An Electron Diffraction Study of the Protective Coating on Metals and Alloys (*Continued*): the Acid-Proof Surface of Ferrosilicon (Duriron).

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Introduction. It is well-known that an alloy(1) of Fe and Si containing about 14% Si is one of the few alloys capable of resisting the corrosive action of sulphuric acid, but the state of this acid-proof surface as well as the surface substance produced here inhibiting the corrosive action of the acid have escaped study, because it is very difficult to detect such thin films by the usual methods except the electron diffraction method. The present study by the latter method can successfully produce the entity of the protective coating obtained over the silicon-iron alloy immersed in sulphuric acid solutions.

When aluminium bronze was heated in the air, electron diffraction analyses only γ-Al_2O_3 over the surfaces of these alloys.(2) The mechanism of this "selective oxidation" is at present being discussed by many investigators throughout the world, but no interpretation regarding this phenomenon can be held as conclusive.(3)(4)(5) A selective oxidation by sulphuric acid solution, not by air, was found through the present study, and consequently this phenomenon can be considered from a point of view other than those assumed by the above investigators.

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(1) Woldman and Dornblatt, "Engineering alloys," 1936.
(2) I. Iitaka and S. Miyake, *Nature*, **136** (1935), 437; **137** (1936), 457.
(3) G. D. Preston and L. L. Bircumshaw. *Phil. Mag.*, **20** (1935), 706.
(4) S. Dobinski, *Nature*, **141** (1938), 81; **144** (1939), 510.
(5) H. Bienfait, *Nature*, **145** (1940), 190.

Electron Diffraction Experiments. A piece of ferrosilicon ("Duriron") (Si: ca. 15%), whose macro-structure as seen through the microscope consists mainly of Fe-Si solid solution intermixed with a small quantity of Fe_2Si_3, was adopted as a specimen. The corrosive reagent was sulphuric acid at various concentrations (5~20 N); the experimental results obtained were always the same.

Experiment 1. On immersing the specimen in the sulphuric acid solution, a faint generation of gas bubbles (H_2) was observed for 5~10 minutes, and then this phenomenon ceased. The surface of the specimen in this state has a gray colour and possesses a practically perfect acid-proof nature. An electron diffraction analysis was made on this surface. The four spacings corresponding to the four weak rings observed in the diffraction pattern here obtained were determined by repeating the experiment about twenty times.* However, since it was difficult to determine the entity of the substance giving these four rings on the basis of these four spacings alone, further experiment was carried out.

Table

d	d_{obs}	$d_{x\text{-ray}}$	$h\ k\ l$	I_{obs}
—	—	4.90	1 1 0	—
3.60	3.60	3.58	2 0 0	m
—	3.00	2.99	2 1 1	s
2.15	2.16	2.20	3 1 0	s
1.84	1.84	1.87	3 2 1	s
—	1.53	1.56	4 2 0	f
1.35	1.36	1.37	4 3 1	s
—	1.26	1.28	5 2 1	s
—	1.08	1.13	5 3 2	f

d: Spacings characteristic of the surface of the sample.
d_{obs}: Spacings of α-cristobalite crystal.
$d_{x\text{-ray}}$: Spacings of α-cristobalite observed by x-ray.
$h\ k\ i$: Miller Indices.
I_{obs}: Intensity of the rings observed here.

Experiment 2. As may be suggested in Experiment 1, the crystals producing the above four spacings must be a weak electron scatterer, i.e., the existence of silica (SiO_2) on the acid-resisting surface of Duriron is suspected. According to our physical and chemical studies the following modifications of SiO_2 are known:

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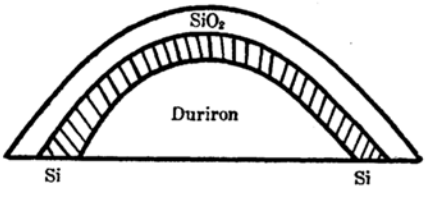
* It was vain to expect that the diffraction rings from α-Fe (body-centred structure) will be observed here. This fact suggests the formation of some protective coating over the specimen, since a heavy metal Fe diffracts intense electron beam.

α- and β-Cristobalite
α- and β-Tridymite
α- and β-Quartz.

Of these six modifications the existence of α-cristobalite is not only the most probable, but also it is the form appearing at low (room) temperature.(6) The present author carried out an experiment here: pure α-cristobalite was chemically prepared and the diffraction pattern, consisting of many obvious rings, from α-cristobalite was directly compared with that from the surface of Duriron passive to sulphuric acid.

The thin film of α-cristobalite for the experiment was produced by making beforehand a film of water-glass over a platinum wire-gauze and then by dropping hydrochloric acid upon it.* The values of spacings determined with the rings from pure α-cristobalite were, as listed in the table, in accordance with those of α-cristobalite by X-ray study. As may be seen in the table, the values of d agree with those of d_{obs} satisfactorily, and therefore there is no room for doubt that the acid-proof surface of ferrosilicon (Duriron) is coated with small crystals of α-cristobalite.

Discussion. Under the same conditions, not only Fe but also Si in the solid solution of the iron silicon alloy must be attacked by the corrosive molecule or ion; but the reaction product of the former is easily soluble in water,** whereas that from the latter is insoluble in water. It is chemically well-known that pure silicon is practically unattacked by common mineral acids (HCl, H_2SO_4, HNO_3, etc.). However, the present study concludes that the silicon surface immersed in acid is coated with SiO_2 (α-cristobalite) small crystals. Since the surface or the superficial layer of Duriron immersed in acid is α-cristobalite small crystals, the second layer lying below the SiO_2 layer should be chiefly silicon or the silicon-rich layer, and below this layer lies the alloy substrate. A picture of the condition of the layers imparting the acid resistant property is shown in the figure.



The iron in the alloy is coated with Si and SiO_2 which are both resistant toward acid; as it were, "a protective double layer" exists on the iron alloy. It is due to this double layer that the iron silicon alloy is able to resist satisfactorily the attack of sulphuric acid.

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(6) T. F. W. Barth, *Am. J. Sci.*, **23** (1932), 350; **24** (1932), 97.

[*] The platinum wire-gauze used here has been explained many times in my previous papers; e.g., *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*).

The NaCl solution produced over the wire-gauze was removed with a small piece of clean filter paper.

[**] Fe in the solid solution exists in the same state as in metallic iron, because the ferrosilicon used here contains no compound between Fe and Si.

As a matter of fact, the corrosive solution (sulphuric acid) altered the colour of ferricyanide solution to blue.

When Fe in the solid solution is removed by the acid and Si remains adhering to the metal substrate, many small protuberances consisting of Si posessing free bond are produced on the surface of this alloy. This silicon atom has a large chemical affinity and can give SiO_2 more easily than ordinary silicon. Although the gaps are partly packed with SiO_2 crystals, the recrystallization of the active silicon, i.e., the metallic bond formation of Si helps partly the packing of the gaps.

The phenomenon of formation of SiO_2 over the ferrosilicon is doubtlessly selective oxidation of the alloy taking place in solution. The "selective oxidation" which has been often discussed only with the oxide obtained in air can here be considered from another point of view.

The selective oxidation of Duriron by sulphuric acid is realized as a result of the following chemical and physical processes:

(1) Fe, a component weak towards acid is removed from the metal surface,

(2) Si, a component strong towards acid remains over the metal surface, becoming a protective coating of SiO_2, and recrystallization of Si and SiO_2 occurs in order to stretch over the surface and covering the metal substrate. If the analogy between this selective oxidation in solution and that in air is permitted, in the latter environment also the processes (1) and (2) should take place. When on the surface of aluminium bronze oxidation by air takes place, process (1) results in that the CuO produced on the surface exfoliates, because it is produced comparatively coarse and does not adhere strongly to the metals substrate, while the γ-Al_2O_3 produced over the alloy adheres strongly to the ground metal, for both of these oxide coatings are very thin, compact and strong as were verified in the previous study of the present author.(7)

In conclusion, I wish to express my deep thanks to Dr. Ichiro Iitaka, under whose direction this work has been undertaken, for his many important suggestions, to Prof. S. Mizushima for his sincere interest. I also take this opportunity in thanking the Nippon Gakuzyutsu Shinkokwai for the financial grant through the auspices of its Corrosion Committee.

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(7) S. Yamaguchi: *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **36** (1939), 463; I. Iitaka and S. Yamaguchi: *Nature*, **144**, (1939), 1090.