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Note

Unit Cell Dimensions Measurement of Less Perfectly Crystallized Artificial Graphite

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INTRODUCTION

The precise unit cell dimension measurement of the reactor graphite is difficult because of a small number of the X-ray diffraction lines. One can use only the small angle reflections (100), (110), (002), and (004).

Investigating highly crystalline graphites Bacon[1,2] got the following results: If the value of c dimension of the unit cell is deduced from a general line, such as (116), it is the same for different graphites, in contrast to the variation of c measured directly from a (00l) line. $c_{(00l)}$ is equal to twice the mean spacing in a stack of parallel graphite layers, some oriented and others disoriented. On the other hand, $c_{(116)}$ refers only to twice the interlayer spacing in a group of oriented layers, and is smaller than $c_{(00l)}$. Bacon also found apparent decreasing of a dimension of the unit cell, as inferred from the (120) line, with the increasing of the proportion of disoriented layers p, in contrast to the constancy of the $a_{(121)}$ values. Bacon's results refer to the highly crystalline samples ranging from $p = 0$ up to $p = 0.2$.

According to the equation for the mean interlayer spacing[2]

$$d = 3.440 - 0.086(1\text{-}p) - 0.064p(1\text{-}p)$$

the Yugoslav reactor graphite we examined had $p = 0.26$ and was not as well crystallized material as Bacon's samples. It was of interest to find if conclusions and results mentioned above had been valid also for such less perfectly crystallized specimens.

EXPERIMENTAL

X-ray photographs were taken using a microfocus X-ray tube with copper anode and *Hilger & Watts* Y 103 camera of diameter (90.00 ± 0.01) mm., for which the temperature stabilisation was realized[3].

Unit cell dimensions measured at (30.00 ± 0.05)°C were converted to the standard temperature of 25°C by means of the known thermal expansion coefficients[4].

In order to avoid the errors due to eccentricity, two X-ray photographs were taken for each specimen: one photograph with the specimen in the initial position, and one photograph after the rotation of the specimen for 180°.

The influence of the vertical beam divergence on the positions of lines was minimized using a collimator with height of 0.3 mm.

The positions of the diffraction arcs on the photographs were measured to 0.05 mm. by means of a film measuring rule and a converging lens as a magnifier. The accuracy was increased by means of a microfotometer, with 2 cm. continuous movement, for the measurement of the distances between the diffraction lines and razor blade scratches, drawn on the film.

We did not observe any significant orientation of the crystallites due to powder extrusion[5] procedure, whereby at the surface of the specimen there is an excess of the graphite layers parallel to the lenght of the specimen.

Errors due to absorption and the horizontal beam divergence were eliminated by the Bacon's method of accurate determination of unit cell dimensions for non-cubic substances[6]. As the internal standard was used a germanium powder giving non-overlapping lines in the whole angular range[3]. The effective camera diameter, including the effect of shrinkage, was determined individually for each photograph using the asymmetric placement[7] of films.

The arc diameter of the (004) line could be measured with error of 0.02 mm., and the arc diameter of the (110) line with error of 0.015 mm. We got the following values of the unit cell dimensions, converted to 25°C:

$$a_{(110)} = (2.4604 \pm 0.0003)\ \text{Å}$$
$$\left(\frac{c}{2}\right)_{(004)} = (3.3629 \pm 0.0007)\ \text{Å}$$

In order to record the low intensity lines (101) and (112) the solid specimens also were used thus avoiding the additional background produced by the germanium and the gum tragacanth binder.

A series of the photographs were taken of the five turned and ground specimens with diameter 1.0 mm.; 0.7 mm.; 0.5 mm.; 0.3 mm. and 0.2 mm. The errors due to absorption and horizontal beam divergence were eliminated by the extrapolation to the diameter of the specimen equal to zero. The films of all solid graphite specimens were developed together with one photograph of the germanium powder, which was used for the elimination of the film shrinkage error.

DISCUSSION

The extrapolation procedure is shown in Fig. 1 for (100) and (110) reflections (after convertion to the 25°C value). It is seen that the equal values of a dimensions were got using (100) or (110) line. Both values are in agreement

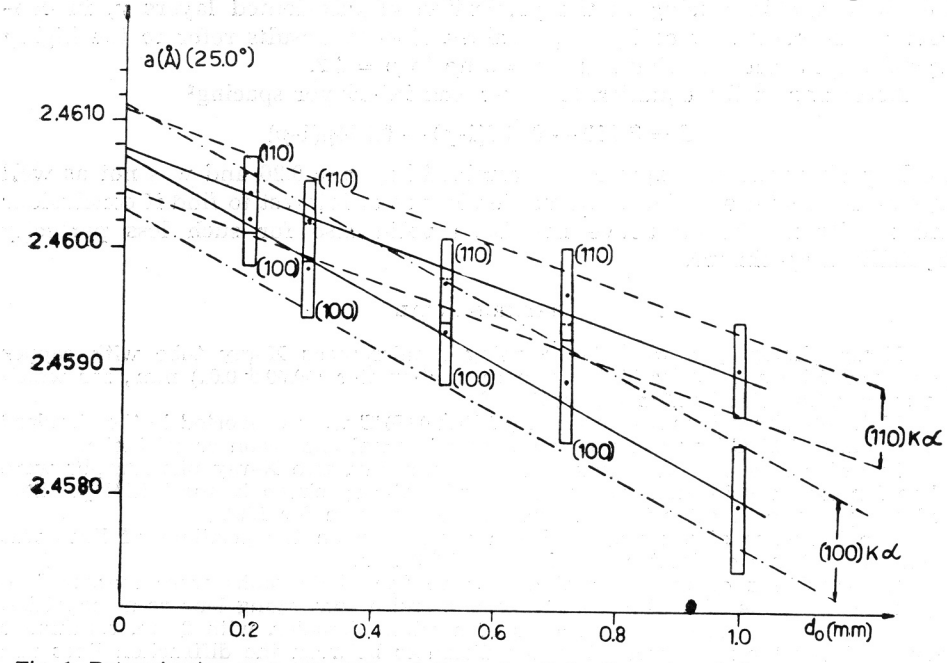

Fig. 1. Determination of a dimension of the unit cell by the extrapolation to the diameter of the specimen equal to zero for (100) and (110) reflections.

with that one obtained by the mixture method. The rectangular areas drawn around the points on the figure indicate the estimated accuracy of the measurements.

By the extrapolation procedure the arc diameters of the (101) and (112) lines could be measured with error of 0.02 mm. Using the Bragg angles of both reflections we deduced the following unit cell dimensions converted to 25°C:

$$a_{(101)\,(112)} = (2.4615 \pm 0.0006)\ \text{Å}$$

$$\left(\frac{c}{2}\right)_{(101)\,(112)} = (3.3542 \pm 0.0008)\ \text{Å}$$

The upper value of c dimension is substantially different from the previously deduced value $c_{(004)}$. One can also consider that the difference between observed values $a_{(101)\,(112)}$ and $a_{(110)}$ is greater than the experimental error magnitude. Those results are in agreement with Bacon's findings for the highly crystallized graphites.

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IZVOD

Mjerenje dimenzija elementarne ćelije slabije kristaliziranog umjetnoga grafita

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Snimanje uzoraka reaktorskoga grafita izvedeno je korištenjem mikrofokusne rendgenske cijevi pomoću kamere sa stabiliziranom temperaturom. Pogreške uslijed vertikalne i horizontalne divergencije snopa, apsorpcije, ekscentričnosti uzorka i stezanja filma eliminirane su prikladnim postupcima. Da se registriraju slabo intenzivne linije, snimani su i kruti uzorci, a pogreške uslijed apsorpcije i horizontalne divergencije uklonjene su ekstrapolacijom na promjer uzorka jednak nuli. Dimenzije elementarne ćelije a i c, izvedene iz linija (110), odnosno (004), razlikuju se od vrijednosti dobivenih korištenjem linija s općim indeksima (101) i (112), što je u skladu s opažanjima Bacona za bolje kristalizirane grafite.

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