

## Chemical Transport Reaction of Niobium Oxides

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The transport experiment of niobium oxides using  $\text{TeCl}_4$  as a transport agent and the mass spectrometric analysis of gas species in the closed tube were carried out.

In the transport reaction, the starting material,  $\text{NbO}_3$ , at the hot zone was partially oxidized to  $\text{Nb}_{12}\text{O}_{29}$ . A portion of oxygen source was water vapor in the silica tube. The single crystals of  $\text{Nb}_{12}\text{O}_{29}$  were deposited at the cold zone, when the oxide phase at the hot zone was  $\text{NbO}_2$ - $\text{Nb}_{12}\text{O}_{29}$  mixture. About 10 days later, the oxide at the hot zone became a single phase of  $\text{NbO}_2$  and the deposition of  $\text{NbO}_2$  crystals started. It was found by the mass spectroscopy that gas species of  $\text{NbOCl}_3$  and  $\text{NbCl}_5$  were concerned with the transport reaction of  $\text{Nb}_{12}\text{O}_{29}$ . When the mixture of  $\text{NbO}$  and  $\text{NbO}_2$  corresponding to the composition of  $\text{NbO}_{1.8}$  was used as the starting material, the single crystals of  $\text{NbO}_2$  were from the first deposited at the cold zone. The transport rate of  $\text{NbO}_2$  using  $\text{NbO}_{1.8}$  as the starting material was lower than using  $\text{NbO}_2$ . The transport mechanism was discussed from the results of gas analysis.

KEY WORDS: Chemical transport reaction/ Niobium oxide/ Mass spectrometric analysis/

### I. INTRODUCTION

There have recently been several reports on the chemical transport reaction of  $\text{NbO}_2$  material. Sakata *et al.*<sup>1)</sup> succeeded in the growth of single crystals of  $\text{NbO}_2$  and  $\text{Nb}_{12}\text{O}_{29}$  using  $\text{TeCl}_4$  as a transport agent. Kodama *et al.*<sup>2,3)</sup> prepared  $\text{NbO}$  and  $\text{NbO}_2$  crystals using other transport agents such as  $\text{NH}_4\text{Cl}$ . Ritschel *et al.*<sup>4)</sup> reported that the single crystals of  $\text{Nb}_{12}\text{O}_{29}$  were at first deposited and the deposition of  $\text{NbO}_2$  followed. They predicted the gas species equilibrated in the  $\text{NbO}_2$ - $\text{TeCl}_4$  system based on the thermochemical consideration. The difference in composition between a starting material and single crystals obtained have often been observed in the chemical transport reaction. The representative example is the chemical transport of  $\text{Ti}_n\text{O}_{2n-1}$  using  $\text{TeCl}_4$ .<sup>5,6)</sup> As one of the important factors of composition difference, it was found that the starting material was oxidized at the hot zone in the initial stage of the transport.<sup>7)</sup> The second is due to the equilibrium condition that the compositions of oxide in the two component system depends on the oxygen partial pressure and the temperature.<sup>6,7)</sup>

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In the closed system, the oxygen partial pressure is the same in the cold and hot zone, and therefore the composition of the oxide in the cold zone should be different from that in the hot zone. In the transport of  $Ti_nO_{2n-1}$ , the difference of the composition between the hot and cold zones appeared clearly, because of the large temperature dependence of the composition under the same oxygen partial pressure.

This phenomenon may not on the rare case. To clarify the mechanism on the composition change in the transport of  $NbO_2$ , the detailed transport experiments and the gas analysis on the  $NbO_2$ - $TeCl_4$  system were carried out.

## 2. EXPERIMENTALS

### 2.1 Preparation of Starting Materials

The mixtures of niobium metal and  $Nb_2O_5$  powders corresponding to  $NbO_2$  and  $NbO_{1.8}$  compositions were sealed in evacuated silica tubes and heated at  $1000^\circ C$  for 2 days. The sample was pulverized and the same heat treatment was repeated for the sample homogenization. The products were identified by the X-ray powder diffraction method. The sample corresponding to  $NbO_{1.8}$  composition was two phases of  $NbO$  and  $NbO_2$ .

### 2.2 Transport Experiment and Mass Spectrometric Analysis of Gaseous Species

The starting material of 1200 mg and  $TeCl_4$  of 200 mg were charged in a silica tube of 165~175 mm in length and 12.5 mm in diameter. The tube was evacuated to  $10^{-5}$  Torr and then sealed. The tube was placed in the electric furnace with the temperature gradient and after appropriate time of transport reaction the tube was rapidly quenched in water. The single crystals transported and residual starting material were treated with a hydrochloric acid and identified by X-ray diffraction. The compositions of residual starting materials were determined from the weight gain in oxidation of the materials to  $Nb_2O_5$ .<sup>8,9)</sup>

The gas analysis system with a quadrupole spectrometer for the chemical transport reaction is the same as described in the previous paper.<sup>10)</sup> The gas analysis was carried out for the chemical transport of  $NbO_2$  and the mixture of  $NbO_2$  and  $NbO$ . The starting material of 50~70 mg and  $TeCl_4$  of 10~15 mg were used for the gas analysis. The temperatures of the hot and cold zones were  $1050^\circ C$  and  $870^\circ C$  for the  $NbO_2$ - $TeCl_4$  system, and  $1100^\circ C$  and  $870^\circ C$  for the mixed oxides ( $NbO$ - $NbO_2$ )- $TeCl_4$  system.

## 3. RESULTS

### 3.1 Transport Behavior in the $NbO_2$ - $TeCl_4$ System

The change of the transport behavior with time is summarized in Table I. In Run No. 6 and 7, the single crystals of  $NbO_2$  and  $Nb_{12}O_{29}$  were individually depos-

Table I. Results of the transport of NbO<sub>2</sub> using TeCl<sub>4</sub>.  
(NbO<sub>2</sub>: 1200 mg, TeCl<sub>4</sub>: 200 mg, temperature gradient: 1100°C–1030°C)

Run No.	Transport period	Starting material composition		Single crystals	
		phase (by X-ray)	Nb <sub>12</sub> O <sub>29</sub> /NbO <sub>2</sub> (wt)	phase	quantity
1	2.8 (h)	NbO <sub>2</sub> +Nb <sub>12</sub> O <sub>29</sub>	0.19	—	— (mg)
2	50	"	0.27	Nb <sub>12</sub> O <sub>29</sub>	102.7
3	71	"	0.29	"	122.9
4	102	NbO <sub>2</sub>	0.12	"	273.5
5	184	"	0.06	"	296
6	247	"	0.04	Nb <sub>12</sub> O <sub>29</sub>	332.3
				NbO <sub>2</sub>	17.9
7	303	"	0	Nb <sub>12</sub> O <sub>29</sub>	331.2
				NbO <sub>2</sub>	153.1

ited. The shapes of NbO<sub>2</sub> and Nb<sub>12</sub>O<sub>29</sub> were different and two oxide crystals could be therefore separated from each other under a microscope.

At the initial stage of the chemical transport reaction, the starting material of NbO<sub>2</sub> was oxidized and became the mixture of NbO<sub>2</sub> and Nb<sub>12</sub>O<sub>29</sub>. The oxidation of the starting material lasted for 70 h, while the crystals of Nb<sub>12</sub>O<sub>29</sub> deposited at the cold zone. The crystals of Nb<sub>12</sub>O<sub>29</sub> continued to deposit as long as Nb<sub>12</sub>O<sub>29</sub> was contained in the starting material at the hot zone. The transport rate of NbO<sub>2</sub> was 2.5 mg/h. The result that deposition of NbO<sub>2</sub> followed that of Nb<sub>12</sub>O<sub>29</sub> had also been found by Ritschel *et al.*<sup>4)</sup>

### 3.2 Role of Water Content in Silica for Oxidation of Starting Material

The oxygen source for oxidation of the starting materials might be oxygen gas produced from reaction of NbO<sub>2</sub> with TeCl<sub>4</sub>. The other oxygen source may be water vapor coming from silica tube. Therefore, the chemical transport behavior using a special silica tube (Toshiba Ceramics T-2030) which contained 5 ppm water was compared with using a normal one containing 100~150 ppm water. The result is shown in Table II. The degree of oxidation of the starting material using the special silica tube was lower than using the normal silica tube. It was confirmed that the water contained in the silica contributed to oxidation of the starting material, but was not the main oxygen source.

Table II. Effect of transport by water content.  
(NbO<sub>2</sub>: 1200 mg, TeCl<sub>4</sub>: 200 mg, temperature gradient: 1100–1030°C, transport time: 71 h)

Silica tube	Starting material composition		Single crystal	
	phase (by X-ray)	Nb <sub>12</sub> O <sub>29</sub> /NbO <sub>2</sub> (wt)	phase	quantity (mg)
Normal silica (H <sub>2</sub> O: 100~150 ppm)	NbO <sub>2</sub> +Nb <sub>12</sub> O <sub>29</sub>	0.19	Nb <sub>12</sub> O <sub>29</sub>	115
Special silica (H <sub>2</sub> O: ~5 ppm)	NbO <sub>2</sub> +Nb <sub>12</sub> O <sub>29</sub>	0.29	Nb <sub>12</sub> O <sub>29</sub>	123

### 3.3 Chemical Transport of NbO–NbO<sub>2</sub> Mixture

Table III shows the results of the transport using the mixture of NbO and NbO<sub>2</sub> as the starting material. The residuals at the hot zone and the crystals produced were only NbO<sub>2</sub> independent of the period of the transport reaction. It is interesting that the transport rate of NbO<sub>2</sub> (0.07 mg/h) is greatly lower than in the case of the transport using NbO<sub>2</sub> as a starting material. This suggests the difference of the transport mechanism.

Table III. Results of the transport using mixture of NbO<sub>2</sub>+NbO (composition of NbO<sub>1.8</sub>) as starting material (NbO<sub>1.8</sub>: 1050 mg, TeCl<sub>4</sub>: 200 mg, temperature gradient: 1000°C–1030°C)

Transport period	Starting material phase	Single crystals	Transport rate
93 (h)	NbO <sub>2</sub>	NbO <sub>2</sub>	0.065 (mg/h)
246	NbO <sub>2</sub>	NbO <sub>2</sub>	0.071

### 3.4 Gas Analysis in the NbO<sub>2</sub>–TeCl<sub>4</sub> System

The mass spectrum is shown in Fig. 1. The ions, O<sub>2</sub><sup>+</sup>, HCl<sup>+</sup>, Nb<sup>+</sup>, NbO<sup>+</sup>, NbCl<sup>+</sup>, NbOCl<sup>+</sup>, NbCl<sub>2</sub><sup>+</sup>, NbCl<sub>3</sub><sup>+</sup>, NbOCl<sub>3</sub><sup>+</sup>, NbCl<sub>4</sub><sup>+</sup> and Te<sub>2</sub><sup>+</sup> were observed. The relative intensities of the ions are shown in Table IV. The ions, O<sub>2</sub><sup>+</sup>, HCl<sup>+</sup> and Te<sub>2</sub><sup>+</sup> indicated the presence of the gas of O<sub>2</sub>, HCl and Te<sub>2</sub> in the closed tube, respectively.

The niobium species observed may suggest the presence of NbOCl<sub>3</sub>, NbCl<sub>5</sub>, NbCl<sub>4</sub>, NbCl<sub>3</sub> and NbCl<sub>2</sub> gas as gas species. The mass spectra were separately measured for NbCl<sub>5</sub> and NbCl<sub>4</sub>. The relative intensities of ions observed are shown in Table V. The intensity of HCl<sup>+</sup> is strong compared with the other ions. In the

Table IV. Ions species and their relative intensities

Ion species (70 eV)	NbO <sub>2</sub> –TeCl <sub>4</sub> 1100/870°C	NbO <sub>1.8</sub> –TeCl <sub>4</sub> 1100/870°C
NbCl <sub>4</sub> <sup>+</sup>	0.7	—
NbOCl <sub>3</sub> <sup>+</sup>	98.0	—
NbCl <sub>3</sub> <sup>+</sup>	3.7	—
NbOCl <sub>2</sub> <sup>+</sup>	100	2.7
NbCl <sub>2</sub> <sup>+</sup>	24.3	1.7
NbOCl <sup>+</sup>	55.0	10.9
NbCl <sup>+</sup>	51.6	35.8
NbO <sup>+</sup>	44.5	88.3
Nb <sup>+</sup>	45.2	100
O <sub>2</sub> <sup>+</sup>	27.1	trace
HCl <sup>+</sup>	215.7	1900
Te <sub>2</sub> <sup>+</sup>	1.6	—
Te <sup>+</sup>	—	15.2

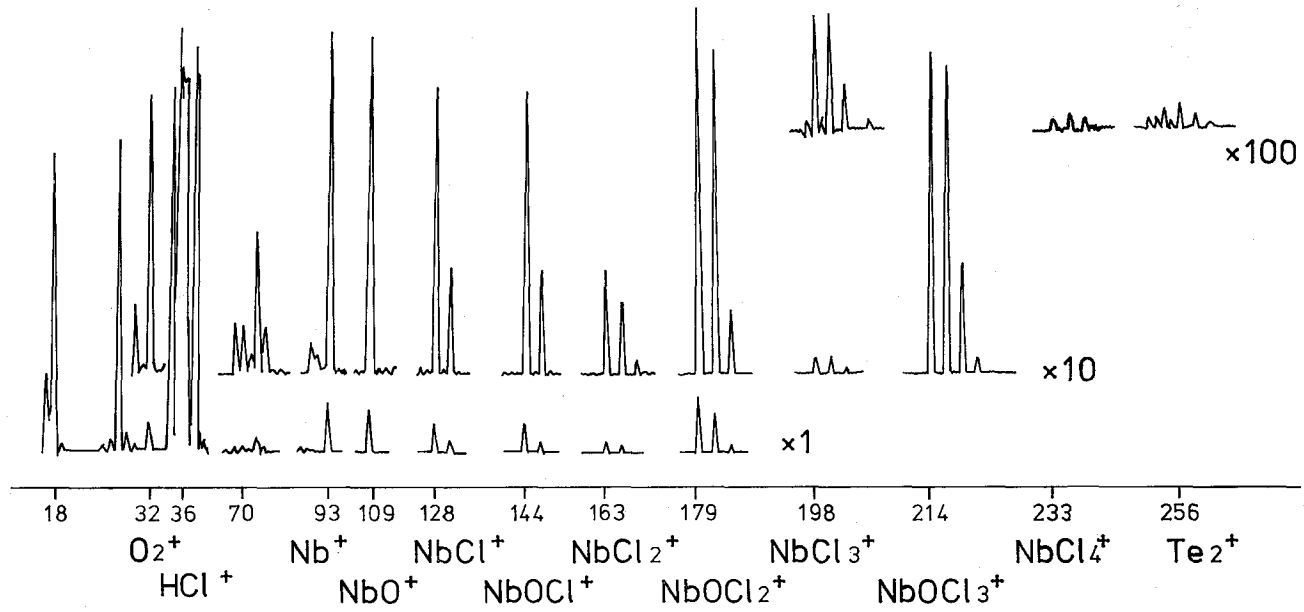


Fig. 1. Mass spectrum of gases in the  $\text{NbO}_2\text{-TeCl}_4$  system (Temperature gradient:  $1050^\circ\text{C}\text{-}870^\circ\text{C}$ , Ionization energy:  $70\text{ eV}$ ).

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Table V. Mass analysis of NbCl<sub>5</sub> and NbOCl<sub>3</sub>

Substance	Temperature	Ions observed and the relative intensities
NbCl <sub>5</sub>	830°C	NbCl <sub>4</sub> <sup>+</sup> (5.3), NbOCl <sub>3</sub> <sup>+</sup> (2.8), NbCl <sub>3</sub> <sup>+</sup> (10.2), NbOCl <sub>2</sub> <sup>+</sup> (13.9), NbCl <sub>2</sub> <sup>+</sup> (37.4), NbOCl <sup>+</sup> (16.5), NbCl <sup>+</sup> (70.4), NbO <sup>+</sup> (27.4), Nb <sup>+</sup> (100)
NbOCl <sub>3</sub>	1050°C	NbOCl <sub>3</sub> <sup>+</sup> (10.0), NbCl <sub>3</sub> <sup>+</sup> (1.0), NbOCl <sub>2</sub> <sup>+</sup> (58.8), NbCl <sub>2</sub> <sup>+</sup> (20.3), NbOCl <sup>+</sup> (57.6), NbCl <sup>+</sup> (100), NbO <sup>+</sup> (13.9), Nb <sup>+</sup> (17.6)

spectrum of NbOCl<sub>3</sub>, NbOCl<sub>3</sub><sup>+</sup> and the fragment ions with the lower mass were observed. For NbCl<sub>5</sub>, the fragment ions of NbCl<sub>5</sub> and the ion species corresponding to NbCl<sub>3</sub> were observed. The ion species of NbCl<sub>3</sub><sup>+</sup>, NbOCl<sub>2</sub><sup>+</sup>, NbOCl<sup>+</sup> are derived from NbCl<sub>3</sub> molecule which is produced by reaction of NbCl<sub>5</sub> and H<sub>2</sub>O. Gaseous species of NbCl<sub>4</sub> are unstable and decompose into NbCl<sub>5</sub>, NbCl<sub>3</sub> and NbCl<sub>2</sub> gases at high temperature.<sup>11)</sup>

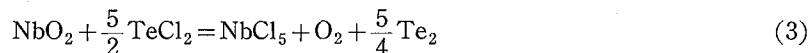
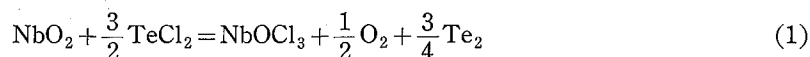
Compared with the relative intensity of the niobium ion species in Table V, the results of the spectrum in Table VI indicated that NbOCl<sub>3</sub> and NbCl<sub>5</sub> molecules were the main niobium gaseous species in the NbO<sub>2</sub>-TeCl<sub>4</sub> system. The ions of NbCl<sub>2</sub><sup>+</sup> and NbCl<sub>3</sub><sup>+</sup> may be mainly the fragments from NbCl<sub>5</sub> and NbOCl<sub>3</sub> molecules.

### 3.5 Gas Analysis in the (NbO-NbO<sub>2</sub>)-TeCl<sub>4</sub> System

The mass spectrum and the relative intensities of the ions are shown in Fig. 2 and Table IV, respectively. The ions observed are NbOCl<sub>2</sub><sup>+</sup>, NbOCl<sub>2</sub><sup>+</sup>, NbCl<sup>+</sup>, NbO<sup>+</sup>, Nb<sup>+</sup>, Te<sup>+</sup>, HCl<sup>+</sup> and trace of O<sub>2</sub><sup>+</sup>. The ions of NbOCl<sub>2</sub><sup>+</sup> suggested the presence of NbOCl<sub>3</sub>, although NbOCl<sub>3</sub><sup>+</sup> was not observed. The intensity of HCl<sup>+</sup> was far strong compared with that of the niobium ion species.

## 4. DISCUSSION

As 90% of TeCl<sub>4</sub> dissociates into TeCl<sub>2</sub> and Cl<sub>2</sub> at 900°C, the reactions should be represented by following equations.



All the reactions produce the oxygen gas. This oxygen gas is considered to be oxygen source for oxidation of the starting material of NbO<sub>2</sub>. As the oxygen gas is consumed for oxidation of NbO<sub>2</sub> and the reaction proceeds forwards, the gas of TeCl<sub>2</sub> and Cl<sub>2</sub> would be almost consumed. In fact, the ions of TeCl<sub>2</sub><sup>+</sup> and TeCl<sup>+</sup>

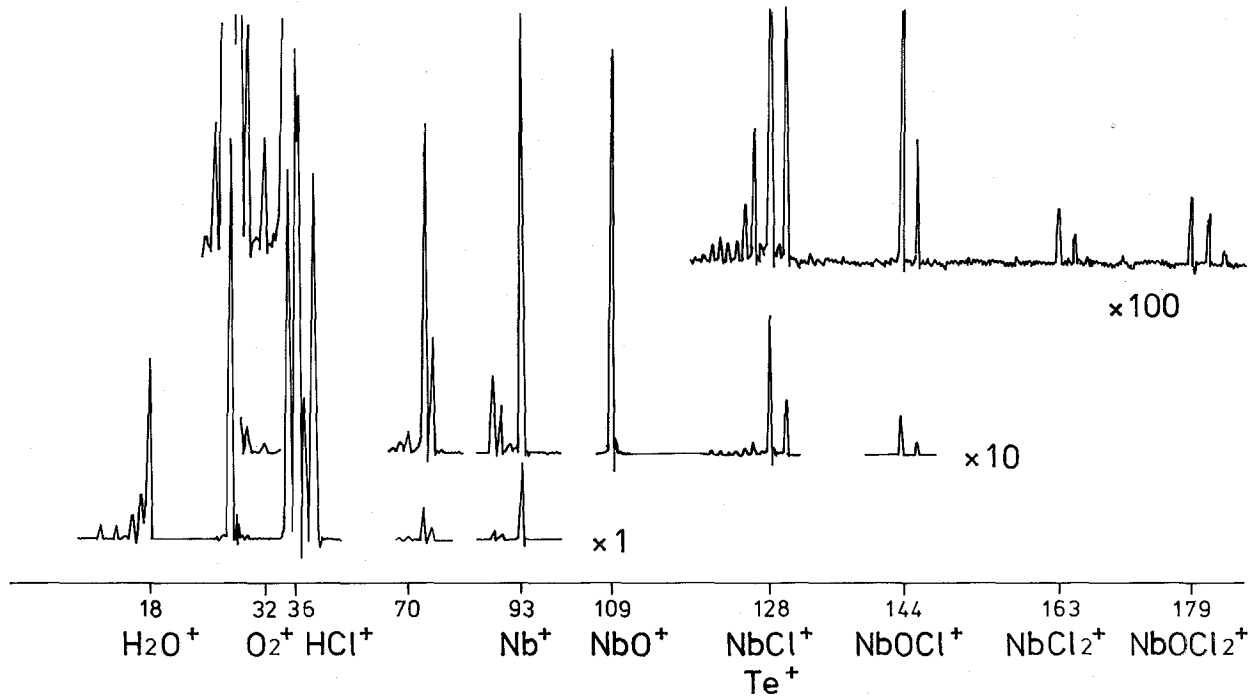
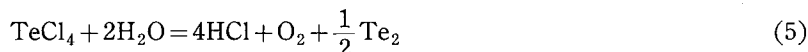


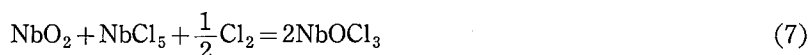
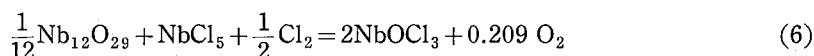
Fig. 2. Mass spectrum of gases in the Nb<sub>1.8</sub>-TeCl<sub>4</sub> system (Temperature gradient: 1100°C-890°C, Ionization energy: 70 eV).

were not observed and the intensities of the ion species derived from  $\text{NbOCl}_3$  and  $\text{NbCl}_5$  were very strong.

On the other hand, the existence of  $\text{HCl}$  gas means that  $\text{TeCl}_4$  is partly hydrolyzed by water vapor in the closed tube.<sup>12)</sup>



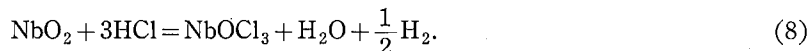
This oxygen gas from water vapor also oxidizes  $\text{NbO}_2$ . It is reported that  $\text{NbCl}_5$  and  $\text{HCl}$  can act as transport agents of  $\text{NbO}_2$ , respectively.<sup>3)</sup> It is therefore considered that the transport system  $\text{NbO}_2\text{-TeCl}_4$  changes to mainly the systems  $\text{Nb}_{12}\text{O}_{29}\text{-NbCl}_5$  which will be followed by the system  $\text{NbO}_2\text{-NbCl}_5$ . The examples of assumed transport reaction is then as follows:



In the deposition of  $\text{Nb}_{12}\text{O}_{29}$ , the oxygen gas coming from  $\text{H}_2\text{O}$  and reaction (1)~(4) acts not only as the oxidizing agent of starting material but also as the oxygen source necessary for formation of  $\text{Nb}_{12}\text{O}_{29}$  crystal. The supply of oxygen gas will stop after the  $\text{Nb}_{12}\text{O}_{29}$  phase at the hot zone is used up, and the transport of  $\text{NbO}_2$  will start according to the reaction (7).

In the  $(\text{NbO}\text{-NbO}_2)\text{-TeCl}_4$  system, the starting material changed to the single phase of  $\text{NbO}_2$  by oxidation of  $\text{NbO}$ . The very strong intensity of the  $\text{HCl}^+$  species in the mass spectrum indicated that the predominant gas species as transport agent was  $\text{HCl}$ . The transport system  $(\text{NbO}\text{-NbO}_2)\text{-TeCl}_4$  changed to mainly the system  $\text{NbO}_2\text{-HCl}$ .

The transport reaction is as follows:



The difference in the transport rate of  $\text{NbO}_2$  between the  $\text{NbO}_2\text{-TeCl}_4$  system may be mainly due to the difference of the transport agents.

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