On the Etched Surfaces of Nickel Single Crystals Revealed by Means of Electron Diffraction and Microscopy

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The etched surfaces of nickel single crystals were here examined by means of electron diffraction and oxide replica of microscopy. The electron diffraction method identified the crystalline substances found in the etched surfaces of specimens and determined their crystallographic orientation. The oxide replica method of electron microscopy clarified the forms and orientation of the metal crystals on the etched surfaces of specimens. It was demonstrated in the present study that the combination of electron diffraction and microscopy made it possible to assign the crystallographic indices to the etched surfaces of single crystals of nickel. It is important to ascertain the particular crystallographic arrangement characteristic to the atoms on the etched surface, because the physical and chemical properties (*e. g.*, catalysis,(1) corrosion-resistance(2) *etc.*) of nickel crystal should be discussed in relation to the atomic arrangement experimentally determined.(3)

(1) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).
(2) S. Yamaguchi, T. Nakayama and T. Katsurai, *J. Electrochem. Soc.*, **95**, 21 (1949).
(3) T. N. Rhodin, *J. Appl. Phys.*, **21**, 971 (1950).

Experiments

The three types of nickel single crystals(4) employed in the present experiments were the three metal discs (diameter: 10 mm., thickness: 2 mm.) cut along the (001), (110) and (111) planes respectively. These specimens were named No. 1, 2 and 3 here. The surfaces of these three types of disc specimens were buffed and then etched with ethanol-bromine (10 : 1 by vol.) for 10-20 seconds. These specimens gave respectively different etching figures to naked eyes. These etched surfaces were observed at first by means of electron diffraction and then oxide replica method of electron microscopy.

The specimen No. 1 gave the diffraction patterns shown in Photos. 1-4. These diffraction patterns verified the existence of pure nickel crystal in the etched surface of specimen. Photo. 1 coincides with the diffraction pattern which should be given by the electron beam running parallel to the (001) and (110) planes of nickel single crystal. The electron beam in obtaining Photo. 1 was nearly parallel to the macroscopic surface of etched specimen. Photos. 2 and 3 were obtained from the specimen surfaces rotated respectively by 15° and 30° from the position of Photo. 1. Photo. 4 was obtained from the specimen whose macroscopic surface was inclined by 2° to the incident beam in the position of Photo. 2. These four diffraction patterns verified that the macroscopic etched surface of specimen No. 1 was approximately parallel to the (001) planes of nickel single crystal.

The etched surface giving the diffraction patterns of Photos. 1-4 was treated in an autoclave (water vapor pressure: 15-20 atm., duration of reaction: 5hrs.) in order to form the structureless oxide film on the specimen surface. This oxide film was stripped from the substrate by Mahla-Nielsen's method(5) with ethanol-bromine solution. The isolated film was magnified by means of electron microscopy. The electron micrograph obtained is shown in Photo. 5. It is seen in Photo. 5 that the crystals of cubic form (size: 30 mμ-300 mμ) are oriented in one direction. Some side planes of the single crystals recognized in Photo 5 are distinctively more opaque than the other planes. This means that the crystallographic indices for the opaque planes are different from those for transparent planes, since the former planes have been oxidized more deeply than the latter. It is, therefore, concluded in reference to the results of diffraction experiments described above that the etched surface of specimen No. 1 is composed of the (001) and (110) planes, as is shown in Fig. 1. It is surmised here that the (110) faces are more easily oxidized than the (001) planes.

The specimen No. 2 gave the diffraction patterns shown in Photos. 6-8. Many fine grooves arranged

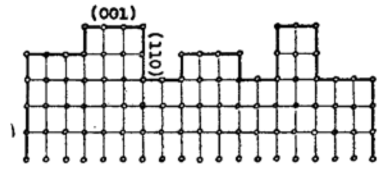

Fig. 1.—Profile of specimen No. 1 sectioned parallel to (1̄10) plane. Atom distances: 3.52 Å. and 2.49 Å.

parallel with each other were observed by naked eyes on the etched surface of the specimen. The electron beam running parallel to these grooves gave the diffraction shown in Photo. 6. The beam intersecting at the angles of 45° and 90° to the direction of the grooves gave the patterns of Photos. 7 and 8 respectively. These diffraction patterns verified that the macroscopic surface of specimen No. 2 was parallel to the (110) planes of nickel crystal and the direction of the grooves was parallel to the (1̄10) direction.

The etched surface of specimen No. 2 was magnified by means of electron microscopy, as is shown in Photo. 9. The long crystals oriented parallel to each other in Photo. 9 might be seen as etching grooves with naked eyes. In this way the profile of specimen No. 2 sectioned parallel to cube face was shown schematically in Fig. 2, *i. e.*, the etched surface of specimen No. 2 is composed of the (110) and (1̄10) planes.

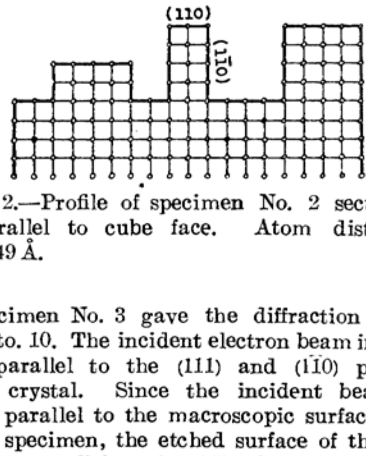

Fig. 2.—Profile of specimen No. 2 sectioned parallel to cube face. Atom distance: 2.49 Å.

Speccimen No. 3 gave the diffraction pattern of Photo. 10. The incident electron beam in Photo. 10 is parallel to the (111) and (1̄10) planes of nickel crystal. Since the incident beam was nearly parallel to the macroscopic surface of the etched specimen, the etched surface of the specimen was parallel to the (111) planes and perpendicular to the (1̄10) planes. The Kikuchi-lines are found in Photo. 10. This means that the etched surface of the specimen is rather flat than thorny.

The magnified reprints of the etched surface of specimen No. 3 are shown in Photos 11 and 12. There are many lamellar crystals of triangular form in Photos 11 and 12. The faces of the lamellae had to be assigned with (111) indices in reference to the results of the diffraction experiments. The surface of specimen No. 3 was composed of the (111) and (1̄10) planes, as is shown schematically in Figs. 3 and 4.

(4) These single crystals were prepared by S. Kaya, and J. Horiuti used these crystals for the samples in the experiments on chemical kinetics.

(5) E. M. Mahla and N. A. Nielsen, *J. Appl. Phys.*, **19**, 378 (1948).

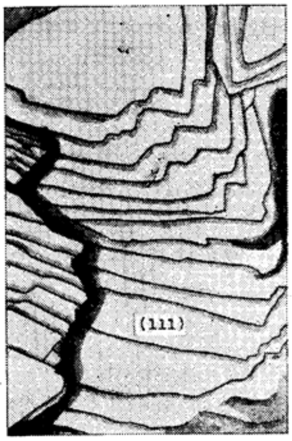

Fig. 3.—An exaggerated sketch of Photo 11.

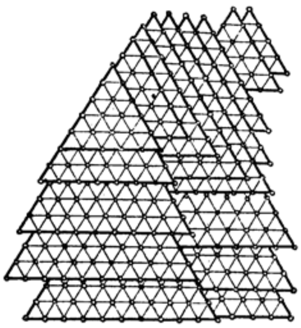

Fig. 4.—Projection of the etched surface of specimen No. 3 showing the (111) faces. Atom distances, 2.49 Å.

Discussion

The crystallographic assignment of the boundary planes of the powder crystals was able to be carried out by means of electron microscopy and microscopic diffraction.(6) In order to assign crystallographically the boundary planes of bulk single crystal, however, it was necessary to rely on the oxide replica method and the electron reflection method of diffraction as given in the present study.

The temper colors obtained on the etched surfaces of the specimens on exposure to the air were here observed. The etched surface of specimen No. 2, which was composed of the (110) and $(1\bar{1}0)$ faces, became mat rapidly in the air at room temperature. On the other hand, the etched surface of specimen No. 3, which was composed of the (111) and $(1\bar{1}0)$ faces, became mat very slowly in the air at room temperature. These facts indicated that the (110) face, whose atomic arragement is coarse, is chemically most active, and the (111) face, which consists of the closest packed atoms, is most inert among the principal faces of nickel crystal.

Summary

(1) It was possible to assign the crystallographic indices to the etched surfaces of single crystals by the combination of electron microscopy and diffraction.

(2) The (110) plane of nickel crystal was most active and the (111) plane was most inactive among the principal planes of crystal.

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(6) A. C. Dorsten, H. Nieudorp and A. Verhoeff, *Philips Tech. Rev.*, **12**, 33 (1950).

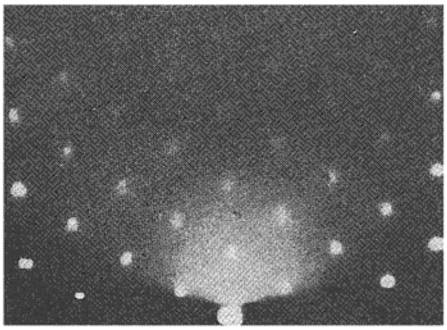

Photo. 1.—Incident beam is parallel to (001) and (110) planes. Macroscopic surface is parallel to (001) planes.

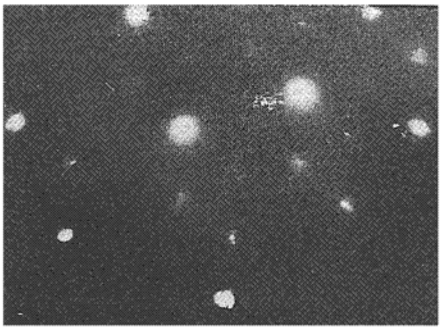

Photo. 2.—Diffraction from the specimen surface rotated by 15° from the position of Photo. 1.

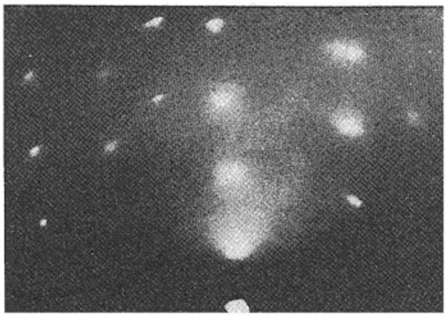

Photo. 3.—Diffraction from the specimen surface rotated by 30° from the position of Photo. 1.

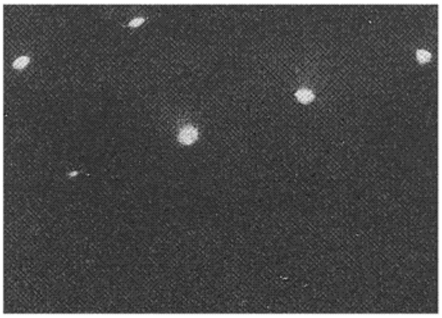

Photo. 4.—Diffraction from the specimen surface inclined by 2° to incident beam in the position of Photo. 2.

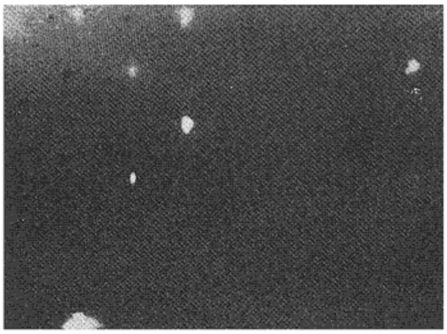

Photo. 6.—Diffraction of the incident beam parallel to the etching grooves of specimen No. 2.

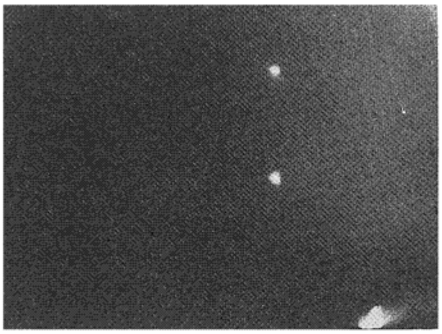

Photo. 7.—Diffraction from the specimen surface rotated by 45° from the position of Photo. 6.

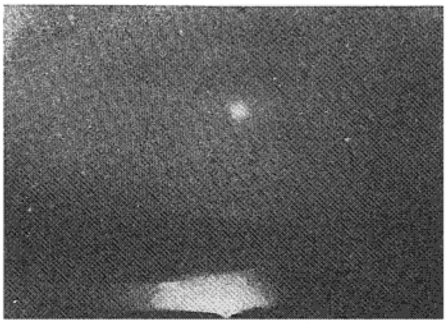

Photo. 8.—Diffraction from the specimen surface rotated by 90° from the position of Photo. 6.

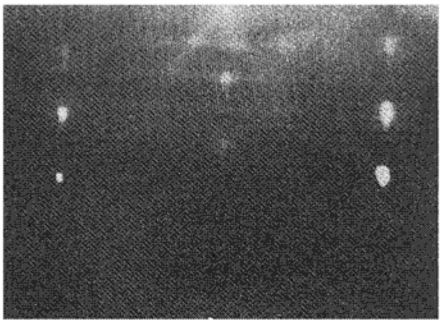

Photo. 10.—Diffraction from the etched surface of specimen No. 3. Macroscopic surface of specimen is parallel to (111) planes

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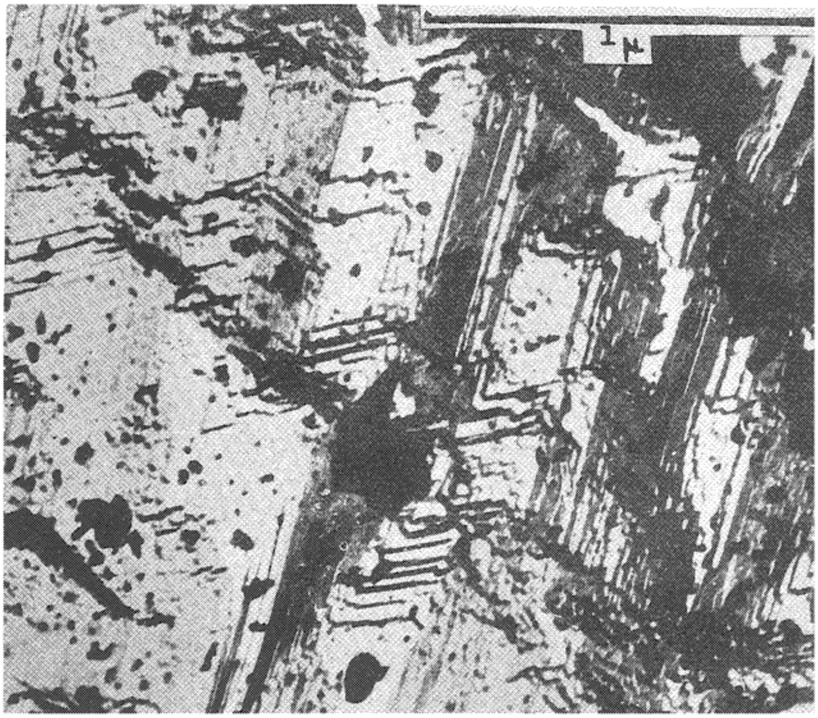

Photo. 5.—Electron micrograph of the etched surface of specimen No. 1.

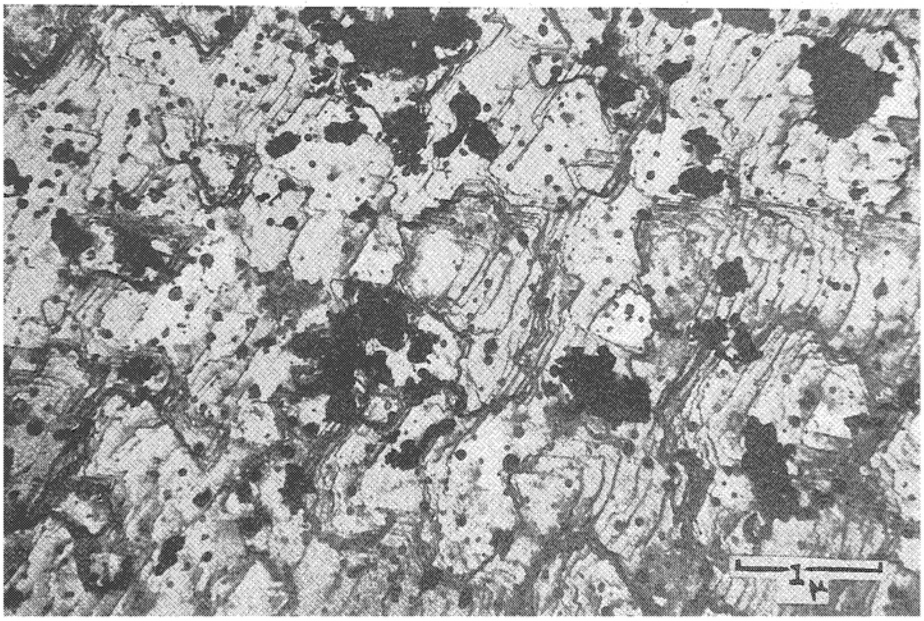

Photo. 11.—Electron micrograph of the etched surface of specimen No. 3. There are many lamellar crystals.

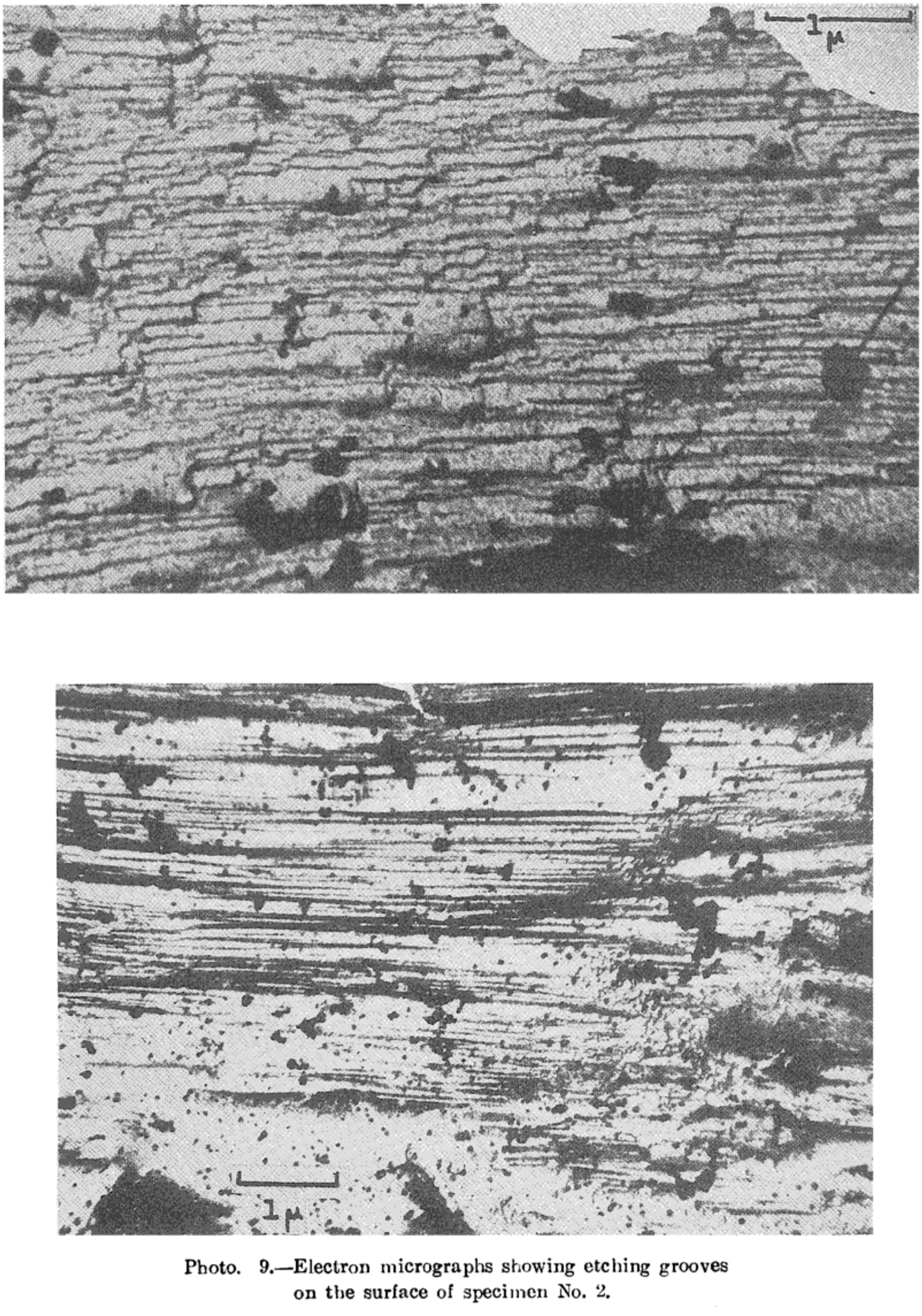

Photo. 9.—Electron micrographs showing etching grooves on the surface of specimen No. 2.

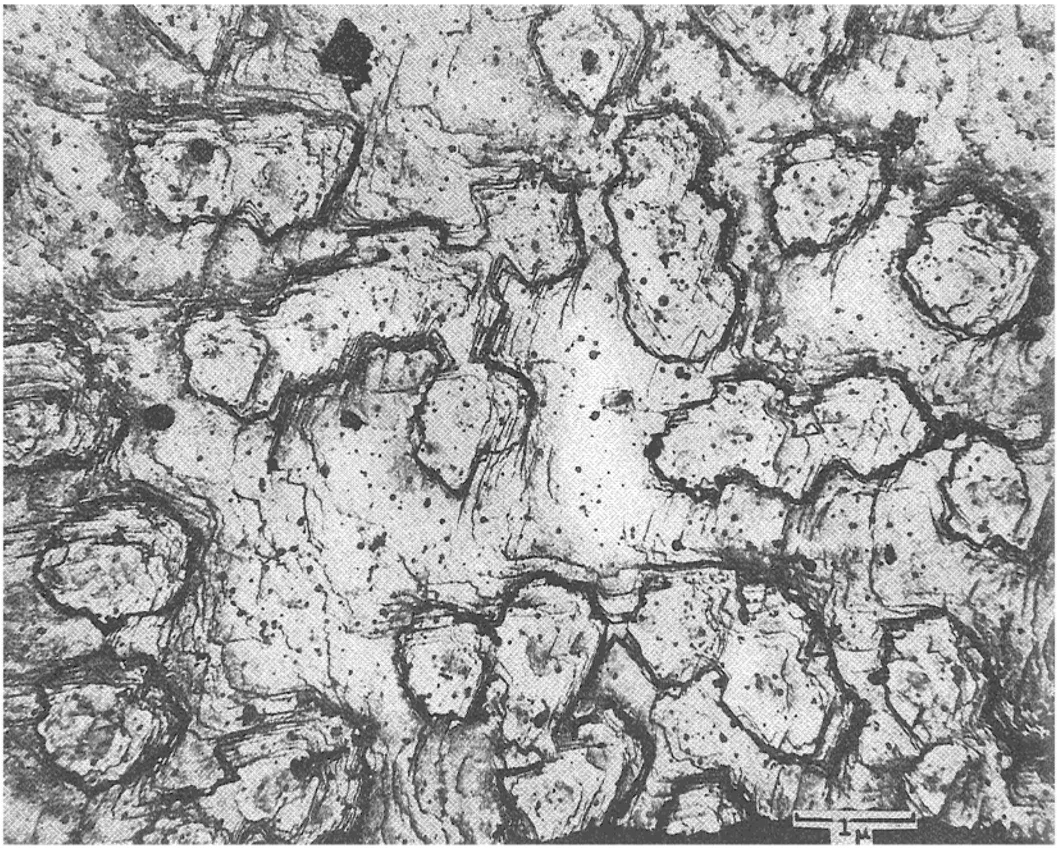

Photo. 12.—Electron micrograph of the etched surface of specimen No. 3. There are lamellae of triangular form.