Habit and Orientation in Electron Diffraction

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Electron diffraction patterns of etched tungsten surfaces apparently indicate a preferred orientation of the crystallites, with [100] ⊥ surface. Actually, the etching leaves, on grains of a certain orientation, a structure exceptionally favorable for diffraction, and these selected grains dominate in the scattering. Analogous examples of weighted sampling, rather than random sampling, appear in studies of clays and of graphite. We suggest that crystal habit may frequently replace preferred crystal orientation as the cause of arcing in reflection patterns.

1. ETCHED METAL SURFACES

IN the course of studying electron diffraction by metal surfaces treated in various ways we examined a block of polycrystalline tungsten cut from a rolled strip 3 mm thick. One flat side was polished and then etched for 1 min. in 3 percent H_2O_2 solution, boiling. The semicircles of the reflection pattern had diameters appropriate for the body-centered cubic tungsten lattice, but were broken into well-defined arcs, indicating a preferred orientation of the surface crystallites involved in the diffraction. These crystallites, according to the pattern, have a [100] axis preferentially normal to the surface, and grains deviating from this orientation by more than 25° contribute only negligibly to the scattering. The arc pattern remained entirely unchanged as the sample was rotated in its own plane. We had to conclude that the surface crystallites concerned in the pattern have only the single fiber axis, [100] ⊥ surface, and are turned at random angles about the surface normal.

Rolling a metal commonly orients its crystallites in two directions: one crystallographic axis turns preferentially with respect to the direction of rolling and another turns preferentially with respect to the plane of rolling. We should have found a strong preference for [110] in the rolling direction and a less pronounced preference for [100] perpendicular to the plane of rolling.[1] The discrepancy between this expectation, based on x-ray studies of bulk samples, and our finding that only the surface normal appears as a fiber axis, made us suspect that the surface crystallites involved in the diffraction are not a true sample of the metal grains. To test this proposition we cut a 1-cm cube from a piece of wrought tungsten, polished three mutually perpendicular faces, etched for 1 min. in the boiling H_2O_2 solution, and made patterns of the three surfaces; again, we prepared in a similar way a cube from a block of tungsten sintered but not wrought, and made patterns of three mutually perpendicular faces. These six patterns were indistinguishable and were indistinguishable from the first-mentioned patterns of etched rolled stock. Finally, we made a pattern of the polished and etched end of a drawn tungsten rod in which the crystallites have, as a result of the drawing, a preferred orientation, [110] along the rod axis.[2] Still the pattern showed [100] ⊥ surface. Evidently the preferred orientation indicated by the diffraction patterns is not noticeably influenced by preferred orientation that may be present in the bulk sample.

Three explanations suggest themselves. The first is that the polishing may break up the surface crystallites and reorient the fragments, the rearranged layer persisting through the etching. Simple microscopic examination is sufficient to discount this surmise. The etching reveals the original grains of the bulk sample, producing a serrated structure that varies in tilt and course from one grain to another—in short, the diffraction samples, microscopically, are typical etched polycrystalline surfaces. A second hypothesis, so implausible as to require no discussion, is that the etchant somehow leaves submicroscopic ad-crystals on the surface, and

[1] Clark, *Applied X-Rays* (McGraw-Hill, New York, 1932), second edition, p. 379.

[2] M. Ettisch, M. Polanyi, and K. Weissenberg, Zeits. f. physik. Chemie **99**, 332 (1921).

that the lattice orientation of these ad-crystals is determined relative to the mean surface normal.

The correct explanation, we believe, is that diffracted electrons reach the photographic plate dominantly from those surface crystallites which after the etching display relatively long, sharp peaks emerging nearly perpendicular to the mean surface. Such grains will hide their more bluntly etched neighbors from the beam, and moreover the electrons will penetrate the tips of thin peaks more easily than the broader summits of flatter promontories.

It may, of course, be held simply that any etching which attacks the various crystal surfaces at different rates will leave only grains of a certain orientation projecting above the mean surface level and accessible to the electron beam. We cannot strictly insist that the difference between thin peaks and blunt summits is essential, though our experience with the preparation of metal samples to yield electron diffraction patterns suggests strongly that the details of surface structure within a grain determine the quality of the pattern, and even determine whether or not a crystalline pattern appears.

It remains to prove whether etching of a tungsten crystal in boiling H_2O_2 solution will produce a habit of the postulated sort. We had at hand a single-crystal tungsten wire 0.015 cm in diameter, made by the Pintsch process. When this had been etched in the solution long enough to reduce its cross section by some 50 percent the original circular boundary had given way to a rhombus of acute angle $76°\pm2°$, with slightly bulging sides. A back-reflection Laue pattern of the etched wire, made by Mr. Eric Asp of this Laboratory, identified the long diagonal of the rhombus as [100], the short diagonal as $[01\bar{1}]$, and the wire axis as [011]; the bulging faces are approximately of the (111) type. This result with the single-crystal wire indicates that the etching of a polycrystalline sample will produce on each grain an array of pyramids bounded by approximate (111)-type faces. It follows immediately that the most salient pyramids will indeed occur on grains that have a [100] axis most nearly perpendicular to the sample surface.

Boiling H_2O_2 is not the only etchant which produces on tungsten a surface yielding the pseudo-orientation patterns. We found the same effect after etching with the conventional $HF+HNO_3+H_2O$ mixture. When the single-crystal wire was etched in this solution its cross section again tended toward a bulged rhombus with diagonals in the [100] and the [110] directions. Electrolytic etching of tungsten in NaOH solution produces, under certain conditions, a matte finish, and such a surface also gives a diffraction pattern quite like that of the H_2O_2-etched samples. In fact, in every case where we have obtained a good pattern of bulk polycrystalline tungsten the same apparent preferred orientation, with approximately the same spread about the mean, has appeared.

Molybdenum, also, when etched in boiling H_2O_2 and quickly plunged into cold water to prevent formation of a colored film, yields a similar pattern, again indicating a fiber axis, [100] $\perp$ surface. We have not tested Mo so thoroughly as W, but the few patterns we have made are alike in this respect.

2. SETTLED CLAY SAMPLES

Another case of pseudo-orientation effects has appeared incidentally in some current studies of clay minerals. A drop of a thin water suspension of montmorillonite, of a certain range of particle size, is dried down onto a Formvar pellicle and the resulting sample is examined by transmission, at various angles relative to the electron beam. The diffraction patterns show beyond question that most of the particles, which have a platy habit, lie nearly flat on the Formvar film.[3] When a similar sample, made by drying down a drop of the same suspension on a polished metal block, is examined by reflection, the pattern contrastingly indicates that the flakes are standing preferentially edge-up on the surface, and moreover are preferentially perpendicular to the beam, no matter what the azimuth of the beam with respect to the settled deposit. All these conclusions cannot plausibly be maintained. The difficulty is resolved by assuming that the beam cannot get through the lamellar particles except nearly along the direction in

[3] S. B. Hendricks and C. S. Ross, Zeits. f. Krist. **100**, 251 (1938–39).

which they are thinnest. In the reflection case, flakes which happen to stand nearly edge-up and nearly perpendicular to the beam then dominate in the diffraction, though these particles are by no means representative of the settled aggregate. This explanation is entirely consistent with the known approximate dimensions of the flakes and the known approximate penetration range of the electron beam. When similar samples are made from a monodisperse fraction of montmorillonite, separated centrifugally and known to have a mean particle diameter in the neighborhood of 100A, the reflection pattern agrees with the transmission patterns in showing that the platelets lie preferentially flat on the surface. Diffraction features corresponding to lattice planes parallel to the plate faces now appear prominently in the reflection pattern, though these features were entirely absent from the reflection pattern of the larger particles.

3. GRAPHITE

Flake graphite, such as is used for lubricating small machine bearings, gives patterns analogous to those of the larger clay particles. Transmission patterns of a sample settled from air suspension onto a Formvar film prove that the flakes are predominantly flat on the surface, while a reflection pattern of a similar sample settled onto a polished metal block indicates that the flakes stand preferentially on edge. The discrepancy is again to be explained on the view that the beam can easily penetrate only those flakes that it strikes nearly perpendicularly; such flakes therefore have a weight in the reflection pattern far out of proportion to their frequency of occurrence in the sample.

A fine-grained block of graphitized petroleum coke after smoothing on No. 0 emery paper gives a reflection pattern indicating a preferred orientation of graphite lamellae normal to the surface and to the beam; this indication certainly does not agree with any reasonable picture of the actual surface condition. When, however, the same specimen is polished by rubbing on glass (which quickly coats with an adherent film of graphite) its pattern is that of flakes lying flat on the surface. The polishing, we must say, levels the surface and reduces the exposed flakes to a penetrable diameter. White and Germer,[4] studying carbon black deposits in which the pseudo-graphitic flakes are so small that the electrons can easily traverse them in any direction, get reflection patterns showing prominent $(00\cdot l)$ features and transmission patterns in which $(hk\cdot 0)$ rings are dominant. With graphitic carbon, as with the montmorillonite clay, when the particles are sufficiently small, transmission and reflection patterns tell consistent stories about the preferred orientation.

4. REMARKS

Our results with clays and with graphite are not without precedent: several investigators have remarked upon the absence or extreme weakness of reflections from the basal planes of layer-lattice materials and have attributed this anomaly, as we do, to a lamellar shape of the crystals in the sample.[5] It has not previously been noticed, so far as we know, that peculiarities of crystal habit even in materials of the cubic system can give rise to pseudo-orientation patterns.

We venture to wonder whether weighted sampling of crystallites, in place of random sampling, may not occur rather generally in the diffraction of electrons by surface layers. For example, the thin oxide films formed on polished metals by heating in air often give reflection patterns indicating a preferred orientation with respect to the surface normal. We suggest, in view of the observations described here, that such patterns may need to be interpreted cautiously.

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[4] A. H. White and L. H. Germer, J. Chem. Phys. **9**, 492 (1941).

[5] See L. H. Germer and K. H. Storks, Ind. Eng. Chem., Anal. Ed. **11**, 583 (1939) and references given in discussion on p. 588.