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Preparation of Titanium Tetrachloride

—Some Experiments for the Determination of its Mechanism—

By

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Abstract

As one of the fundamental experiments on the preparation of titanium tetrachloride, several chlorinations such as that with and without carbon by chlorine gas, that by the mixed gas of chlorine and carbon monoxide, and that by carbon tetrachloride vapour are examined using titanium dioxide and its lower oxides as the material. By the results, it is known that the ignition temperature generally becomes lower as the titanium content in the oxides increases, but it is exceptional in case of the chlorination by the mixed gas of chlorine and carbon monoxide.

1. Introduction

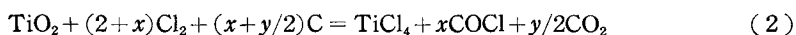
The present production of titanium in Japan is entirely depending upon the Kroll process. As the materials for its purpose, the iron sand containing titanium oxide, found in Tohoku district and Hokkaido, and the ilmenite mined in Malay and India are mainly used. These ores are separated into the pig iron and titanium slag by the electric arc furnace smelting. The titanium slag got by this smelting contains from 70 to 90% titanium dioxide, and by the chlorination of it the titanium tetrachloride is prepared. The case in which the titanium slag is chlorinated is more complicated than that in which the rutile is chlorinated. In this paper, several conditions concerning to the chlorination were examined.

Previous to this paper the effect of the carbon quantity added on the chlorination of titanium dioxide, the chlorination of low titanium slag (TiO_2 , 20% around), and the effects of the potassium chloride, sodium chloride or ammonium chloride etc. added to the titanium oxide mixed with carbon on the progress of the reaction, these were determined.¹⁾ As the results by these experiments above mentioned, the fact that the addition of potassium chloride served to progress the reaction velocity of the chlorination was found. Next to these experiments, the thermodynamical considera-

tion on the reactions of the titanium tetrachloride preparation was given.²⁾ As the results by the thermodynamical calculation, the following reactions were considered to be taken place: in the range between 136° and 400°C,



in the range between 400° and 480°C,



in the range between 480° and 1000°C,



in the range above 1000°C,



Then, it was held that several examinations on the chlorination of the compounds which are considered to be prepared in the high titanium slags such as $\text{MgO} \cdot \text{TiO}_2$, $\text{MgO} \cdot 2\text{TiO}_2$, $\text{CaO} \cdot \text{TiO}_2$ and $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$, etc.³⁾ The chlorination rate was getting better in order of $\text{MgO} \cdot \text{TiO}_2$, $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ and $\text{MgO}_2 \cdot \text{TiO}_2$ respectively, and that of $\text{CaO} \cdot \text{TiO}$ keeps from the chlorination. Besides, the effects of the calcium oxide and magnesium oxide quantity on the chlorination rate of the actual high titanium slag, and the effect of the basicity of the slag on the chlorination rate were examined, however, no clear conclusion was obtained. And also, the authors suggested qualitatively the fact that existence of the titanium lower oxides served to drop the ignition temperature of the chlorination reaction.^{4),5)}

In this paper, several experimental results are reported as the first step for the determination of the chlorination mechanism in case of the preparation of titanium tetrachloride. In case of the chlorination of metal oxide, two types are considered, that is, one is that chlorinated as it is like iron zinc, copper, or manganese oxide, and another is that not chlorinated unless carbon is added to the oxide like titanium, zirconium or silicon oxide. This fact is simply described as following formulas thermodynamically:⁶⁾

Formula of the reaction	Free energy change	
	at 500°C,	at 1000°C,
$\text{MnO} + \text{Cl}_2 = \text{MnCl}_2 + \frac{1}{2}\text{O}_2$	-12,300 cal.	-9,900 cal.
$\text{FeO} + \text{Cl}_2 = \text{FeCl}_2 + \frac{1}{2}\text{O}_2$	-7,600 cal.	-5,200 cal.
$\frac{1}{2}\text{TiO}_2 + \text{Cl}_2 = \frac{1}{2}\text{TiCl}_4 + \frac{1}{2}\text{O}_2$	+19,000 cal.	+15,900 cal.
$\frac{1}{2}\text{Al}_2\text{O}_3 + \text{Cl}_2 = \frac{1}{2}\text{AlCl}_3 + \frac{1}{2}\text{O}_2$		+9,400 cal.
$\frac{1}{2}\text{SiO}_2 + \text{Cl}_2 = \frac{1}{2}\text{SiCl}_4 + \frac{1}{2}\text{O}_2$	+24,300 cal.	+21,400 cal.

Among the above formulas, the titanium oxide or some others are not chlorinated

as they are, but the chlorination reaction would proceed if carbon is added to such oxides. Thermodynamically, the reason to add carbon to the oxides is that, adding the formulas: $C + 1/2O_2 = CO$ or $1/2C + 1/2O_2 = 1/2CO_2$ to the formulas above cited, the value of the free energy change of the formula goes from plus to minus and the reaction goes to form the chloride. This is the thermodynamical meaning of the reactions, $1/2TiO_2 + C + Cl_2 = 1/2TiCl_4 + CO$ and $TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2$. What part has the carbon in the chlorination reaction? As the authours and real operators had already suggested, the presence of the titanium lower oxides serves to drop the ignition temperature and to progress the reactivity, however, does the carbon act as the reducing agent on?

In order to determine the action of the carbon, the authors had the several experiments as follows:

(a) The preparation of the titanium lower oxides by the hydrogen reduction of titanium white (TiO_2 99.9%, pure Anatase for jewel production).

(b) Examinations on the ignition temperature and reactivity of the titanium lower oxide mixed with carbon in the chlorination.

(c) The chlorination of the titanium lower oxides with chlorine gas only.

(d) The chlorination of the titanium lower oxides with the mixed gas of chlorine and carbon monoxide.

(e) The chlorination of the titanium lower oxides with carbon tetrachloride vapour.

2. Apparatus and Procedure

Figure 1 is the apparatus of hydrogen reduction of titanium dioxide used. Approximately 100 cc. per minute hydrogen gas from the hydrogen bomb is heated and cleaned and dried through the copper net, calcium chloride and phosphorous oxide, and introduced into the reduction furnace, in which the titanium dioxide powder charged on the high alumina boat is kept and reduced by the hydrogen gas at the

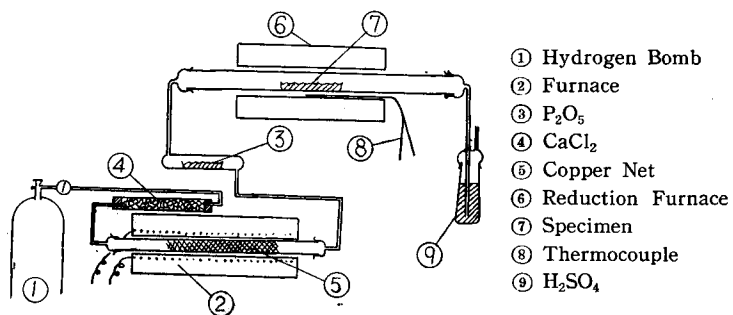


Fig. 1.

temperature, 900°, 1000°, 1100°, 1200°, 1300°, and 1400°C., respectively during 3, 5, 7, and 9 hours respectively at each temperature. After keeping the specimen in the reducing atmosphere at each temperature and during each hours, and reducing it, it is removed from the reduction furnace after cooling it in the reducing atmosphere to reserve in the desiccator. Reduction furnace is kept at constant temperature within plus minus 5 degree centigrade. Hydrogen gas after reducing is exhausted through concentrate sulphuric acid. Then the specimens reduced are analyzed by the volumetric and weighing method, in the former the titanium per cent is determined with the standard potassium permanganate solution and in the later the titanium per cent is determined by calculation as the reduced oxide becomes the titanium dioxide after heating at high temperature.

Figure 2 is the apparatus used for the chlorination of titanium dioxide and its

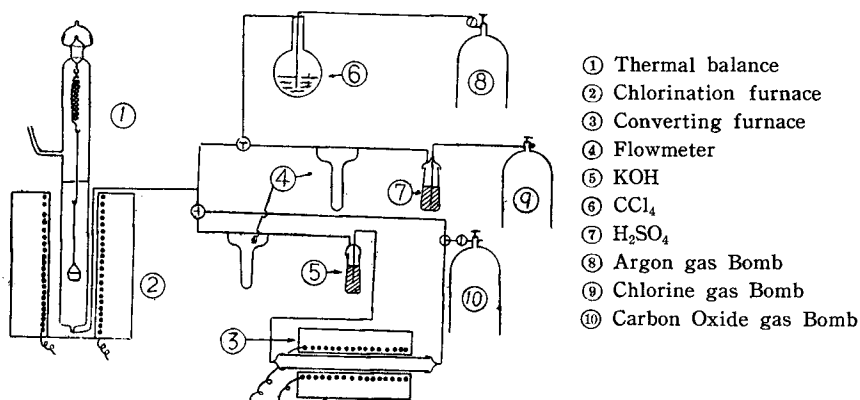


Fig. 2.

lower oxides. In the apparatus the main part is the chlorination furnace and it consists of two parts, the electric furnace and the thermal balance. The thermal balance consists of silica spring, rods and basket, and the spring has 500 gamma sensitivity combining with cathetometre. The specimen is put in the basket and suspended in the chlorination tube, in which it is chlorinated with the chlorine gas or mixed gas or carbon tetrachloride vapour introduced. The process of the reaction is caught by the scale on cathetometre as the constant point at a certain part of spring or rod goes up and down according to the reaction. The volume of the gas introduced is from 50 to 75 cc. per min. in case of chlorine gas only, 150 cc. per min. in case of the mixed gas of chlorine and carbon monoxide, and each gas is introduced after drying through the concentrate sulphuric acid. The carbon monoxide gas is generated from the concentrate sulphuric acid and formic acid. The chlorination furnace is heated with electricity at the rate of 25 degree centigrade per three minutes. The ignition

temperature is that at which the reaction occurs and the change appears in the cathetometre at first. In case of the chlorination with carbon tetrachloride, it is heated to vapourize at around 78°C. and the argon gas is used as the carrier of it.

3. Experimental Results and Considerations

a) Hydrogen reduction of titanium dioxide (Anatase).

Table 1 is the results of analysis and the relation between the reduction time and the reduction rate at each reduction temperature is summarized in the figure 3, where the reduction rate is expressed as the total titanium per cent. The hydrogen at any given temperature, from 900° to 1400°C., can only reduce the titanium dioxide to material with the chemical composition at the highest Ti_3O_5 or Ti_7O_{12} , and the reduction to TiO cannot be expected by hydrogen in this temperature range.

For examples, the reduction at 1400°C. for 9 hours results the lower oxide contain about 98% Ti_2O_3 converting the total titanium pct., and it needs 7 hours or at 1200°C., 5 hours or more at 1300°C., and 1400°C. or higher temperature to reduce the dioxide to Ti_3O_5 . There are some irregular point in figure 3, which are due to, under the burning solidification, the fact that the specimen is, at the high

temperature, apt to make the film of reduced oxide on the surface and through it enough hydrogen cannot easily penetrate and diffuse into the oxide in the boat. As the figure 3 shows under the experimental condition used, the reduction proceeds to the equilibrium with the hydrogen concentration used by 9 hours.

Table 1.

Temp. of Red.	Hrs. of Red.	Titanium Pct.	Temp. of Red.	Hrs. of Red.	Titanium Pct.
900°	3	61.79	1200°	3	63.34
"	5	62.25	"	5	64.00
"	7	62.50	"	7	64.45
"	9	62.74	"	9	64.62
1000°	3	62.42	1300°	3	63.56
"	5	63.06	"	5	64.33
"	7	63.40	"	7	64.70
"	9	63.62	"	9	64.92
1100°	3	62.94	1400°	3	64.30
"	5	63.61	"	5	64.82
"	7	64.12	"	7	65.35
"	9	64.30	"	9	65.70

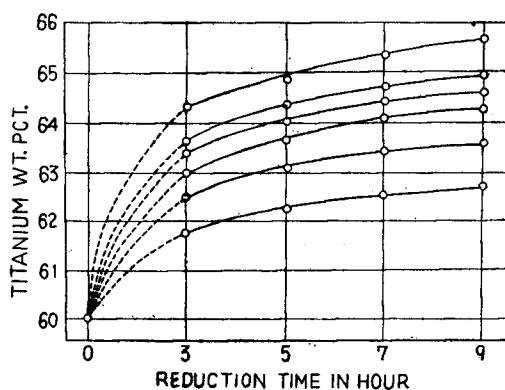
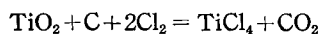


Fig. 3.

b) The chlorination of the lower oxide mixed with carbon.

The chlorination just as used in the Kroll process is held with lower oxides got by the hydrogen reduction. The specimen used consists of lower oxide and carbon powder and is weighed 500 mg. The carbon added is the minus 200 mesh powder of charcoal, and its quantity is as twice as theoretically needs to achieve the reaction:



The results of the chlorination are shown in the Table 2 and the figure 4, where almost liner relation is obtained between the ignition temperature and titanium per cent.

Table 2.

Specimen Sign	Tianium Pct.	Iguition Temp. °C
A	61.79	425
B	62.74	400
C	63.06	375
D	63.61	350
E	64.00	340
F	64.30	325
G	65.35	290
H	65.70	275

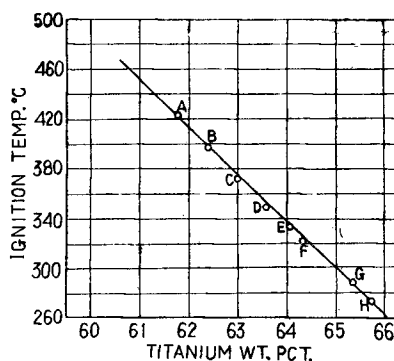


Fig. 4.

This relation can be written into the equation as follows:

$$t^\circ = -38.3a + 2790, \quad a = 60 \sim 66$$

where t° is the temperature in degree centigrade and a is the titanium per cent in the lower oxide. The processes of the chlorination of the lower oxides reduced at each temperatures are shown in the figure 5, 6, 7, 8, 9 and 10 respectively. As it is obvious from each figures, the chlorination of the lower oxides mixed with carbon has the

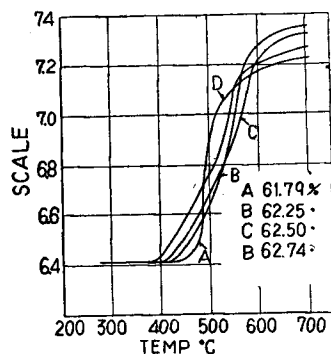


Fig. 5.

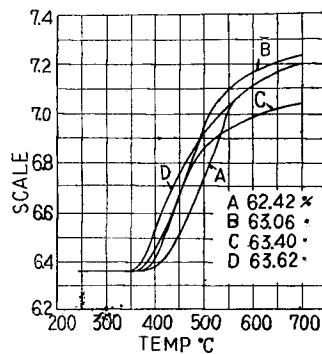


Fig. 6

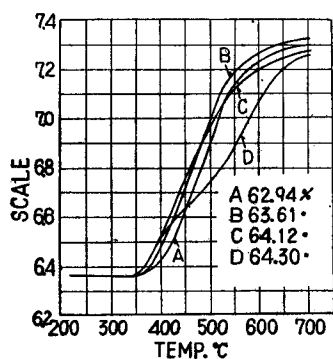


Fig. 7.

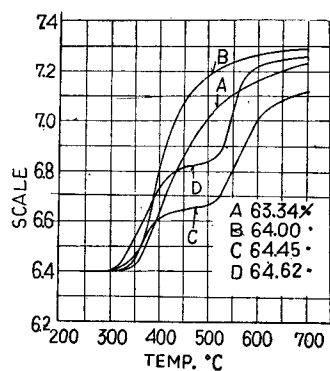


Fig. 8.

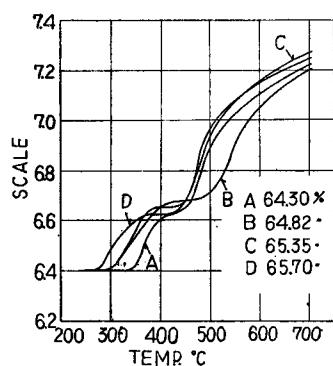


Fig. 9.

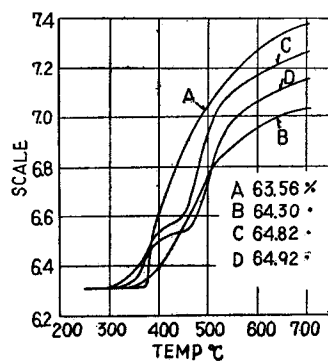


Fig. 10.

ignition temperature between 275° and 450°C. and proceeds very smoothly after once the reaction occurs, and about 80–90% of the total reaction finishes by 600°C. The interesting phenomena are seen in the figure 7–10, where the lower oxides containing 64% titanium or more have the tendencies to decrease the reaction velocity between 400° and 500°C., and the striking example of this tendency is seen in the figure 10. As the reason why such tendency appears, it is thought that the lower chlorides are formed in such gas atmosphere as used in the series of this experiment. Though there is no clear and sure proof, such phenomena are due to the so-called disproportional reaction of the chlorides. From the results, it is understood that the ignition temperature goes to lower according to titanium pct. increase in case of the chlorination of the lower oxides mixed with carbon and the reaction velocity becomes almost constant beyond 500°C. Hitherto, it is believed that the titanium dioxide is reduced by the carbon or carbon monoxide gas in case of mixing carbon and then the lower oxides are attacked by the chlorine gas. If so, is the lower oxide attacked by the chlorine gas only?

c) The chlorination of the titanium lower oxides with chlorine gas only.

The specimens are the titanium lower oxides got by the hydrogen reduction and their composition is shown in the Table 3. The figure 11 is shown the relation between the ignition temperature and the titanium per cent. The processes of the chlorination are shown in the figure 12 in the scale as 1/10 as in the figure 5-10. As it is obvious from the figure 11 and 12, the ignition temperatures of the reaction are higher

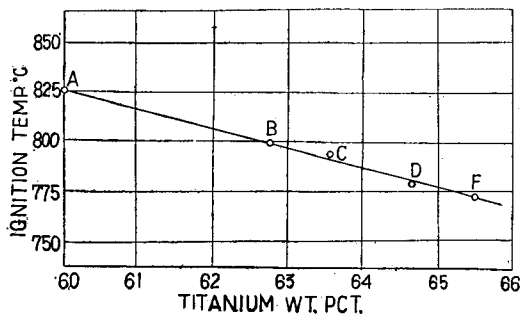


Fig. 11.

Table 3.

Specimen sign	Titanium Pct.	Ignition Temp °C
A	TiO ₂	825°C
E	62.74	800°C
C	63.62	800°C
D	64.82	780°C
E	65.70	775°C

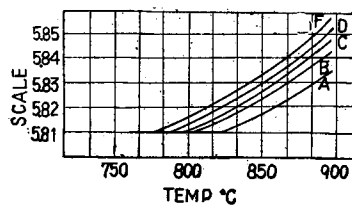
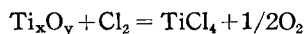


Fig. 12.

and the velocity of the reaction is exceedingly slow. In the series of experiment, the relation between the ignition temperature and the titanium pct. is liner in the range between 60 and 66% Ti and can be written in the equation as follows:

$$t^{\circ} = -9.26a + 1380.6,$$

where t° is the ignition temperature in degree centigrade and a is the titanium pct. As the reaction, it is considered that the reaction



takes place. Therefore, introducing the carbon monoxide gas into the reaction system, the next experiments are held to remove oxygen that is evolved in the reaction.

d) The chlorination of the titanium lower oxides with the mixed gas of chlorine and carbon monoxide.

The specimens used in the experiment are shown in the Table 4, where the oxides contain 60-65.4% titanium. The relation between the ignition temperature and the titanium per cent is shown in the figure 13. From it forcibly speaking the liner relation between

Table 4.

Specimen sign	Titanium Pct.	Ignition Temp. °C
A	60.00	250
E	62.45	275
C	63.40	300
D	64.80	325
E	65.40	350

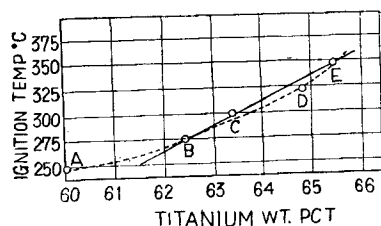


Fig. 13.

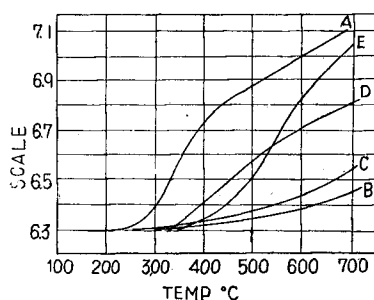


Fig. 14.

the ignition temperature and the titanium per cent is obtained and it is found that this relation is quite contrary to that previously obtained and the ignition temperature goes higher, according to the titanium per cent increase. The processes of the chlorination are shown in the figure 14, where the oxide (TiO_2) ignites at 250°C . and proceeds the reaction smoothly, and the more the oxide has the titanium per cent, the higher the ignition temperature becomes. The lower oxides that contain 62–64 per cent titanium have very slow reaction velocity, and the reaction velocity of the lower oxides in case of that contains 65 or more per cent titanium becomes to quicken again.

e) The chlorination of the titanium lower oxides with carbon tetrachloride vapour.

The specimens used in this experiment are shown in the Table 5, where the oxides contain 60–66 per cent titanium. The relation between the ignition temperature and the titanium per cent is shown in the figure 15, where the liner relation between the

Table 5.

Specimen sign	Titanium Wt. Pct.	Ignition Temp. °C
A	60.00	400
B	61.80	375
C	62.80	350
D	64.00	340
E	64.85	325
F	65.75	300

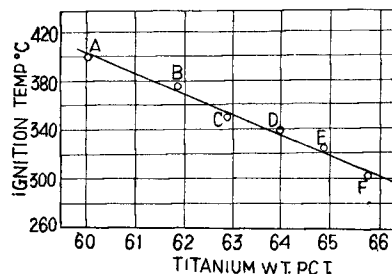


Fig. 15.

ignition temperature and the titanium per cent is obtained and can be written as following equation :

$$t^\circ = -16a + 1360, \quad a = 60 - 66$$

where t° is the ignition temperature in degree centigrade and a is the titanium per cent. The processes of the chlorination are shown in the figure 16 where it is found

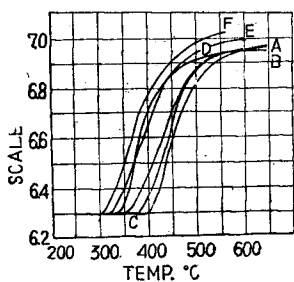


Fig. 16.

that the reactions proceed very smoothly after ignition and finish almostly by 500°C. It is very interesting, understanding from the results, that the chlorination of the titanium oxides do not always need the solid carbon. The chlorinations of titanium dioxide with the carbon tetrachloride vapour had been reported by Proc. W. Va. Acad. Scie.⁷⁾ and Belchetz,⁸⁾ in their paper the chlorination reactions are held at 700 degree centigrade and 1200 degree Fahrenheit, respectively.

4. Conclusion

For the determination of the mechanism in the preparation of titanium tetrachloride from the titanium oxides, several experiments are held and concluded as follows:

(1) By the hydrogen reduction of titanium dioxide, the lower oxide of the chemical composition Ti_2O_3 is got at 1400°C. and for 9 hours and it is impossible to get TiO in this temperature range.

(2) In case of the chlorination mixing with carbon, the lower the oxides are, the faster the ignition of the reaction occurs. There is the liner relation between the ignition temperature and the titanium per cent. and it is written as follows:

$$t^\circ = -38.3a + 2790$$

and the lower oxides containing 64 or more per cent titanium have very slow relation velocity between 400° and 500°C. and it might due to a kind of the disproportional reaction.

(3) In the chlorination, the carbon does not react as only reducing agent. Namely, in case of the chlorination of the titanium lower oxides without carbon, the ignition temperature of the reaction is very high and the reaction velocity is quite slow. There is also the liner relation between the ignition temperature and the titanium per cent and it is written as follows:

$$t^\circ = -9.26a + 1381$$

(4) In case of the chlorination with the carbon monoxide gas instead of the carbon, the behaviour of the reaction is very complicate and there is the contry relation between the ignition temperature and the titanium per cent. That is, the ignition temperature becomes higher as the titanium per cent increases and reaction velocity varies complicately with the titanium contents.

(5) Carbon tetrachloride is a good reagent for the chlorination and no deposition of the carbon in the tetrachloride is seen during the reaction. There is the liner rela-

tion between the ignition temperature and the titanium per cent. and it is written as follows :

$$t^{\circ} = -16a + 1360.$$

Summarizing the experimental results, several facts are understood as above mentioned, however, no sure conclusion on the mechanism has got yet.

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