SHORT COMMUNICATIONS

THE OXIDATION OF POLYCRYSTALLINE BERYLLIUM IN CARBON DIOXIDE*

By W. J. VAN PEER†

The growth and structure of beryllium oxide on polycrystalline beryllium was studied, using weight gain versus time curves, electron diffraction, and X-ray diffraction.

The rates of oxidation varied widely for the different materials used and the ways in which the metal was produced.

Here the specimens were cut off from extruded bar of french flake powder, which was hot pressed and oxidized very rapidly in moist carbon dioxide at 700 °C in a furnace with a large constant temperature zone, at atmospheric pressure.

The electron diffraction camera used was an R.C.A. type E.M.C. electron microscope, converted into a diffraction camera by Dr. C. S. Lees at Harwell (1954) and modified by the author.

Working at a fixed voltage of 30 kV and a camera length of 25 cm, λL was of the order of 1·7Å cm. The central spot diameter varied between 0·02 and 0·025 cm.

The oxide grew with a preferred 001 orientation and an estimate of crystal sizes was made at regular intervals.

This was calculated from the ring breadths, using the formula $t \simeq \lambda L/B'$, where B' is the corrected half-breadth of the *hkl* ring and t is the effective mean thickness of the crystal in a direction normal to the *hkl* plane.

Scherrer's formula was applied for correction $B' = B - b$, where B is the observed half-breadth of the ring and b the instrumental broadening due to the diameter of the electron beam.

The ring chosen for measurement was the 100 reflection, giving an estimate of the thickness normal to the c axis.

Specimens examined before oxidation, being etched in a suitable solution to take off the work-hardened layers, showed beryllium oxide present on the surface with a crystal size of a few hundred Ångström units (Plate 1, Fig. 1).

The interplanar spacings from the patterns always corresponded to the A.S.T.M. X-ray data for crystalline hexagonal beryllium oxide.

In the electron diffraction case, however, the 002 diffraction arcs were very weak or missing. This must be due to the beryllium oxide crystals being plate shaped, with large smooth 001 faces, parallel to the beryllium substrate.

* Manuscript received October 11, 1960.

† Australian Atomic Energy Commission.

Diffractions such as 100 and 101 will then arise by transmission through the tips of flakes oriented with an edge projecting from the surface, while the 002 can arise only by a grazing Bragg reflection from 001 faces of flakes lying flat in the surface and will therefore suffer severe refraction and more broadening than the other diffractions. This causes the 002 diffraction to be very much diffused and weakened. It has been found by X-ray diffraction that the rod has a definite fibre texture with the orientation axis at right angles to the rod axis.

The next specimens were heated for 10 min at 700 °C in carbon dioxide at atmospheric pressure and show that a large number of very small beryllium oxide crystals appear in a mean preferred 001 orientation with a crystal size of 20–50 Å. (Plate 1, Fig. 2.)

After 1 hr at 700 °C the specimens show that beryllium oxide needles have grown, probably on dislocations with a crystal size of 100–200 Å.

After some hours the needles have grown into large beryllium oxide flakes. The rings become very spotty as Plate 1, Figure 3, shows, particularly the 100 and 110 reflections. The size of the flakes was estimated at 1000 Å.

Plate 1, Figure 4, shows a transmission pattern of a thin film of beryllium oxide taken from specimen 2.

No beryllium carbide rings appeared in the patterns, because the carbide formed on the surface readily hydrolysed to beryllium oxide in the moist carbon dioxide atmosphere. Its presence was made evident, particularly for the stronger reflections, in an X-ray diffractometer.

In the oxidation of beryllium with carbon dioxide the following thermodynamically possible reactions occur:

$$(1)\quad Be+CO_2\rightarrow BeO+CO,$$
$$(2)\quad 2Be+CO_2\rightarrow 2BEO+C.$$

The beryllium carbide which is formed in the oxide layer comes from the reaction

$$(3)\quad 2Be+C\rightarrow Be_2C.$$

An appreciable percentage of the deposited carbon in the specimens is present as beryllium carbide. The reaction between beryllium and graphite powders is known to start at about 600 °C.

Because of the water vapour in these experiments (2%) the beryllium carbide in the outer surface is converted into methane,

$$Be_2C+2H_2O\rightarrow 2BeO+CH_4.$$

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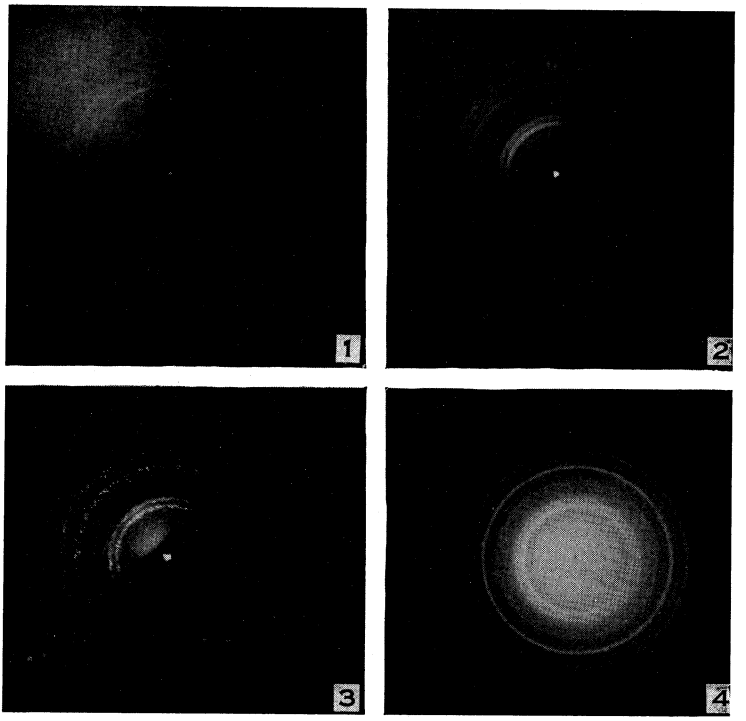

Electron diffraction patterns of beryllium oxide.