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Influence of Crystallographic Orientation on the Corrosion Rate of Aluminum in Acids and Alkalies

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The corrosion of single crystals of high-purity aluminum in strong acid and alkali media is disclosed as an orderly process, the rate of attack being dependent on the orientation of the corroding surface. For a 15-percent NaOH solution, corrosion apparently progressed by revealing facet surfaces of the [335] type, resulting in gross corrosion of spheres into cubes; in contrast, substantiating other investigations, corrosion in aqua regia-hydrofluoric acid mixture revealed etch pits with surfaces of the [100] type, resulting in gross corrosion of spheres into equilateral octahedra. Observations of the corrosion by acid and alkali solutions of disks with central holes, and rectangular prisms, both of monocrystalline aluminum, result in interesting conclusions and comparisons with respect to the corrosion process.

1. Introduction

Corrosion is such an extremely complex destructive process, influenced by so many factors, that a study of metals and alloys in their commercially usable state affords little information concerning the basic nature of the process. The fundamental corrosion characteristics of metals can best be determined by a study of the least complex form of the metal that has the basic characteristics of the whole, i. e., of single crystals. By such a study many of the corrosion-influencing characteristics of polycrystalline materials, aside from the environmental factors, are eliminated or at least minimized, and the basic behavior of the metal can be observed.

Those concerned with the study of metals have observed, particularly under the microscope, over-etched specimens whose individual grain surfaces appear to be at different elevations, as though the individual grains had been attacked at different rates, such as may be seen in figure 1. In this specimen the grains were at several different levels, with the central grain at the highest level of all. Further, it can be observed that there has been a preferential attack within an individual grain as revealed by variations in rates of etching in an orderly pattern. Those familiar with the preparation of surfaces for metallographic examination are also aware of the variation in behavior of different etchants (corrodents) on the surface. It thus becomes apparent that not only is a metal preferentially attacked when subjected to a corrosive medium, but also that different corrosive media attack the metal in different ways.

The above suggests that the corrosion of aluminum is an ordered attack on the structure in accordance with a definite pattern, the pattern varying with the nature of the corrodent.

Extensive work by Gwathmey and his associates [1,2,3,4] [1] has shown that the atomic arrangement on affected surfaces has great influence on the oxidation and electrochemical characteristics of copper, and significantly affects the catalytic behavior of metals.

[1] Figures in brackets indicate the literature references at the end of this paper.

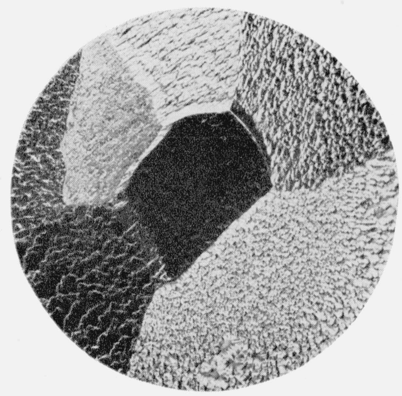

FIGURE 1. *High-purity, polycrystalline aluminum deep-etched in an aqua regia-HF solution.* ×3.

Glauner and Glocker [5] investigated single-crystal spheres of copper and found that the rate of attack by various etchants varied with crystallographic face. Kostron, Hoffler, and Sautter [6] demonstrated that crystallographic orientation had significant influence on the corrosion of single-crystal spheres of aluminum. Politycki and Fischer [7] also did excellent work on the behavior of various acids on monocrystalline aluminum. Straumanis [8] investigated monocrystalline zinc and measured the electrochemical potential of various crystal faces as corrosion progressed.

It is the purpose of this paper to report on the results of an investigation undertaken to determine the basic differences between the corrosion of aluminum in acids and in alkalies.

2. Orientation Relationships in Test Specimens

In investigating the relation between corrosion rates for various surfaces of a single-crystal corresponding to different crystallographic planes, it was believed that a qualitative study alone might yield much useful information; quantitative studies related to surfaces of single crystals had been attempted by the author and found to be very difficult to undertake and interpret.

Judging from experience obtained with metallographic etching, it could be presumed that the corrosion of aluminum single crystals would occur in a very orderly fashion, being dependent upon the orientation of atoms in the surfaces of the test specimen being attacked. The change in shape effected by corrosion on a single crystal of simple geometrical shape would permit a qualitative evaluation of the relative rates of corrosion in various crystallographic directions.

In this investigation the relative rates of corrosion of variously oriented surfaces were determined by corroding spheres, disks, cubes, and rectangular prisms of monocrystalline aluminum.

The sphere is an ideally shaped specimen for such work because every crystallographic plane of the system is tangent to the sphere at some point on its surface.

As it developed, the circular monocrystalline disk proved to be the most satisfactory of the geometrical forms utilized in this investigation because it best illustrated the differences in corrosion rates among the various planes.

Figure 2 is a sketch of a sphere showing the relationship of the cubic planes to the sphere, the position of two of the cubic planes being shown by the shaded areas passing through the pertinent great circles; the third cubic plane is in the plane of the paper. The cubic planes will thus be tangent to the spherical surface at the six points where the intercepts of the three mutually perpendicular meridional planes intersect the surface.

Figures 3, 4, and 5 are plan views of the sphere shown in figure 2, positioned with the cubic, dodecahedral, and octahedral planes, respectively, parallel to the plane of the paper, the azimuthal orientations being as indicated.

There are also shown in each of the diagrams, lying within the plane of the diagram, the poles of various principal crystallographic planes. Inasmuch as the correspondingly numbered planes are perpendicular to the plane of the diagram, they are said to be lying within its zone. Thus in figure 3 can be observed the poles of certain cubic (100) and dodecahedral (110) planes, which planes are in the zone of the cubic plane of the diagram.

These diagrams will become useful in the study of spherical single crystals of aluminum corroded by acids or alkalies.

Figures 6, 7, and 8 show a monocrystalline aluminum sphere, corroded in an aqua regia-hydrofluoric acid mixture, positioned to conform to the orientations indicated in figures 3, 4, and 5. They are shown here for comparison with the sketches and will be discussed later.

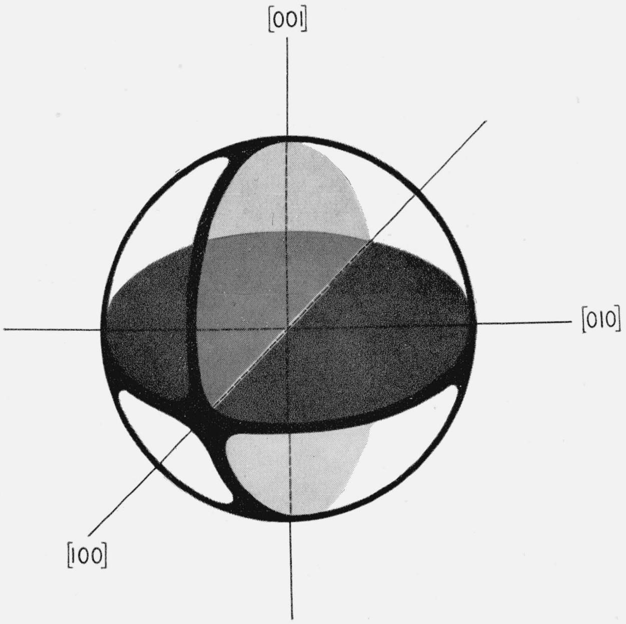

FIGURE 2. *Sketch of sphere showing the location of the cubic planes.*

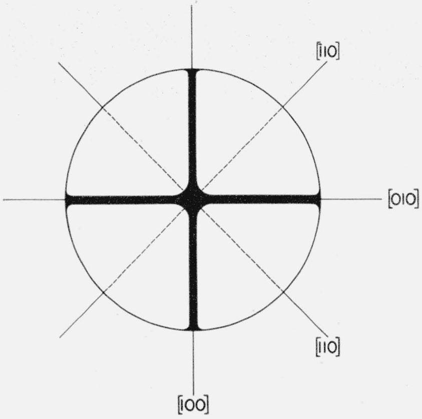

FIGURE 3. *Sketch of sphere shown in figure 6, oriented with cubic plane parallel to paper and showing loci of the cubic and dodecahedral directions.*

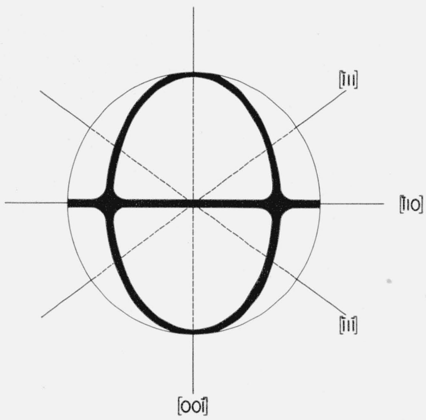

FIGURE 4. *Sketch of sphere shown in figure 7, oriented with the dodecahedral plane parallel to the paper and showing loci of cubic, dodecahedral, and octahedral directions.*

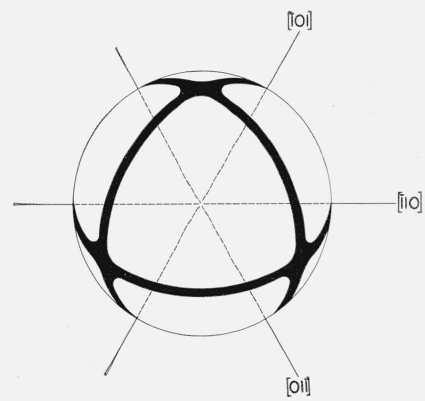

FIGURE 5. *Sketch of sphere shown in figure 8, oriented with the octahedral plane parallel to the paper and showing loci of the dodecahedral directions.*

The relationship between corrosion characteristics of all the low-index planes can be shown by corroding a series of disks, the flat surfaces of which are parallel to the cubic, dodecahedral, or octahedral planes.

Figure 9, a, represents the plan and edge views of a monocrystalline aluminum disk whose flat surfaces are parallel to a cubic plane. The various figures grouped about the plan view represent principal planes within the crystal, which are parallel to the cylindrical surface of the disk at the eight indicated positions. These are the cubic (A) and dodecahedral (B) planes; they lie within the zone of the cubic plane of the disk surface. All other crystallographic planes (not shown), which lie parallel to the cylindrical surface of the disk at other parts on its periphery, also lie in this cubic zone.

Figures 9, b, and 9, c, represent the corresponding relationships for monocrystalline aluminum disks whose flat surfaces are parallel to the dodecahedral and octahedral planes, respectively. Thus, cubic (A), dodecahedral (B), and octahedral (C) planes lie in the zone of the surface dodecahedral plane of figure 9, b, whereas dodecahedral planes (B) lie in the zone of the surface octahedral plane of figure 9, c. The unit cell shown at D in the front view of the disk of figure 9, c, is as the cell would appear when viewing it in a direction normal to the one plane of {112} which is tangent to the cylindrical surface of the disk at that position. There are 6 locations (D) where planes of {112} are tangent to the cylindrical surface of the disk, 1 each being equidistant between the 6 locations where the dodecahedral planes are tangent to the cylindrical surface of the disk. The comparative corrosion rates between {110} and {112}, and such other lesser planes, as {123}, {134}, and {235}, which lie in the octahedral zone and are therefore tangent to the cylindrical surface of such a disk, will be shown by corroding such a disk.

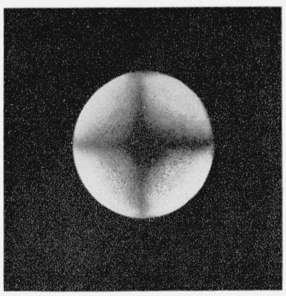

FIGURE 6. *Monocrystalline aluminum sphere after corrosion in aqua regia*-HF *solution.*

Cubic plane parallel to paper. ×¾.

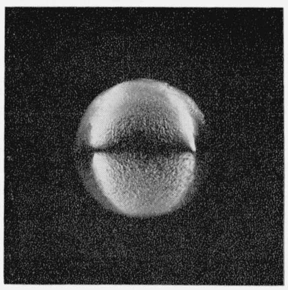

FIGURE 7. *Monocrystalline aluminum sphere after corrosion in aqua regia*-HF *solution.*

Dodecahedral plane parallel to paper. ×¾.

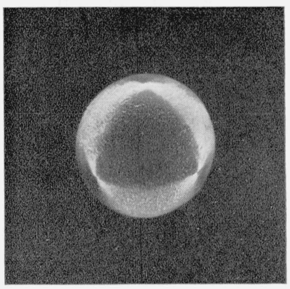

FIGURE 8. *Monocrystalline aluminum sphere after corrosion in aqua regia*-HF *solution.*

Octahedral plane parallel to paper. ×¾.

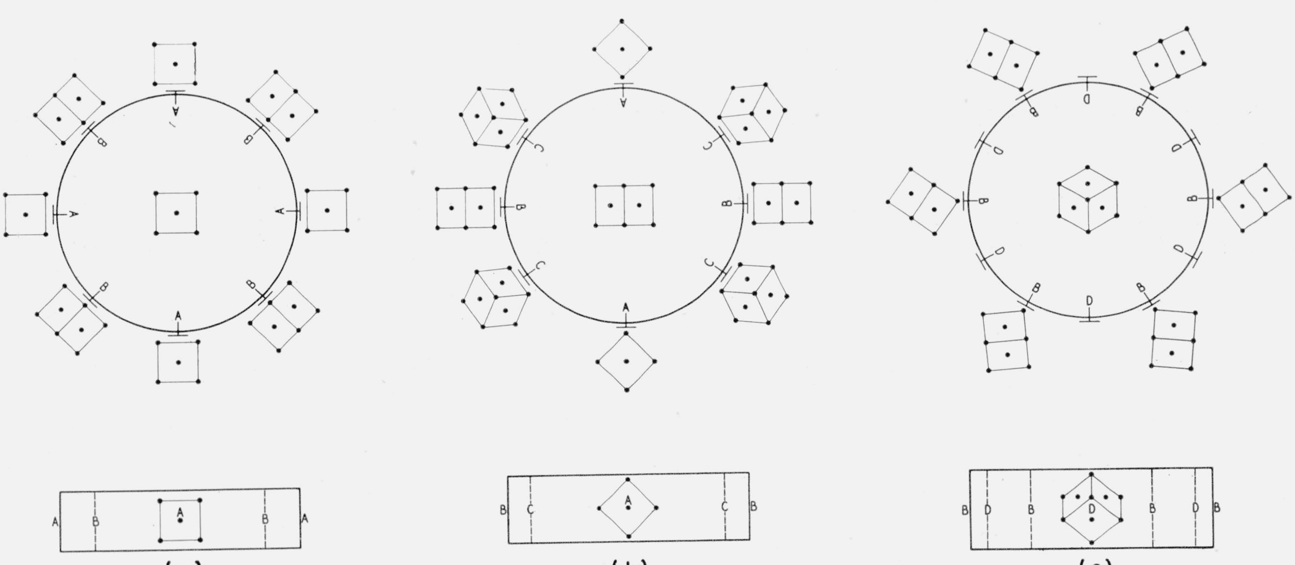

FIGURE 9. *Orthographic projection of disks having various surface orientations and showing the unit-cell arrangement when viewed in directions normal to the flat and cylindrical surfaces of the disks.*

(a) Surface parallel to a cubic plane; (b) surface parallel to the dodecahedral plane; (c) surface parallel to the octahedral plane.

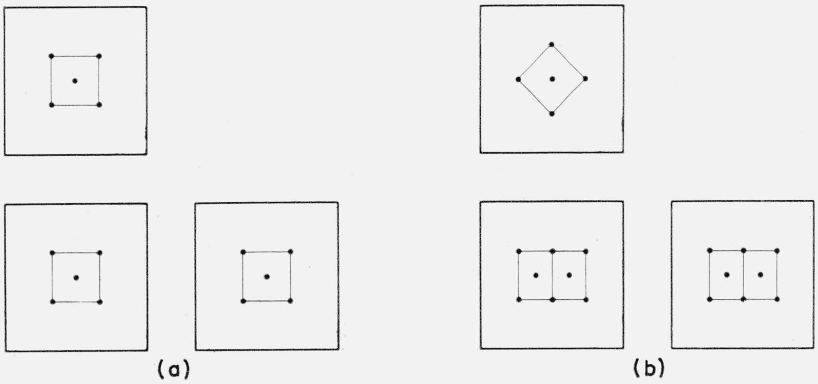

FIGURE 10. *Orthographic projections of cubes having faces parallel to cubic and dodecahedral planes and showing the unit-cell arrangement when viewed in directions normal to these planes.*

(a) All faces parallel to cubic planes; (b) two faces parallel to cubic planes and four faces parallel to dodecahedral planes.

The use of cubes or rectangular prisms was of value only for determining the relative corrodibilities of surfaces parallel only to planes that are mutually normal. Figures 10, a, and 10, b, are orthographic projections of two such cubes, 10, a, being of a cube that has all 6 faces parallel to the cubic plane, and 10, b, that of a cube that has 2 faces parallel to a cubic plane and 4 faces parallel to the dodecahedral planes. The views of the unit cell indicate the crystal orientation on the faces of the cubes in these two sketches.

3. Preparation of Test Specimens

For this investigation monocrystalline spheres of high-purity aluminum 1 in. in diameter were grown by what is known as the Bridgman method [9] of slow cooling from the melt. The aluminum used was furnished by the Aluminum Company of America and was of 99.99+ percent purity. The disks, cubes, and rectangular parallelopipeds were machined from cylindrically shaped ingots, 1¼ in. in diameter, grown by the same method. Any desired orientation of a single crystal specimen was obtained by seeding the melt.

4. Corrosion of Single-Crystal Specimens

4.1. Acid Media

A sphere of monocrystalline aluminum subjected to the corrosive action of aqua regia (65 ml HCl, sp gr 1.18, plus 35 ml HNO_3, sp gr 1.41), to which HF had been added in the ratio of 5 ml of 48-percent HF to 100 ml of aqua regia, corroded in such a manner as to produce the surfaces shown in figures 6, 7, and 8. In these photographs the corroded sphere has been positioned to conform to the orientations of figures 3, 4, and 5, respectively. It will be observed, particularly in figures 7 and 8, that those areas coinciding with the loci of the cubic poles in the sketches stand out in relief to other surfaces of the sphere. This indicates that the attack has been slowest in in these areas, or in a direction normal to the cubic planes.

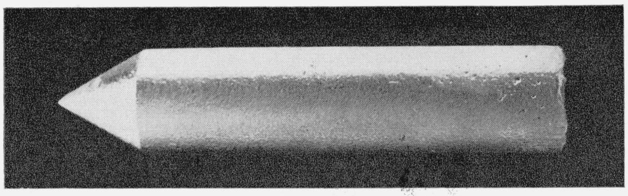

FIGURE 11. *Aluminum monocrystal used for machining of specimens.* ×½.

It could be observed in figures 7 and 8, and, less noticeably, in figure 6, that the areas other than those in the immediate vicinity of the cubic poles (compare with figs. 3 to 5) are uniformly pitted, there being some semblance of pattern to the attack. In the areas around the cubic poles there was no evidence of the pitting type of attack.

This lack of pitting around the cubic-pole areas is because only surfaces parallel to the cubic planes are exposed when aluminum is attacked by acids [10,6,7]. This exposure of cubic planes is demonstrated by the etching characteristics of plane surfaces parallel to the cubic, dodecahedral, and octahedral planes.

A monocrystalline cylindrical ingot (see fig. 11) was sectioned to produce disks whose surfaces were approximately parallel to the cubic, dodecahedral, and octahedral planes. The specimens were electropolished to remove cold work induced by the cutting and grinding operations, and back-reflection Laue diffraction patterns, using unfiltered radiation from a copper target, were obtained from specimens whose flat surfaces were normal to the X-ray beam. The actual orientations of the flat surfaces of the disks were obtained by using the Greninger [11] method, and the specimens were subsequently reground, repolished, and again X-rayed, as became necessary, until the surfaces were within ½° of being parallel to the desired crystallographic planes.

The above specimens were then subjected to the corrosive action of the aqua regia-HF mixture, and then examined with an optical goniometer [12]. This operation revealed that only the cubic planes were exposed as the result of the attack; the same planes

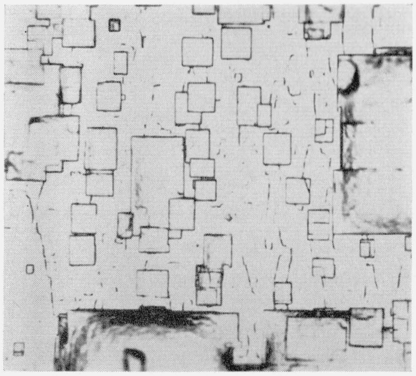

FIGURE 12. *Photomicrograph of etched surface of monocrystalline aluminum approximately parallel to (100).*

Etchant—a solution of aqua regia, HF, and $FeCl_3$. ×200.

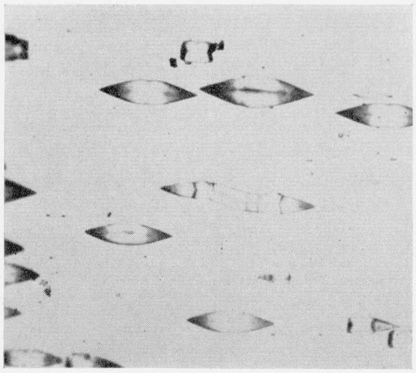

FIGURE 13. *Photomicrograph of etched surface of monocrystalline aluminum approximately parallel to (110).*

Etchant—a solution of aqua regia, HF, and $FeCl_3$. ×200.

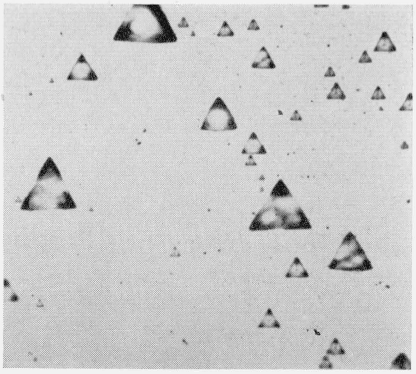

FIGURE 14. *Photomicrograph of etched surface of monocrystalline aluminum approximately parallel to (111).*

Etchant—a solution of aqua regia, HF, and $FeCl_3$. ×200.

were exposed when similar specimens were subjected to concentrated HCl in preliminary experiments. All of the planes exposed were mutually perpendicular; this type of attack was described by Mahl [13] and by Mahl and Pawlek [14] and observed by Roald and Streicher [15] in their work on the corrosion of aluminum in HCl.

Since the attack by the aqua regia-HF mixture was much more rapid than that by the concentrated HCl and the pattern of attack so much more clearly discernible, the acid mixture was employed in this investigation for all experiments relating to the acidic type of attack on aluminum.

Photomicrographs of the above specimens, etched with the aqua regia-HF mixture, to which a small amount of $FeCl_3$ had been added to improve the detail of the microstructure, are shown in figures 12, 13, and 14. The etch pits in the figures possess fourfold, twofold, and threefold symmetry details, respectively, similar to those observed in figures 3, 4, and 5.

The sketch of a cube sectioned so as to reveal the cubic, dodecahedral, and octahedral faces, figure 15, shows the configuration of etch pits on these faces. Comparing these pits with those on the corresponding specimens, it can be observed that the confines of each pit are composed of cubic faces only. The single etch pit on the dodecahedral face of the sketch is a schematic conception of the ellipse-like character of the pits shown in figure 13, the illusion of roundness or ellipticity being the result of a multiplicity of minute facets, all parallel to cubic planes, and diminishing in size toward the ends of the pit.

Because only cubic planes are exposed as a result of corrosion in the aqua regia-HF mixture, and because corrosion consequently progresses at the slowest rate in a direction normal to these planes, it should be evident that the corrosion rates in directions normal to all other planes will exceed that in directions normal to cubic planes.

Prolonged exposure of the sphere to the corrosive action of the aqua regia-HF mixture caused it to evolve into the form shown in figure 16. It is

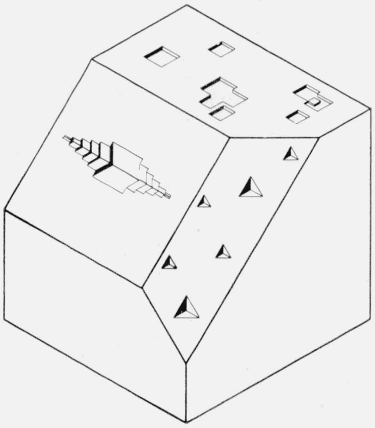

FIGURE 15. *Sketch of cube showing etch pits bounded by cubic planes on cubic, dodecahedral, and octahedral faces.*

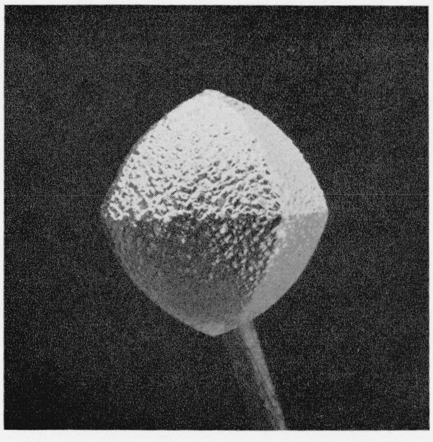

FIGURE 16. *Monocrystalline aluminum sphere deeply corroded in an aqua regia-*HF *mixture.* ×2.

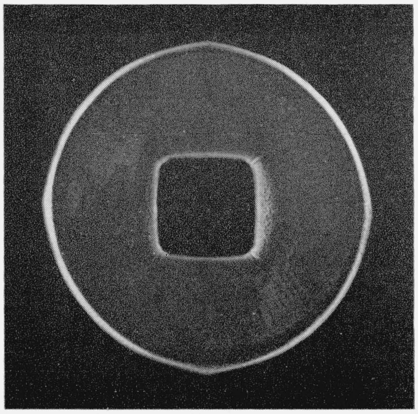

FIGURE 17. *Disk with surface parallel to cubic plane after corrosion in aqua regia-*HF *solution.*

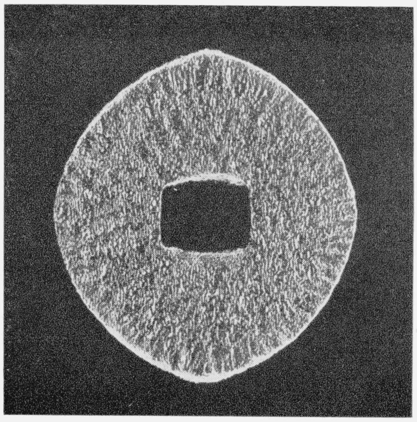

FIGURE 18. *Disk with surface parallel to dodecahedral plane after corrosion in aqua regia-*HF *solution.*

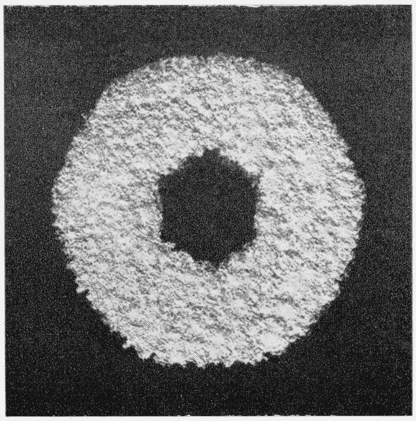

FIGURE 19. *Disk with surface parallel to octahedral plane after corrosion in aqua regia-*HF *solution.*

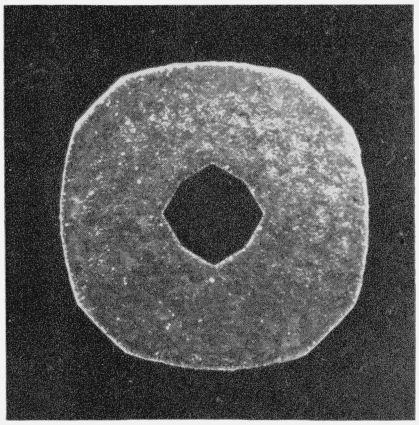

FIGURE 20. *Disk with surface parallel to cubic plane after corrosion in 15-percent* NaOH *solution.*

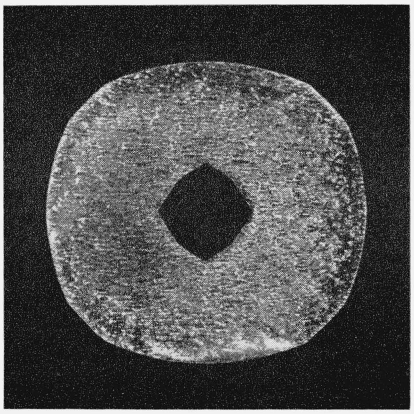

FIGURE 21. *Disk with surface parallel to dodecahedral plane after corrosion in 15-percent* NaOH *solution.*

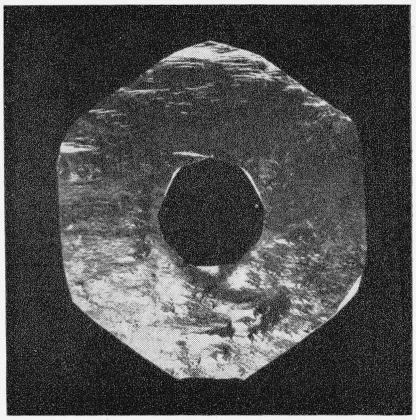

FIGURE 22. *Disk with surface parallel to octahedral plane after corrosion in 15-percent* NaOH *solution.*

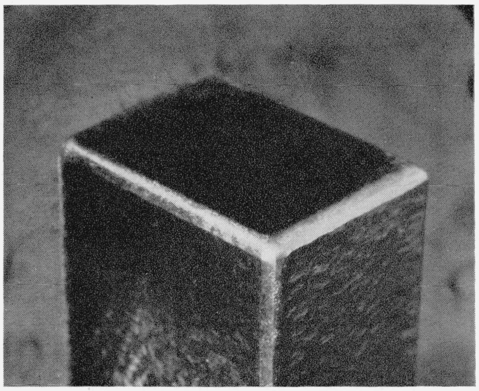

FIGURE 23. *Rectangular parallelopiped with six faces parallel to cubic planes after exposure to an aqua regia-*HF *mixture.* $\times 3$.

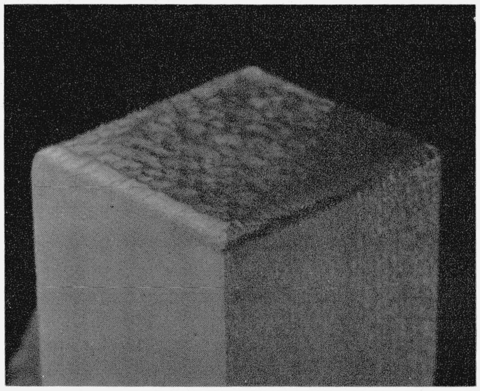

FIGURE 24. *Rectangular parallelopiped with two faces parallel to cubic planes and four faces parallel to dodecahedral planes after exposure to an aqua regia-*HF *mixture.* $\times 3$.

apparent that an octahedron is evolving from the sphere, indicating that corrosion is progressing at the fastest rate in a direction normal to the surfaces that are parallel to the octahedral planes. This observation is in full accordance with the findings of Kostron, et al. [6] and others, that when aluminum is subjected to a corrosive medium which exposes the cubic planes only, the rate of corrosion is fastest in a direction normal to the octahedral planes, slowest in a direction normal to the cubic planes, and at some intermediate rate in a direction normal to the dodecahedral planes.

To further substantiate these findings, disks of monocrystalline aluminum 1⅛ in. in diameter by ¼ in. thick were machined from ingots that were grown in such a manner that the axes of the ingots were parallel to the cubic, dodecahedral, and octahedral axes. A very small diameter hole was drilled through the center of the face of each disk. Disks having these orientations were discussed earlier. Their orientations are shown schematically in figures 9, a, b, and c, respectively.

When disks of such surface orientations are corroded in an aqua regia-HF mixture, the behavior of the cylindrical surfaces of the disks should be comparable to that which was observed when a monocrystalline sphere was corroded in the same medium. That is, the corrosion rates will vary, depending upon the orientation of the planes tangent to the cylindrical surfaces, and on examination after immersion in the corroding medium the cylindrical disks will no longer have circular right sections. Thus, in a disk having its flat surfaces parallel to a cubic plane, figure 9, a, corrosion in a direction normal to the dodecahedral planes will be faster than that in a direction normal to the cubic planes and, after prolonged exposure in the aqua regia-HF mixture, the disk will corrode to the shape shown in figure 17. Note that the originally small, round hole in the center of the disk has corroded so that its plan is now roughly a square. The diagonals of this square coincide with the dodecahedral directions, the directions in which the corrosion is progressing at the fastest rate for a disk of this particular surface orientation. The cylindrical surface of the disk, while not as radically corroded as the hole in the center, nevertheless shows that corrosion progressed at a slower rate in a direction normal to the cubic planes than it did in a direction normal to the dodecahedral planes.

A photograph of a disk having its surface parallel to the dodecahedral plane and oriented as is the sketch in figure 9, b, after prolonged exposure to an aqua regia-HF mixture, is shown in figure 18. This particular disk, as explained above, is the most favorable for illustrating the relationship between rates of corrosion in directions normal to low-index planes of the face-centered cubic system.

By referring to figure 9, b, the shape of such a corroded disk reveals that corrosion has progressed at the slowest rate in a direction normal to the cubic planes (A), and at the fastest rate in a direction normal to the octahedral planes (C), as observed by the remaining radial width of the disk at these positions. It may be similarly deduced that corrosion in a direction normal to the dodecahedral planes (B) has progressed at an intermediate rate.

A third disk, one having its surface parallel to an octahedral plane and oriented as in figure 9, c, is shown in figure 19 as it appeared after prolonged exposure in an aqua regia-HF mixture. It is evident that corrosion in a direction normal to the dodecahedral planes (B) was at a slower rate than that in a direction normal to $\{112\}$, (D).

Figures 20, 21, and 22 show similarly oriented disks corroded in an alkaline medium and are placed in the same diagram as figures 17, 18, and 19 for purposes of comparison; they are discussed later.

In order to determine the relative corrodibility of surfaces that are mutually normal, rectangular prisms oriented as in figures 10, a, and 10, b, were exposed to the acid mixture. In figure 23 is the specimen having all faces parallel to cubic planes (see fig. 10, a). Corrosion at cube edges and corners is evidently greater than on cube faces. Figure 24 shows the specimen having four sides parallel to dodecahedral planes. After prolonged exposure, the edges where these sides join are still sharp, thus indicating a greater rate of corrosion normal to dodecahedral planes than to any other plane in the cubic zone. The edges where the top joins the sides are beveled, inasmuch as corrosion in directions normal to dodecahedral planes is less than for directions normal to other planes in the dodecahedral zone such as the octahedral plane. As would be expected, corrosion in such directions is also somewhat greater than in those normal to the cubic planes.

4.2. Alkaline Media

It is well known that the grain-boundary structure of aluminum is generally developed readily in acid media. The grain boundary is distinguishable because each adjoining grain reflects light in different directions. Because the acid attacks the metal with the exposure of cubic planes only, the light from any one grain is thus reflected from a maximum of only three reflecting surfaces. In alkaline media, however, it is difficult to distinguish grain boundaries on etch-polished surfaces of aluminum. This is due to the inability to distinguish between adjoining grains, all of which have a satiny or frosted appearance. This would indicate that light is being reflected from many more facets than in the case of an acid etchant.

To illustrate the radical difference between the modes of attack of acids and alkalies, spheres and various oriented disks of monocrystalline aluminum were corroded in a 15-percent NaOH solution. Figures 25, 26, and 27 are different views of a sphere after prolonged exposure to such a solution. Figure 25 shows the sphere oriented with its cubic pole normal to the paper and its azimuthal orientation as in figure 3. It has the same orientation as the acid-corroded sphere shown in figure 6. Figure 26 has the dodecahedral pole of the crystal normal to the paper, its azimuthal orientation is as in figure 4, and it is oriented the same as that of the acid-corroded sphere in figure 7. The octahedral pole of the sphere in figure 27 is normal to the paper, its azimuthal orientation is as in figure 5, and it is oriented the same as the acid-corroded sphere shown in figure 8. Figures 28, 29, and 30, representing deeply corroded spheres in the acid mixture, are placed on the same diagram as figures 25, 26, and 27, for comparison with the alkali-corroded spheres; reference will be made to these photographs later in the paper.

A study of the different views of the sphere discloses little difference between the corrosion rates normal to the cubic and dodecahedral planes. The rates in both of these directions appear to be about the same, but both are definitely faster than that in a direction normal to the octahedral plane. However, examination of appropriately oriented disks comparably exposed to attack does indicate that there is a difference between the rate of corrosion in a direction normal to the cubic plane and that in a direction normal to the dodecahedral plane.

Figure 20, which shows a disk with its surface parallel to a cubic plane, as in figure 9, a, clearly indicates that corrosion in a direction normal to the cubic planes has been at a greater rate than that in a direction normal to the dodecahedral planes. The configuration of the hole in the center of the disk especially demonstrates this difference in corrosion rates. Figure 31, which is a sketch of the corroded hole, the shaded area indicating the portion of the disk that has corroded away, shows that corrosion has progressed at a faster rate in a direction normal to the cubic planes than it has in a direction normal to the dodecahedral planes, because the A dimensions are greater than the B dimensions. The sketch is oriented as in figures 9, a, and 20.

A disk whose surface is parallel to a dodecahedral plane, figure 21, shows clearly that a difference exists in the rates of corrosion in directions normal to the cubic, dodecahedral, and octahedral planes. Figure 32, a sketch of this hole, oriented as in figure 9, b, clearly shows that corrosion has progressed further in a direction normal to the cubic planes than it has in a

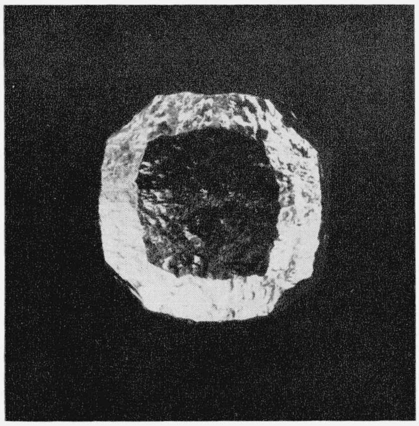

FIGURE 25. *Monocrystalline aluminum sphere corroded in 15-percent* NaOH.

Cubic plane parallel to paper. ×2.

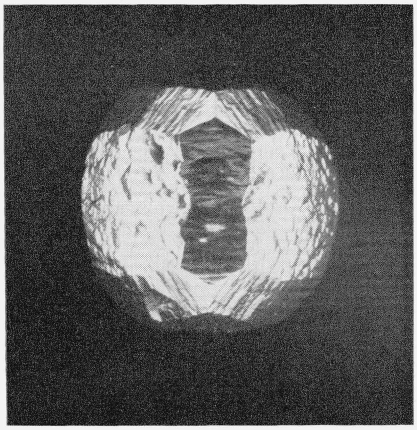

FIGURE 26. *Monocrystalline aluminum sphere corroded in 15-percent* NaOH.

Dodecahedral plane parallel to paper. ×2.

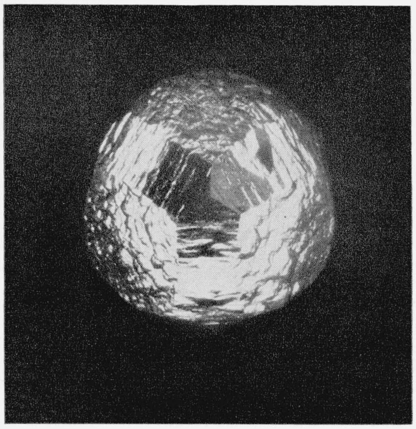

FIGURE 27. *Monocrystalline aluminum sphere corroded in 15-percent* NaOH.

Octahedral plane parallel to paper. ×2.

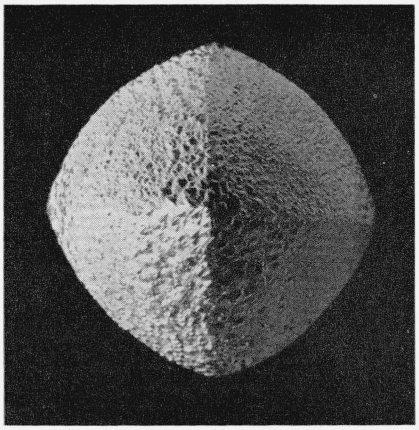

FIGURE 28. *Deeply corroded version of sphere shown in figure 6.*

Cubic plane parallel to paper. ×3.

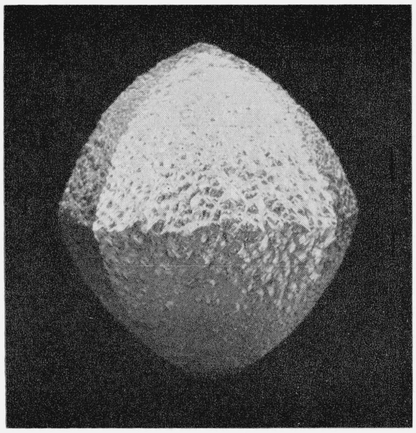

FIGURE 29. *Deeply corroded version of sphere shown in figure 7.*

Dodecahedral plane parallel to paper. ×3.

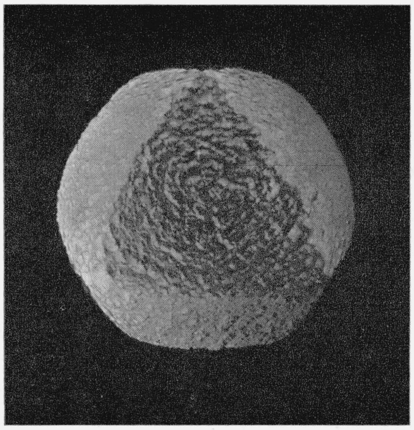

FIGURE 30. *Deeply corroded version of sphere shown in figure 8.*

Octahedral plane parallel to paper. ×3.

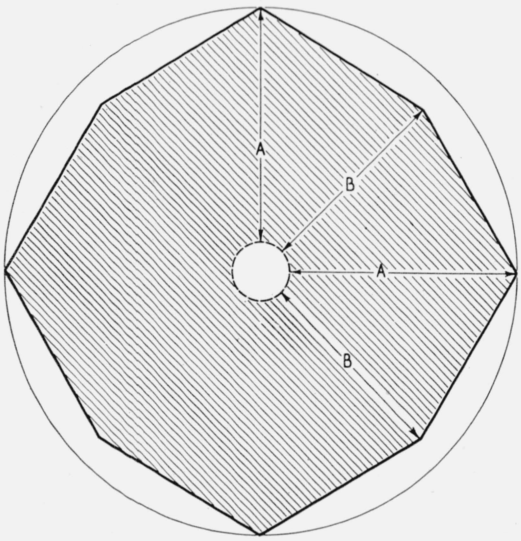

FIGURE 31. *Sketch of hole in disk whose surface is parallel to cubic plane after corrosion in 15-percent* NaOH.

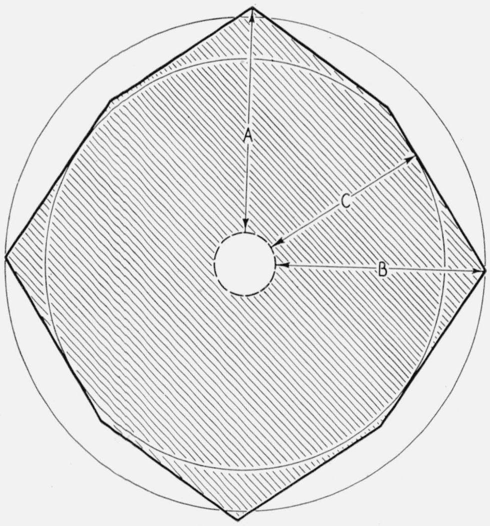

FIGURE 32. *Sketch of hole in disk whose surface is parallel to dodecahedral plane after corrosion in 15-percent* NaOH.

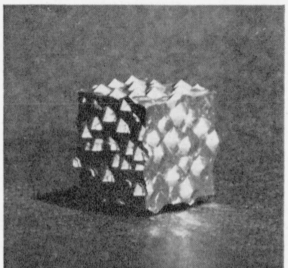

FIGURE 33. *Cube with six faces parallel to* {100} *after exposure to a 15-percent* NaOH *solution.* ×1½.

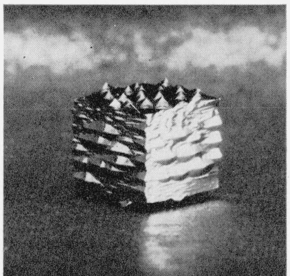

FIGURE 34. *Cube with two faces parallel to* {100} *and four faces parallel to* {110} *after exposure to 15-percent* NaOH *solution.* ×1½.

direction normal to the dodecahedral planes because dimension A is greater than dimension B. Both rates of corrosion are at a faster rate than in a direction normal to the octahedral planes since dimension C, which lies approximately in the octahedral direction, is somewhat less than both dimensions A and B.

The specimen in figure 22 oriented as in figure 9, c, shows the relationship between the rates of corrosion in directions normal to planes in the octahedral zone.

It is quite evident, both from the peripheral appearance and from the corroded hole, that corrosion in a direction normal to the dodecahedral planes (B) has been at a faster rate than that in a direction normal to {112}, (D). Thus, for such a disk, it is apparent that corrosion progresses at the fastest rate in a direction normal to the dodecahedral planes, and at the slowest rate in a direction normal to {112}.

The determination of the relative corrodibility of mutually normal surfaces was obtained by exposing cubes oriented as in figures 10, a, and 10, b, to 15-percent NaOH for a prolonged period. The specimen having all sides parallel to cubic planes is shown in figure 33, corrosion apparently having occurred at an equal rate in all three cubic directions with the three dimensions remaining essentially equal. The specimen having its four sides parallel to dodecahedral planes is shown in figure 34, its height having become considerably less than its lateral dimensions, indicating a more rapid corrosion rate normal to the cubic planes than to the dodecahedral planes.

Another feature of the exposure of these cubes, which is also evident in the exposure of spheres and disks in an alkaline medium, is the appearance of protruding facets on the surfaces of these specimens. The lack of beveling, as might be expected on the vertical edges of the cube specimen in figure 34, is apparently due to the predominant effect of the occurrence of such facets in these regions.

5. Discussion of Results

In the investigation of the corrosion of aluminum in the aqua regia-HF mixture, the originally round holes in the centers of the disk corroded to various geometrical shapes after prolonged immersion in the corrodent, the shape of the hole bearing a direct relationship to the orientation of the surface of the disk. These variously shaped holes, caused by corrosion with the exposure of cubic planes only, conformed to the projected shape of the outermost boundaries of a cube, the crystallographic orientation of the cube determining the shape of the hole.

Shadow photographs of a cube oriented so that either cubic, dodecahedral, or octahedral planes lie in the plane of the projection are shown in figures 35, a, b, and c, respectively; these are similar in shape to the projections of the unit cubes shown in the centers of the plan views of figures 9, a, b, and c. It will be observed that these also conform approximately to the shapes of the center holes of specimens corroded in acid media in figures 17, 18, and 19.

Applying the above logic to the disks corroded in 15-percent NaOH, in an effort to determine the

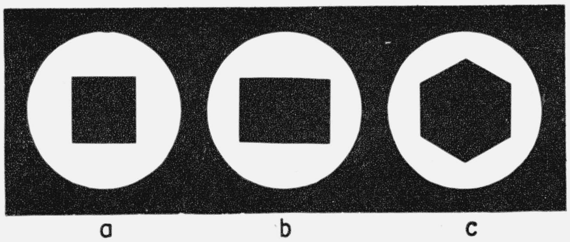

FIGURE 35. *Shadow photographs of cube.*
(a) Cubic plane; (b) dodecahedral plane; (c) octahedral plane parallel to paper

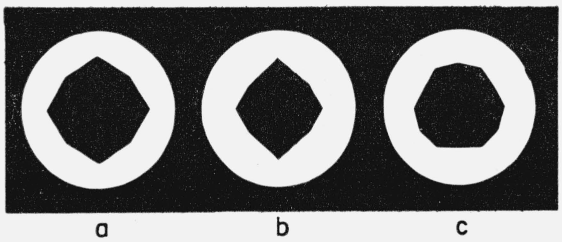

FIGURE 36. *Shadow photographs of tetragonal trisoctahedron having sides parallel to* {335}.
(a) Cubic plane; (b) dodecahedral plane; (c) octahedral plane parallel to paper.

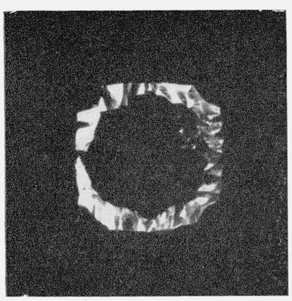

FIGURE 37. *Corroded sphere shown in figure 25 after longer exposure to 15-percent* NaOH. ×3.

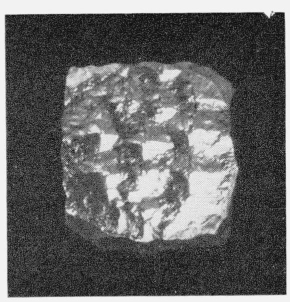

FIGURE 38. *Corroded sphere shown in figure 37 after still longer exposure to 15-percent* NaOH. ×5.

crystallographic planes exposed during corrosion in this medium, a study was made of the corroded holes in the specimens of figures 20, 21, and 22, comparing them with the appropriately projected shapes of polyhedra with faces corresponding to various crystallographic indices.

The most suitable polyhedron appears to be one whose faces are parallel to {335}. In figure 36 is shown a shadow photograph of such a polyhedron, oriented so that either cubic (a), dodecahedral (b), or octahedral (c) planes lie in the plane of projection. Figures 36 a and c correspond closely with the holes in the disks of figures 20 and 22. However, some discrepancy occurs between figure 36, b, and the hole in the disk of figure 21, in that the relative lengths of the sides and the angles between sides are not similar for the two figures. No simple mode of corrosion process can be hypothesized to explain

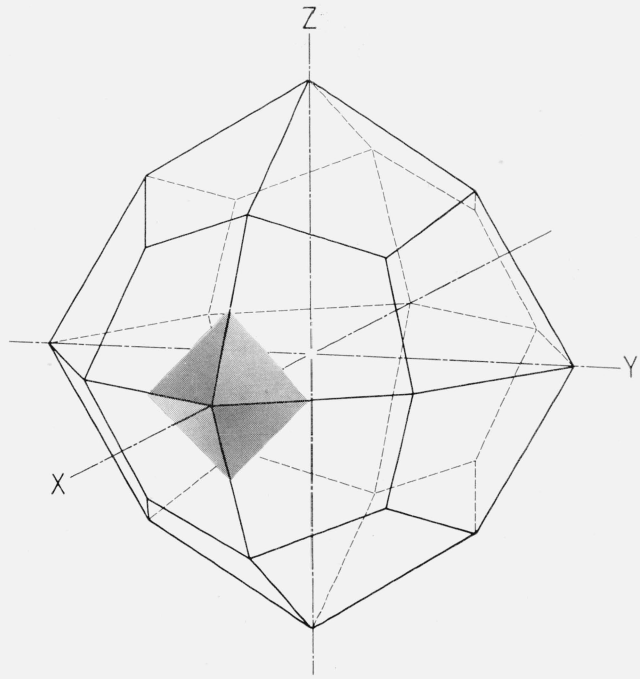

FIGURE 39. *Sketch of tetragonal trisoctahedron showing hillock as viewed in a direction normal to the cubic plane.*

how such a polyhedron might be formed wherein the hole produced would conform to the assumed model on only two of the three planes of projection.

It will be recalled that, whereas acid corrosion of monocrystalline aluminum resulted in producing etch pits exposing only cubic planes, its gross features consisted of the most rapid rate of corrosion in a direction normal to octahedral planes. Figures 28, 29, and 30 show the specimen of figure 16, when oriented in the positions corresponding to figures 3, 4, and 5, respectively. This clearly shows that an octahedron-like shape is evolving from the original sphere.

Conversely, specimens subjected to alkaline corrosion revealed protuberances having facets which are presumed to parallel {335} planes, whereas in its gross features, corrosion apparently progressed most rapidly in the cubic direction. Figure 37 shows a view parallel to the cubic plane of the specimen of figure 25 after a somewhat longer exposure. It apparently has become more cube-like inasmuch as the areas lying on other than cubic planes have become smaller owing to the further development of such cube faces. After the specimen becomes essentially cubic in form, as shown in figure 38, further corrosion would only decrease the dimensions of the cube. The least rapid corrosion apparently occurs in directions normal to the octahedral plane, whereas an intermediate corrosion rate occurs normal to the dodecahedral plane.

The protrusions on all faces of specimens in figures 33 and 34 are considered to be the facets exposed during the attack by the alkali. As stated above, they are identified as being probably parallel to

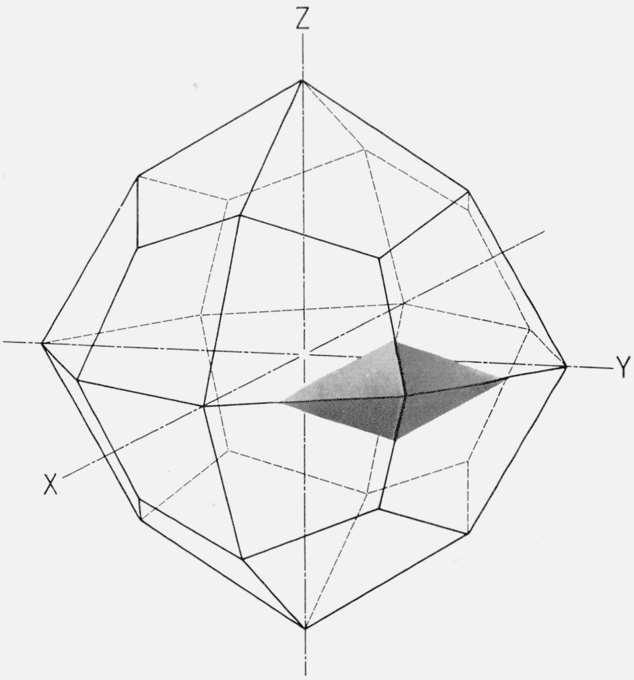

FIGURE 40. *Sketch of tetragonal trisoctahedron showing hillock as viewed in a direction normal to the dodecahedral plane.*

{335}. The difference between the appearance of the protrusions on the vertical sides of the specimen in figure 34 and all the other protrusions on both specimens, will be clarified by viewing figures 39 and 40. This shows two views of the polyhedron formed by such planes. The shaded areas in figure 39 cover four intersecting planes of the tetragonal trisoctahedron whose faces are parallel to {335} when cut by a cubic plane. Its appearance is similar to the shape of all the protrusions on the specimen in figure 33 and the protrusions on the top face of the specimen in figure 34. They are the facets exposed when the corrosion progressed in a direction normal to the cubic planes. The shaded area of the polyhedron in figure 40 covers four intersecting planes when cut by a dodecahedral plane. Its configuration is similar to the protrusions on the sides of the specimen in figure 34.

6. Conclusions

An investigation of the influence of corrosion by a 15-percent NaOH solution and by an aqua regia-hydrofluoric acid mixture on high purity monocrystalline aluminum in various geometrical shapes results in the following conclusions:

1. The process of corrosion is an orderly one, the rate of attack being dependent on the arrangement of the atoms relative to the surface upon which the attack is taking place.

2. For the alkali mixture, the attack is such as to reveal facets whose surfaces probably are parallel to {335} planes, with the most rapid corrosion taking place in directions normal to cubic planes. Thus, when thin single-crystal disks having various surface orientations and containing small central holes were exposed to the NaOH mixture, these holes corroded so as to form shapes roughly similar to the trace of a polyhedron bounded by {335} planes when intersected by a plane oriented to correspond to the surface of the disk.

3. For the acid mixture, a pitting type of attack occurs which exposes only the cubic planes. However, corrosion is observed to progress at a very slow rate in directions normal to such planes, the most rapid corrosion occurring in directions normal to octahedral planes. This is similar to the attack observed by earlier investigators when using various acids.

Thus, when thin single-crystal disks having various surface orientations and containing small central holes were exposed to the acid mixture, these holes corroded so as to form shapes similar to those of the trace of a cube when intersected by a plane oriented to correspond to the surface of the disk.

4. The gross effect of corrosion by these media on spherical single crystals is such as to cause them to acquire the general shape of equilateral octahedra, when attacked by the acid mixture and of cubes when attacked by the NaOH solution.

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