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Crystal Growth of the Phosphate Coating on Iron and Steel*1

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Crystal growth of the phosphate coating on steel and pure iron was investigated by microscopic observation and X-ray diffraction. β-Hopeite was recognized as a main constituent of the phosphate coating. From the experimental results obtained in this investigation and the crystal structure of β-hopeite proposed by Gamidov and Galovachev (*Dokl. Akad. Nauk, SSSR*, **150**, 2, 381, (1963)), it was concluded that the bonding of the (010) plane of β-hopeite to the (100) plane of iron is most favorable for atomic arrangement of the phosphate coating.

Many attempts have been made to establish a theory of crystal growth since the first research by P. Curie at the end of the 19th century, and the results obtained in the course of those attempts have recently come to be applied to polymer chemistry and electronic engineering. The process of crystal growth has to be taken into account to understand the mechanism that crystals are produced on a metal surface by corrosion. The phosphate coating may be regarded as one of the most excellent utilizations of corrosion products. According to the research by Neuhaus and his coworkers,[1] phosphorus atoms in phosphate ions of the coating combine with iron atoms on the surface in such a manner that is known as Wustite bond. Notwithstanding the comprehensive investigation by Neuhaus, the detailed construction of the boundary layer between iron and phosphate coating has still remained obscure. In the present paper microscopic observation on the crystal growth of phosphates on iron surface and X-ray diffraction patterns of the phosphate coating are described and, based on our experimental results and the crystal structure of β-hopeite determined by Gamidov and Galovachev,[2] an adhesive mechanism between iron and phosphate is presented.

*1 Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

1) A. Neuhaus and M. Gebhardt, *Dechema. Monograph*, **51**, 117 (1964).

2) R. S. Gamidov and V. P. Galovachev, *Dokl. Akad. Nauk, SSSR*, **150**, 2, 381 (1963).

Experimental

A) Microscopic Observation on Crystal Growth. The compositions of specimens of iron and steel, size of which being 3 mm×5 mm×20 mm, and that of phosphating solution are shown in Tables 1 and 2,

TABLE 1. COMPOSITIONS OF SPECIMENS (wt %)

	O	Si	Mn	F	S	Cu	Cr	Ni
iron	0.007	trace	trace	trace	0.006	0	trace	0
steel	0.20	trace	0.80	0.016	0.024	0.06	0.06	0.03

TABLE 2. COMPOSITION OF PHOSPHATING SOLUTION

Zn^{2+} (g/l)	PO_4^{3-} (g/l)	Na_2CO_3 (g/l)	Total acidity (point)	Free acidity (point)
5.9	15.7	2.74	32.1	2.2

respectively. The specimens were polished with emery paper (0/5) and buff. When necessary, they were further etched with Nital or Picral. About 0.05 ml of the phosphating solution was dropped on the surface of the specimen placed on a deck glass. The visual field of the microscope was fixed at the same position during the observation. Most of the microscopic photographs were taken every 2 min.

B) X-Ray Diffraction. The coating obtained in the phosphating solution was scratched and stripped off with an edge of glass plate. The X-ray diffraction patterns of the powdered coating were taken with the "Geigerflex" manufactured by Rigaku Denki Co., Ltd. The diffraction data were compared with those of ASTM cards.

C) Observation on Phosphate Crystals under Polarized Light. The powdered coating used for X-ray diffraction pattern was also observed with a polarization microscope inserted with a gypsum plate. The directions of optical elasticity axes of β-hopeite were identified by comparison of the refractive indices obtained in this experiment with those in the data shown in ASTM card (9-497). The refractive indices were measured by the immersion method under the polarization microscope.

D) Calculation of the Velocity of Crystal Growth. The velocity of crystal growth of β-hopeite was calculated from the differences of the crystal length shown in microscopic photographs which were taken by the method described above.

Results and Discussion

A series of microscopic photographs from Figs. 1 to 4 shows the crystal growth of phosphate on the buff-polished carbon steel. At first, a certain number of small core crystals appeared. They grew radially, forming dendrites, and finally covered the whole surface of iron. The number of round crystals formed at the beginning remained constant during the phosphating process. A similar behavior of crystal growth was found on the buff-polished pure iron, etched carbon steel and etched pure iron. Figures 5 and 6 show the phosphate crystals which appeared on the buff-polished pure iron. The initiation of crystallization on pure iron surface was considerably delayed, compared with that on carbon steel. In Figs. 7, 8, 9 and 10, the crystals on the etched surfaces of carbon steel and of pure iron are shown. The round phosphate crystals were apt to appear in the neighborhood of grain boundaries or on the scratches of polishing.

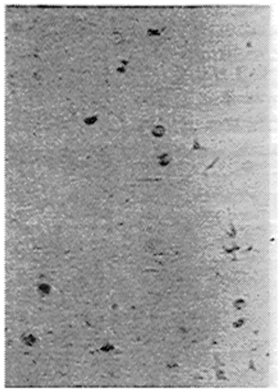

Fig. 1. Crystal growth of phosphate coating on polished carbon steel (2 min). (×180)

Fig. 2. Crystal growth of phosphate coating on polished carbon steel (6 min). (×180)

Fig. 3. Crystal growth of phosphate coating on polished carbon steel (10 min). (×180)

Fig. 4. Crystal growth of phosphate coating on polished carbon steel (24 min). (×180)

Fig. 5. Crystal growth of phosphate coating on polished pure iron (10 min). (×180)

Fig. 6. Crystal growth of phosphate coating on polished pure iron (26 min). (×180)

The order of increasing size of the phosphate crystal particles on various iron surfaces was obtained as follows: etched carbon steel, etched pure iron, buff-polished carbon steel and buff-polished pure iron. The initiation of crystallization of various iron surfaces was delayed with increasing size of the crystals. The X-ray powder diffraction pattern of the stripped coating is shown in Fig. 11. By comparison of this pattern with that in ASTM card (9-497), β-hopeite was recognized as a main constituent of the phosphate coating and a trace of vivianite was also found on it. Under the polarized microscope the direction of elongation of all β-hopeite crystals was parallel to the direction of wave motion of lower velocity, of which refractive index was 1.580. For β-hopeite two kinds of

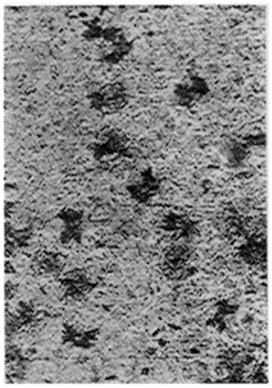

Fig. 7. Crystal growth of phosphate coating on etched carbon steel (3 min). (×180)

Fig. 8. Crystal growth of phosphate coating on etched carbon steel (9 min). (×180)

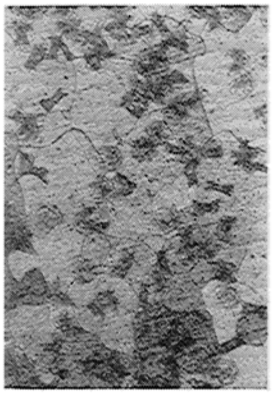

Fig. 9. Crystal growth of phosphate coating on etched pure iron (4 min). (×180)

Fig. 10. Crystal growth of phosphate coating on etched pure iron (14 min). (×180)

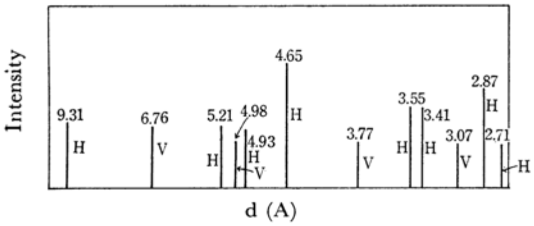

Fig. 11. X-ray diffraction pattern of stripped coating.

H: β-Hopeite V: Vivianite

optical orientation are shown in the reference:[3] $X=b$, $Y=c$, $Z=a$, or $X=b$, $Y=a$, $Z=c$. The refractive indices of β-hopeite (ASTM card 9-497) are as follows: $\alpha=1.574$, $\beta=1.582$, $\gamma=1.582$. Therefore, it is considered that the direction of elongation and also the c axis were parallel to Z axis with the minimum velocity of wave motion. The optical elasticity axes of the stripped β-hopeite were identified to be $X=b$, $Y=a$ and $Z=c$. The relations between crystal growth of β-hopeite on polished carbon steel and phosphatizing time are shown in Fig. 12. The elongation of the c axis increased linearly with time and the velocity was much greater than that in the direction perpendicular to the c axis. An overlapped projection of the (010) plane of β-hopeite and the (100) plane of iron is schematically shown in Fig. 13. In this mode of adhesion, oxygen atoms located at the apices of tetrahedra of phosphate ion can be transferred into the interstices of an iron lattice. Although some other modes of adhesion in the phosphate coating have already been presented, this mechanism may be most favorable for atomic arrangements of both iron and β-hopeite crystal.

Conclusion

The mechanism of phosphate film formation was studied with the concept that the phosphating reaction may be a kind of corrosion. Conclusions obtained from the present investigation are as follows: (a) In the phosphate coating process, small round phosphate crystals appear at the beginning as nuclei in the neighborhood of grain boundaries corroded by etching solution or on the scratches produced by polishing. (b) The nuclei of phosphate coating grow to form dendrites. The total number of nuclei does not increase during the course of phosphatization. (c) The dendritic crystals are identified as β-hopeite from a comparison of the X-ray diffraction spacings with the data of ASTM card and from the microscopic observation under polarized light. (d) Comparing the crystal structure of β-hopeite proposed by Gamidov with the results obtained in this investigation, it is concluded that the (010) plane of β-hopeite sticks on the (100) plane of iron.

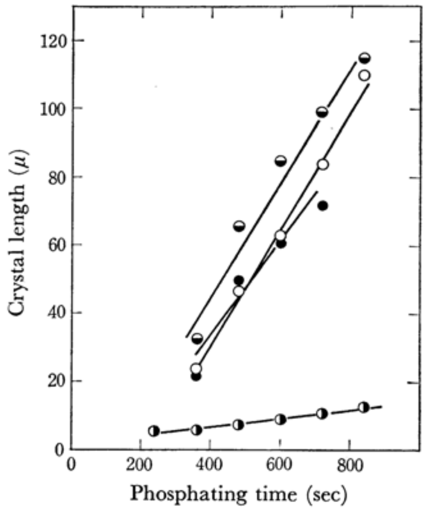

Fig. 12. Crystal growth of β-hopeite on polished carbon steel.

◒ ○ ● } c-axis of various crystals

◑ direction vertical to c-axis

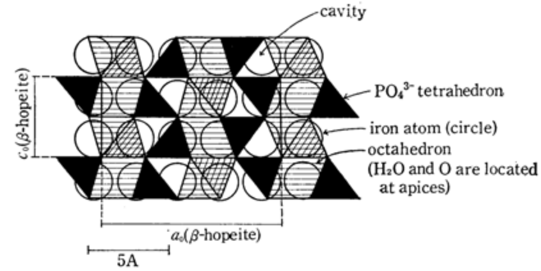

Fig. 13. Overlapped projection of the (010) plane of β-hopeite and the (100) plane of iron.

β-Hopeite: $a=10.64$A, $b=18.36$, $c=5.04$A, $Z=4$.

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3) E. S. Larsen and H. Berman, "The Microscopic Determination of Nonopaque Minerals," 163, 2nd Ed. (1934).