

**Original Paper**

## Thermal Decomposition of NbCl<sub>5</sub> in Reductive Atmosphere by Using Hydrogen Gas

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### Abstract

The present investigation is a preliminary study of metallic niobium purification process from ferroniobium, by thermal decomposition of niobium pentachloride in reductive atmosphere. Niobium pentachlorides was produced from the chloride separation and distillation of ferroniobium chlorination process. The study aims to provide some basic data related with the experimental condition of niobium pentachloride reduction. The thermal treatment process was conducted at 1373–1523 K for about 6 hours. The gas utilized in the process was 40% H<sub>2</sub> balanced with Ar or commercial quality (CQ) H<sub>2</sub> which was flowed at 0.3 l/min. The optimum experimental condition was found at the temperature of 1473–1523 K by using CQ H<sub>2</sub>. The products of thermal decomposition consist of chips, black, gray and yellow/white powders. In this condition, chips were recovered as the highest content of niobium product, that reach at about 98 mass% niobium. The chip product is composed of a mixture phase of Nb and NbO with the average of mass fraction of about 0.85 and 0.15, respectively. NbO seems to be formed mainly due to dechlorination of niobium oxychloride compound, as an impurity of the raw material.

**Key words:** Niobium, chloride metallurgy, thermal treatment, dechlorination, dry method

### 1. Introduction

Niobium alloys become of major interest recently and are utilized in many industrial sector, such as nuclear reactor materials and superconductor<sup>1)</sup>. It is due to a low neutron absorption cross section area and low transition temperature properties. This metal is classified as refractory metals because of its stability in high temperature and also applied to high strength steel as an alloying element.

The most important natural sources of ferroniobium and niobium are pyrochlore, columbite ore and tin slag. In the case of ferroniobium recovery from tin slag, chloro and pyrometallurgical processes are widely applied<sup>1)</sup>. However, recently, the separation of valuable metals such as rare earths and thorium from ore has changed the raw materi-

als of niobium recovery. Many producer countries tend to process the ore first and then exported as a ferroniobium. Since then, the recovery and purification of niobium from ferroniobium becomes widespread. In this process, niobium is separated from ferroniobium by flowing the chlorine gas to produce niobium pentachloride. In the next step, the chloride compounds are reduced, for instance by means of hydrogen reduction.

One of the study of niobium separation from ferroniobium has been conducted by Sato and Nanjo<sup>2)</sup>. They showed that the niobium separation is feasible at relatively low temperature at about 578 K. Niobium pentachlorides was selectively condensed and separated from ferric chloride because of temperature gradient. With the addition of iron, ferric chloride was reduced to ferrous chloride and pure niobium pentachloride was produced by a distillation method. Further, purification

of niobium pentachlorides by using hydrogen gas has also been investigated<sup>3</sup>). The reduction of niobium pentachloride by hydrogen reduction was undertaken with the presence of metallic niobium surface. The metallic niobium was deposited on the feed in the form of heated niobium sheet at temperature range of 1273–1873 K. It was reported that the maximum deposit rate was about 21.3 kg/m<sup>2</sup> (= 2.13 g/mm<sup>2</sup>). There are also several reduction processes of niobium pentachloride, which have been patented so far<sup>4,5</sup>). However, they consist only a few information about the process details.

The present study aims to provide information of the fundamental process taking place during thermal treatment of niobium pentachloride by hydrogen gas which is produced from chlorination of ferroniobium in a laboratory scale. The attempt is focused on the examination and evaluation of the decomposition phenomena and experimental conditions that allow optimum niobium recovery. It is also expected that the results obtained to be useful for the process in a higher scale.

## 2. Thermodynamic consideration

Fig. 1 shows the stability diagram of Nb-Cl<sub>2</sub> system which were calculated based on thermodynamic data<sup>6</sup>). There are several niobium compounds which are plotted in the figure such as, NbCl<sub>5</sub>(g), NbCl<sub>3,13</sub>(s), NbCl<sub>2,67</sub>(s), NbCl<sub>2</sub>(s) and Nb(s). Because of the limitation of the thermodynamic data, some lines (NbCl<sub>2,67</sub> and NbCl<sub>2</sub>) were drawn by using extrapolation data, especially for the temperature more than 1000 K<sup>6</sup>).

The melting and boiling point of NbCl<sub>5</sub>, which are not shown in the figure, are at 479 and 521 K, respectively. The estimation of the partial pressure of chlorine during experiment are plotted by dotted lines with the assumption that the reaction of H<sub>2</sub>(g) + Cl<sub>2</sub>(g) = 2HCl(g) is taken place under condition of x = 1 and x = 100, where  $x = p_{\text{H}_2}/p_{\text{HCl}}^2$ . The partial pressure of chlorine gas increases in the higher temperature.

The cross line between reaction line of Nb/NbCl<sub>2</sub> (extrapolated) and H<sub>2</sub>/HCl leads to the dechlorination temperature of NbCl<sub>2</sub> at 1453 K. Keeping this in mind, a temperature range of thermal treatment used in this study is set at 1373–1523 K. It can be predicted that the partial pressure of chlorine in equilibrium condition (x = 1) is in the range of  $1.58 \times 10^{-9}$ – $1.26 \times 10^{-8}$  MPa at 1373–1523 K. This condition is feasible enough to dechlorinate NbCl<sub>5</sub> to Nb. As shown in the figure, at 1373 K, the reaction product may contain lower sub-

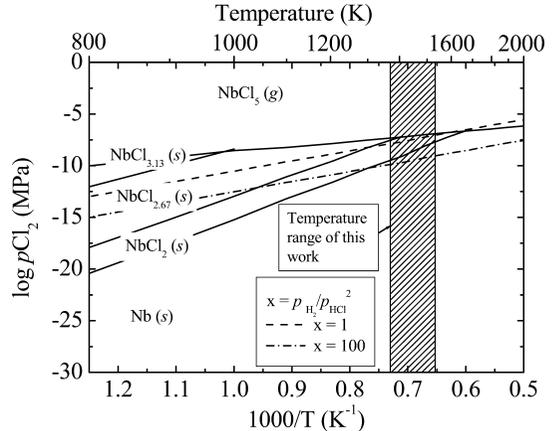


Fig. 1 Stability diagram of Nb-Cl<sub>2</sub> system.

chloride such as NbCl<sub>2</sub>. At higher temperature, it is possible to obtain metallic niobium from the dechlorination process directly.

## 3. Experimental

### 3.1 Material and apparatus

Niobium pentachlorides (NbCl<sub>5</sub>) were supplied from JEMCO Inc. They were produced from chlorination of ferroniobium by using chlorine gas under NaCl existence. The chlorination process was based on the (previous reported) literature<sup>7</sup>). By applying fractional distillation of the chlorides, yellow powder of niobium pentachlorides was produced in the condenser.

The composition of niobium in niobium pentachlorides (as received) was 34.5 mass%. Other impurities such as of Al, Fe, Na are less than 1 ppm. Si and total S are about 25 ppm and 125 ppm, respectively. This raw material was kept and stored carefully in a desiccator in the glove box before it used in the experiments. Since NbCl<sub>5</sub> is very reactive with air/moisture, it should be considered that the degradation of its purity may occur in the storage due to a small portion contamination of air/moisture. The ICP analysis of raw materials, which had been stored for a certain time, was conducted. It showed that niobium content in the raw materials became 35.6 mass%. It is quite reasonable that the raw materials may contain NbOCl<sub>3</sub>, according to the reaction (1) or (2)<sup>9</sup>. Both of reactions occur spontaneously at room temperature, since the  $\Delta G^\circ$  of reaction (1) and (2) (298 K) are  $-58.43$  kJ/mol and  $-96.46$  kJ/mol, respectively. Thus, the sample is a mixture of NbCl<sub>5</sub> and NbOCl<sub>3</sub>.





By considering the niobium content of 34.5 mass% and 35.6 mass% in the mixture of NbCl<sub>5</sub> and NbOCl<sub>3</sub>, it gives that the content of NbCl<sub>5</sub> in the raw materials (mixture of NbCl<sub>5</sub> and NbOCl<sub>3</sub>) is in the range of 86.4 mass%–98.9 mass%. It also means that the niobium content in the raw material is 35.3 mol%–35.5 mol%. Further, it can be calculated that the oxygen content in the raw materials is about 1.01 mass% (or about 2 mmol for 3 g sample with the purity of NbCl<sub>5</sub> 86.4%).

The conditions of the experiments, that are represented the optimum condition for the experiment were determined from several preliminary experiments and calculation. The detail thermal treatment conditions used in the experiments are listed in Table 1.

Fig. 2 shows the schematic diagram of the apparatus. The apparatus consists of heating furnace and quartz reaction tube (inner dia. = 30 mm; length = 60 cm). A sample tube (inner dia. = 5 mm; length = 10 cm) made of quartz was inserted in the

extended nozzle in the middle area of the reaction tube. The end of the reaction tube was closed by quartz lid. Vacuum seal was also added between reaction tube and lid.

Flow of hydrogen gas was controlled by using flow-meter. Dehydration agent (silica gel) was placed in the gas flow system to eliminate moisture in the gas flow. The gases from the reaction tube was kept flowing into HCl trap. The HCl trap was filled with distilled water (1.2 dm<sup>3</sup>) to observe the chlorine ion in the off gas during heat treatment. Some valves were utilized to prevent air contamination into the HCl trap and reverse flow of moisture into reaction tube direction during solution sampling. Other gas traps were used after HCl trap before the flue gas flowed into the atmosphere.

### 3.2 Procedure

Sample preparation was undertaken in a glove box filled with nitrogen gas for each run of experiment. About 2–3 grams of niobium pentachloride powder was put in the sample tube. The sample tube then was inserted into nozzle extension in the reaction tube and placed at about 20 cm from the edge (left side) of the reaction tube (see Fig. 2). The reaction tube was sealed and closed by a lid with valves in the glove box, then it was moved into the furnace. Nitrogen gas evacuation and argon and hydrogen (purity min. 99.9%) gas flushing were applied before thermal treatment for several minutes into the tube reaction. 40% H<sub>2</sub>-Ar (hydrogen and argon-base mixture, purity min. 99.9%) and H<sub>2</sub> commercial quality (CQ, purity min. 99.9%) were used as dechlorination agents. The data of oxygen and moisture in the gases used in the experiments were not available. For analysis purpose, it can be assumed that they were not more than 100 ppm (0.01%). The gas flow rate was set at 0.3 L/min.

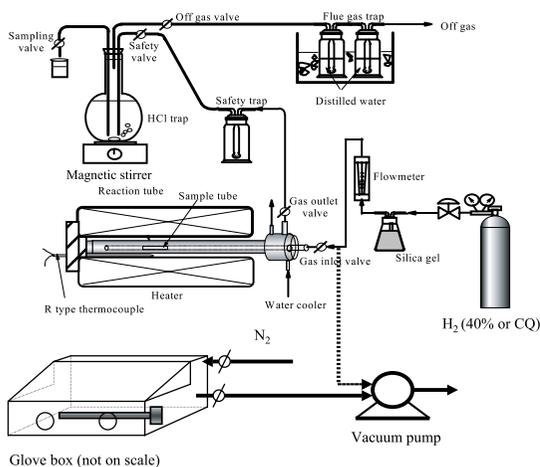
The temperature inside the quartz tube near the sample tube was measured by R type thermocouple. Previously, some preliminary tests were conducted to evaluate and compare the temperature in the furnace and inside the reaction tube. It was found that the temperature difference between furnace and inside of quartz tube, under steady state thermal condition, was negligible. Other preliminary tests were also undertaken to observe temperature gradient inside the reaction tube. Considering this condition, the sample was placed at equitemperature zone of the furnace. The position of sample tube was in the same position as the thermocouple. A constant heating rate was applied during the experiment. The system was heated slowly and carefully. The regulated temperature

**Table 1** Thermal treatment conditions.

Exp. #	Thermal treatment conditions			
	Temp. $T_{tr}$ (K)	Atmosphere	Flow rate (L/min.)	Time $T_{tr}$ (h)
A	1373	H <sub>2</sub> -40% <sup>1)</sup>	0.3	6
B	1473	H <sub>2</sub> -40%	0.3	6
C	1523	H <sub>2</sub> -40%	0.3	6
D	1473	H <sub>2</sub> -CQ <sup>2)</sup>	0.3	6
E	1523	H <sub>2</sub> -CQ	0.3	6

<sup>1)</sup> Hydrogen gas in argon based mixture.

<sup>2)</sup> CQ: commercial quality.



**Fig. 2** Experimental apparatus used in the thermal treatment process.

was controlled precisely and was kept at 1373, 1473 and 1523 K for 6 hours.

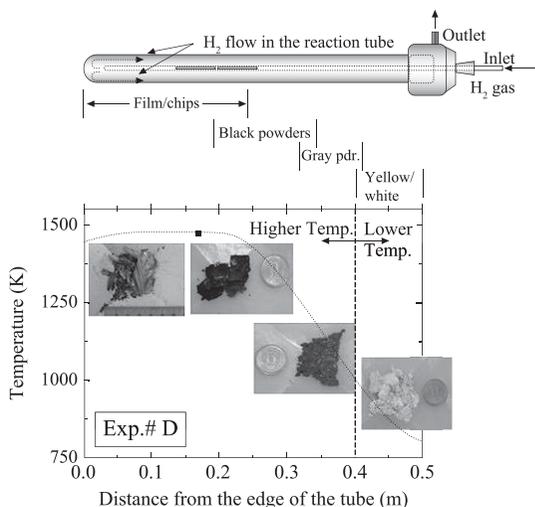
During the thermal treatment, about 10 ml solution in the HCl trap was taken out, periodically. The sampling was conducted in a such that no air contamination into the gas flow system by controlling the valves. Cl ion content in the sample solution was measured by  $\text{AgNO}_3$  titration, several times. The experiment was terminated and the gas flow was stopped when the temperature in the reaction tube was less than 323 K. After the reaction tube cooled down to the room temperature, the deposit products were taken out by using quartz spatula and weighed. Finally, to maintain reproducibility after each run of experiment, the reaction tube was cleaned and washed by using 4% HF and  $\text{HNO}_3$  solution mixture in an ultrasonic cleaner for several hours.

The composition of the products were analyzed qualitatively by X-ray Diffractometer (XRD, JEOL JDX-3500). Observation of morphology and quantitative analysis of the products were conducted by using Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometry (SEM/EDX, JEOL JSM-5900 LV). For comparison, some of the products were analyzed by Inductively Coupled Plasma (ICP, Seiko Instrument, Inc. SPS 3000 Plasma spectrometer).

#### 4. Result and discussions

At the temperature higher than 521 K (boiling point of  $\text{NbCl}_5 = 521$  K),  $\text{NbCl}_5$  in gas phase began to be dechlorinated by hydrogen. As shown in Fig. 2, hydrogen gas flows from right-hand side to left hand-side in the reaction tube. Some of  $\text{NbCl}_5$  in gas phase flows are undechlorinated to the right-hand side, others are dechlorinated and deposited onto the surface of the reaction tube. For all experiment conditions, metallic films are formed and attached on the reaction tube wall. The reaction time which was set for 6 hours is long enough to adhere the dechlorination products in the reaction tube.

Fig. 3 shows the estimation of temperature distribution and typical deposition location of each product in the case of Exp. #D. The vertical dashed line in the figure indicates the end position of heating zone. Actually, the products deposited in the reaction tube without a definite boundary. Their location in the reaction tube were based on average distance which was measured during sampling. The mixture of the deposition products in one location were also observed in the reaction tube, such as metallic chips/film—black powder,

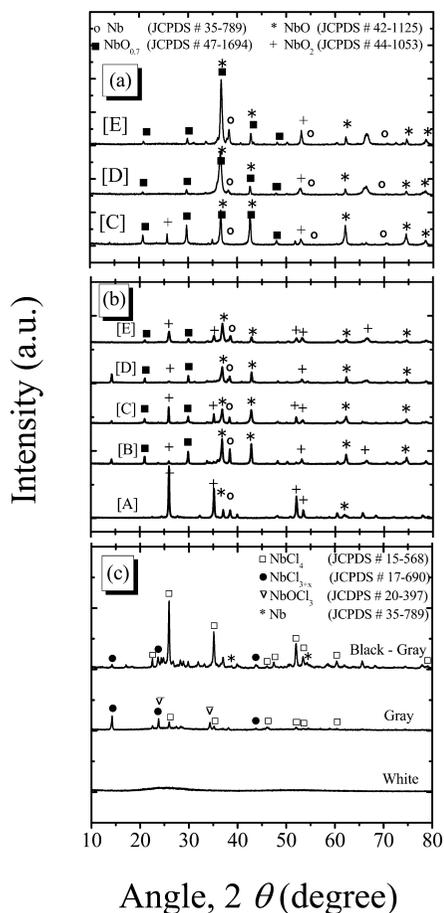


**Fig. 3** Estimation of temperature distribution and location of reaction products obtained in Exp. #D (1473 K).

black-gray powder or gray-yellow/white powder. Metallic film/chips were observed to be deposited in an equitemperature zone. Black powders were deposited in the vicinity of equitemperature zone to the right hand-side. Other products were condensed and deposited in boundary area and in a lower temperature in the right hand side of the reaction tube.

##### 4.1 Products composition

The products, which were stored in a desiccator and without any pretreatments were analyzed qualitatively by using XRD. The compound species which were detected from chips, black powders and other powders, such as mixture of black and gray, gray and yellow/white are shown in Fig. 4 (a), (b) and (c), respectively. The analysis for yellow/white products gave the amorphous structure. Some of  $\text{NbOCl}_3$  peaks were also detected in the gray powders (Fig. 4 (c)). Actually, in case of the mixture powder of black and gray, niobium subchlorides were detected among niobium oxide (Fig. 4 (c)). Although, the peak position ( $2\theta$ ) of  $\text{NbO}_2$  (JCPDS #44-1053) and  $\text{NbCl}_4$  (JCPDS #15-568) is almost similar, that is at  $25.98^\circ$  and  $25.99^\circ$ , respectively, the  $\text{NbO}_2$  can be distinguished from  $\text{NbCl}_4$  by its pattern as shown in Fig. 4 (b). From both samples (black powder and chips), Nb, NbO and  $\text{NbO}_2$  compounds were detected. In case of chip products (Fig. 4 (a)), the peaks of  $\text{NbO}_{0.7}$  and NbO were detected. The strongest peak ( $2\theta = 36.8^\circ$ ) coincided with that of  $\text{NbO}_{0.7}$  and NbO. It shows that the chips may also contain  $\text{NbO}_{0.7}$  and NbO.



**Fig. 4** X-ray diffractograms of chips (a), black powders (b), and other powders from Exp. #E (c). Exp. #A and B produced too less amount of chips for XRD analysis.

Then, the products were analyzed quantitatively by using EDS. The composition of niobium, oxygen and chlorine in the chips/film and black powder from all experiment conditions are listed in Table 2. The analysis was covered only for higher content of niobium such as chips and black powders. Although, film was formed in Exp. #A, the chip product was not found. In this case, analysis was undertaken for only black powders.

Niobium content in black powders and chips reached to 75–89 mass% and 90–98 mass%, respectively. From the results listed in Table 2, the products were also consisted of chlorine and oxygen. In black powder and chips products, the presence of chlorine seems not to form a compound with niobium, as detected in XRD analysis.

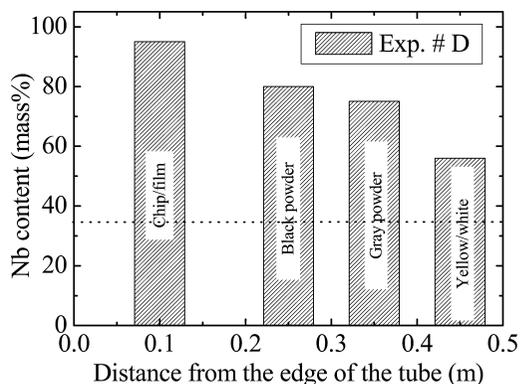
The results listed in Table 2 also suggests that decomposition at higher temperature increases

**Table 2** Composition of Nb, O and Cl in the products (analyzed by EDS).

Exp. #	Deposits	Analytical Result, C <sub>i</sub> (mass%)		
		Niobium C <sub>Nb</sub>	Oxygen C <sub>O</sub>	Chlorine C <sub>Cl</sub>
A	Black	74.7(73.5) <sup>1)</sup>	25.2	0.08
	Chips	n.a. <sup>2)</sup>	n.a.	n.a.
B	Black	85.6(84.3)	12.3	1.88
	Chips	90.0	8.95	1.01
C	Black	82.3(78.1)	17.0	0.73
	Chips	90.7	8.08	1.48
D	Black	86.8(82.9)	10.3	2.96
	Chips	95.4(91.3)	4.33	0.24
E	Black	88.6(97.6)	10.5	1.44
	Chips	97.8(96.6)	2.22	0.02

<sup>1)</sup> ICP analysis is listed in parentheses for comparison.

<sup>2)</sup> Chips was not observed to be formed in Exp. #A.



**Fig. 5** Composition of niobium in each reaction products from Exp. #D (1473 K; H<sub>2</sub> CQ) and estimation of their deposition location in the reaction tube. Average content of niobium in the starting material is drawn as dashed line.

niobium composition of chips and black powder which were treated by using H<sub>2</sub> CQ (Exp. #D and E). This phenomenon is not observed in decomposition process by using H<sub>2</sub> 40% (Exp. #A, B and C).

Fig. 5 shows the distribution of niobium composition in each product of Exp. #D in the reaction tube. The highest composition of niobium, that was detected from chips, reached 97.8 mass%. It was assumed that the composition of niobium of chips and film is similar. The composition of niobium in the black, gray and yellow/white powders was decreased as shown in Fig. 5. It was observed that the composition of niobium in yellow/white

products was still higher than the raw material of  $\text{NbCl}_5$  (35.6 mass%). This observation suggests that it was not only volatilized and condensed but also decomposed to subchlorides.

#### 4.2 Niobium distribution and balance

The mass distribution of niobium in the raw material and in the deposit products are listed in Table 3. Comparing to the molar quantity of each products with niobium in the raw materials, the molar fraction of the products are obtained. Fig. 6 (a) exhibits the distribution of molar fraction of niobium in the deposits from left hand side (film/chips, black, gray and yellow/white) for the case of Exp. #D. They are 0.33, 0.12, 0.10 and 0.45, respectively. In this case, almost a half of the niobium in the raw materials were poorly decomposed. The comparison for all conditions of experiment are shown in Fig. 6 (b).

In a higher temperature of thermal treatment, the molar fraction of films/chips increases, for instance Exp. C and D. However thermal treatment to the formation of film/chips is not effective in

the temperature lower than 1473 K. Yellow/white product which can be represented as a product loss also increases in higher temperature more than 1473 K. Moreover, the fraction of gray products decreases in higher temperature, while the fraction of black powder is almost the same. This indicates that temperature control is an important part in the process, because it can directly affect the product with higher niobium content. Utilization of higher concentration of hydrogen increases the effectivity of dechlorination reaction in term of the fraction to the metallic film/chips. It seems also effective in the temperature more than 1523 K.

#### 4.3 Formation of niobium oxide

To find out the origin of oxygen which produce oxide compounds in the products, such as chips and black powder, a mass balance of oxygen in the experiments was calculated. Based on this calculation the gas tightness during experiments can be also evaluated. The mass balance of oxygen is shown in Table 3.

According to the mass balance of oxygen in Table 3, the oxygen input is still relatively higher than that of in the chips/film and black powders. Other portion of oxygen likely took place in the formation reaction of other products, such as gray and yellow/white powder. It can be also noted that not all oxygen which was consisted in the supply side reacted with niobium in chips/film and/or black powder to form  $\text{NbO}$ . It seems that the oxygen from raw materials plays more important role than that from the gas in the formation of  $\text{NbO}$ .

Although, some of the data in the oxygen balance are based on the assumption, they may represent the condition during the experiment. Actually, the apparatus was not designed to be a high vacuum system. However, from the oxygen balance, it shows that the gas tightness of the apparatus is adequate to support the experiment, in terms of reproducibility of the results.

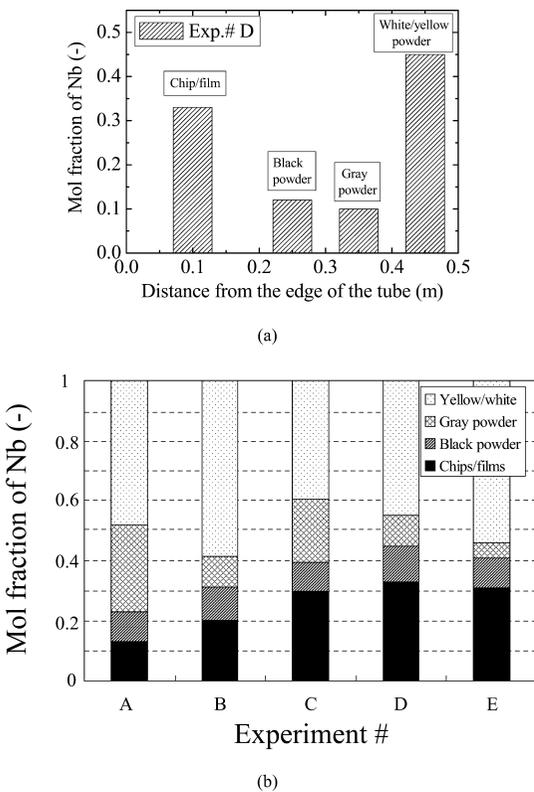
#### 4.4 Dechlorination degree

A cumulative analysis of the chlorine ion in the gas trap was undertaken to estimate the degree of dechlorination process during the experiments. The dechlorination degree ( $\alpha$ ) is defined as the ratio of the removed amount Cl ( $\Delta n_{\text{Cl}}$ ) to the total amount of Cl ( $\Sigma n_{\text{Cl}}$ ) in the starting materials,

$$\alpha = \Delta n_{\text{Cl}} / \Sigma n_{\text{Cl}} = n_{\text{HCl}} / (c_{\text{Cl}} m_0) \quad (\text{i})$$

where  $c_{\text{Cl}}$  and  $m_0$  is the composition of Cl and mass of starting materials, respectively.

The dechlorination degrees of the experiment which was measured periodically are shown in Fig. 7. Both of HCl and/or  $\text{Cl}_2$  may dissolve to the distilled water in the trap. For the higher temperatures (1473 and 1523 K), dechlorination degree



**Fig. 6** Distribution of mole fraction of niobium in the reaction products and estimation of their deposition location in the reaction tube for Exp. #D (a), and distribution of mole fraction of niobium in the reaction products from all experiments (b).

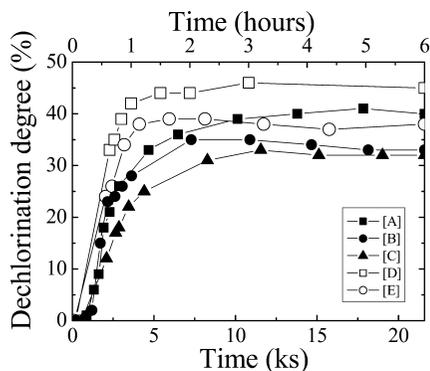
**Table 3** Mass of niobium in the raw material and deposit products.

Exp.#	Raw material		Deposit products <sup>3)</sup>			
	Sample mass (mg)	Niobium mass <sup>1)</sup> (mg)	Chips/Film (mg)	Black (mg)	Gray (mg)	Yellow/white (mg)
A	1979	705 (7.58) <sup>2)</sup>	88.5 (0.95)	69.0 (0.74)	206 (2.22)	341 (3.67)
B	1791	638 (6.86)	129 (1.39)	71.3 (0.77)	65.5 (0.70)	372 (4.00)
C	1741	620 (6.67)	187 (2.01)	59.0 (0.63)	129 (1.39)	245 (2.64)
D	2671	951 (10.2)	312 (3.36)	112 (1.21)	99.8 (1.07)	426 (4.59)
E	3189	1135 (12.2)	350 (3.76)	112 (1.21)	55.5 (0.60)	617 (6.64)

<sup>1)</sup> Niobium content in sample is 35.6 mass%.

<sup>2)</sup> The niobium quantity in mmol is shown in parentheses.

<sup>3)</sup> The composition of niobium in chips/film and black powder is based on EDS analysis listed in Table 2, whereas average niobium mass in gray and yellow/white powder are 75.0 mass% and 56.2 mass%, respectively.

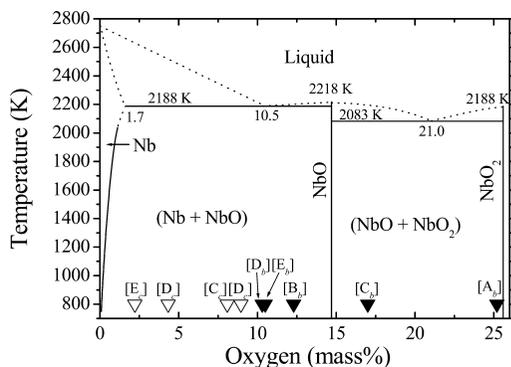


**Fig. 7** Dechlorination degree of all experiments for 6 hours.

decreases significantly. However, it is still not clear whether re-chlorination of the products, such as chips/film, also took place during thermal decomposition, especially in the higher temperature.

#### 4.5 Niobium recovery

Due to the presence of niobium oxide in the products, the recovery of niobium metallic in the experiment can be predicted by using the phase diagram of Nb-O. The calculation is focused to chips, *i.e.*, the products which contain the highest amount of niobium. As shown in Fig. 8, the data of niobium composition in Table 2 are plotted to the phase diagram. The diagram shows that at the room temperature the mass% of oxygen of NbO is 14.7 mass%. By applying lever rule to the plot in the phase diagram, the fraction of Nb and NbO can be calculated. Thus, the recovery of niobium from dechlorination process can be estimated. The frac-



**Fig. 8** Plotting of oxygen content of the chip and black powder products in the Nb-O phase diagram<sup>9)</sup>. The oxygen content of each experiment shows in blank dots for chips and black dot for black powders.

tion of NbO<sub>0.7</sub> was also represented and included in the total fraction of Nb and NbO, since NbO<sub>0.7</sub> also consists of Nb and NbO phases. It can be shown by plotting its oxygen mass% (10.8 mass%) in the Nb-O phase diagram.

Niobium recovery is calculated by the ratio of niobium obtained after reaction with the niobium in the starting materials.

Recovery (%)

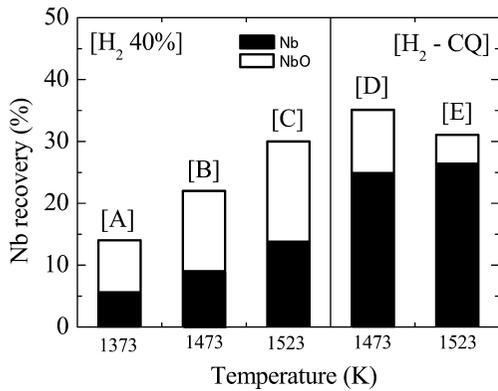
$$= (\text{fraction in phase diagram}) \times (m_p \cdot C_p) / (m_o \cdot C_o) \times 100\% \quad (\text{ii})$$

where  $m_p$ ,  $C_p$  is the mass and concentration niobium in the products, and  $m_o$ ,  $C_o$  is the mass and concentration of niobium in the starting materials.

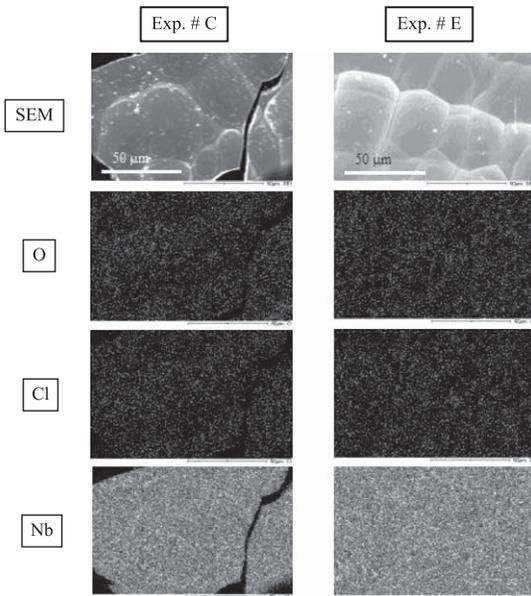
From the calculation, the total mixture phase of

niobium (Nb) and niobium oxide (NbO) in the chips of Exp. #E (2.2 mass% oxygen) was in the fraction of 0.85 and 0.15, respectively. In this study, niobium which was recovered in the chip/film products from dechlorination of niobium pentachlorides was about 25–26% at 1473–1523 K by hydrogen commercial quality gas (see Fig. 9). It was observed that the recovery of niobium tends to increase at higher temperature and by applying higher concentration and purity of hydrogen gas.

Fig. 10 exhibits SEM micrograph of chips from Exp. #C and D. Grain boundaries were found in



**Fig. 9** Estimation of metallic niobium recovery in the chips/films from the dechlorination experiments. Exp. #A is calculated by using the phase fraction of Exp. #B for comparison.

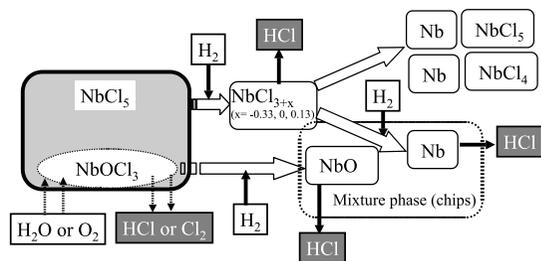
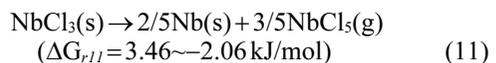
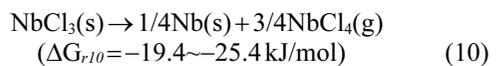
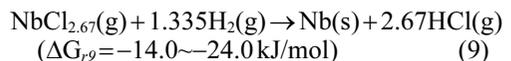
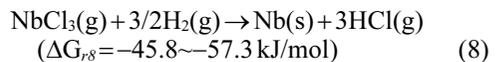
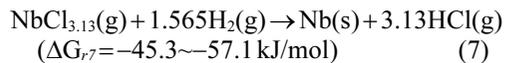
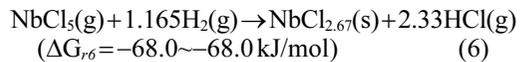
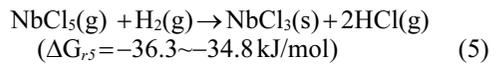
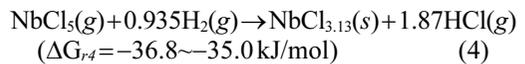
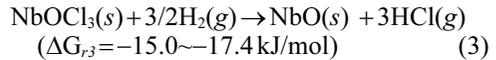


**Fig. 10** SEM micrographs and elements mapping (Nb, O and Cl) of chips from Exp. #C and E.

the chip surface. The elements mapping shows that the higher intensity of image (brighter) indicates the higher composition of element. Furthermore, no segregations are observed in the intergranular region.

#### 4.6 Reaction scheme during thermal decomposition

Based on the product species which were obtained and detected from XRD analysis, a scheme of several reactions that have possibility to take place during thermal decomposition of  $\text{NbCl}_5$  in a reductive atmosphere is drawn in Fig. 11. It is a kind of a compilation of the reaction which were obtained from the experiment results and other report<sup>8)</sup>. Further investigation should be conducted to confirm the detail reaction mechanism during thermal decomposition. The possible reactions and their free energies ( $\Delta G_{r,i}$ ,  $i$ =reaction number) at the range temperature of 1473–1523 K are shown below.



**Fig. 11** Reaction scheme during thermal treatment.

**Table 4** Oxygen balance in the main products during thermal treatment.

Exp. #	Sample mass (mg)	Oxygen input			Total oxygen input (mmol)	Oxygen output <sup>4)</sup> (in the deposit products)		Total oxygen output (mmol)
		Oxygen in samples <sup>1)</sup>		Oxygen in gas flow <sup>2,3)</sup>		Chips/Film	Black powder	
		(mg)	(mmol)	(mmol)		(mmol)	(mmol)	
A	1979	20.0	1.25	0.88	2.13	0.55	1.45	2.00
B	1791	18.1	1.13	0.88	2.01	0.80	0.63	1.43
C	1741	17.6	1.10	0.88	1.98	1.04	0.76	1.80
D	2671	27.0	1.69	0.88	2.57	0.89	0.83	1.72
E	3189	32.2	2.01	0.88	2.89	0.50	0.83	1.32
Average		Oxygen input			2.32	Oxygen output		1.65

<sup>1)</sup> Oxygen content in samples is based on the assumption that the raw material (NbCl<sub>5</sub> and NbClO<sub>3</sub> mixture) contains NbOCl<sub>3</sub> as much as 13.4 mass%.

<sup>2)</sup> Oxygen gas is assumed as much as 100 ppm (0.01%) in the flow of gas, that was used in the thermal treatment.

<sup>3)</sup> The flow time of the gas in the experiment was 12 hours totally, which is including flushing before thermal treatment, heating, soaking and cooling step during thermal treatment.

<sup>4)</sup> The amount of oxygen in other products, such as gray and yellow/white powders is not available.

The free energy of the reactions exhibits that most of the reactions occur spontaneously in the given temperature range. The scheme describes that the formation of the NbO occurs due to the reduction of NbOCl<sub>3</sub> in the raw materials (mixture of NbCl<sub>5</sub> and NbOCl<sub>3</sub>) by hydrogen, according to the reaction (3). It also shows that some intermediate compounds of niobium chlorides, such as NbCl<sub>3+x</sub> (x = -0.33, 0 and 0.13) may take part during decomposition of NbCl<sub>5</sub> to Nb (see reaction (4)–(6)). The formation of niobium subchlorides was detected from XRD analysis from gray powder (Fig. 4). Further, the intermediate compounds (NbCl<sub>3+x</sub>, x = -0.33, 0 and 0.13) were reduced by hydrogen to niobium (reaction (7)–(9)). Some portion of NbCl<sub>3</sub> was decomposed to niobium and higher subchloride as illustrated in reaction (10) and (11), respectively.

## 5. Conclusion

The examination and evaluation of thermal decomposition of NbCl<sub>5</sub> in a reductive atmosphere by using hydrogen gas was conducted. The present study that aims as a preliminary study of hydrogen reduction of NbCl<sub>5</sub>, gives the results that can be summarized as follow.

(1) The process produced niobium in the form of chip with the composition of 98 mass% (Exp. #E: 1523 K; H<sub>2</sub> CQ). It was found that the chips consist of a phase mixture of Nb and NbO by the fraction of 0.85 and 0.15, respectively. Thus, the highest recovery of niobium (Exp.#E) reaches 26%. Niobium oxide in the chips was formed mainly from the reduction of oxychloride in the raw materials.

(2) Utilization of hydrogen and raw materials in higher concentration and purity may increase the niobium fraction in the chip products.

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## References

1. W. Rockenbauer: *Proc. of Int. Symp., Niobium '81*, Nov. 8–11, pp. 1–21 (1981).
2. N. Sato and M. Nanjo: *Metallurgical Transaction B*, **16B**, 9, pp. 639–644 (1985)
3. L.A. Niselson, Ya. M. Polyakov, A.N. Krestovnikov: *Z. Prikladnoi Khimii.*, **37**, 3, pp. 670–672 (1964)
4. R.L. Ripley: USP. 3.104.165 (1963)
5. K.F. Griffiths: USP. 3.085.871 (1963)
6. I. Barin and O. Knacke: *Thermochemical properties of inorganic substances*, Springer Verlag (Weinheim) (1989)
7. C.A. Sutherland and A.G. White: USP. 3.085.855 (1965)
8. W.D. Jamrack: *Rare metal extraction by chemical engineering*, Pergamon press (Oxford), pp. 60–61, 249 (1963)
9. T.B. Massalski (eds.): *Binary alloy phase diagrams*, ASM Int. (Ohio), pp. 2748–49 (1990)