C.), a one-degree (101) orientation of the oxide crystals was also observed. It was not possible to detect any sign of epitaxy of the (101) BeO on the (001) Be at this stage of growth, but it is possible that in the very early stages of growth such an epitaxy had occurred, similar to that found by Acharya (1948), for (101)-orientated ZnO formed on (001) Zn cleavages which had been heated in air after slight attack by H_2S gas or S from thiophene impurity in liquid benzene. With increasing film thickness it is found that the (101) orientation shows an increasingly greater spread from the mean and eventually becomes random. In general the more rapid the rate of growth, the more it tends to be disoriented (Wilman, 1940).

When the electropolished (001) Be surface was heated in air at 350 °C., the parallel growth of (001) BeO on (001) Be with [100] BeO parallel to [100] Be was less well-defined than with the cleavage face and a greater degree of disorientation was observed. In the first experiment on this (001) face, a proportion of BeO was in one-degree (001) orientation, while on the second face no azimuthal preference of the (001) BeO could be detected at all. This was evidently due to the fact that although judged on a microscopic scale the electropolished face appeared to be the smoother, microscopically the cleavage face possessed a very large number of small but perfect (001) faces upon which the (001) BeO could grow. The chemically prepared crystal faces presumably presented, to the reacting gas, a large proportion of surface elements other than (001).

No (101) one-degree orientation of the BeO, such as that seen in the diffraction patterns from the heated (001) cleavage face, was observed on the electropolished (001) surfaces, although in one experiment a trace of (100) orientation of the BeO was found in addition to the main (001) orientation.

A one-degree (103) orientation of the BeO crystals was observed on the electropolished (100) and (110) faces after heating them for 30 min. at 350 °C. The (103) orientation of BeO was also observed by Kerr & Wilman (1956) upon a vacuum-condensed (110)-orientated beryllium deposit. These writers suggested that the (103) BeO probably grew epitaxially on well-defined (110) facets of the beryllium crystals such that [100] BeO was parallel to a [210] Be lattice row. Such a (103) orientation would be similar to the epitaxial growth of (103) ZnO upon the (110) cleavage face of ZnS, found by many investigators (Yamaguti, 1935; Uyeda, Takagi & Hagihara, 1941; Evans & Wilman, 1950). However, in the present work, one-degree (103)-orientated BeO was observed on both the (100) and (110) Be crystal faces. Although the elongation of the Be spots in the diffraction patterns shows that at least some of the surface elements, formed during the electropolishing procedure, are parallel to the mean surface, those surface elements which are inclined to the mean surface will undoubtedly affect the observed orientation of the BeO growth.

The oxide produced on the (001) Be cleavage face after 30 min. heating at 350 °C., was not appreciably affected by further heating (2 hr.) at the same temperature. This is presumably due to the protective nature of the thin BeO film formed under these conditions, the volume ratio of oxide to metal being greater than unity (Pilling & Bedworth, 1923), in this case 1·68 (Kubaschewski & Hopkins, 1953).

The increased rate of growth and crystal size of the BeO with increase in temperature is presumably due to the increased rate of diffusion of Be ions through the oxide layer.

At still higher temperatures (above 600 °C.), the BeO layer affords little protection to the Be substrate. The increased rate of reaction of the beryllium with oxygen at these higher temperatures results in outward growth of the oxide as can clearly be seen in the electron micrographs, which show that the BeO crystals formed at 600 °C. and above, develop as projecting needles and flakes on the Be surface.

The diffraction patterns showed the needles to possess a ⟨110⟩ axis with a limited azimuthal spread of (110) planes around the ⟨110⟩ normal. The parallel lines joining the diffraction spots implies that considerable disorder exists in the crystal. It has been suggested (for the case of copper oxide on copper by Cowley, 1954) that such disorder may take the form of screw dislocations parallel to the axis of the needle-like crystals. The flake-like crystals were seen to consist of thin lamellae, while the multiple single-crystal type of spot pattern indicated that considerable distortion exists in the crystal flake. Similar observations have been reported by Takagi (1954) for ZnO on Zn and brass, and he concluded that the needle-shaped ZnO crystals have a ⟨110⟩ axis. This author also reported the occurrence of plate-shaped ZnO crystals showing rotational slip, on a mechanically-distorted substrate of Zn or brass. Takagi's results are in contrast to those of Cowley, Rees & Spink (1951) who concluded that the axes of their ZnO smoke needles were [001].

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Solid Solutions in Bromine-Iodine Mixtures. II

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At −23·5 °C. the unit-cell volumes fall on a discontinuous plot which is not inconsistent with the existence of 3 ranges of solid solutions containing a predominance of Br–Br, Br–I and I–I molecules respectively.

Introduction

In the earlier part of the present work (Heavens & Cheesman, 1950) it was found possible to follow compositions only as far as 38 atomic% of bromine. A 9 cm. camera has now been developed in which it is possible to maintain temperatures down to −100 °C. or lower, and it has been found that with this the whole range of Br_2–I_2 mixtures can be readily photographed at −23·5 °C. In the region where the measurements overlap those previously obtained at room temperature, the new values lie on a line parallel with the earlier ones, the coefficients of expansion being in good agreement with those given by Straumanis (1943) for iodine. The observed values for a, b and c for the various compositions are shown in Table 1.

Fig. 1 shows the product of a, b, c, viz. the effective unit-cell volume as a function of composition; three straight lines have been drawn through groups of points, in accordance with the hypothesis that three types of lattice arrangement succeed one another as the composition changes. Plots of the individual lattice constants exhibit similar breaks at the same