Electron Diffraction Study on Titanium Attacked by Various Acids

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Synopsis

Titanium immersed in various acids were examined by electron diffraction. Surfaces attacked by hydrofluoric, hydrochloric, sulphuric or phosphoric acid suffered considerable corrosion and yielded Debye rings of a face-centred cubic lattice, which was deduced as belong to titanium hydride (TiH_2) formed in the course of corrosion. At the surfaces immersed in nitric acid at room temperature for a long period, however, hexagonal rings of titanium alone were observed, and these surfaces were taken as the standard for further corrosion tests. In the following cases the surfaces became passive, and protective films were formed: When the specimens were attacked by boiling nitric acid or aqua regia, anatase was formed, while a mixture of this and a rutile was seen after immersion in boiling 10 per cent solution of chromic acid. The surfaces immersed in boiling 10 per cent solution of ferric chloride for 1 hour yielded many sharp rings, which, however, could not be assigned to any known compound of titanium at the present stage.

I. Introduction

It is a well-known fact and is now being watched with keen industrial interest that metallic titanium (below 880°C, hexagonal close-packed, $a = 2.92$ Å, $c = 4.67$ Å[1]) exhibits excellent oxidation- and corrosion-resistance. The structure of its surface oxidized at high temperatures has thoroughly been elucidated through the electron diffraction studies by Hickman and Gulbransen[2] and by Nakayama[3], and the oxidation-resistive surface was found to be covered with titanium dioxide film which has the crystal lattice of rutile type.

The corrosion-resistance of the metal to various chemical reagents has so far been studied only by the weighing method, and especially, recently by Obinata et al.[4] On the other hand, there has scarcely been an electron diffraction study on this topic, although such a study seems to be indispensable to elucidate the nature of surface films formed in the course of corrosion. In the present paper titanium surfaces were examined by the reflection method: they were attacked by hydro-fluoric acid, hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid, aqua regia, chromic acid, sodium chloride solution or ferric chloride solution. The results obtained were compared with those obtained by other corrosion tests.

(1) R. W. G. Wyckoff, Crystal Structures, Vol. 1 (1951).
(2) J. W. Hickman and E. A. Gulbransen, Analy. Chem., 20 (1948), 158.
(3) T. Nakayama, Read at the Meeting of Japan Inst. Metals at Tokyo, April, 1953.
(4) I. Obinata, K. Nishimura, O. Izumi and Y. Takeuchi, J. Jap. Inst. Metals, 18 (1954), 452. (in Japanese)

II. Experimental

A diffraction camera of the camera length of 309 mm, made by Hitachi Co. (ED-C type) was used. The voltage accelerating electrons was about 50 KV. A gold film formed by evaporation was used as the standard for measuring the lattice spacings.

Specimen plates were dispensed by Prof. I. Obinata in our Institute. Titanium ingot prepared by means of arc melting of sponge titanium (made in Japan and having the nominal purity above 99.5 per cent) in argon atmosphere was forged and rolled at about 800°C, worked upon by alternate cold-working and annealing, and finally finished up to a plate, 0.5 mm in thickness, by cold-rolling of 38 per cent. The results of chemical analysis of the plate are shown in Table 1. The plates

Table 1. The results of chemical analysis for the specimen.

C	W	Fe	Si	Cl	Mg
0.034	0.008	0.053	0.016	0.010	—

used in diffraction tests were $10 \times 6 \times 0.5$ mm³ in size. After immersed in various reagents, they were washed successively with running water, methanol and ether, and finally dried with warm air. The results of diffraction tests will be described in the following.

1. Corrosion due to hydrofluoric, hydrochloric, sulphuric or phosphoric acid

In general, it is strongly necessary that every specimen must be of the same condition before exposed to corrosion, that is, that its diffraction pattern must initially be only of pure titanium. For this purpose, the rolled plates were etched with hydrofluoric, hydrochloric, sulphuric or phosphoric acid. The structures of the etched surfaces were as follows :

(i) When the rolled plate was immersed in concentrated hydrofluoric acid at ordinary temperature for a few seconds or about 1 minute, vigorous corrosion took place and coarse crystal grains appeared. Such a surface yielded sharp rings of a face-centred cubic lattice with the lattice constant ranging from 4.38 to 4.42Å. A weak ring corresponding to the spacing of 1.74 Å was often observed, which seemed to be caused by the hexagonal close-packed lattice of titanium.

(ii) When the plate was immersed in concentrated hydrochloric acid at ordinary temperature for about 17 hours, the surface became somewhat dark and yielded spotty rings of a f.c.c. lattice in its diffraction pattern. Sharp rings of this lattice also appeared, when immersed in the boiling concentrated acid (Photo. 1), in the dilute acid of 50 per cent or in the boiling acid of 10 per cent. In the case of 50 per cent the surface became gray.

(iii) When the plate was immersed in the sulphuric acid of 30 per cent at 45°C for 30 minutes, sharp rings of a f.c.c. lattice were also observed.

(iv) At the surface immersed in boiling phosphoric acid of 80 per cent for a short period, f.c.c. rings were also observed.

The lattice constants measured in the above-stated cases are shown in Table 2.

In every case the surface was considerably corroded, the crystal structure being face-centred cubic.
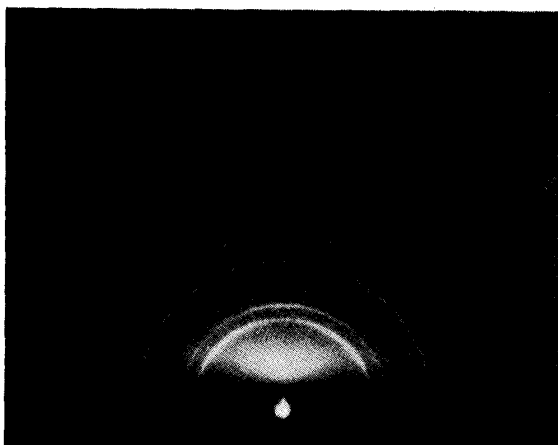

Photo. 1. Diffraction pattern of TiH_2 produced on Ti after immersion in boiling conc. HCl.

Titanium has two types of lattice, i.e., one is stable at low temperature and is hexagonal close-packed, and the other exists above 880°C and is body-centred cubic, but face-centred cubic titanium has not so far been found. The f.c.c. substance was suspected once to be titanium monoxide (rocksalt type, $a = 4.235$ Å), but this deduction was not reasonable, because, besides the discrepancy between the lattice constants, in such a lattice of rocksalt type the reflections of odd indices should be diminished in intensity, com-

Table 2. Observed lattice constants of face-centred cubic surface products.

	Temperature	Immersion time	Observed lattice constant a (Å)
Conc. HF	room temp.	a few seconds	4.38~4.42
Conc. HCl	”	17 hrs.	4.39
”	boiling temp.	a few seconds	4.43~4.46
50% HCl	room temp.	4 hrs.	4.40
”	boiling temp.	30 min.	4.43
10% HCl	”	40 min.	4.43
30% H_2SO_4	~45°C	30 min.	4.42
80% H_3PO_4	boiling temp.	a few seconds	4.43

pared with those of even indices, which was not the case in the present f.c.c. substance. If it were of rocksalt type, the partner of titanium in the compound should be an element of far smaller atomic number than oxygen. Hägg[5] reported in his X-ray study on the reaction product of titanium and hydrogen that the β
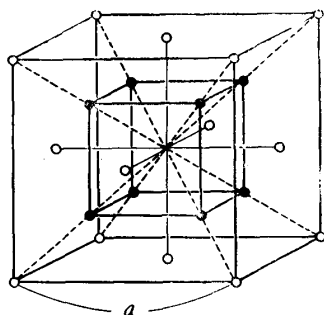

Fig. 1. The lattice of CaF_2 type.
○ ; Ca atom
● ; F atom

phase absorbing 50 or more atomic per cent of hydrogen yielded f.c.c. lines corresponding to the lattice constant ranging from 4.397 to 4.460 Å. He deduced that the structure corresponding to 66.7 atomic per cent of hydrogen (TiH_2) was completely of fluorite type (Fig. 1), and that, in the less content of hydrogen, the vacant sites of hydrogen atom were produced, resulting in an incomplete lattice. The diffraction pattern of this compound produced by X-rays or electron beam is expected to be mainly of the lattice of the metal atoms alone, hydrogen atoms being almost unable to contribute to the intensities. The corrosion

(5) G. Hägg, Z. phys. Chem., B 11 (1930), 433.

product of f.c.c. type obtained in the present case corresponds probably to this compound, although the positions of hydrogen atoms in the lattice remained indeterminable in both Hägg's and the present cases. As shown in Table 2, the lattice constant of the product became large, with the quantity of absorbed hydrogen, i.e., when the specimen was immersed in boiling acids.

Gulbransen and Andrew[6] investigated the reaction kinetics between titanium and oxygen, nitrogen and hydrogen, and observed no pattern characteristic of the reaction product of the metal and hydrogen in the electron diffraction study. It will be interesting that titanium hydride can be easily formed on the surface attacked by acids in the present case. They reported, moreover, that hydrogen absorbed by titanium was evolved in vacuum (10^{-6} mmHg) at temperatures above 350°C. In order to examine if titanium hydride obtained by the present experiment would be decomposed in such conditions, the specimen plates covered with titanium hydride were heated in vacuum at temperatures above 450°C for several hours. The diffraction patterns completely changed after heating, as shown in Photos. 2
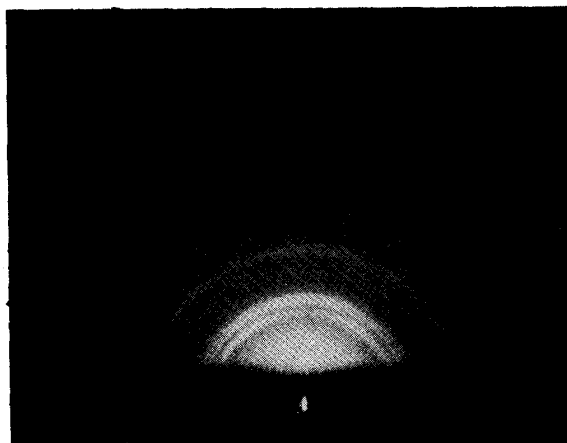

Photo. 2. Diffraction pattern obtained from surface heated in vacuum at 500°C for 3 hrs. after immersion in boiling conc. HCl. Ti+TiC (NaCl-type, a=4.29 Å)

Photo. 3. Diffraction pattern obtained from surface heated in vacuum at 800°C for 2 hrs. after immersion in 50% HCl. TiC (NaCl-type, a=4.31 Å)

and 3 and Table 3. At 450 as well as 500°C the rings consisted of both titanium and a substance of rocksalt type of the lattice constant of 4.29~4.30 Å, while at 600 as well as 800°C the rings corresponding to the former disappeared, those of the latter alone remaining (a = 4.31~4.32 Å). It has been known that monoxide, nitride and carbide of titanium crystallize in the rocksalt type, the lattice constants being 4.235, 4.235 and
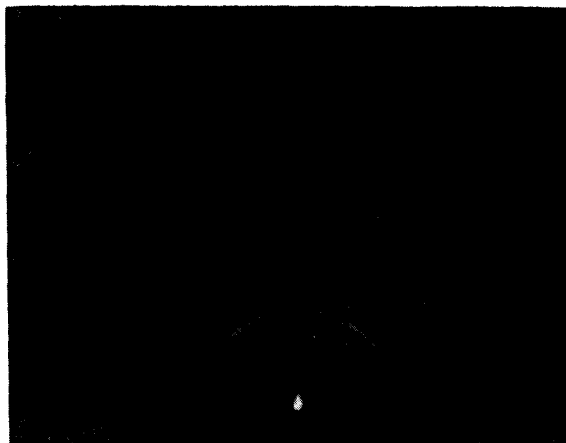
Table 3. Lattice spacings obtained from surface heated in vacuum at 500°C for 3 hrs. after immersion in boiling conc. HCl.

d(Å)	I(obs.)	hkl(Ti)	hkl (NaCl-type, TiC)
2.55	M. St.	(10,0)	
2.47	M. St.		(111)
2.26	St.	(10,1)	
2.14	St.		(200)
1.741	W.	(10,2)	
1.522	M. St.		(220)
1.488	W.	(11,0)	
1.352	V. W.	(10,3)	
1.302	V. W.		(311)
1.242	V. W.	(20,1)	(222)
			a(mean)$=4.29$Å

(6) E. A. Gulbransen and K. F. Andrew, J. Metals, 1 (1949); A. I. M. E., Metals Trans., 185, 741.

4.319Å[1] respectively. From these values the above substance might be deduced to be titanium carbide (TiC). As already mentioned, the reflections of odd indices must be depressed in intensity in the case of rocksalt type. The integrated intensities of Debye rings can be calculated by the following equation.

$$I = k \frac{|S|^2}{\sin 2\theta} \frac{p}{\theta} \approx k' \frac{p}{\theta^2} |S|^2,$$

where θ is the Bragg angle, p the multiplicity of net plane, S^* the structure amplitude, and k and k' constants. Table 4 shows the calculated intensities and observed ones. The coincidence between both is good for the reflections of higher indices** (e.g. $I_{(311)} : I_{(222)}$).

Table 4. Relative intensities of diffraction rings due to TiC (NaCl-type).

hkl	I(calcu.)	I(obs.)
200	100	St.
220	42	St.
311	9	M. St.
222	11	M. St.
400	4	V. W.
331	3	V. W.
420	9	M. St.
422	5	W.

The above fact shows that titanium hydride is decomposed in the course of vacuum heating, evolving hydrogen gas, that metallic titanium appears at the surface, and that this reacts upon any active vapor of grease or pumping oil, titanium carbide being ultimately formed.

2. Corrosion due to nitric acid (at ordinary temperature)

Titanium plates polished or as rolled yielded a diffraction pattern of titanium alone when immersed in concentrated nitric acid or its dilute solution of 50 per cent for a long period (4~10 days)at room temperature. Specimens, on which titanium itself and its carbide were formed as the result of decomposition of the hydride after vacuum heating, as stated above, also gave the similar results, i.e., the rings corresponding to the carbide disappeared, as shown in Photo. 4 and Table 5. In these cases some weak rings often appeared, which could not be assigned to titanium ($d=$ 4.2, 3.3, 1.67 Å).
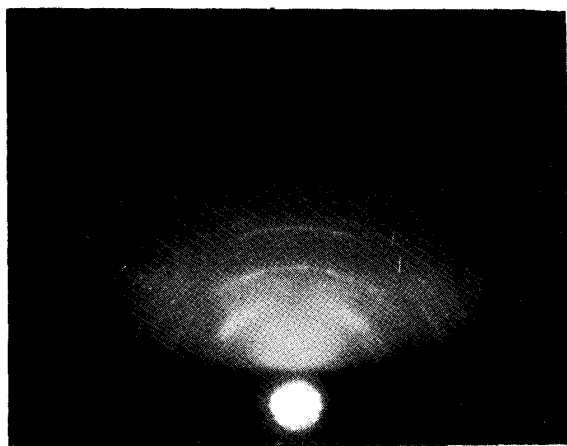

Photo. 4. Diffraction pattern of Ti obtained from surface immersed in conc. HNO$_3$ for 100 hrs. at room temperature.

* For the reflections of odd indices $|S| = 4|E_{Ti} - E_0|$ and for even indices $|S| = 4|E_{Ti} + E_0|$, where E is the atomic scattering factor for electron. This is defined as $\frac{8\pi^2 me^2}{h^2} \frac{Z - f(s)}{s^2}$, where Z is the atomic number, $f(s)$ the atomic scattering factor for X-rays and $s = 4\pi \sin\theta/\lambda$.
** From various physical properties the lattice cohesion of titanium carbide may be judged to be metallic rather than ionic, though not clear. The binding manner of the atoms in the lattice influences the value of E in the range of $\sin\theta/\lambda$ smaller than 0.2, but almost not in the range of larger $\sin\theta/\lambda$. In Table 4 are used values of $f(s)$ for Ti^{++} and C$_{neutral}$ (W. H. Bragg and W. L. Bragg, The Crystalline State, 1 (1939), Appendix IV), and hence the comparison between calculation and observation should be made in higher indices than (200).

As already stated, in the diffraction test of corrosion the metal surface should be covered with no film and, therefore, the surface obtained as above was used as

Table 5. Lattice spacings obtained from surface immersed in
conc. HNO_3 for 100 hrs. at room temperature.

(hk,l)	Electron diffraction data (observed)		X-ray diffraction data for Ti[7]	
	d(Å)	I	d(Å)	I
10,0	2.54	St.	2.54	0.27
00,2	2.37	St.	2.34	0.20
10,1	2.24	V. St.	2.23	1.00
10,2	1.72	M. St.	1.72	0.13
11,0	1.471	M. St.	1.470	0.13
10,3	1.328	St.	1.330	0.13
20,0	1.268	V. W.	1.275	0.01
11,2	1.239	M. St.	1.248	0.11
10,4	1.071	W.	—	—

the standard in the subsequent tests, i.e., all tests were done after the surface was confirmed to yield diffraction rings of titanium alone by the treatment in concentrated nitric acid. The following experiments were done mainly about the passive state.

3. Corrosion due to nitric acid (at boiling temperature)

The immersion of specimen plates in boiling nitric acid of 50 per cent for 1 hour made the surface passive and its colour light-brown, and gave somewhat diffused Debye rings in the diffraction pattern. Measured spacings and observed intensities are shown in Table 6. These rings can be explained as those of anatase

Table 6. Observed lattice spacings of surface films produced after
immersion in HNO_3 or aqua regia at various conditions.

50% HNO3 60 min. boil.		conc. HNO3 2 hrs. boil.		aqua regia 1.5 hrs. boil.		TiO2 (anatase).[7] tetragonal a=3.776Å c=9.486Å		Ti, (hexagonal)[7] a=2.92Å c=4.67Å	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
3.56	V. St.	3.52	V. St.	3.56	V. St.	3.52	1.00		
				2.57	M. St.			2.54	0.27
2.40	M. St.	2.38	M. St. diff.	2.40	St.	2.37	0.24	2.34	0.20
				2.24	M. St.			2.23	1.00
1.90	M. St.	1.89	M. St.	1.92	M. St.	1.88	0.40		
1.69	St.	1.69	St. diff.	1.71	V. St. diff.	1.70	0.28	1.72	0.13
						1.66	0.24		
1.492	M. St.	1.486	M. St.	1.490	M. St.	1.48	0.24	1.470	0.13
				1.376	W.	1.362	0.08	1.330	0.13
1.359	W.	1.353	M. St.	1.351	M. St.	1.335	0.08	1.275	0.01
1.269	W.	1.268	M. St.	1.272	M. St.	1.262	0.11	1.248	0.11
1.172	V. W.	1.165	W.	1.180	W.	1.164	0.06	1.230	0.05
TiO2(anatase)		TiO2(anatase)		Ti+TiO2(anatase)					

(tetragonal, $a = 3.776$ Å, $c = 9.486$ Å[1]), though the disagreement in the innermost ring is remarkable ($d_{cal.} = 3.52$ Å, $d_{obs.} = 3.56 \sim 3.58$ Å). Weak rings of titanium often remained in this pattern and the oxide rings were, in general, diffuse and,

(7) J. D. Hanawalt, H. W. Rinn and L. K. Frevel, Ind. Eng. Chem. analyt. edit., **10** (1938), 457.

therefore, the anatase film seemed to be considerably thin and to consist of minute crystals. When the specimen was immersed in boiling concentrated nitric acid, its surface became passive and was covered with a dark-purple film after 2 hours, and the diffraction pattern coincided very well with that of anatase, especially in the innermost ring, as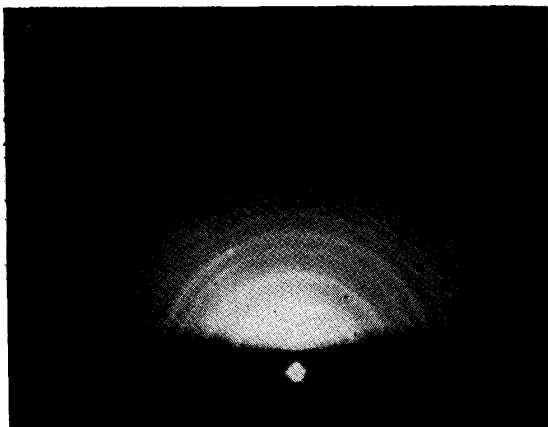 shown in Table 6 and Photo. 5. This surface was again activated by immersion in boiling hydrochloric acid for about 10 seconds and yielded weak diffraction rings of titanium and rings of anatase. The spacing corresponding to the innermost ring of the latter became again large, i.e., $d = 3.57$ Å. When the immersion was for 20 seconds, the pattern transformed into that of the f.c.c. type (TiH_2).

Photo. 5. Diffraction pattern of TiO_2 (anatase) produced on Ti surface after immersion in boiling conc. HNO_3 for 2 hrs.

4. Corrosion due to aqua regia

Even when immersed in aqua regia at room temperature for 100 hours, the specimen remained unchanged in the appearance and diffraction rings of the substrate metal and very weak ones probably of anatase were observed. When this specimen was immersed in boiling aqua regia for about 30 minutes, diffraction rings of anatase, the spacing of the innermost ring of which was 3.57Å, increased their intensities to the same grade as those of titanium, though the surface colour seemed to be unchanged. After 1.5 hours the anatase rings exceeded the titanium ones in intensity, as shown in Table 6 and Photo. 6, while the surface appearance remained as unchanged as ever.

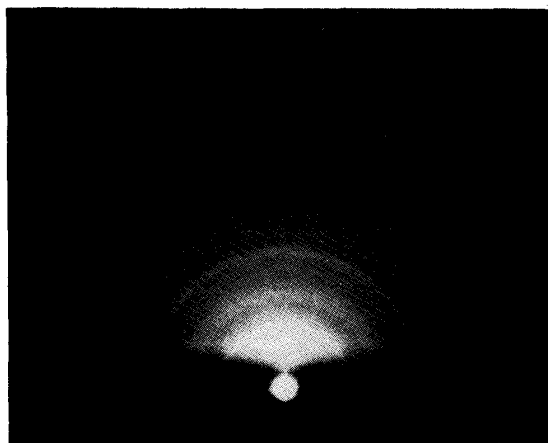5. Corrosion due to 10 per cent solution of chromic acid

Photo. 6. Diffraction pattern of TiO_2 (anatase) produced on Ti surface after immersion in boiling aqua regia for 1.5 hrs. Diffraction rings due to the titanium substrate are visible.

The immersion in the boiling acid hardly changed the surface appearance, but produced considerable changes in the diffraction pattern in the following manner : for the immersion of 1 hour, rings corresponding respectively to the spacings of 3.3 Å and 1.70 Å appeared, being superposed on the pattern of the substratum; for 4 hours, the patterns of both anatase, the innermost ring of which had the spacing of 3.57 Å, and rutile (tetragonal, $a = 4.492$ Å, $c = 2.893$ Å[(1)]) became distinct, the former exceeding the latter in intensity, and titanium rings still remained; for 10 hours, these disappeared and the patterns of the two kinds of oxide remained, while the spacing corresponding to the innermost ring of anatase decreased to

3.52 Å. The manner of change of the pattern is depicted in Fig. 2 and an example of the photographs is shown in Photo. 7.

	Immer-sion time	Corrosion products
	10^{hr}	Anatase + Rutile
	4^{hr}	Ti + Rutile + Anatase
	1^{hr}	Ti + a small quantity of oxide
		TiO_2 (Rutile)[7]
		TiO_2 (Anatase)[7]
		Ti[7]

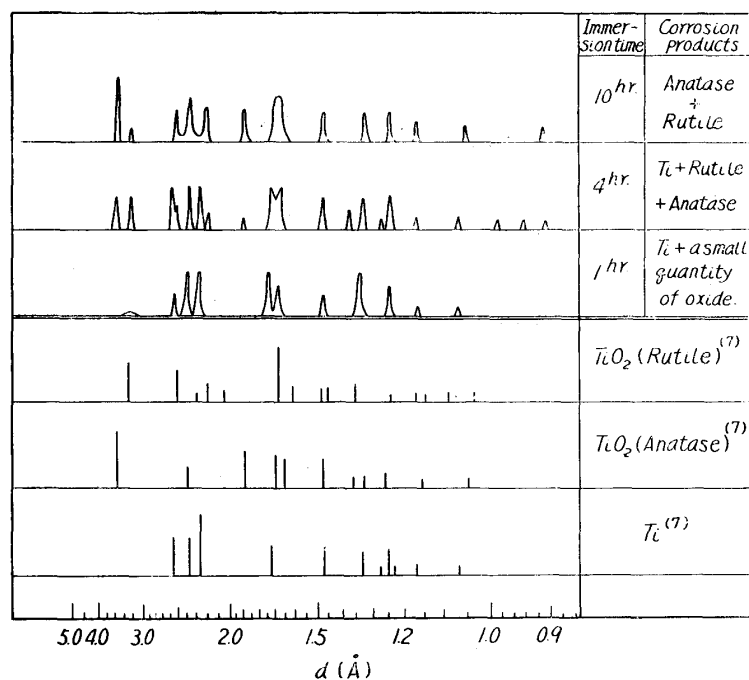5.0 4.0 3.0   2.0   1.5   1.2   1.0   0.9

d (Å)

Fig. 2. Diffraction pattern diagrams obtained from surfaces immersed in boiling 10% solution of chromic acid. (Height of figures should be understood to represent relative intensities within a single diagram only). X-ray patterns of three referred substances are shown in the lower part of the figure.

6. Corrosion due to aqueous solution saturated with sodium chloride

Nakayama[3] reported that titanium plate immersed for 30 minutes at 200°C in the aqueous solution saturated with sodium chloride was covered with rutile film. In the present experiment the plate was immersed for a long period (up to 10 hours) in this solution heated at 100°C. The surface appearance did not change. For 30 minutes, a weak ring corresponding to the spacing of 1.69 Å was seen besides the spotty pattern of titanium; for 10 hours, several weak rings correspond-

Photo. 7. Diffraction pattern of TiO_2 (anatase and rutile) produced on Ti surface after immersion in boiling 10% CrO_3-solution for 10 hrs.

ing respectively to the spacings of 3.4, 2.59 and 1.54 Å appeared moreover. These results suggested the formation of some surface film consisting probably of rutile crystallites, though could not be confirmed, owing to the insufficient data.

7. Corrosion due to 10 per cent solution of ferric chloride

The plate immersed for 10~20 minutes in this boiling solution scarcely became discoloured but showed a red-brown appearance in the case of 1 hour. The diffraction pattern exhibited many, sharp Debye rings and did not change with the immersion time. Spacings corresponding to these rings and one of the patterns are shown in Table 7 and Photo. 8 respectively. Some of the rings seemed to arise from the substrate metal, but the others were not attributable to any compound of titanium so far found. It was difficult to understand that the rings of the substratum appeared, while the surface was evidently covered with some film of considerable thickness. The elucidation of the structure of this surface will be brought over to the future.

Table 7. Observed lattice spacings of surface film produced after immersion in boiling 10% solution of $FeCl_3$ for 1 hr.

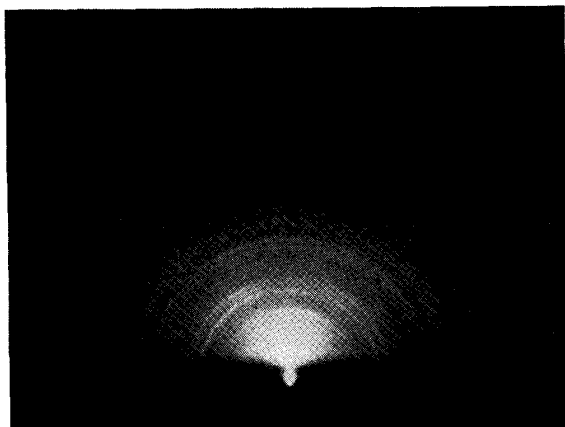| $d(Å)$	I	$d(Å)$	I
7.6	V. St.	1.64	V. St.
5.3	M. St.	1.50	St.
3.35	V. St.	1.444	St.
2.63	St.	1.374	M. St.
2.54	V. St.	1.303	W.
2.38	M. St.	1.223	W.
2.28	V. St.	1.144	W.
2.10	M. St.	1.059	W.
1.95	St.	1.018	W.
1.74	M. St.		

Photo. 8. Diffraction pattern of unknown substance produced on Ti surface after immersion in boiling 10% $FeCl_3$-solution for 20 min.

III. Considerations for the results

The above results obtained by electron diffraction should be compared with those confirmed mainly by chemical tests. It has so far been known that hydrofluoric, hydrochloric, sulphuric and phosphoric acids markedly attack titanium, and it has become clear by the present experiment that titanium hydride is formed on the surfaces attacked by these acids. It is also noticeable that the substrate metal is just exposed without any surface film after the immersion in nitric acid at room temperature for several days. The weight loss does not occur after immersion in boiling nitric acid, aqua regia, dilute chromic acid and saturated solution of sodium chloride, and the surfaces were found by electron diffraction to become passive as the result of the formation of protective films. In the case of boiling concentrated nitric acid, a film of anatase grows up so thickly that the surface becomes discoloured and titanium rings disappear. In other cases, however, the film of anatase or rutile is so thinly formed that the surface does not become discoloured and rings arising from the substratum still remain even in the case of a long period of immersion. In the case of 10 per cent solution of ferric chloride the passive state is also attained, due probably to the formation of some protecting film, although its nature is not yet clear at the present stage.

Titanium dioxide has three modifications, i.e., anatase, rutile and brookite (orthorhombic). According to Hickman and Gulbransen[2], rutile was formed by air oxidation of the metal at temperatures between 300 and 700°C. A similar result was also reported by Nakayama[3]. In the present corrosion tests rutile was hardly formed, but anatase was easily formed. It is noticeable that the spacing of the innermost ring of anatase ranges between 3.56 and 3.58 Å, being larger than its proper value, 3.52 Å, at an early stage of immersion, and that it diminishes to the proper value as the immersion time is prolonged. A similar behaviour was also found in the spacings of the other rings of anatase after a careful examination of the data. These facts lead to the anomalous expansion of the lattice of anatase at an early stage of immersion. Ehrlich[8] studied titanium oxides, including monoxide, sesquioxide and dioxide by X-rays, varying continuously the oxygen content through the reaction between the metal and various types of its oxide, and determined the composition-range of each type of oxide as well as the variation of the lattice constants. The above change of the spacings of the anatase rings may be related probably to the change of the oxygen content. It is, however, not clear, because anatase was not formed in Ehrlich's case.

In conclusion, the present authors wish to express their sincere thanks to Professor I. Obinata of the Institute for his kind dispensation of the specimens and for his useful suggestions. Their thanks are also due to Mr. Y. Takeuchi, whose advice was of great benefit to accomplish the present work.

(8) P. Ehrlich, Z. f. Elektrochem., **45** (1939), 362.