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PHYSICAL METALLURGY DIVISION

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Ion Bombardment of Single Crystals of Aluminum*

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(Received 6 November 1962)

This paper presents the results of bombarding the (100), (110), and (111) surfaces of aluminum single crystals with a narrow beam of 8-kV argon ions. The crystals were tilted at the angles required to bring [110], [100], [112], and [111] directions parallel to the beam. The experiments were designed to study the effect of incident ion direction on ejection directions and etching rates.

Ejection directions, as determined from the positions of deposits on hemispherical collectors, were found to be independent of incident ion direction for a given surface orientation. The quantity of material ejected along equivalent ejection directions was observed to decrease as the angle of deviation between the incident ion beam and the ejection direction increased. The principal ejection directions observed were [110]. Apparent [116] ejection directions were observed when (110) and (111) surfaces were bombarded. These were caused by an abrupt deflection of momentum from [110] directions of the crystal to directions close to [110] of elementary twins. These are formed by surface atoms in twin positions on (111) surfaces developed, in the case of the (110) surface, during bombardment. The [110] directions of an elementary twin are parallel to certain [114] directions of the crystal, and, had multilayer twins been formed, the resulting ejection would have been along apparent [114] directions as a result of Silsbee focusing. Ejection along apparent [116] directions was not observed from (100) surfaces presumably because predominant [100] surface grooves produced by bombardment could not contain (111) facets. Under these conditions [100] ejection was detected.

Etching rates, as judged by the occurrence of matte spots, were least when the beam was parallel to the close-packed [110] directions and greatest when parallel to high index directions making large angles with the [110] directions. Low etching rates were also observed when the beam became parallel to [100] and [112] directions. Any anisotropy in surface migration rates was shown to be negligible in controlling etching rates under the conditions of these experiments.

I. INTRODUCTION

THE directional ejection of atoms from single crystals of several metals when subjected to ion bombardment has been reported.[1–12] In some instances[1–4] the specimen was immersed in a high-density vacuum arc plasma, in others the specimen served as cathode[5–8] and therefore the published data refer largely to bombardment normal to the crystal surface. Nelson and Thompson,[9] using an ion source arranged to give an output beam of canal rays, bombarded polycrystalline gold foils of strongly preferred crystal orientation, at 20° and 70° to the specimen surface along chosen crystallographic directions. Using an electromagnetic separator as a source, Rol *et al.*[10] and Almen and Bruce[11] varied the angle of attack on single crystals of copper along single zones. Yurasova, Pleshivtsev, and Orfanov[12] bombarded a single crystal of copper with a beam of ions at various angles to a (100) surface and reported on the variation of ejection directions with energy.

Etching effects on single crystals when subjected to

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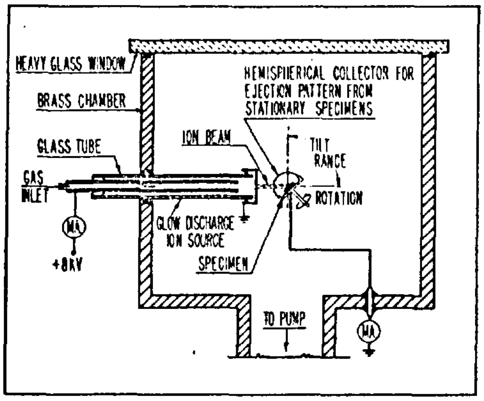

FIG. 1. Schematic diagram of ion source and reaction chamber. Argon gas input is regulated by fixed capillary and pressure control.

ion bombardment have been reported.[13–24] Here again the reported data refer largely to surface normal bombardment. However, Haymann[22,23] and Haymann and Lecomte[24] did report on etching effects on single crystals of silver using a well-defined beam of argon ions directed along chosen crystallographic directions. Experiments using narrow ion beams directed along chosen crystallographic directions were thus needed to supplement the papers cited above.

II. APPARATUS AND TECHNIQUES

The apparatus consisted of a vacuum chamber (Fig. 1) containing a two-circle goniometer which permitted the specimens to be oriented with any crystallographic direction parallel to the ion beam or to be rotated at a fixed angle of tilt to the beam.

The source consisted of a glow discharge tube operated at 8 kV with argon. The cathode was pierced with a 1-mm hole to permit the passage of ions into the bombardment chamber. The design was similar to that of Gervais and Trillat.[25] Argon, of mass spectrometer grade, was fed into the gun and the un-ionized gas passed into the bombardment chamber along with the ions. Having passed through the pierced cathode, the ions formed a slightly diverging beam which impinged on the specimen held at essentially the same potential as the cathode. It was thus possible to tilt the specimen for bombardment at any desired angle without modifying the path of the ions since the region between the cathode and the specimen was free of any significant field. The total current to the gun was held at 1 mA and the current to the specimens was usually stable and in the range of 100–200 μA. The cross section of the beam at the specimen was about 2 mm^2.

Although the pressure within the ion gun was necessarily some tens of microns of mercury, the pressure in the chamber was maintained at 0.2–0.3 μ by creating a pressure drop along the small hole in the cathode by rapid pumping. Low chamber pressure was necessary to prevent back-scattering of material onto the surface of the specimen. A liquid nitrogen trap was placed between the silicone oil diffusion pump and the specimen chamber. The background pressure in the system was about 0.01 μ. No significant atmospheric contamination was expected because the heavy current density used in these experiments continually exposed a fresh surface.

Ejection patterns were developed on the inner surfaces of hemispherical collectors cut from ping-pong balls. These were placed over the specimens with the point of bombardment at the center of curvature. A hole in the hemisphere admitted the ion beam in the desired crystallographic direction. The patterns were conveniently analysed by making pinholes through the hemispheres at the center of each spot in the pattern and then placing the hemispheres over a point source of light located so as to produce standard stereographic projections on a ground glass screen.

In principle, relative ejection rates for different incident directions could be determined by comparing the length of time taken to develop visible matte spots on different specimens. However, bombardment times were not satisfactorily reproducible from specimen to specimen, due perhaps to surface contamination during electropolishing or handling. These uncertainties were eliminated by a technique involving a single bombardment. The beam was made to strike a flat specimen, rotating about its normal and tilted in respect to the beam, at a point about 2 mm from the center of rotation so that a narrow ring about 4 mm in diameter was swept out on the surface. Thus, in one revolution, the beam became parallel to all the crystallographic directions corresponding to the tilt of a given specimen, and matte surfaces appeared first where the beam became parallel to the directions of most rapid etching. The trace of the beam passed through the center of rotation so that any forward surface migration of atoms did not interfere with other bombarded areas.

A Siemens Elmiskop I electron microscope was used for surface examination. Formvar replicas were shadowed with chromium at 30° in a direction opposite to that of the ion beam. A knowledge of the direction of bombardment was preserved by cutting a slit in the grids used as replica supports and orienting them on the specimen parallel to the direction of attack. Latex

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spheres, about $0.25\,\mu$ in diameter, were placed on the replicas prior to shadowing as a means of distinguishing between elevations and depressions on the replica.

Single-crystal specimens (10-×10-×5-mm) with (100), (110), and (111) planes in their surfaces were cut with a fine jeweller's saw from a large rectangular aluminum crystal grown from a seed in a horizontal graphite boat. The growth and surface normal directions were closely parallel to the cubic directions as determined by a Laue back-reflection photograph. After cutting from the large crystal, each specimen was ground to increase the accuracy of orientation to within 2° and then planed in an electric spark crystal-cutting machine to remove most of the cold-worked metal. These surfaces were then lightly polished on a series of five emery papers, followed by electropolishing for four minutes in a perchloric acid–alcohol–water solution, which, by Laue patterns, was found to have removed all cold-worked material. The analysis of the single crystal was determined spectroscopically and it was found to contain 0.001% Si, 0.001% Mn, 0.001% Mg, 0.001% Fe, 0.005% Cu, and 0.0006% Ni.

III. RESULTS

A. Ejection

1. *Ejection Directions*

Early in the investigation two bombardments were made at 45° to a (100) surface at different locations, the first being parallel to a [110] and the second after rotating the specimen 45° about its surface normal. It was found that a matte spot developed much more rapidly when bombarding in the latter direction than when parallel to the [110]. As a first step towards determining the cause of this phenomenon, a survey was undertaken to see whether or not the same ejection directions were operating over a wide range of incident ion directions and surface orientations. The incident ion directions chosen were the three most densely packed directions in the fcc system, viz, [110], [100], and [112], in order of decreasing density, and the [111], the normal to the closest packed plane. Ejection patterns were obtained on hemispherical collectors. Table I and Fig. 2 summarize these results.

The locations of ejection deposit maxima for all bombardments of each surface are plotted on the stereographic pole figures in Figs 2(a), (b), and (c). Typical ejection deposit patterns on hemispherical collectors, from which these data were obtained, are shown in Figs. 2 (d), (e), and (f); these patterns were formed with the incident ion beam parallel to [112], but all other incident directions gave similar results except for relative intensity of the spots.

It can be seen from the pole figures of Fig. 2 that the [110] directions registered accurately for all crystals and this gives an estimate for the experimental error of about 3°. In Fig. 2 (a) a [100] deposit is also recorded. For the (111) surface the only other directions recorded are close to [116] directions, differing by 6° from the theoretically significant [114] directions which is discussed later. For the (110) surface the elongated deposits between two [116] are attributed to overlapping of two neighboring [116] ejections only, as there was no detectable deposit around the [100] pole. Ejection has been reported along [114] directions by Koedam.[5] Anderson's results[4] are close to [116] and measurements on the diagrams published by Nelson and Thompson[9] indicate similar results.

TABLE I. Tabulation of incident ion and ejection directions for single crystals of aluminum with surfaces prepared parallel to (100), (110), and (111).

Plane in surface	Ion beam parallel to	Angle between ion beams and surface	Ejection directions
(100)	[112]	24°16′	Four [110], one [100]
	[111]	35°16′	Four [110], one [100]
	[110]	45°0′	Four [110], one [100]
	[112]	54°44′	Four [110], one [100]
(110)	[110]	30°0′	Five [110], four [116][a]
	[112]	35°16′	Five [110], four [116]
	[100]	45°0′	Five [110], four [116]
	[111]	54°44′	Five [110], four [116]
(111)	[112]	28°08′	Three [110], three [116][a]
	[100]	35°16′	Three [110], three [116]
	[110]	54°44′	Three [110], three [116]

[a] [116] of the parent crystal is near [110] of the surface twin. See text.

Koedam,[5] using single crystals of copper, reported [114] ejection from (111) surfaces only, attributing it to stacking faults at the surface and pointing out that they could not modify the direction of output from (100) and (110) surfaces. Anderson[4] attributed his deviation from [114] ejection from (100), (110), and (111) surfaces to an effective Cu atom diameter of less than 0.8 in the process of ejecting an individual surface atom from a twin position on receiving impulses along [110] directions. On the same basis, the Al atoms appear to have an effective diameter of about 0.85.

The occurrence of [116] ejection from the (110) surface suggests that the [110] grooves developed during bombardment probably contain (111) facets on which surface atoms take up twin positions. Furthermore, no [116] deposits were found in the case of the (100) surface, which develops grooves with axes predominantly along [100]. A very few faint grooves with [110] axes develop also, when the beam trace lies close to a [110] direction in the (100) surface, but these were too few to make a detectable contribution to [116] ejection. Theoretically, for (100) surfaces, smooth grooves with [100] axes cannot contain (111) facets and it would, therefore, not be possible for individual atoms to take up twin positions on them. Deviations from ideal grooves were apparently insufficient to permit detection of [116] ejection. These conditions favored the record-

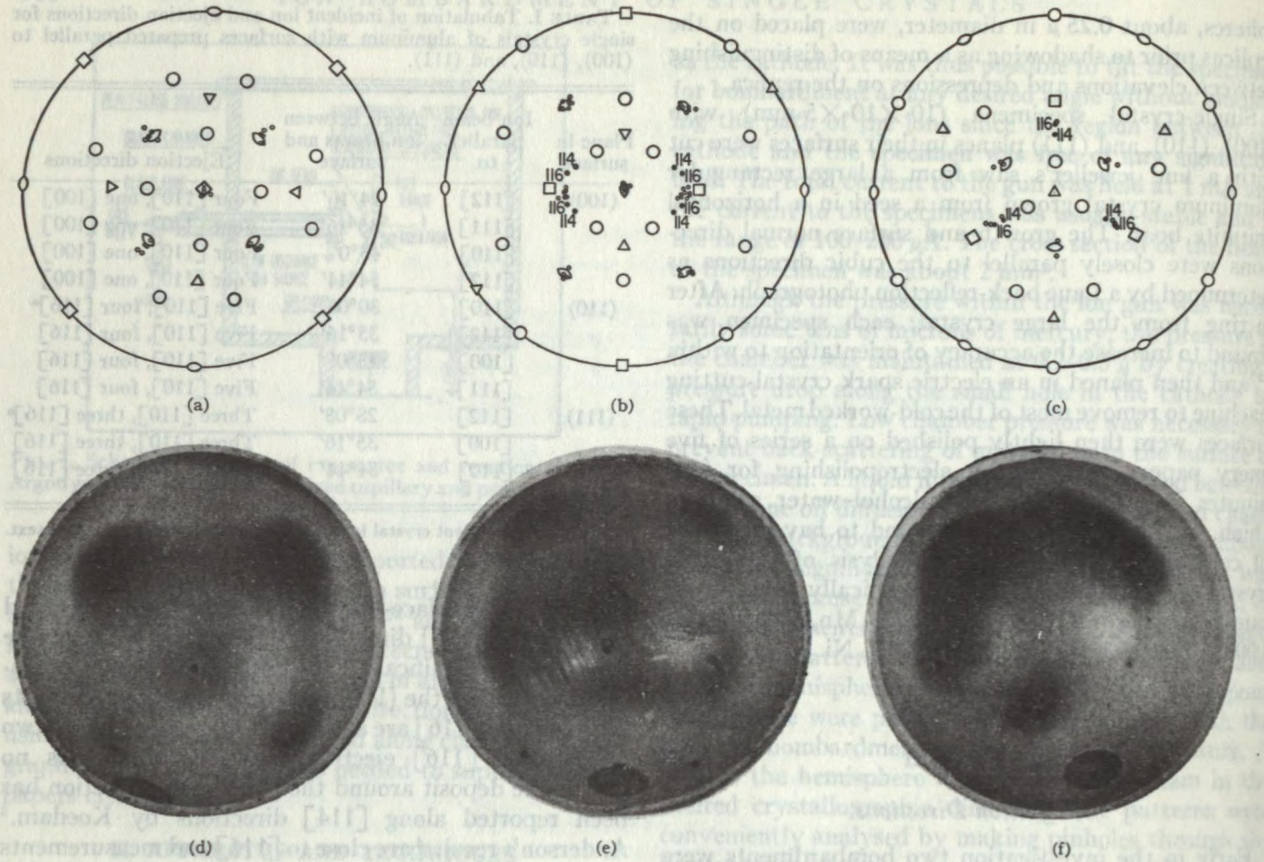

FIG. 2. Stereographic plots of ejection data from all experiments, including those of Table I. (a), (100); (b), (110); (c), (111). Typical corresponding ejection deposit patterns on hemispherical collectors are shown in (d), (e), and (f) with incident ions parallel to [112] in all cases. Entrance holes for incident beams can be seen. (□, ⊂⊃, △, and ○ refer to [100], [110], [111], and [112], respectively).

ing of the nearby weak [100] ejection from the (100) surface and it is possible that very weak undetected [100] ejections may also have occurred in the case of the (110) and (111) surfaces, although low energy transfer does not favor [100] ejection.[4]

The metallographic results are summarized in Table II.

Thus, it appears that nearly all ejection depends on the efficient propagation of momentum along [110] directions within the crystal, the significance of a [116] being only that it is close to a [110] in the surface twin along which momentum transfer is taking place. Had Silsbee focusing[26] been completed along a [110] in the twin, the ejection would apparently have been along a [114].

TABLE II. Correlation of metallographic features with [116] ejection.

Surface	Groove axes	Groove development	Source of [116] ejection detected
(100)	[100]	Strong	...
	[110]	Weak	...
(110)	[110]	Strong	Atoms in twin positions on (111) facets developed during bombardment
	[100]	Very weak	...
(111)	[110]	Strong	Atoms in twin positions on original (111) surface

2. *Ejection Intensities*

Since the phenomenon of varying rates of development of matte spots on the same crystal surface, even at constant angle, could not be accounted for by differences in the number or nature of the ejection directions, a comparison of incident ion directions in influencing intensity of ejection should be considered.

Equivalent output directions have been shown to give heavier deposits where a smaller angle of deviation from the direction of the original beam is involved,[1] as would be expected for a momentum transfer process. This is well illustrated [Fig. 2(d)] in the case of a [112] incident ion beam making different angles with each of the four [110] ejection directions, the maximum angle of deviation being 150° and the minimum being 73°.

No attempt was made to obtain accurate intensity measurements nor an accurate relationship between the angle of deviation θ, and intensity I, as visual judge-

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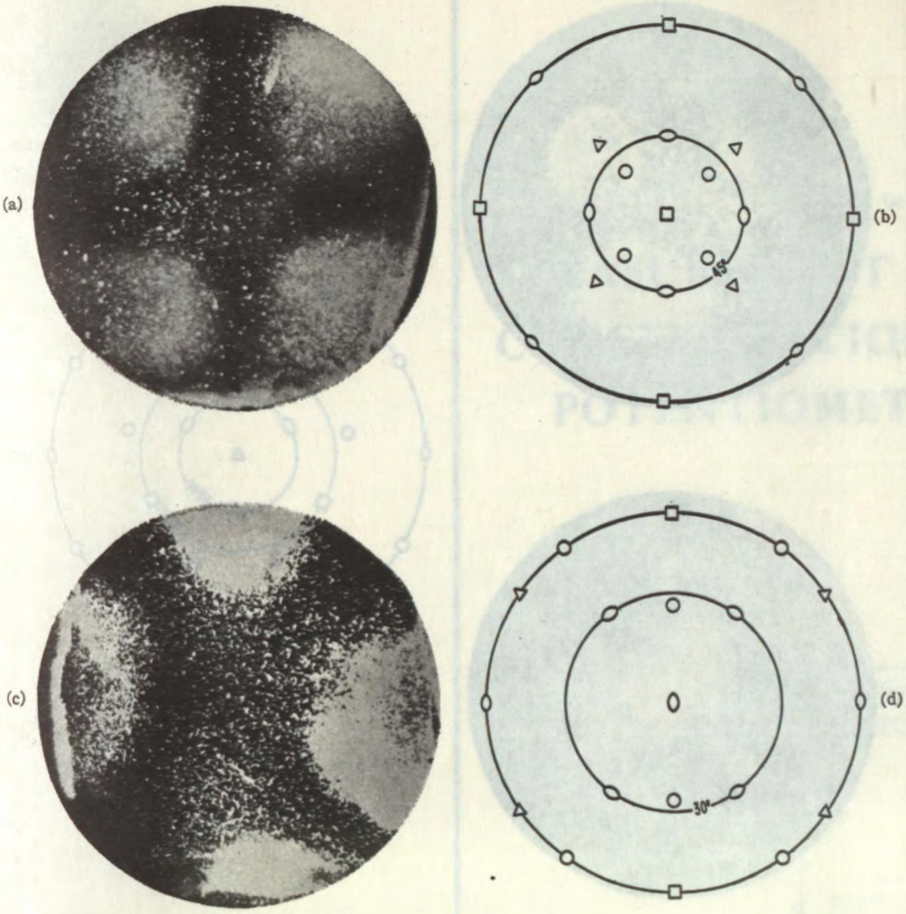

FIG. 3. Surface patterns developed on rotating (100) and (110) specimens. (a) (100) Surface bombarded at 45° so as to bring beam parallel to four [110] directions per revolution [see (b)]. (c) (110) Surface bombarded at 30° so as to bring beam parallel to four [110] directions and close to two [112] directions per revolution. [see (d)]. Etching patterns indicate ejection rates are relatively low when the beam is parallel or close to [110] directions.

ment of intensity did not warrant this. The empirical linear equation $I=k(1-0.0055\theta)$ was found to be sufficient for the purpose.

Applying this approximate relationship to the original bombardment of a (100) surface at 45° along [110] and after rotating through 45°, it was estimated that the total outputs of the four [110] in the two cases, and hence the etching rates, should have been within about 10% of each other, if the two incident directions had been the same in their efficiences in initiating ejection. Hence, the (110) input direction must be much less efficient in producing ejection than the other at the same angle to the surface. The [110] direction, being the most closely packed direction in a fcc crystal, has been shown[1] to be the direction along which momentum can be transferred most efficiently. The transfer of momentum from an incident [110] into [110] ejection directions must, therefore, occur by more numerous and smaller energy steps and, on the average, more deeply than in other directions. Hence, a longer series of collisions along ejection directions would be required to carry these small amounts of energy to the surface and little energy would be available for ejection; hence, the low efficiency of [110] as an incident direction for subsequent ejection.

These observations are consistent with the fact that glancing angle bombardment of polycrystals gives higher etching rates than vertical bombardment since the depth of penetration is a function of both the angle of incidence and the path length in the crystal.

B. Etching

1. *A Comparison of the Influence of Incident Ion Direction and Surface Migration on Etching Rates*

The previous experiments make it appear that redistribution of momentum close to the surface is a necessary condition for high ejection rates. However, there was the possibility that surface migration might be significant and it was necessary to evaluate the comparative importance of these two factors. Since the specimen surfaces chosen contained closely and loosely packed crystallographic directions, it could reasonably be expected that surface atom migration might be anisotropic and would, therefore, strongly affect the etching efficiency in different directions. The variation of etching efficiency with incident ion direction at a constant angle to given surfaces is illustrated in Fig. 3 (a) and (c) and Fig. 4 (a) and (b). They show the etched surfaces of (100), (110), and (111) rotated crystals after bombardment by a beam of ions striking the crystal off-center so as to sweep out an annular area on the crystal.

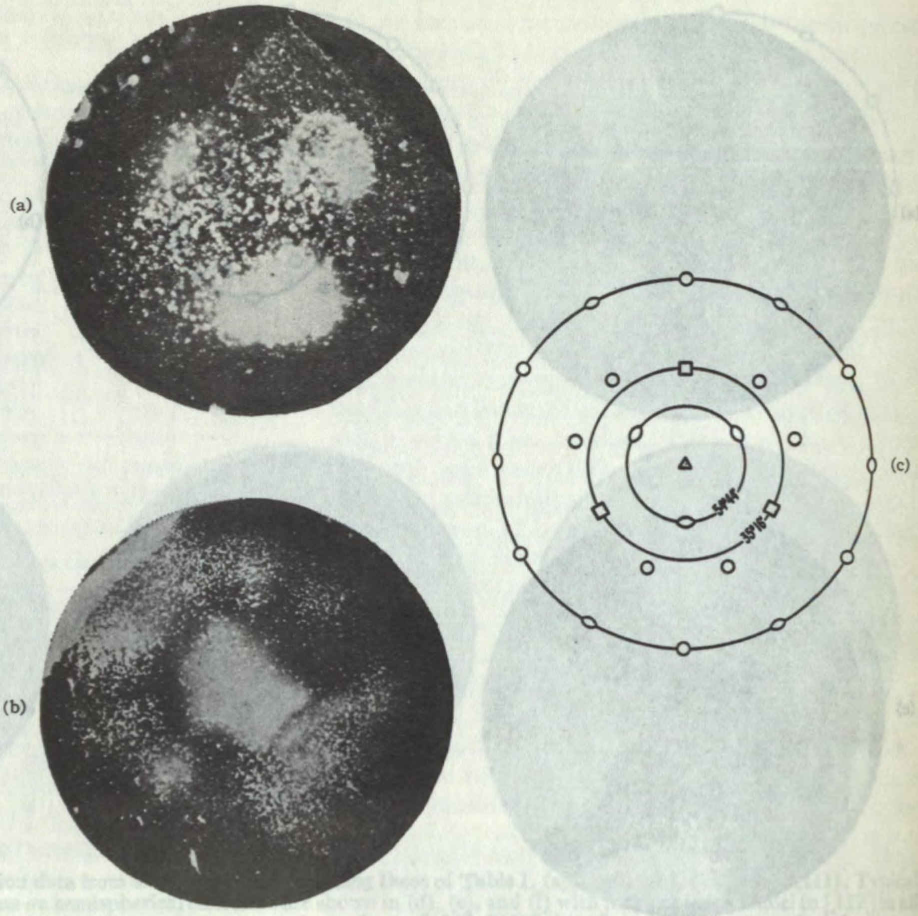

FIG. 4. Surface patterns developed on rotating (111) specimens. (a) bombarded at 54°44′ so as to bring beam parallel to three [110] directions per revolution [see (c)]. (b) bombarded at 35°16′ so as to bring beam parallel to three [100] directions and close to six [112] directions per revolution [see (c)]. Etching patterns indicate ejection rates are relatively low when the beam is parallel or close to [100], [110], and [112] directions.

The circles on the three stereographic projections, Fig. 3 (b) and (d) and Fig. 4 (c), indicate the directions to which the beam becomes parallel during the course of one revolution at the angles indicated. Exposure continued until a matte surface developed on those areas where the beam struck the surface in the directions of comparatively rapid etching.

The (111) surface is particularly suitable for the evaluation of the relative importance of penetration and surface migration, because in one revolution the trace of the beam becomes parallel to six [110] and six [112] surface directions, so that twelve matte spots might be expected if surface migration was the predominant factor. On the other hand, if low penetration was the predominant factor, three matte spots might be expected in the case of a (111) surface, bombarded at 55°, in the positions intermediate to the three [110] directions through which the beam passes during one revolution. Similarly, nine intermediate matte spots might be expected, when bombarding at 35°, as the beam would become parallel to three [100] directions and, within 7°, six [112] directions. In fact, two patterns containing three and nine spots, respectively, were obtained and are shown in Fig. 4 (a) and (b). Furthermore, the (111) surface produces no matte spot in a reasonable length of time when the beam is directed along a [110] at 55° to the surface, but does produce a matte spot after rotating the specimen 60° about its normal, although in both cases the traces of the beams have identical angular relationships to the [110] and [112] surface directions [Fig. 4(c)].

It was also found that no correlation existed between closeness of packing in surface rows and positions of matte spots on (100) and (110) surfaces. Hence, the results are consistent with the theory that the depth of momentum transfer into the crystal is much more important than anisotropy of surface migration in determining etching rates.

ACKNOWLEDGMENTS

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