On the Solution-Body Phenomenon and Anisotropy of Solution Rate in Bismuth Crystals

On the Solution-Body Phenomenon and Anisotropy of Solution Rate in Bismuth Crystals*

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Synopsis

The solution-body phenomenon has been investigated with bismuth single crystals, of circular-rod and sphere forms, etched with various reagents and some information concerning the anisotropy of solution rate has been obtained. It has been found that 31.6 percent nitric acid is only one reagent that produced clear-cut solution-bodies characteristic to the trigonal symmetry of bismuth crystal and that the rates of solution along various crystallographic directions in this reagent are in the order of

$$V_{\langle\bar{h}kl\rangle} > V_{\langle\bar{2}11\rangle} > V_{\langle -2+m,\, 1+m,\, 1+m\rangle} > \begin{matrix} V_{\langle\bar{1}01\rangle} > \\ \\ V_{\langle -3+n,\, n,\, 3+n\rangle} \end{matrix} > V_{\langle 111\rangle},$$

where $\bar{h}+k+l=0$ and m and n = any rational number. It is also shown that solution rates in 50 percent aqueous solution of 1 : 2 mixture of hydrochloric acid and nitric acid are in the same order as in 31.6 percent nitric acid, though the anisortopy is far smaller.

I. Introduction

Generally, when a crystal of a cylindrical rod form or of a sphere form is etched with a reagent, the cylindrical rod will gradually be converted into a regular polygonal rod and the sphere will transform into a polyhedron. This phenomenon, usually called a solution body (*der Lösungskörper* in German) is caused by the fact that the rate of solution or corrosion generally varies with crystallographic directions so that crystal planes normal to directions whose rates of solution are greater develop preferentially(1). Thus, from the shape of a solution body, an information as to the anisotropy of solution rate can be obtained if the crystal orientation of the solution body is known beforehand, and conversely, the crystal orientation can be fixed when the crystallographic indices of faces or edges constructing the solution body are known. As for the solution-body phenomena of metallic crystals only cubic crystals of tungsten(2) and copper(3) and hexagonal crystals of zinc(4,5) were hitherto examined, and the anisotropy of solution rate

* The 755th report of the Research Institute for Iron, Steel and Other Metals. A preliminary short note (in English) and the original report (in Japanese) was published previously in Nippon Kinzoku Gakkai-shi (J. Japan Inst. Metals), **16** (1952), 234 and **17** (1953), 118, respectively.

(1) H.C. Desch, *The Chemistry of Solids*, Cornell Univ. Press, New York, (1934), p. 69.
(2) R. Gross, F. Koref and K. Moers, Z. Phys., **22** (1924), 317; W. Böttgar, Z. Elektrochem., **23** (1917), 121.
(3) G. Tammann and F. Sartorius, Z. anorg. allg. Chem., **175** (1928), 97.
(4) G. Aminoff, Z. Krist., **65** (1927), 23.
(5) M. Straumanis, Z. phys. Chem., **147** (1930), 161.

have so far been studied only on cubic copper[6] and hexagonal zinc[4,5] and magnesium[7] crystals. It is to be noted that the rate of solution is appreciably anisotropic even in cubic crystals and a direction of the greatest solution rate is never constant but varies with the kind of etching reagent.

Now, we have investigated for the first time with single crystals of trigonal bismuth. Clear-cut and less clear-cut solution-bodies have been obtained in some cases of etching, and some informations concerning the anisotropy of solution rate have been derived from them.

II. Crystal specimens and the experimental procedure

Bismuth single crystals used as specimens were circular rods, 5 mm in diameter and several cm in length, as grown by the suction method[8] and by the Bridgman method[9], and spheres, 15~20 mm in diameter, as prepared by the Tammann method[10], from two lots of bismuth of 99.98 and 99.99 percent purity. Orientations of circular-rod crystals as determined by the light-figure method[11] are represented in Table 1 and Fig. 1, which show that rod axes are nearly parallel to ⟨111⟩, ⟨$\bar{2}$11⟩ and ⟨$\bar{1}$01⟩ directions and parallel to a direction intermediate between those three principal crystal directions. These rod crystals will be simply called the ⟨111⟩, ⟨$\bar{2}$11⟩, ⟨$\bar{1}$01⟩, and intermediately oriented crystals in the following.

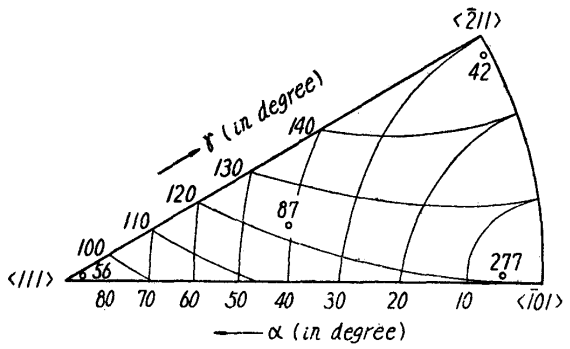


Fig. 1. Orientations of bismuth single crystals of the round-bar form used as specimens.

Table 1. Orientations of bismuth single crystals of the round-bar form used as specimens.
θ, α, β and γ denote angles which the rod axis makes with [111], [10$\bar{1}$], [0$\bar{1}$1] and [$\bar{1}$10] axes, respectively.

Nominal orientation	Crystal No.	θ degree	α degree	β degree	γ degree
⟨111⟩	56	4.7	86.0	90.0	93.9
⟨$\bar{2}$11⟩	42	88.5	28.0	92.0	148.0
⟨$\bar{1}$01⟩	277	84.8	5.4	118.3	121.4
Intermediately oriented	87	50.7	41.2	102.7	122 2

(6) R. Glauner and R. Glocker, Z. Krist., **80** (1931), 377.
(7) E. Schiehold and G. Siebel, Z. Phys., **69** (1931), 458.
(8) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **B14** (1950), No. 10 (in Japanese); Sci. Rep. RITU, **A3** (1951), 165.
(9) The preparation of bismuth single crystals by the Bridgman method will be reported in the near future.
(10) M. Yamamoto and J. Watanabé, Sci. Rep. RITU, **A3** (1951), 655; Nippon Kinzoku Gakkai-shi, **17** (1953), 1 (in Japanese).
(11) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **B15** (1951), 572 (in Japanese); Sci. Rep. RITU, **A5** (1953), 135.

The surface of sphere crystals was very carefully polished with a file and subsequently with emery papers of 3~05 in order to make the diameter uniform.

Specimen crystals were dipped into an etching solution of about 100 cc at room temperature. After an elapse of proper time, they were picked up from the solution, washed by running water and dried. Then, the change in shape of the specimens was observed and the relation between the shape and crystal directions was examined by means of light figures[12]. With sphere crystals, moreover, the reductions in linear size along principal crystal directions were measured with a callipers. This procedure was repeated at proper intervals of etching time.

As etching reagents we employed strongly oxidizing ones such as nitric acid, a mixture of nitric acid and hydrochloric acid, and nitric acid containing a small quantity of mercury or various salts according to the results of our previous investigation[12].

III. Experimental results and considerations

A. *Experiments with circular-rod crystals; etching with 31.6 percent nitric acid.*

In the first place, circular rod crystals were subjected to etching with 31.6 percent nitric acid.

(1) $\langle 111 \rangle$ crystal

The $\langle 111 \rangle$ crystal (No. 56) etched with this reagent for a short time showed a six-fold alternation of maximum glitter of light over its surface when rotated around its rod axis. This glitter is caused by the reflection of light from crystal faces belonging to the $\{\bar{1}01\}$ zone, particulary from the $\{uu\bar{v}\}$ faces[13], as developed by the etching, as may be seen readily from the form of light figures[12] produced by the same etching[14].

With an elapse of etching time, glittering portions of the crystal surface gradually became angular, accompanied by a spreading out of the glitter, and thus finally at 30~35 minutes the originally circular rod converted into a nearly regular hexagonal prism such as shown in Photo. 1(a). (In this set of photographs, the upper and lower parts are, respectively, the front and side views of the solution bodies produced.) The relation of the shape of this solution body to the crystal axes is as shown in Fig. 2(a): In a normal cross section forming a nearly regular hexagon, a direction conneting its center with an apex coincides with a $\langle \bar{2}11 \rangle$ direction and a direction connecting the center with a middle point of a side is a $\langle \bar{1}01 \rangle$ direction. From this relation it is readily seen that the rate of solution along the $\langle \bar{1}01 \rangle$ direction, $V_{\langle \bar{1}01 \rangle}$, is greater than that along the $\langle \bar{2}11 \rangle$ direction, $V_{\langle \bar{2}11 \rangle}$, and that along any direction intermediate between the $\langle \bar{1}01 \rangle$ and

(12) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **B15** (1951), 514 and 519 (in Japanese); Sci. Rep. RITU, **A4** (1952), 127; **A5** (1953), 124.

(13) This means a series of crystal faces containing the $\{44\bar{1}\}$ or $\{55\bar{1}\}$ or $\{66\bar{1}\}$ plane and its nearby crystal planes.

(14) The glitter phenomenon in single crystals of several metals including bismuth will be reported shortly.

its neighbouring $\langle\bar{2}11\rangle$ directions, $V_{\langle\bar{h}kl\rangle}$ ($\bar{h}+k+l=0$), is intermediate, namely

$$V_{\langle\bar{1}10\rangle} > V_{\langle\bar{h}kl\rangle} > V_{\langle\bar{2}11\rangle} \text{ , where } \bar{h}+k+l=0. \quad (1)$$

(2) $\langle\bar{2}11\rangle$ crystal

The $\langle\bar{2}11\rangle$ crystal (No. 42) subjected to a short-time etching showed a two-fold alternation of the maximum glitter of light over its surface by rotation around its rod axis, as might be expected from the above-mentioned. Glittering portions of the surface became angular and the glitter itself spread out with an increasing etching time, similar to the case of the $\langle111\rangle$ crystal, and finally a nearly elliptic prism as shown in Photo. 1 (b) was formed by etching for 25~35 minutes. The correspondence of the shape of this solution body to the crystal axes is illustrated in Fig. 2 (b), which shows that the direction of the major axis of a nearly ellipse as a normal cross-section of the solution body coincides with the $\langle111\rangle$ direction and that of the minor axis with a $\langle\bar{1}01\rangle$ direction. This indicates at once that the rate of solution along the $\langle111\rangle$ direction, $V_{\langle111\rangle}$, is less than $V_{\langle\bar{1}01\rangle}$, and that along any direction intermediate between the $\langle111\rangle$ and $\langle\bar{1}01\rangle$ directions, $V_{\langle-3+n,\,n,\,3+n\rangle}$ (n=any rational number), is intermediate, namely

$$V_{\langle\bar{1}01\rangle} > V_{\langle-3+n,\,n,\,3+n\rangle} > V_{\langle111\rangle}, \text{ where } n=\text{any rational number.} \quad (2)$$

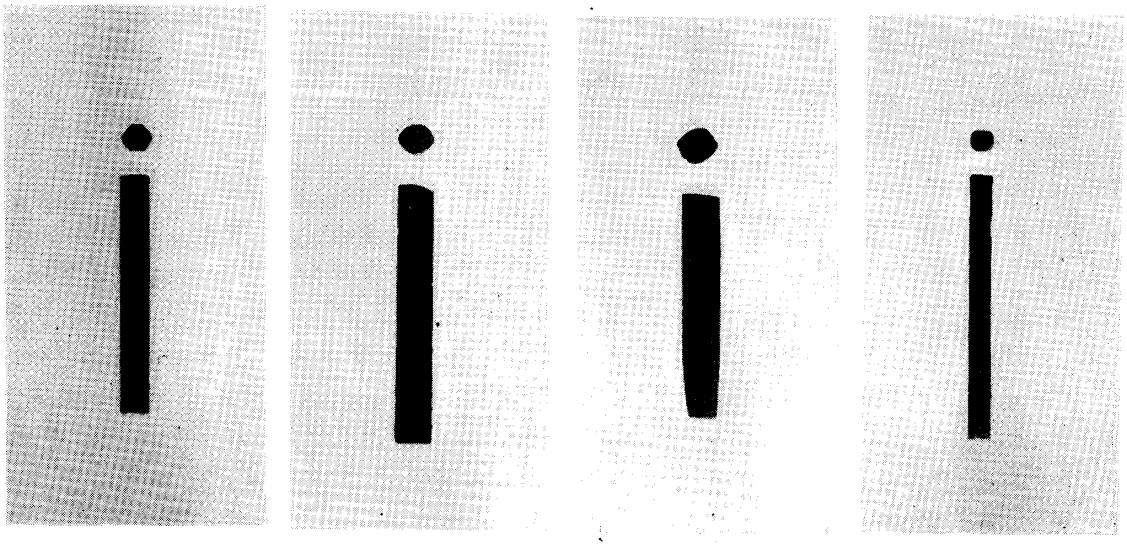
(3) $\langle\bar{1}01\rangle$ crystal

The etched surface of the $\langle\bar{1}01\rangle$ crystal (No. 277) also showed a two-fold alternation of the maximum glitter of light by rotation around its rod axis, as might be expected. The manner of variations in the glitter and in the shape with etching were almost the same as in the case of the $\langle\bar{2}11\rangle$ crystal. The originally circular rod became a slightly distorted elliptic prism as shown in Photo. 1 (c) after 45 minutes' etching. The deviation of the shape of this solution body from an "elliptic" prism may be due to the fact that the rod axis of this crystal inclined somewhat more to the $\langle\bar{1}01\rangle$ direction, as seen at once from Fig. 1. The relation of the shape of this solution body to the crystal axes is shown in Fig. 2 (c), which indicates that $V_{\langle111\rangle}$ is less than $V_{\langle\bar{2}11\rangle}$ and the rate of solution along any direction intermediate between the $\langle111\rangle$ and $\langle\bar{2}11\rangle$ directions, $V_{\langle-2+m,\,1+m,\,1+m\rangle}$ (m=any rational number), is intermediate, namely

$$V_{\langle\bar{2}11\rangle} > V_{\langle-2+m,\,1+m,\,1+m\rangle} > V_{\langle111\rangle}, \text{ where } m=\text{any rational number.} \quad (3)$$

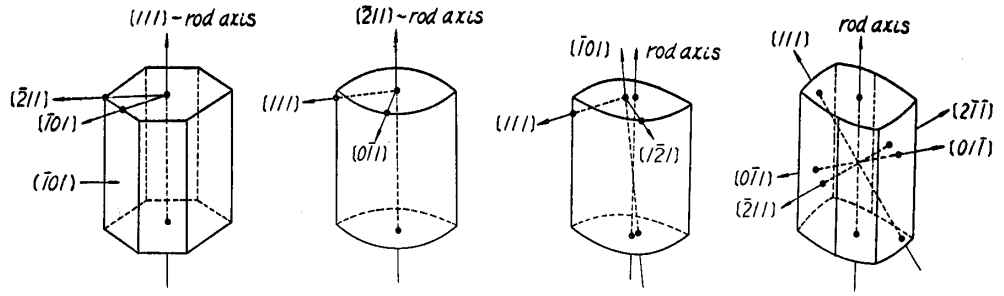
(4) Intermediately oriented crystal

Finally, the intermediately oriented crystal (No. 87) when etched for a short time presented a four-fold alternation of the maximum glitter of light over its surface by rotation around its rod axis, though the glitter of this crystal was weaker than that of other crystals. It eventually changed into a rounded rectangular-prism-like shape as shown in Photo. 1(d) after about one hour's etching. The correspondence of this solution body to the crystal axes is illustrated in Fig. 2(d), but no definite information concerning the anisotropy of solution rate can be obtained directly from this figure. It is to be noted, however, that the shape of this solution body is really a rounded hexagonal prism in which two



(a) ⟨111⟩ crystal (b) ⟨$\bar{2}$11⟩ crystal (c) ⟨$\bar{1}$01⟩ crystal (d) Intermediately oriented crystal

Photo. 1. Solution bodies produced by etching with 31.6% HNO_3 of originally round-bar crystals of bismuth. (×1)



(a) ⟨111⟩ crystal (b) ⟨$\bar{2}$11⟩ crystal (c) ⟨$\bar{1}$01⟩ crystal (d) Intermediately oriented crystal

Fig. 2. Solution bodies produced by etching with 31.6% HNO_3 of originally round-bar crystals of bismuth in relation to the crystal axes.

neighbouring sets of facing surfaces apparently degenerate into one set, as will be shown later.

Summarizing formulae (1), (2) and (3), the rates of solution along various crystal directions of bismuth crystal in 31.6 percent nitric acid are found to be in the order of

$$V_{\langle\bar{1}01\rangle} > \begin{matrix} V_{\langle\bar{h}kl\rangle} > V_{\langle\bar{2}11\rangle} > V_{\langle -2+m,\, 1+m,\, 1+m\rangle} \\ V_{\langle -3+n,\, n,\, 3+n\rangle} \end{matrix} > V_{\langle 111\rangle}, \qquad (4)$$

where $\bar{h} + k + l = 0$ and m and n = any rational number. Previously Goetz[15] reported that $V_{\langle\bar{1}11\rangle} > V_{\langle 111\rangle}$, and this is in accordance with Eq. (3) or (4). It is to be noted that the series of solution rate (4) for trigonal crystal corresponds to

$$V_{\langle 11\bar{2}0\rangle} > \begin{matrix} V_{\langle hk\bar{i}0\rangle} > V_{\langle 10\bar{1}0\rangle} > V_{\langle 10\bar{1}l\rangle} \\ V_{\langle 11\bar{2}l\rangle} \end{matrix} > V_{\langle 0001\rangle} \qquad (5)$$

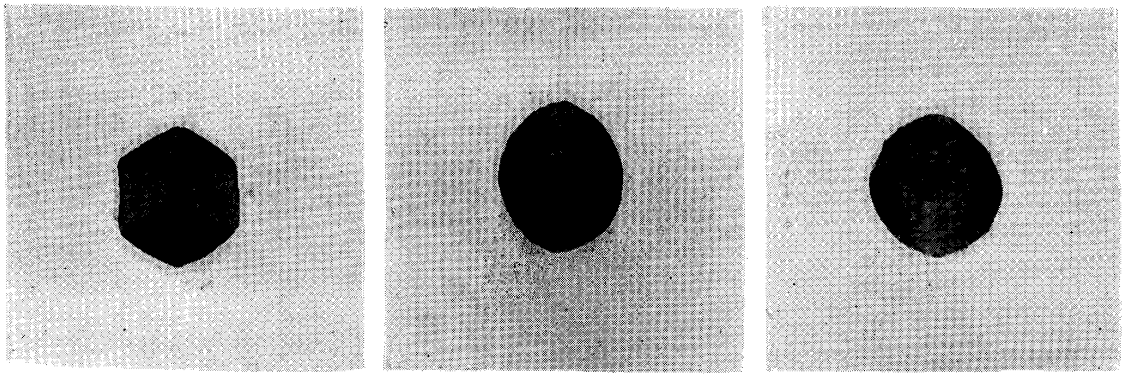
for hexagonal crystal, and that the series of solution rates (5) was found to hold for the solution of zinc crystal in hydrochloric acid by the present authors[16].

(15) A. Goetz, Proc. Nat. Acad. Amer., **16** (1930), 99.
(16) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **17** (1953), 315 (in Japanese).

B. *Experiments with sphere crystals*

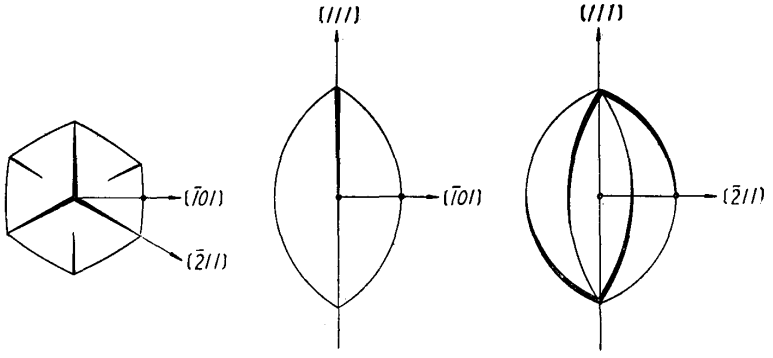
(1) Etching with 31.6 percent nitric acid

The above-described results of experiments with circular-rod crystals in the case of etching with 31.6 percent nitric acid indicate that a sphere crystal, when etched for a long time with the same reagent, would take a shape like a rugby ball of which the axis coincides with the $\langle 111 \rangle$ direction and the surface is surrounded by six curved faces, six edges bordering the curved faces running from the (111) pole to the $(\bar{1}\bar{1}\bar{1})$ pole through $\{2\bar{1}\bar{1}\}$ poles. In fact, we obtained, by etching a sphere crystal with 31.6 percent nitric acid for more than one and half hours, a clear-cut solution-body having the expected shape as shown in Photo. 2 and Fig. 3. It is to be noticed that one set of alternative three edges is sharp and the other set of alternative three edges is less sharp in the (111) pole side and the situation is reverse in the $(1\bar{1}\bar{1})$ pole side, indicating evidently the trigonal symmetry of bismuth crystal.



(a) $\langle 111 \rangle$ (b) $\langle \bar{2}11 \rangle$ (c) $\langle \bar{1}01 \rangle$

Photo. 2. Solution body produced by etching with 31.6% HNO_3 of an originally sphere crystal of bismuth. (a), (b) and (c) are views along the $\langle 111 \rangle$, $\langle \bar{2}11 \rangle$ and $\langle \bar{1}01 \rangle$ directions, respectively. (×1.5)



(a) $\langle 111 \rangle$ (b) $\langle \bar{2}11 \rangle$ (c) $\langle \bar{1}01 \rangle$

Fig. 3. Solution body produced by etching with 31.6% HNO_3 of an originally sphere crystal of bismuth in relation to the crystal axes. (a), (b) and (c) are views along the $\langle 111 \rangle$, $\langle \bar{2}11 \rangle$ and $\langle \bar{1}01 \rangle$ directions, respectively.

A cross-section of this solution body parallel to the (111) plane is a regular hexagon-like figure with slightly curved sides (Photo. 2 (a) and Fig. 3 (a)), in which a direction connecting the center with an apex coincides with a $\langle\bar{2}11\rangle$ direction and that connecting the center with a middle point of a side is a $\langle\bar{1}01\rangle$ direction. This corresponds to a normal cross-section of the solution body of the $\langle 111\rangle$ rod crystal described in A (Photo. 1 (a) and Fig. 2 (a)). While, a cross section parallel to the $(\bar{2}11)$ or to the $(\bar{1}01)$ plane is an ellipse-like figure (Photo. 2(b) and Fig. 2(b) or Photo. 3(c) and Fig. 3(c)), of which a direction of the major axis corresponds to the $\langle 111\rangle$ direction and that of the minor axis coincides with a $\langle\bar{1}01\rangle$ or with a $\langle\bar{2}11\rangle$ direction. This corresponds to a normal cross-section of the solution body of the $\langle\bar{2}11\rangle$ or $\langle\bar{1}01\rangle$ rod crystal described in A (Photo. 1 (b) and Fig. 2 (b) or Photo. 1 (c) and Fig. 2 (c)). Finally, a cross-section normal to the "intermediate" orientation represented by a point 87 in Fig. 1 is a rounded hexagon as shown in Fig. 4. In this figure four corners designated as sharp correspond to the sharp parts, and two corners designated as less sharp to the less sharp parts, of edges of the solution body, and thus the two sets of facing sides separated by the two less sharp corners practically degenerate into one set of facing sides, thus the cross-section as a whole appearing as a rounded rectangle. This corresponds to a normal cross-section of the solution body of the intermediately oriented rod crystal described in A (Photo. 1(d) and Fig. 2(d)).

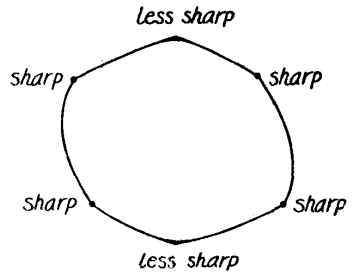


Fig. 4. A cross-section normal to the "intermediate" orientation of a solution body produced by etching with 31.6% HNO_3 of an originally sphere crystal of bismuth.

That the cross-sections parallel to the $(\bar{2}11)$ and to the $(\bar{1}01)$ plane are practically ellipses was confirmed as follows. If a cross-section were an ellipse, and if the half length of its major axis ($\langle 111\rangle$ direction) is a and that of its minor axis ($\langle\bar{1}01\rangle$ or $\langle\bar{2}11\rangle$ direction) b, the distance from its center to a point on its circumference r, and an angle between the direction of the radius vector and the major axis θ, then a following relationship should hold

$$r^2\left(\frac{\cos^2\theta}{a^2}+\frac{\sin^2\theta}{b^2}\right)=1. \qquad (6)$$

Accordingly, the correspondence can be confirmed if for r as a function of θ the measured values and values calculated from Eq. (6) are compared with each other. The measured values as obtained on photographs enlarged by 5.1 times and the calculated ones are as given in Table 2, from which it may be seen that both the measured and calculated values are in agreement with each other within the limits of experimental error.

Further, in order to obtain a quantitative information concerning the anisotropy of solution rate, the reduction in linear size as a function of the etching time was measured along $\langle 111\rangle$, $\langle\bar{2}11\rangle$ and $\langle\bar{1}01\rangle$ directions of a sphere crystal having the initial diameter of 14.93 ± 0.14 mm. The results are shown in Fig. 5. The

Table 2. Correspondence to ellipses of the cross-sections parallel to the $(\bar{1}01)$ and $(\bar{2}11)$ planes of a solution body produced by etching with 31.6% HNO_3 of an originally sphere single crystal of bismuth.

θ degree	r (mm)			
	Section parallel to $(\bar{1}01)$		Section parallel to $(\bar{2}11)$	
	Measured value	Computed value	Measured value	Computed value
0	27.5(a)	—	27.4(a)	—
30	26.1	26.8	25.3	26.1
45	26.0	26.1	24.4	24.9
60	25.6	25.6	23.5	23.9
90	25.0(b)	—	23.0(b)	—

reduction in linear size is the least along the $\langle 111\rangle$ direction and becomes greater in the order of the $\langle\bar{2}11\rangle$ and $\langle\bar{1}01\rangle$ directions. This is in accordance with Eq. (4). Every solution curve shows a sharp rise at the start, but with an increase of etching time it gradually becomes slower and finally almost linear. It should be noted that every solution curve shows an inflexion point at an early stage of

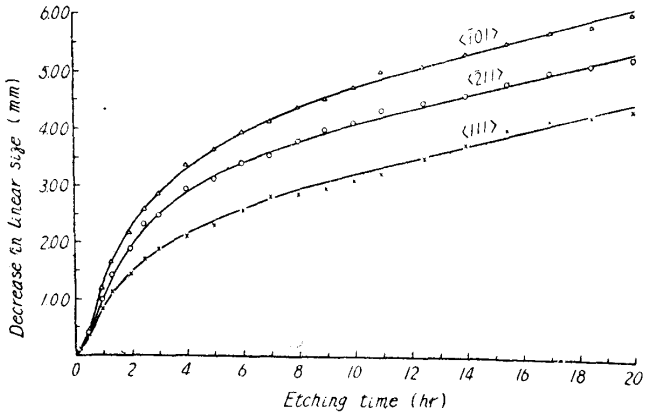
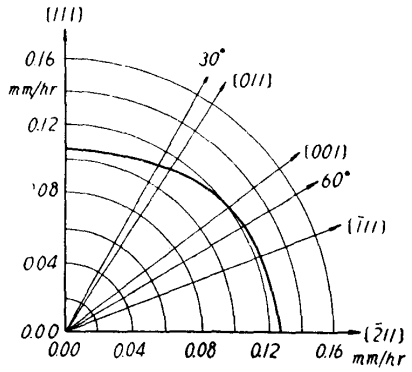
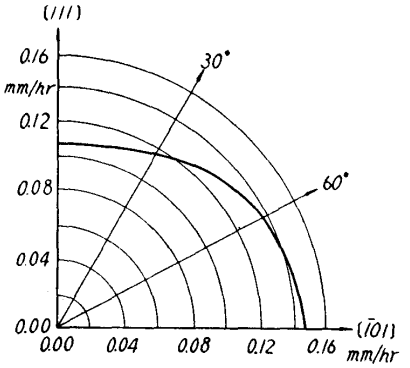


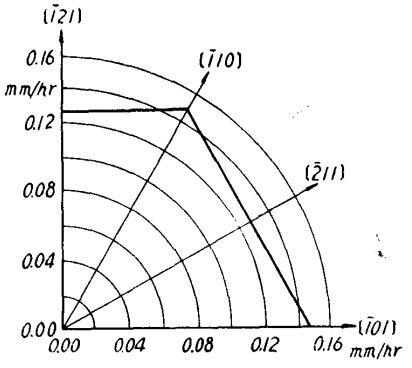
Fig. 5. Solution curves for the $\langle 111\rangle$, $\langle\bar{2}11\rangle$ and $\langle\bar{1}01\rangle$ directions of an originally sphere crystal of bismuth in 31.6% HNO_3.



(a) $(\bar{1}01)$ plane



(b) $(\bar{2}11)$ plane



(c) (111) plane

Fig. 6. Relative rate of solution of bismuth crystals in 31.6% HNO_3 in relation to the crystal direction.

etching. Although the absolute values of solution rate can not be obtained from these curves, the values of average solution rate during up to 20 hours for the ⟨111⟩, ⟨$\bar{2}$11⟩, and ⟨$\bar{1}$01⟩ directions are found to be in a ratio of 1.0 : 1.2 : 1.4. Further, relative average solution rates for various crystal directions can be computed from this ratio by taking into account of the above-mentioned form of the solution body. The anisotropy of solution rate of bismuth crystals in 31.6 percent nitric acid determined in this way is shown in Fig. 6.

(2) Etching with other reagents

The etching with 61.7 percent nitric acid was vigorous, and produced many irregular projections on the crystal surface.

In the case of etching with 50 percent aqueous solution of the 1 : 2 mixture of hydrochloric acid (29.6 percent) and nitric acid (61.7 percent), we obtained a solution body approximately similar to, but not so clear-cut as, that obtained in the case of etching with 31.6 percent nitric acid. The relationships between the reduction in linear size and etching time obtained with a sphere crystal, 19.99 ± 0.20 mm in the original diameter, are plotted in Fig. 7, which shows that the reduction in linear size along the ⟨111⟩ direction is the least and that along the ⟨$\bar{1}$01⟩ direction is very slightly larger than that along the ⟨$\bar{2}$11⟩ direction, namely the order of solution rates in this case is the same as that in the case of etching with 31.6 percent nitric acid (Eq. (4)), though the anisotropy of solution rate is much smaller.

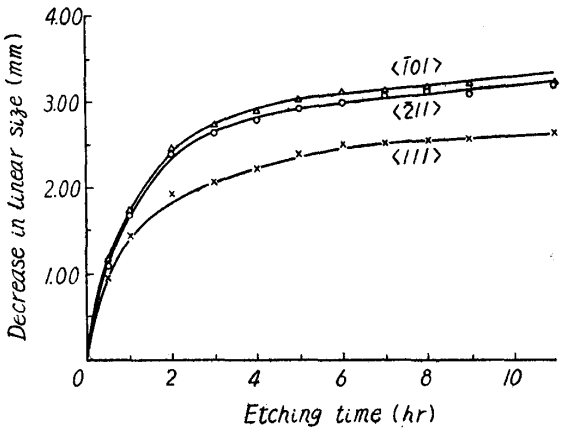


Fig. 7. Solution curves for the ⟨111⟩, ⟨$\bar{2}$11⟩ and ⟨$\bar{1}$01⟩ directions of an originally sphere crystal of bismuth in 50% aqueous solution of $1\text{-}HCl + 2\text{-}HNO_3$.

Finally, after Hausser and Scholz's[17] experiments on the anisotropic deposition of silver or mercury on the surface of sphere single crystals of copper etched with nitric acid containing a small quantity of silver nitrate or mercury, we made similar experiments with sphere crystal of bismuth. Etching with 31.6 percent nitric acid containing 10 weight percent of silver nitrate for six hours produced a solution body, which was similar to, but not so clear-cut as, that obtained in the case of etching with 31.6 percent nitric acid only, and of which the surface was uniformly silver-plated. In cases of etching with 31.6 percent nitric acid containing 20 weight percent of mercury and with 31.6 percent nitric acid containing 10 weight percent of cuprous chloride, we obtained no solution body, although an uniform deposition of mercury and of a white film was produced on the crystal surface in the former and latter cases, respectively. Finally, etching with 31.6 percent nitric acid containing 20 weight percent of zinc chloride for two hours produced a

(17) K. W. Hausser and P. Scholz, Wiss. Veröff. Siemens-Konzern, **5** (1927), 144.

solution body, which was similar to, but not so clear-cut as, that obtained in the case of etching with 31.6 percent nitric acid only, and of which the surface was covered with a greyish-white film.

Summary

The solution-body phenomenon has been investigated with bismuth single crystals, of circular-rod and sphere forms, etched with various reagents and some information concerning the anisotropy of solution rate has been obtained.

First, circular-rod crystals, of which rod axes are nearly parallel to the ⟨111⟩, ⟨$\bar{1}$01⟩, ⟨$\bar{2}$11⟩ and an intermediate directions, were etched with 31.6 percent nitric acid. The ⟨111⟩ crystal converted into a nearly hexagonal prism. In its normal cross-section forming a nearly regular hexagon, a direction connecting the center with an apex coincides with a ⟨$\bar{2}$11⟩ direction and a direction connecting the center with a middle point of a side is a ⟨$\bar{1}$01⟩ direction. Both ⟨$\bar{2}$11⟩ and ⟨$\bar{1}$01⟩ crystals transformed into nearly elliptic prisms. In a nearly ellipse as a normal cross-section of these solution bodies, the direction of the major axis coincides with a ⟨111⟩ direction for both crystals, but that of the minor axis corresponds to a ⟨$\bar{1}$01⟩ direction for the ⟨$\bar{2}$11⟩ crystal and to a ⟨$\bar{2}$11⟩ direction for the ⟨$\bar{1}$01⟩ crystal. The intermediately oriented crystal changed into a rounded rectangular prism. It was found, from the relationships between such shapes of solution bodies and crystal directions, that the rates of solution in 31.6 percent nitric acid were in the order of

$$V_{\langle\bar{1}01\rangle} > \begin{matrix} V_{\langle\bar{h}kl\rangle} > V_{\langle\bar{2}11\rangle} > V_{\langle -2+m,\,1+m,\,1+m\rangle} \\ V_{\langle -3+n,\,n,\,3+n\rangle} \end{matrix} > V_{\langle 111\rangle} ,$$

where $\bar{h}+k+l=0$ and m and n = any rational number. This series of solution rate for trigonal crystal corresponds to

$$V_{\langle 11\bar{2}0\rangle} > \begin{matrix} V_{\langle hki\bar{0}\rangle} > V_{\langle 10\bar{1}0\rangle} > V_{\langle 10\bar{1}l\rangle} \\ V_{\langle 11\bar{2}l\rangle} \end{matrix} > V_{\langle 0001\rangle}$$

for hexagonal crystal, which was found previously by the authors to hold for the solution of zinc crystal in hydrochloric acid.

Next, sphere single crystals were etched with 31.6 or 61.7 percent nitric acid, with 50 percent aqueous solution of 1 : 2 mixture of hydrochloric acid and nitric acid, and with 31.6 percent nitric acid containing a small quantity of silver nitrate, mercury, cuprous chloride or zinc chloride. 31.6 percent nitric acid was only one reagent that produced a clear-cut solution body. As expected from the experimental results with circular-rod crystals, the shape of the solution body is like a rugby ball, of which the axis coincides with the ⟨111⟩ direction and the surface is surrounded by six curved faces, six edges bordering the curved faces running from the (111) pole to the ($\bar{1}\bar{1}\bar{1}$) pole through {2$\bar{1}\bar{1}$} poles. Of these six edges, one set of alternative three edges is sharp and the other set of alternative three edges is less sharp in the (111) pole side, while the situation is reverse in the ($\bar{1}\bar{1}\bar{1}$) pole side, indicating evidently a trigonal symmetry of bismuth crystal.

A cross-section of this solution body parallel to the (111) plane is a nearly regular hexagon and those parallel to the $(\bar{2}11)$ and $(\bar{1}01)$ planes are practically ellipses. It was found from the observed decrease in linear size of a sphere crystal etched with 31.6 percent nitric acid that values of the average solution rate during up to 20 hours for the $\langle 111 \rangle$, $\langle \bar{2}11 \rangle$, and $\langle \bar{1}01 \rangle$ directions is in a ratio of 1.0 : 1.2 : 1.4. Further, the rate of solution in 50 percent aqueous solution of 1 : 2 mixture of hydrochloric acid and nitric acid have been found to be in the same order of as in 31.6 percent nitric acid, although the anisotropy is far smaller and hence a not so clear-cut solution body is produced.