Crystal Growth of β-Hopeite on (0001) Plane of a Single Crystal of Zinc

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The epitaxy and the orientation of β-hopeite grown on the (0001) plane of a single crystal of zinc were studied. The epitaxy was found to be (0001)-Zn//(010)-β-hopeite, and the orientation was [10.0]//[100] or [12.0]//[100]. The nature of the chemical bond between β-hopeite and zinc is considered to be similar to that of the wurtzite type rather than to that of the wüstite type in view of the structure of the boundary surfaces.

One of the present authors previously studied the influence of impurities on the phosphatizing of steel,[1,2] the composition and the orientation of phsophate,[3] and also the electrochemical behavior of phosphatizing.[4] Machu,[5] Jaenicke and Lorenz,[6] and Khain[7] have studied the mechanism of phosphatization, and Neuhaus and Gebhardt[8-10] have presented a unique opinion on the epitaxies of phosphate coated on such base metals as Fe, Zn, and Cu.

From the above-mentioned investigations into the orientation of β-hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, on iron and steel, it has become obvious that the (010) plane of β-hopeite combines with the metal surface. In those studies, however, since polycrystalline pieces have been used as the base metal, the experimental determination of the epitaxies between phosphate and metal was difficult. Consequently, their estimation was carried out from their lattice constants. In order to examine the orientation and epitaxy between coating and metal precisely, the use of a single crystal as the base metal is necessary. In the present paper the following investigations will be reported: the orientation and the epitaxy of β-hopeite grown on the (0001) plane of zinc single crystal were studied by a microscopic observation of the crystal growth of β-hopeite, based on our experimental results and the crystal structure of β-hopeite, an adhesive mechanism between β-hopeite and zinc was also investigated.

Experimental

Phosphatizing Solution. The phosphatizing solution was prepared from a 0.1 mol/*l* solution of phosphoric acid by adjusting its pH with anhydrous sodium carbonate.

Microscopic Observation of the Crystal Growth. A single crystal of zinc (3 mm × 3 mm × 100 mm) was prepared by a modification of the method of Czochralski', the *c*-axis of zinc in the single crystal is perpendicular to the base plane. It was split just before the experiment, and a split chip of 2 mm was dipped in the phosphatizing solution, and held in a crystallizing dish. Then, under a microscope whose object glass was immersed into the phosphatizing solution, the crystal growth was observed, photographed, and filmed using a FUJICA Single 8, Z 2-type 8 mm movie camera by means of the memo-motion technique.

Results and Discussion

Observation of the Growth Direction of β-Hopeite. Photographs of crystals grown on the (0001) plane of zinc treated with the phosphatizing solution at various pH's are shown in Figs. 1—4. At pH 3.5, β-hopeite did not form, except for the appearance of etch pits. In the pH range of 4.5—5.0, the growth of a relatively large crystal of β-hopeite was observed.

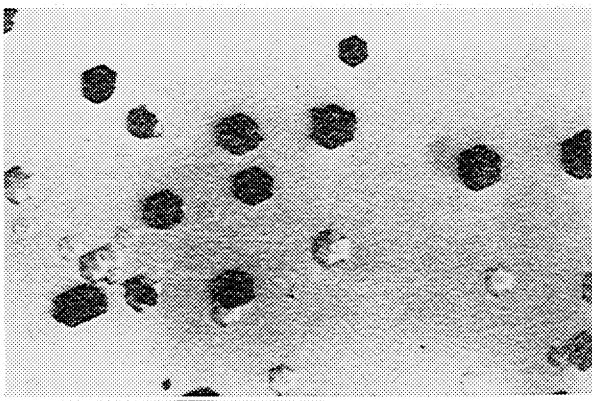

Fig. 1. Crystal growth of β-hopeite on the (0001)-Zn at pH 3.5 (45 min). (×180)

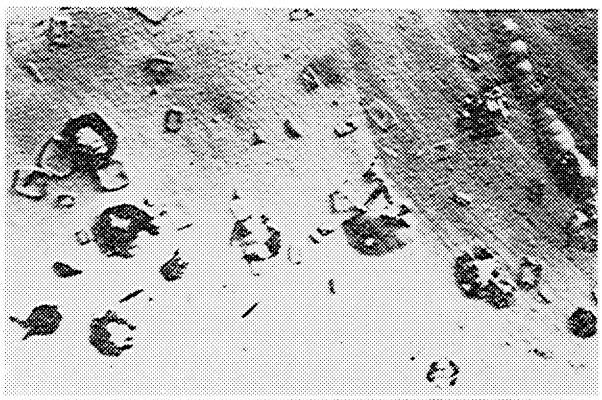

Fig. 2. Crystal growth of β-hopeite on the (0001)-Zn at pH 4.0 (45 min). (×180)

1) T. Umegaki, H. Ito, and T. Okabe, This Bulletin, **42**, 1555 (1968).
2) T. Umegaki, H. Ito, and T. Okabe, *ibid.*, **42**, 2364 (1969).
3) T. Umegaki, T. Okabe, and K. Omori, *ibid.*, **42**, 1304 (1969).
4) R. Shirakawa, S. Takeda, T. Umegaki, and T. Okabe, *ibid.*, **44**, 1007 (1971).
5) W. Machu, *Chem. Fabrik*, **13**, 461 (1940).
6) W. Jaenicke and B. Lorenz, *Werkstoffe u. Korrosion*, **10**, 681, **10**, 761 (1959).
7) I. I. Khain, *J. Appl. Chem. USSR*, **32**, 2531, 2542, 2662 (1959).
8) A. Neuhaus, E. Jumpertz, and M. Gebhardt, *Z. Elektrochem.*, **66**, 593 (1962).
9) A. Neuhaus and M. Gebhardt, *Naturwiss.*, **51**, 358 (1964).
10) M. Gebhardt, *Farbe Lack*, **74**, 217 (1968).

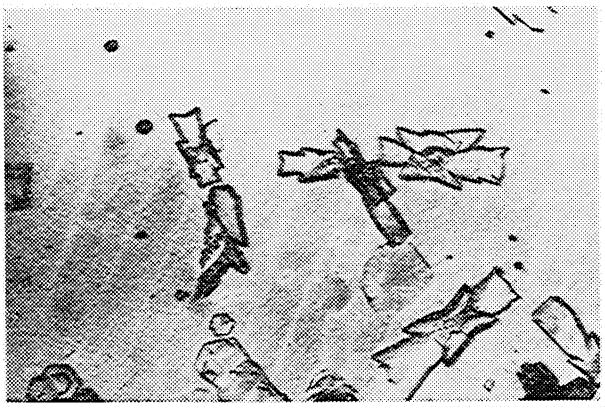

Fig. 3. Crystal growth of β-hopeite on the (0001)-Zn at pH 4.5 (45 min). (×180)

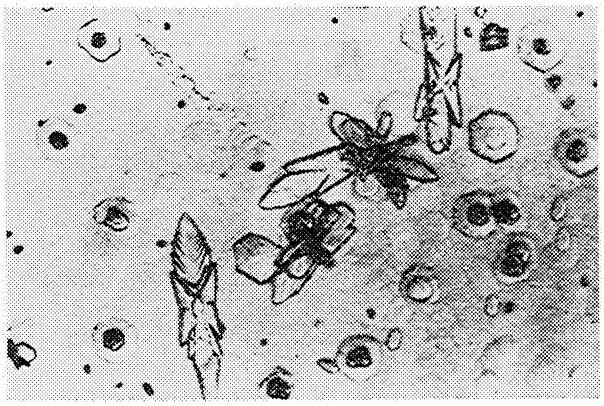

Fig. 4. Crystal growth of β-hopeite on the (0001)-Zn at pH 5.0 (45 min). (×180)

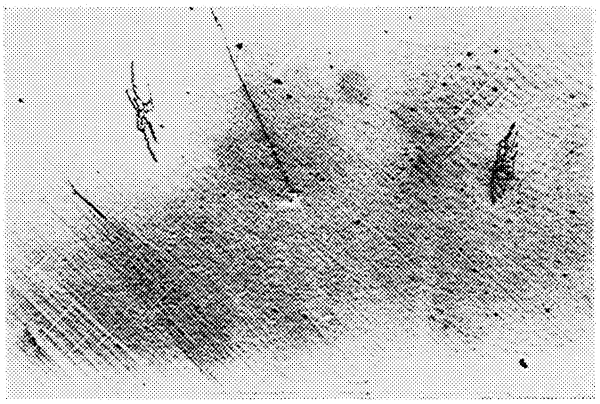

Fig. 5. Crystal growth of β-hopeite on the (0001)-Zn at pH 4.72 (10 min). (×180)

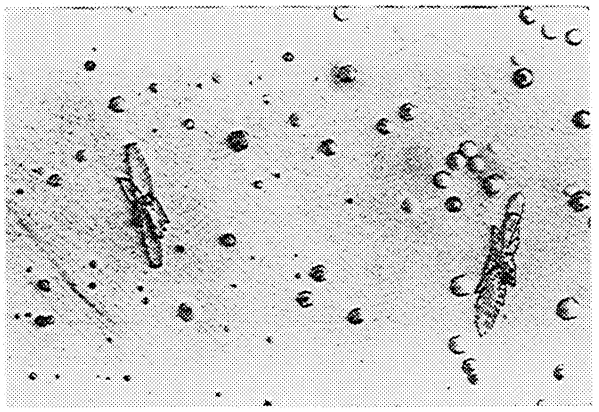

Fig. 6. Crystal growth of β-hopeite on the (0001)-Zn at pH 4.72 (20 min). (×180)

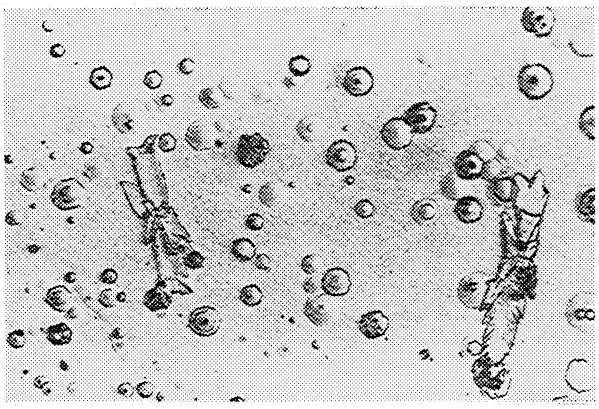

Fig. 7. Crystal growth of β-hopeite on the (0001)-Zn at pH 4.72 (30 min). (×180)

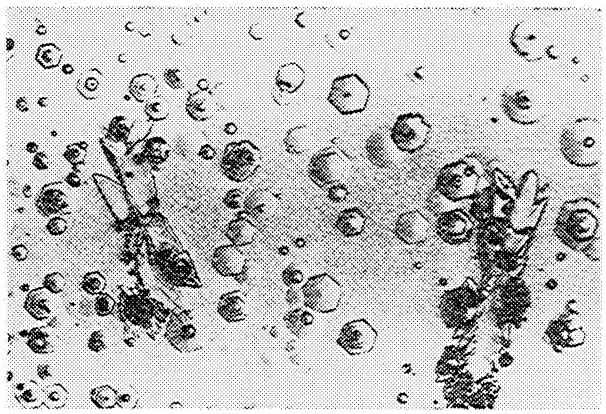

Fig. 8. Crystal growth of β-hopeite on the (0001)-Zn at pH 4.72 (40 min). (×180)

The series of microscopic photographs shown in Figs. 5 to 8 are the crystal growth of β-hopeite on the (0001) plane of zinc at pH 4.72, 20°C. The orientation of the *a*-axis on the (0001) plane of zinc can easily be recognized from the etch pits formed. Yamamoto and Watanabe[11] reported that etch pits appeared as regular hexagons when the (0001) plane of zinc was etched with a dilute hydrogen chloride solution. In these cases, the three *a*-axes of the zinc crystal are at right angles to the sides of the hexagon. When a zinc single crystal revealing a (0001) plane was dipped in the phosphatizing solution, etch pits with the same orientation as has been described above appeared, as is shown in Fig. 1. In Figs. 9 and 10, obtained by tracing Figs. 4 and 7 respectively, the directions of the crystal growth of β-hopeite are shown as dotted lines, and the three *a*-axes, a_1, a_2, and a_3, of the zinc crystal are drawn on an enlarged regular hexagon of the etch pit.

Two kinds of direction of the crystal growth can be observed in these figures; one of them coincides with the direction of the three *a*-axes, while the other makes an angle of 30° with the *a*-axes. From these results, it can be said that β-hopeite crystal grows along the [10.0] or [12.0] direction on the (0001) plane of zinc.

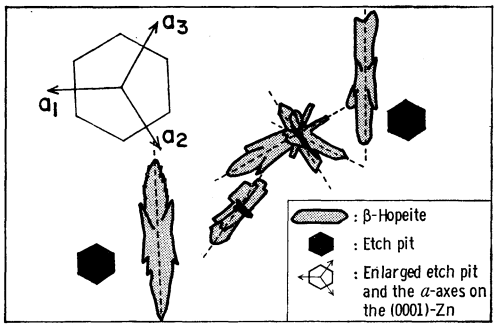

Fig. 9. Relation between the direction of crystal growth and that of the a-axes on the (0001)-Zn.

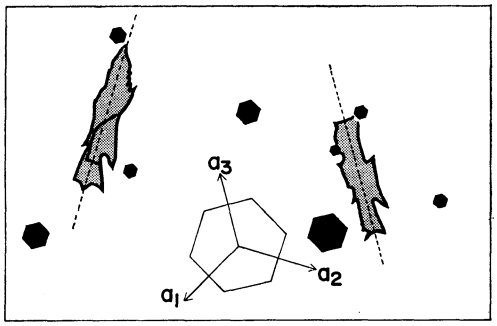

Fig. 10. Relation between the direction of crystal growth and that of the a-axes on the (0001)-Zn.
The illustrations of shapes are the same as in Fig. 9

Epitaxy. The epitaxies of β-hopeite on the (0001) plane of zinc are shown by two modes in Fig. 11 and Table 1. The black spots in Fig. 11 are zinc atoms on the (0001) plane, while the regular hexagon and the rectangle with perimeters of thick lines indicate an etch pit and the unit cell of β-hopeite projected on the (010) plane respectively.

The length of the a-axis in β-hopeite is equivalent to

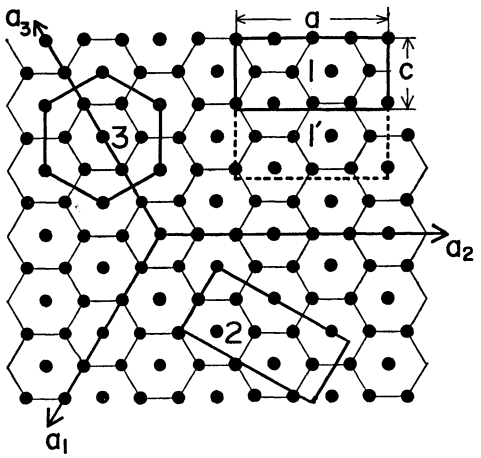

Fig. 11. The epitaxies of β-hopeite on the (0001)-Zn.
a_{1-3}: a-axes on the (0001)-Zn
a,c: lattice constant of β-hopeite

Zn	β-Hopeite
1: [10.0]	// [100]
1′: [10.0]	// [100]
2: [12.0]	// [100]
3: etch pit	

β-Hopeite: a=10.64 Å, b=18.36 Å, c=5.04 Å, Zinc: a=2.665 Å, c=4.947 Å.

Table 1. Epitaxies between β-hopeite and zinc

Mode	Epitaxy Zinc	Epitaxy β-Hopeite	Period Zinc	Period β-Hopeite	Misfitting (%)
1	$[1\bar{2}10]$	// [100]	10.66	10.64	0
	$[10\bar{1}0]$	// [001]	4.62	5.04	+9
1′	$[10\bar{1}0]$	// [001]	10.01	10.08	+1
2	$[01\bar{1}0]$	// [100]	10.01	10.64	+6
	$[\bar{2}110]$	// [001]	5.33	5.04	−5

4 times the a-axis in zinc in the 1 mode. This mode of orientation accords with that published by Neuhaus and Gebhardt.[9] As for the direction of the c-axis in β-hopeite, considering zinc atoms on the (0002) plane in relation to such epitaxy as the 1′ mode, the misfitting in the epitaxy becomes smaller than that in the 1 mode, as is shown in Table 1. In the 2 mode, β-hopeite grows along the [12.0] direction; perhaps this relation is a new finding. Although, many other modes can be observed in the epitaxies between β-hopeite and zinc, the two modes described above seem to be the simplest ones, with the least misfitting.

The growth of crystals of a fin shape is observed in some figures of this paper; the crystal joins at an angle of about 30° with the [001] direction of β-hopeite. The angle between [100] and [101] in β-hopeite is smaller than 30°, that between [10.0] and [12.0] in zinc, therefore, the rate of crystal growth in the direction of [001] is more rapid than that in the direction of [101] in a β-hopeite crystal. Seemingly, the quantity of β-hopeite formed on the (0001) plane of zinc by the epitaxies of either mode, 1 or 1′, is larger than that formed by the epitaxy of the 2 mode, and the growth rate of the former is larger than that of the latter judging from an observation of Figs. 4—8 and several other photographs and movies, although some of them are not cited here. This may be due to the fact that the misfitting in the 1 or 1′ mode is smaller than that in the 2 mode.

Adhesive Mechanism. Neuhaus and Gebhardt have found that the (010) plane of β-hopeite usually combines with the surface of metals in phosphatization.[9] Such phenomena seem to be attributable to the crystal structure of β-hopeite, which was analysed by Gamidov and Galovachev.[12] The projection of the phosphate

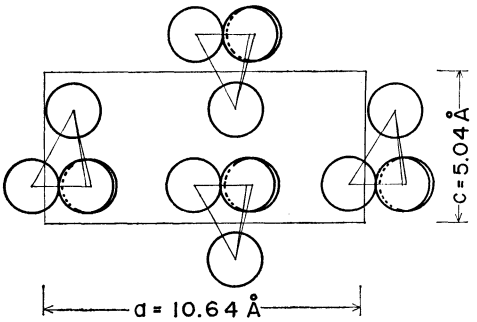

Fig. 12. The projection of phosphate ion on the (010) plane of β-hopeite.

11) M. Yamamoto and J. Watanabe, *J. Japan Inst. Metals*, **17**, 628 (1953).
12) R. S. Gamidov and V. P. Galovachev, *Dokl. Akad. Nauk. USSR*, **150**, 381 (1963).

ion to the (010) plane is shown in Fig. 12 in aid in the consideration of the adhesive mechanism.

As it is impossible to project all the atoms because of the mutual hindrance, only phosphate ions combined to metallic zinc are projected.

A brief explanation of the combination of the (010) plane of β-hopeite with a metal surface is given below from the standpoints of the density and the distribution of oxygen atoms, and the bond length and the coordination between metal and oxygen atoms of the phosphate ion in β-hopeite. On the (001) plane, all the oxygen atoms are located on the 1/4 and 3/4 *c* levels; therefore, it is difficult for this plane to combine with the metal surface. Similarly, on the (100) plane, the low density of the oxygen atom and its localization at one corner are observed. On the (010) plane, however, the density of the oxygen atom is the highest, and the distribution of these atoms is relatively uniform, as is shown in Fig. 12, consequently, the strongest combination is that between the (0001) plane of zinc and the (010) plane of β-hopeite occurs, as is indicated in Figs. 13 and 14.

The positions of the oxygen atom of phosphate in these figures were determined so that the bond distance between the oxygen and zinc atoms was about 2 Å. The lattices, however, combine with each other in a

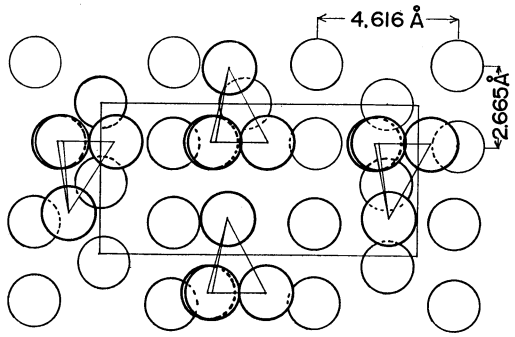

Fig. 13. Overlapped projection of the (010) plane of β-hopeite and the (0001) plane of zinc.

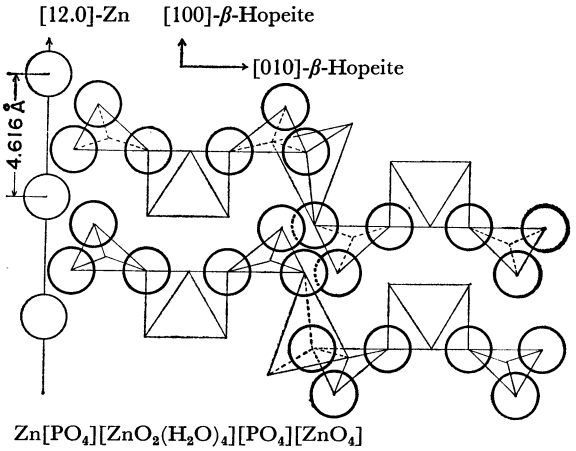

Fig. 14. Side view of the overlapped projection.

rather distorted manner, and the nature of the chemical bond may be of a strong chemisorption. Neuhaus and Gebhardt[13] have proposed that the chemical bond between β-hopeite and the metal surface is of the wüstite type and that a mesomery exists between $Me^{(+)}\cdots O^{(-)}\cdots PO_3$ and $MeO^{(-)}\cdots P^{(+)}\cdots O_3$. It is, however, reasonable that the bond is not of an wüstite type but of an wurtzite one for the following reasons:

1. Zinc atoms are abundant on the boundary surface between β-hopeite and zinc, as is shown in Fig. 13. This may be analogous to an wurtzite enriched with zinc atoms, having an oxygen vacancy and behaving as a negative semiconductor. On the other hand, an wüstite enriched with oxygen atoms is positive.[14]
2. It is reasonable to say that zinc combined with the oxygen in the phosphate ion located at the boundary has a coordination number of 4, in the light of the crystal structures of β-hopeite and wurtzite.

13) A. Neuhaus, *Dechema Monograph.*, **51**, 119 (1964).
14) A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, (1962), p. 165.