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Hydrogen Reduction of Niobium Pentachloride*

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The reduction of gaseous niobium pentachloride with hydrogen was carried out under various conditions. The behavior of niobium tritaoctachloride obtained by the hydrogen reduction of the pentachloride at the temperature of 550°C was examined under an argon or hydrogen atmosphere. Also, some thermodynamic considerations concerning the reaction between niobium pentachloride and hydrogen were made. The reaction between gaseous niobium pentachloride and hydrogen began at a temperature of about 400°C. At the temperature range between about 400° and 550°C, it may be considered that the pentachloride was reduced with hydrogen to the tetrachloride which, in turn, disproportionated into the tritaoctachloride and pentachloride. At temperatures above about 600°C, the reactions may be considered as follows: The pentachloride was reduced with hydrogen to the tritaoctachloride which disproportionated into niobium, the pentachloride and the tetrachloride. Then, the pentachloride and tetrachloride produced were reduced with hydrogen to the tritaoctachloride which disproportionated in the same way.

1. Introduction

On hydrogen reduction of niobium pentachloride, only a small number of studies have been reported. Süe¹⁾, Schäfer et al.²⁾ and Brubaker et al.³⁾ found that niobium trichloride may be obtained by hydrogen reduction of the pentachloride at a temperature of about 500°C. McIntosh et al.⁴⁾

described that niobium was obtained by hydrogen reduction of the trichloride at temperatures between about 600° and 700°C. Recently, Schäfer et al.⁵⁾ showed that NbCl_{2.67}, having a smaller content of chlorine than the trichloride, was obtained by hydrogen reduction of the pentachloride at temperatures between 500° and 550°C, and that the so-called niobium trichloride

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is a general name of nonstoichiometric compounds ranging between $\text{NbCl}_{3.13}$ and $\text{NbCl}_{2.67}$. Schäfer et al.⁵⁾ and the CIBA Ltd.⁶⁾ also showed that the $\text{NbCl}_{2.67}$ may be represented as the formula of Nb_3Cl_8 .

In this research, in order to clarify the mechanism of the reaction between niobium pentachloride and hydrogen, the reaction product was examined under various reduction conditions. The behavior of niobium tritaoctachloride which is considered to play an important role was examined. Also, some thermodynamic considerations concerning the reaction between niobium pentachloride and hydrogen were made.

2. Experimental and Result of Hydrogen Reduction of Niobium Pentachloride

The niobium pentachloride used was obtained from the Stauffer Chemical Co.. The impurities in the pentachloride were $\text{Fe}<15$, $\text{B}<15$, $\text{P}<30$, $\text{Si}<30$, $\text{Ta}<150$, $\text{V}<30$,

$\text{Zr}<40$, $\text{Mo}<30$, $\text{W}<160$ and $\text{C}<140$ ppm. The hydrogen used was purified up to a dew point below -70°C using a hydrogen purifier made by the Japan Pure Hydrogen Co..

Fig. 1 shows a schematic drawing of the hydrogen reduction apparatus. The reaction tube of 28 mm inner diameter and 1,000 mm length was made of quartz, and the pyrex or quartz inner tube was inserted to the reaction tube to make the removal of the reaction product easier.

Fig. 1 Apparatus for hydrogen reduction of niobium pentachloride.

Table 1 Experimental Results of Hydrogen Reduction of Niobium Pentachloride

Reaction Temperature (°C)	Reaction products and their yields (%)				
	Nb	Nb_3Cl_8	Mixture of Nb_3Cl_8 and NbCl_4	NbCl_4	NbCl_5
400	-	5	detectable	detectable	90
450	-	15	detectable	detectable	80
500	-	30	detectable	5	60
550	-	45	detectable	5	45
600	detectable**	50***	detectable	5	40
650	5**	50***	-	5	35
800	25**	50***	-	detectable	20
900	40**	35***	-	detectable	20
1,000	20* + 30**	30***	-	detectable	15
1,100	40* + 20**	25***	-	detectable	10
1,200	50* + 20**	15***	-	detectable	10

* Obtained as Nb

** Obtained as a mixture of Nb and Nb_3Cl_8

*** Obtained as a mixture of Nb_3Cl_8 and Nb

Treatments of the pentachloride and the reaction product were made in a glove-box of argon atmosphere. The niobium and chlorine contents of the reaction product were analytically determined as niobium pentoxide and silver chloride, respectively. Niobium and the subchlorides except the tetrachloride were fused with potassium carbonate, for they were insoluble in nitric acid solution.

First, niobium pentachloride was transported with an excess of hydrogen through the reaction tube held at a specified temperature for 1 hr. at a hydrogen flow rate of about 350 cc/min and a sublimation temperature of the pentachloride of 190°C (that is, a mean flow rate of the gaseous pentachloride of about 30 cc/min). The results obtained are summarized in Table 1.

The reaction began at a temperature of about 400°C. At temperatures between about 400° and 550°C, the tritaoctachloride in the form of powder or plate was obtained in the reaction zone (plate-like product was obtained at temperatures above 500°C), while a bit of mixture of the tritaoctachloride and the tetrachloride, a small amount of the tetrachloride, and the pentachloride,

all in the form of powder, were obtained outside the reaction zone.

At temperatures between about 600° and 900°C, a mixture of niobium and the tritaoctachloride in the form of powder was obtained in the reaction zone, while a small amount of the tetrachloride, and the pentachloride were obtained outside the reaction zone.

At temperatures above about 1,000°C, niobium in the form of thin plate and a mixture of niobium and the tritaoctachloride were obtained in the reaction zone, while a bit of the tetrachloride and a small amount of the pentachloride were obtained outside the reaction zone.

Next, the pentachloride was transported with an excess of hydrogen through the reaction tube for 1 hr. at a hydrogen flow rate of about 350 cc/min and a sublimation temperature of the pentachloride of 160°C (that is, a mean flow rate of the gaseous pentachloride of about 10 cc/min). The results obtained are summarized in Table 2.

The results are almost identical with those in Table 1.

Since Schäfer et al.⁷⁾ mentioned that the pentachloride slightly decomposes at high temperatures according to the equation,

Table 2 Experimental Results of Hydrogen Reduction of Niobium Pentachloride

Reaction temperature (°C)	Reaction products and their yields (%)				
	Nb	Nb ₃ Cl ₈	Mixture of Nb ₃ Cl ₈ and NbCl ₄	NbCl ₄	NbCl ₅
400	-	5	detectable	detectable	90
450	-	15	detectable	detectable	80
500	-	35	detectable	5	55
550	-	45	detectable	5	45
600	5**	50***	-	detectable	40
650	15**	40***	-	detectable	40
900	40**	35***	-	detectable	20
1,000	30* + 30**	30***	-	detectable	5
1,200	85* + 10***	detectable***	-	detectable	detectable

* Obtained as Nb

** Obtained as a mixture of Nb and Nb₃Cl₈

*** Obtained as a mixture of Nb₃Cl₈ and Nb

Table 3 Experimental Results of Hydrogen Reduction of Niobium Pentachloride

Flow rate of hydrogen (cc/min)	Mean flow rate of NbCl ₅ (g) (cc/min)	Reaction products and their yields (%)			
		Nb	Nb ₃ Cl ₈	NbCl ₄	NbCl ₅
110	30	70* + 15**	detectable***	detectable	10
350	30	50* + 20**	15***	detectable	10
1,100	30	35* + 20**	25***	detectable	15
110	10	50* + 20**	25***	detectable	detectable
230	10	70* + 15**	10***	detectable	detectable
350	10	85* + 10**	detectable***	detectable	detectable
700	10	80* + 10**	detectable***	detectable	5
1,100	10	75* + 10**	detectable***	detectable	10

* Obtained as Nb

** Obtained as a mixture of Nb and Nb₃Cl*** Obtained as a mixture of Nb₃Cl₈ and Nb

$2\text{NbCl}_5(\text{g}) = 2\text{NbCl}_4(\text{g}) + \text{Cl}_2(\text{g})$, the thermal decomposition of the pentachloride was examined at a temperature of 1,200°C and an argon flow rate of 350 cc/min, under nearly the same conditions as those used in the hydrogen reduction of the pentachloride. As the result, a very small amount of the tetrachloride was produced by the thermal decomposition of the pentachloride outside the reaction zone. Because of this result, the thermal decomposition of the pentachloride may be considered to be negligible when the hydrogen reduction of the pentachloride is considered.

From the above mentioned experimental results, the temperatures above 1,000°C being preferable for the production of niobium by hydrogen reduction of the pentachloride, the reduction at a temperature of 1,200°C was examined under a few conditions. The results obtained are summarized in Table 3.

The best yield of niobium was about 95 per cent at a hydrogen flow rate of about 350 cc/min and a mean flow rate of gaseous niobium pentachloride of about 10 cc/min.

3. Thermodynamic Consideration on Hydrogen Reduction of Niobium Pentachloride

Since the reaction between niobium pentachloride and hydrogen was very intricate as mentioned above, some thermodynamic considerations were made on the probable reactions.

First, the reactions at the temperatures between 400° and 550°C were discussed. At this temperature range, the tritaoctachloride was the main product, and the tetrachloride and pentachloride were also obtained. From this experimental result, the following reactions may be considered.

The ΔG° values for the above equations were calculated using thermodynamic values given in Table 4. The calculated values are shown in Fig. 2.

Table 4 Thermodynamic Values

Substance	$\Delta H_{25^\circ\text{C}}$ (kcal)	$S_{25^\circ\text{C}}$ (eu)	C_p (cal/deg)
NbCl_5 (g)	-169.9 ⁷⁾	93 ⁷⁾	$31.6 - 3.7 \times 10^5 T^{-2}$ ⁷⁾
NbCl_4 (g)	-136.6 ⁷⁾	85 ⁷⁾	$25.8 - 2 \times 10^5 T^{-2}$ ⁷⁾
Nb_3Cl_8 (s)	-385.8 ⁸⁾	98 ⁷⁾	$63 + 11.1 \times 10^{-3} T - 4.5 \times 10^5 T^{-2}$ ⁷⁾
NbCl_2 (s)	-97.3 ⁸⁾	28 ⁷⁾	$17.5 + 3.2 \times 10^{-3} T - 1.2 \times 10^5 T^{-2}$ ⁷⁾
Nb (s)	-	8.73 ⁹⁾	$5.66 + 0.96 \times 10^{-3} T$ ⁹⁾
H_2 (g)	-	31.21 ⁹⁾	$6.52 + 0.78 \times 10^{-3} T + 0.12 \times 10^5 T^{-2}$ ⁹⁾
HCl (g)	-22.0 ⁹⁾	44.65 ⁹⁾	$6.34 + 1.10 \times 10^{-3} T + 0.26 \times 10^5 T^{-2}$ ⁹⁾

Fig. 2 ΔG° vs. temperature—1.

These results indicate that all the four reactions may proceed to the right.

Considering the above mentioned experimental results and the fact that the tritaoctachloride did not disproportionate at this temperature range as will be shown later, the reaction may probably be considered to proceed via the equations (1) and (4). It is considered that the tetrachloride produced by the hydrogen reduction of the pentachloride disproportionated into the tritaoctachloride and pentachloride, and

thus the tritaoctachloride, tetrachloride and pentachloride were obtained.

Second, the reactions at the temperatures above 600°C were discussed. At this temperature range, niobium was obtained. The following three reactions and the disproportionations which will be mentioned later may be considered as the reactions producing niobium.

The ΔG° values for the above equations were calculated using thermodynamic values shown in Table 4. The calculated values are shown in Fig. 3.

These results indicate that the reaction (5) may be considered to have a large possibility to proceed to the right, and that the reactions (6) and (7) to have a small possibility to proceed to the right.

For the disproportionation of the tritaoctachloride, Schäfer et al.^{5),7)} thermodynamically and experimentally showed

Fig. 3 ΔG° vs. temperature-2.

that the reaction proceeds via the equations, $\text{Nb}_3\text{Cl}_8(\text{s}) = 2\text{NbCl}_2(\text{s}) + \text{NbCl}_4(\text{g})$ and $3\text{Nb}_3\text{Cl}_8(\text{s}) = 7\text{NbCl}_2(\text{s}) + 2\text{NbCl}_5(\text{g})$, and that the dichloride and tetrachloride produced disproportionate according to the equations, $2\text{NbCl}_2(\text{s}) = \text{Nb}(\text{s}) + \text{NbCl}_4(\text{g})$, $5\text{NbCl}_2(\text{s}) = 3\text{Nb}(\text{s}) + 2\text{NbCl}_5(\text{g})$ and $7\text{NbCl}_4(\text{g}) = \text{Nb}_3\text{Cl}_8(\text{s}) + 4\text{NbCl}_5(\text{g})$.

From these facts, the production of niobium depends on either the hydrogen reduction of the pentachloride or the disproportionation of the tritaoctachloride. However, considering the experimental result at the temperature of 1,000°C, for example, in which a large amount of mixture of niobium and the tritaoctachloride, a small amount of the tetrachloride, and the pentachloride were obtained with niobium, the disproportionation of the tritaoctachloride may be considered significantly to contribute for the production of niobium.

4. Behavior of Niobium Tritaoctachloride

The behavior of niobium tritaoctachloride under an argon or hydrogen atmosphere was examined. The tritaoctachloride used was obtained by the hydrogen reduction of the pentachloride at a temperature of 550°C. Its analysis showed 49.3% Nb and 50.3% Cl, the theoretical values being 49.5% Nb and 50.5% Cl.

Fig. 4 Apparatus for heating of Nb_3Cl_8 under an argon or a hydrogen atmosphere.

The experimental apparatus is shown in Fig. 4.

The tritaoctachloride (10.0 g) was inserted in the quartz tube under an argon atmosphere as shown in Fig. 4, and heated under an argon or hydrogen atmosphere at various temperatures for a period of 2 hrs.

The experimental results of the disproportionation of the tritaoctachloride under the argon atmosphere are summarized in Table 5.

From the results, the disproportionation of the tritaoctachloride began at a temperature of about 600°C, and niobium, the pentachloride and a small amount of the tetrachloride were obtained. With an increase of the temperature, the disproportionation became violent, and the amounts of niobium and the pentachloride produced increased. Niobium was obtained as a mixture of niobium and the tritaoctachloride at temperatures below 800°C and as a pure state at temperatures above 900°C.

Considering the facts that the tritaoctachloride disproportionated into niobium, the pentachloride and a small amount of the tetrachloride and that the dichloride is thermally unstable⁵⁾, the discussion on the disproportionation of the tritaoctachloride by Schäfer et al.^{5),7)} may be accepted as reasonable.

The experimental results of the heating of the tritaoctachloride under the hydrogen atmosphere are summarized in Table 6.

Table 5 Experimental Results of the Disproportionation of Nb_3Cl_8 under an Argon Atmosphere

Temperature (°C)	Reaction products and their weight per cent			Weight per cent of remained Nb_3Cl_8
	Nb	NbCl_4	NbCl_5	
550	-	-	-	100
600	1**	detectable	detectable	95***
700	3**	detectable	5	90***
800	15**	5	20	60***
900	20*	5	65	10
1,000	20*	5	70	5

* Obtained as Nb

** Obtained as a mixture of Nb and Nb_3Cl_8 *** Obtained as a mixture of Nb_3Cl_8 and NbTable 6 Experimental Results of the Heating of Nb_3Cl_8 under a Hydrogen Atmosphere

Temperature (°C)	Reaction products and their weight per cent			Weight per cent of remained Nb_3Cl_8
	Nb	NbCl_4	NbCl_5	
550	-	-	-	100
600	2**	-	detectable	90***
700	10**	detectable	5	75***
800	20* + 10**	5	15	15***
900	35*	5	15	10
1,000	35*	5	20	5

* Obtained as Nb

** Obtained as a mixture of Nb and Nb_3Cl_8 *** Obtained as a mixture of Nb_3Cl_8 and Nb

The results are nearly in accord with the results of the disproportionation of the tritaoctachloride under argon and those of the hydrogen reduction of the pentachloride at temperatures above 600°C.

The amounts of niobium produced by the disproportionation of the tritaoctachloride under argon and by the heating of the tritaoctachloride under hydrogen vs. temperatures are shown in Fig. 5.

When the tritaoctachloride decomposes only by the disproportionation, the weight per cent of niobium produced does not exceed 23 per cent of the weight of the tritaoctachloride used. The maximum weight per cent of niobium obtained by the disproportionation under argon was close to 23 per cent, while that produced by heating under hydrogen apparently exceeded 23 per cent. From these results,

Fig. 5 Weight per cent of niobium produced by the disproportionation of Nb_3Cl_8 under the argon atmosphere and the heating of Nb_3Cl_8 under the hydrogen atmosphere vs. temperature.

the pentachloride and tetrachloride produced by the disproportionation of the tritaoctachloride may be considered to be reduced via the above mentioned equations (1) and (2) to the tritaoctachloride which was consecutively disproportionated to give niobium.

The above discussion probably shows that the production of niobium does not depend on the direct reduction of the pentachloride with hydrogen, but depends on the disproportionation of the tritaoctachloride.

5. Discussion

In the temperature range between 400° and 550°C, it may be considered that the pentachloride was reduced with hydrogen to the tetrachloride which, in turn, disproportionated into the tritaoctachloride and pentachloride.

Many investigators¹⁻⁴⁾ mentioned that

the trichloride may be obtained by hydrogen reduction of the pentachloride at about 500°C. Contrary to these reports, the tritaoctachloride, having a smaller content of chlorine than the trichloride, was obtained. This result agrees with the work by Schäfer et al.⁵⁾ and the patent by the CIBA Ltd..⁶⁾

At temperatures above 600°C, the reactions may be considered as follows: The pentachloride was first reduced with hydrogen to the tritaoctachloride which disproportionated into niobium, the pentachloride and the tetrachloride. Then, the pentachloride and tetrachloride produced were reduced with hydrogen to the tritaoctachloride which disproportionated in the same way. McIntosh et al.⁴⁾ described that niobium was obtained by hydrogen reduction of the trichloride which was prepared by hydrogen reduction of the pentachloride. They found that the reduction process was complicated by the fact that the trichloride disproportionates to give niobium and the pentachloride which is lost by volatilization and thus the efficiency of the reduction is lowered. The description by McIntosh et al. that niobium was directly produced by hydrogen reduction of the trichloride may not be accepted as reasonable, according to the results of this work. The reactions for the production of niobium may be considered as follows: The tritaoctachloride disproportionated into niobium, the pentachloride and the tetrachloride. Then, the pentachloride and tetrachloride produced were reduced with hydrogen to the tritaoctachloride which also disproportionated to give niobium.

6. Summary

The results obtained may be summarized as follows:

1) The reaction between gaseous niobium pentachloride and hydrogen began at a

temperature of about 400°C. At temperatures between 400° and 550°C, the reaction products were the tritaoctachloride, the pentachloride and a small amount of the tetrachloride. In this temperature range, it may be considered that the pentachloride was reduced with hydrogen to the tetrachloride which, in turn, disproportionated into the tritaoctachloride and pentachloride.

2) At temperatures above 600°C, the reaction products were niobium, the tritaoctachloride, the pentachloride and a small amount of the tetrachloride. The amount of niobium obtained increased and the amounts of the tritaoctachloride, the pentachloride and the tetrachloride decreased with the rise of reaction temperature. At temperatures above about 1,000° C, the amount of niobium obtained was relatively large: for example, the yield at a temperature of 1,200°C was about 95 per cent at a hydrogen flow rate of 350 cc/min and a mean flow rate of the gaseous pentachloride of about 10 cc/min. In this temperature range, the main reactions may be considered as follows: The pentachloride was reduced with hydrogen to the tritaoctachloride which disproportionated into niobium, the pentachloride and the tetrachloride. Then, the pentachloride and tetrachloride produced were reduced with hydrogen to the tritaoctachloride which disproportionated in the same way.

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