A method for accurately determining lattice parameters using electron diffraction in a commercial electron microscope

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SUMMARY

In this paper an electron diffraction method is discussed by which the lattice constants of polycrystalline thin films can be accurately determined (0.1%). The method involves the sequential examination of a standard material and the unknown material mounted on separate grids. The error which can arise through the possible difference in height of the two grids can be corrected by means of height and tilting adjustments. The analytical approach of the dependence of the camera constant on the ring diameter as given in literature appears to be insufficient. An experimental correction factor for this dependence is introduced. The accuracy of this method, and the influence of relevant sources of error, are discussed and explained in terms of some experimental results.

1. STANDARD DIFFRACTION MEASUREMENTS IN ELECTRON MICROSCOPY

One of the most accurate procedures for determining lattice parameters with a commercial electron microscope is described by Andrews, Dyson & Keown (1967). A standard material (of which the d-spacings are accurately known) is evaporated onto the unknown specimen. As standard material, thallium chloride (TlCl) is generally used (Kay, 1965).

The resulting diffraction pattern contains the reflections of both materials. The diameters D of the diffraction rings of the polycrystalline TlCl can be measured. The camera-constant 2\( \lambda L_0 \) can be determined using the formula

\[
dD = 2\lambda L_0. \tag{1}
\]

Here \( \lambda \) is the wave-length of the electrons for the particular accelerating voltage, \( L_0 \) is the effective camera length, i.e. the distance from the specimen to the photographic plate. With the measured ring diameter \( D \) of the unknown specimen and obtained camera constant \( 2\lambda L_0 \), formula 1 can be used to calculate the d-spacings of the unknown specimen.

A correction is introduced with respect to the simple formula 1 as the effective camera length \( L_0 \) depends on the ring diameter \( D \) (Andrews et al., 1967). The corrected camera-constant \( 2\lambda L \) can be calculated from the following relation:

\[
2\lambda L = dD = 2\lambda L_0 \left(1 + \frac{3D^2}{32L_0^2}\right). \tag{2}
\]
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For the standard material a graph can be plotted where the corrected camera constant $2\lambda L$ is shown as a function of the ring diameter. For small values of the ring diameter this graph may be approximated by a straight line.

For each measured ring diameter $D$ of the unknown specimen the corresponding camera constant can be read from this graph. With formula 2 it is then possible to calculate the $d$- spacings. By application of the Miller indices to these values, the lattice parameter can now be calculated. It is also possible to determine the average lattice parameter.

For some investigations an accurate determination of the lattice parameter is necessary; e.g. in our laboratory the measurement of small changes in the lattice parameter of manganese ferrite as a result of an annealing treatment was required (Hulscher, Berg & Lodder, 1972). The application of X-ray diffraction offers no solution since the specimens are in the form of thin films (thickness about 75 nm) consisting of small crystals (10–100 nm). Moreover, it was necessary in this particular investigation to take normal transmission electron micrographs of the same specimen and to examine the magnetic micro-structure by Lorentz-microscopy.

2. DISADVANTAGES OF THIS DIFFRACTION PROCEDURE

Some disadvantages of this procedure can be highlighted by referring to the previously mentioned investigation of ferrite films. In order to take electron micrographs and diffraction patterns of this specimen before and after heat treatment (up to 900°C) it was preferable that the specimen should not be covered with TiCl. Furthermore it is difficult to measure separate reflection rings from TiCl and the ferrite films as they practically coincide. This difficulty may occur in other situations with specimens of complicated structure.

To avoid these disadvantages a method must be used where the standard and the specimen are separately introduced into the microscope each on different grids. In contrast to the previously described method, the disadvantage of a possible difference in height of the standard and the specimen is introduced.

The error in effective camera length can now be several percent (Rymer, 1970). In the present investigations, a higher accuracy was demanded. In the following section a method is described where the error mentioned above can be eliminated by correction of the specimen height with the height adjustment control and the tilt facility.

3. THE NEW ACCURATE DIFFRACTION METHOD WITH THE GONIOMETER

The unevenness of the specimen grid, the sagging of the film and the difficulty of introducing the specimen holder in the same manner can all result in a difference in specimen distance to the photographic plate.

For the immersion objective lens this difference in height needs a change in the focal length of the objective lens (Hall, 1966). This results in a difference in the effective camera length $L_0$. One solution of the problem is to construct a graph with the effective camera length as function of the objective lens current (Andrews et al., 1967). From this graph it is then possible to find the camera length for the specimen that is to be examined. This method does not appear to be very accurate. A more accurate and practical method would be to adjust the height of the standard material and the specimen with the height and tilt controls in steps. These two specimen movements are, in general, possible with the so-called goniometer stage.

Two commercial goniometer stages presenting the above mentioned specimen movements are known to the authors. Jeol has developed a side entry goniometer
that can be used in the Jem-100B electron microscope. The Philips goniometer can be installed in the Philips microscopes EM 200 and EM 300.

Other designs of this type of specimen stages are known in the literature, see for example Goringe & Valdré (1968). For our present work we have used a Philips goniometer installed in an EM 200 microscope. The design and operation of this stage are fully described by Rakels, Tiemeyer & Witteveen (1968). The procedure will now be described for obtaining accurate diffraction results.

The specimen is tilted in both directions through a large angle (about 30°). A recognizable specimen detail is projected into the centre of the fluorescent screen. When, during the tilting, this detail remains in the same place the height of the specimen is correct since it then coincides with the axis of tilt. When incorrectly adjusted the specimen detail will shift during tilting. By means of the height adjustment knob the specimen can be altered until the specimen detail fails to move over the screen during tilting. With this procedure the standard and the specimen can both be adjusted to the same height.

In this way the corrected camera constant $2\lambda L$ determined with the standard material can also be used for the measurement of the unknown specimen.

Reproducibility

The height correction appeared quite reproducible. To illustrate this the corrected camera constant as a function of $D$ for TICI is given in Fig. 1. The correct height adjustment is given by means of line 1. Line 2 is measured after the height adjustment of the specimen (in this case TICI) has been brought about 30 µm beneath the tilt-axis of the goniometer. This change of height is corrected by the above mentioned procedure. The change in the corrected camera constant as result of the change in height of 30 µm is 1.3%. The resulting difference in $2\lambda L$ after the height correction is only about 0.1%.

4. Calculation of the Lattice Parameter and the Error Involved

A number of sources of error by which the accuracy of the lattice parameter determination is influenced in this method are given in the literature (Meyerhoff, 1957, Rymer & Butler, 1945).

Relevant sources of error in our method will be discussed. First the microscope must be aligned to minimize the astigmatism. The elliptic form of the diffraction rings as a result of the remaining astigmatism can result in an error of about 1% of the measured ring diameter. This error can be disregarded when the diffraction patterns of the specimen and the standard are measured in the same direction (within a few degrees).

The diffraction patterns are fixed on photographic plates (glass). The measurement of the ring diameters was carried out by means of a microdensitometer (DD2) and a recorder (BD5) both manufactured by Kipp. The absolute accuracy in the measurement of $D$ on the plate for this combination is ±20 µm. By a correct adjustment of the slit size of the densitometer the influence of the curvature of the measured rings may be so small as to be neglected (Rymer & Butler, 1945).

For the calculation of the lattice parameters we have used the following procedure.

The camera-constant and the correction are determined from the calibration, using the accurately known $d$-spacings from literature (Hambling, 1953). In contrast to the analytical correction formula which is given in the literature (equation 2), we have used a general relation:

$$dD = 2\lambda L_0 + cD^2.$$  

(3)
Fig. 1. The camera constant as a function of the ring diameter given for TiCl. Line 1 is obtained by adjusting the specimen height correction knob of the goniometer. When the same specimen is placed about 30 μm beneath the correct adjustment, line 2 is then measured. This difference in height is corrected (Δ, measuring points). ○, Correctly adjusted specimen height; ◊, specimen about 30 μm beneath; △, corrected specimen height of line 2.

Both the camera constant $2\lambda L_0$ and the correction factor $c$ are calculated from the data obtained from the TiCl standard by application of the method of least squares (Squires, 1968). This experimental correction factor appears to be ten to twenty times greater than the corresponding geometrical correction $3\lambda/16L_0$ (see Fig. 2). For an accurate determination of the lattice parameter therefore, this analytical approach is insufficient. An explanation of this difference between the analytical and experimental approach has not yet been found.

The resulting experimental formula (3) is then used to calculate the lattice parameter of the unknown specimen. The weighted average $\bar{a}$ can be calculated from:

$$\bar{a} = \frac{1}{\sum_{i}^{m} S_{a_i}^{-2}} \sum_{i}^{m} \frac{S_{a_i}^{-2}}{a_i}$$

(4)

Here $m$ is the number of lattice parameters which is defined from the measured ring diameters of the specimen. $S_{a_i}$ is the standard deviation of sample in $a_i$ and here called standard error.
Fig. 2. Comparison of the experimental and analytical approach of the dependence of the camera constant on the ring diameter for TiCl. Line 1 shows the experimental approach and line 2 the analytical approach. (1) \( 2\lambda L = dD = 2\lambda L_0 + cD^2 \). (2) \( 2\lambda L = dD = 2\lambda L_0 + (3\lambda/16L_0)D^2 \). \( \bigcirc \), measured values; \( \lambda \), 0.0042 nm; \( L_0 \), 1.314 m; \( c \), \( 11 \times 10^{-12} \); \( (3\lambda/16L_0) = 0.6 \times 10^{-12} \).

The standard error in \( \hat{a} \) can also be defined. The 95% confidence interval of the lattice parameter is given by \( \hat{a} \pm 2S_\hat{a} \). The calculation of \( \hat{a} \) and \( S_\hat{a} \) in the above mentioned procedure is carried out by a computer.

5. RESULTS OF MEASUREMENTS

To test this procedure a number of electron diffraction patterns have been obtained from some vacuum evaporated metals of iron, silver and gold. From the same materials in bulk form we have also obtained X-ray diffraction patterns. The results of the electron diffraction analysis and those from X-ray diffraction measurements are presented in Table 1, where a comparison of the values from the ASTM-index is also given.

Table 1. Comparison of the lattice parameters given by the ASTM index and X-ray diffraction with those obtained by electron diffraction from some vacuum deposited metals and manganese ferrite

<table>
<thead>
<tr>
<th>Materials</th>
<th>ASTM index</th>
<th>X-ray diffraction</th>
<th>Electron diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a ) (nm)</td>
<td>( a ) (nm)</td>
<td>( \hat{a} \pm S_\hat{a} ) (nm)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.28839</td>
<td>0.28846</td>
<td>0.2885 ( \pm ) 0.0006</td>
</tr>
<tr>
<td>Fe</td>
<td>0.28664</td>
<td>0.28655</td>
<td>0.2868 ( \pm ) 0.0005</td>
</tr>
<tr>
<td>Au</td>
<td>0.40786</td>
<td>0.40801</td>
<td>0.4075 ( \pm ) 0.0006</td>
</tr>
<tr>
<td>Ag</td>
<td>0.40862</td>
<td>0.40861</td>
<td>0.4083 ( \pm ) 0.0002</td>
</tr>
<tr>
<td>Mn_{0.85}Fe_{2.15}O_{4+y}</td>
<td>0.8499*</td>
<td></td>
<td>0.8503 ( \pm ) 0.0002</td>
</tr>
</tbody>
</table>

* ASTM 10-319 for MnFe_{2}O_{4}.
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With respect to the previously mentioned investigations on manganese ferrite films, in the same table the result of our measurement is compared with those of the ASTM index. For this measurement on manganese ferrite a standard error in the ring diameter $D$ is found to be 6 µm.

In our calculations it is accepted that the standard error in $D$ is constant for all values of $D$ (Beu, 1962), and that the error in the $d$-spacings obtained from the literature are so small as to be neglected.

By means of these results it is shown that with the proposed diffraction measurement method a satisfactory level of accuracy can be obtained. The accuracy of the whole procedure is determined by the reproducibility of the height correction (about 0.1%).

6. CONCLUSION

A simple procedure has been introduced of achieving a reproducible and accurate electron diffraction method for polycrystalline thin films.

The standard material and the specimen are measured on separate grids. The specimen height is corrected using the height adjustment facility of a goniometer stage.

The accuracy achieved in a lattice parameter determination is 0.1%. A much greater accuracy appears to be unobtainable without many extra provisions. It is suggested that the rise in specimen temperature by irradiation with the electron beam is of great importance especially in the case of specimens with poor thermal conductivity such as oxides.

ACKNOWLEDGMENT

The authors wish to thank Mr B. v.d. Dolder B.t.w. for writing the computer programme.

References


