

Calcium-Deoxidation of Nb and Ti in Ca-saturated CaCl_2 Molten salt

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Abstract

Niobium was deoxidized under Ca(liquid)-CaO(solid) equilibrium at 1273K to a level below the lower limit of quantitative chemical analysis, 50 mass ppm oxygen. Because Ca does not react with Nb and Ti, it is easy to remove the excess Ca and the byproduct CaO. The oxygen concentration in Nb and Ti was the same whether the molten salt was applied or not. Due to direct contact with Ca liquid, however, Nb and Ti were contaminated by carbon and nitrogen. When Ca was supplied as vapor into a CaO-saturated CaCl_2 melt, Ca could saturate in the CaCl_2 melt, and the impurity carbon and nitrogen in Nb was minimized. By Ca-halide flux deoxidation using the Ca-saturated but CaO-unsaturated CaCl_2 melt, the residual resistivity ratio, RRR, of Nb exceeded that of the starting commercial Nb wire by 500. The oxygen content in Nb was estimated to be smaller than a single ppm. The activity of CaO in the molten salt was evaluated at 1273K using the equilibrium oxygen concentration in Ti.

1. Introduction

Niobium is a promising radio-frequency superconductor for applications in quantum physics because of the good ductility and high thermal conductivity of thin sheets [1,2]. Niobium-titanium alloy is one of the practical superconducting materials applicable for power cables. Their mechanical and physical properties are sensitive to the interstitial atoms such as oxygen, nitrogen and carbon [3,4], and oxygen can contaminate the superconductor during the cold deformation and welding. Therefore, the deoxidation method suitable for the superconducting device is needed [1,2].

Calcium has a strong thermodynamic affinity with oxygen. The deoxidation using Ca can be thermodynamically expected to a very low oxygen concentration level [5-7]. In addition, the combination of Nb, Ca and CaO and that of Ti, Ca and CaO can coexist in equilibrium without alloying, respectively [6,7]. The Ca deoxidation of Nb could be operated in an inert gas atmosphere and at a lower temperature, comparing with the external gettering method. The experimental studies of Ca deoxidation, however, showed that the residual oxygen concentration in Nb was still 35-110 mass ppm [6,7]. Because they were not coincident with the theoretical values (below mass ppb level) from the accessed thermodynamic data of Nb [5-7], it is still an open technical improvement.

Okabe *et al.* found that the “halide flux deoxidation” using a molten salt such as CaCl_2 could successively deoxidize Ti to an oxygen level below that obtained by the Ca deoxidation [8,9]. The principle of the halide flux deoxidation is that the activity of the by-product CaO decreases by solving CaO in the halide melt. We expect that the Ca-halide flux deoxidation can be also applied to Nb.

The purpose of this work is to examine experimentally the applicability of the Ca- CaCl_2 flux deoxidation method towards the preparation of extra low oxygen niobium, which can not achieved by the simple Ca deoxidation. Evaluations of the Nb purity under the Ca-CaO- CaCl_2 equilibrium show thermodynamically the highest oxygen concentrations in the Ca deoxidation and in the Ca- CaCl_2 flux deoxidation. Therefore, this work tested also the deoxidation equilibrium in Nb and Ti using the Ca- and CaO-saturated CaCl_2 melt, comparable with previous studies using the coexistence of the liquid Ca and the solid CaO [5-7,10].

2. Concept and Requirements

The principle of Ca-halide flux deoxidation for Ti was previously reported [8,9]. The free energy change associated with the solution of oxygen in Nb, ΔG°_1 , can be shown as,

$$\Delta G^\circ_1 = -RT \ln \frac{f_{\text{O in Nb}} \cdot [\text{mass\% O in Nb}]}{\sqrt{P_{\text{O}_2}}}, \quad (1)$$

where [mass%O in Nb] is the equilibrium concentration of oxygen (mass%) in Nb at temperature T , and $f_{\text{O in Nb}}$ the Henrian activity coefficient of oxygen in Nb. The oxygen partial pressure (p_{O_2}) in the Ca deoxidation is represented as,

$$\Delta G^\circ_f(\text{CaO}) = -RT \ln \frac{a_{\text{CaO}}}{a_{\text{Ca}} \cdot \sqrt{p_{\text{O}_2}}}, \quad (2)$$

where $\Delta G^\circ_f(\text{CaO})$ is the standard free energy of CaO formation, a_{Ca} and a_{CaO} are the activity of Ca and CaO, respectively. By combining the above,

$$\ln [\text{mass\%O in Nb}] = \frac{\Delta G^\circ_f(\text{CaO}) - \Delta G^\circ_1}{RT} + \ln \frac{a_{\text{CaO}}}{a_{\text{Ca}} \cdot f_{\text{O in Nb}}}. \quad (3)$$

When Ca and CaO, for example, coexists as the binary system at 1273 K, p_{O_2} , a_{Ca} and a_{CaO} can be calculated as $10^{-41.21}$ atm, 0.991 and 1.00, respectively, from the thermodynamic database [11-13]. Using Eq. (3) and the assessed ΔG°_1 , the equilibrium oxygen concentration in Nb was estimated as 0.027 mass ppb at 1273 K [6,7,14].

By keeping a_{Ca} nearly unity and $f_{\text{O in Nb}}$ constant, the decrease of a_{CaO} in Eq. (3) causes an intensive deoxidation compared with the Ca-CaO equilibrium. The dissolution of CaO into the CaCl_2 melt to decrease a_{CaO} is here examined around 1273 K. It can remove CaO precipitation on the Nb surface, and assist a continuous oxygen flow over the surface. The evaporation of the molten CaCl_2 can be suppressed below 1600 K [15], while efficient oxygen diffusion in the Nb bulk occurs above 1000 K [6]. The equilibrium vapor pressure of liquid Ca (>1112K) is high enough to deoxidize Nb by the vapor [15]. Although Ca and Nb are mutually almost insoluble[6] and the thermodynamic data in the binary system of Nb-O were well assessed [14], neither the solubility of Nb in CaCl_2 nor that of Cl in Nb are known. Probably they are small and the thermodynamic effect of Nb on the Nb-Ca-Cl-O quaternary system is here neglected.

The available binary phase diagrams related with the ternary Ca-Cl-O system are summarized for 1273 K in **Fig.1** [7]. The activity a_{Ca} was measured at 1473 K under CaO saturation to be 0.86 in both the regions (A) and (B) in Fig.1, while it decreased significantly in the region (D) [16]. This work utilizes three equilibria ((A):Nb+Ca+CaO, (B):Nb+Ca+CaO+ CaCl_2 , (C):Nb+Ca+ CaCl_2), where a_{Ca} is commonly 0.991 at 1273 K. Although Niiyama *et al.* [10] reported on the feasibility of Ca- CaCl_2 flux deoxidation using a CaO crucible, the oxygen concentration in Nb was higher than under Ca-CaO equilibrium. This was because a_{CaO} was kept unity in the region (D), while a_{Ca} was reduced. Here, the region (C) will be studied, where a_{CaO} is smaller than unity but a_{Ca} remains 0.991.

3. Experimental

A Nb wire of 1.5 mm in diameter or a Nb sheet refined by electron-beam vacuum melting (1 mm thick) was used as a starting material. The sample was cut into about 0.1 g pieces suitable for chemical analysis, or cut longer than 180 mm for electric resistivity measurements. The contaminated surface of the specimen was etched by the HF solution before use.

For Ca-CaO deoxidation equilibrium, Nb specimens were inserted into the stainless steel tube (20 mm i.d.) whose one end had been welded. Sufficient amounts of pure Ca and CaO powder (>98%, calcined in air at 1473 K to anhydrate and to remove carbonate) were added so that the molten Ca could cover the whole surface of the Nb specimens. The stainless steel tube arc-welded was heated for the period considering the oxygen diffusion in Nb bulk [6].

Fig. 2 shows the experimental arrangement for halide flux deoxidation. Ten Nb specimens were inserted into the pure Ti crucible (25 mm i.d.), in which about 5 g CaCl_2 (99.9%, anhydrated at 873K in vacuum) was filled. 0-1.5 g CaO powder was added to CaCl_2 in order to control a_{CaO} . Ca was supplied in the gaseous form to the molten CaCl_2 to avoid contamination of the specimens by impurities in Ca. The stainless steel vessel was tightened between the two disks, and heated at 1273 K for 172.8 ks. Resultantly the vessel was sealed completely by the Ca melt. After cooling in the furnace, Ca, CaO and CaCl_2 were separated from the specimens with water and dilute acetic acid.

The oxygen and nitrogen contents were analyzed by an inert gas fusion - infrared absorption method using LECO TC-336. The lowest limits of the quantitative analysis for Nb were 50 ppm and 5 ppm for oxygen and nitrogen, respectively [7]. The carbon and calcium contents were analyzed using a LECO CS-444 and ICP-AES, respectively. The electric resistance $R(T)$ was measured at 273 K, 77 K and 4.2 K by the four probe method. An external magnetic field was applied in the measurement at 4.2 K to break the superconducting state [7,17].

4. Results and Discussion

4.1 Equilibria of Ca-CaO and Ca-CaO- CaCl_2

Table 1 shows the annealing conditions and impurity concentrations in the Nb specimens under Ca-CaO equilibrium ((A) in Fig. 1). When Nb contacted directly with the liquid Ca, all the Nb specimens were deoxidized to a level below 30 mass ppm, which was below the lower limit of the quantitative analysis (50 ppm). Nitrogen concentrations were independent of the experimental conditions, and increased slightly from the initial values. This increase was

caused by the residual nitrogen gas in the reaction tube and/or by the presence of nitrogen in the used materials. As calcium has a weaker affinity with nitrogen than Nb, we cannot expect thermodynamically to remove nitrogen from Nb [9].

Table 2 shows the annealing conditions and impurity concentrations in the Nb specimens, using the molten CaCl_2 . The used composition of 37.3 mol% CaO -62.7 mol% CaCl_2 corresponds to the two phase region of pure CaO + molten CaCl_2 [18]. Because of the strong hydration due to the atmospheric moisture, no compositional analysis could be employed. The significant hydrogen gas evolution by the hydration in water with the mixture of CaO and the molten salt, however, suggested that a large amount of Ca dissolved in the mixture. It is assumed that Ca could be supplied as vapor and that it could saturate in the molten CaCl_2 (about 6 mol% Ca at 1273 K [19]). The oxygen concentrations in Table 2 were taken as the values in equilibrium with Ca saturated in CaCl_2 + pure solid CaO + molten CaCl_2 (Ca saturation), i.e., as the values for the equilibrium (B) in Fig. 1.

The oxygen concentrations in the two cases, (A) Ca - CaO coexistence and (B) Ca - CaO - CaCl_2 coexistence, are compared in **Fig. 3**. When the gaseous Ca reacted with Nb, widely scattered analytical values such as 150-500 ppm oxygen were often recorded [6]. Such significant scatter was not detected in our 5-10 specimens that were heated simultaneously, probably because the Nb specimens were well wet with Ca and/or CaCl_2 . Although most of the data were below the lower limit of the quantitative analysis and some negative values were recorded, no quantitative difference between the two cases can be found. This implies that p_{O_2} in the Ca - CaO - CaCl_2 equilibrium, (B), was not far from p_{O_2} in the Ca - CaO equilibrium, (A).

As shown in Fig. 3, the oxygen concentrations in the both cases were lower than those in previous studies which allowed a direct contact with the molten Ca [5,6]. Note again that the reported oxygen concentrations were about a million times higher than the extrapolation from the thermodynamic assessment [6,7,14]. As the possible reasons of this discrepancy, Ca penetration into the Nb bulk or CaO precipitation in the Nb specimens were suggested [6]. Ca was, however, not detected in the present study as may be derived from Table 1. It should be noted that the reported data cited in Fig. 3 were analyzed by the same method as used in the present study, and they were close to the lower limit of the quantitative analysis.

4.2 Carbon contamination

The direct contact with Ca and CaO caused carbon contamination. A black film was often precipitated on the Nb specimens, when they had reacted with Ca liquid. The carbon concentration exceeded over 1300 mass ppm when the film was not removed (see Table 1). The film was probably a kind of carbide or carbon, although it could not be identified by the

X-ray diffraction analysis. The metallic Ca tends to form calcium carbide or calcium carbonate when exposed to air, while Ca does not have a thermodynamic potential high enough to remove carbon from Nb. Therefore, the impurity carbon in Ca can become transferred into the Nb specimens. The concentrated carbon near the Nb surface might have delayed the oxygen diffusion when liquid Ca was used.

The film formation had been never observed when the molten salt was used, and the increase of carbon concentration was suppressed (see Table 2). This suggests that the CaCl_2 melt reacted as a buffer if it could dissolve carbon, or that a distillation mechanism of Ca vapor effectively prevented from the carbon contamination in Nb.

4.3 Deoxidation in the molten CaCl_2

(a) Deoxidation of Niobium and Titanium

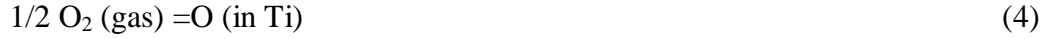
Analytical data before and after the CaCl_2 flux deoxidation were listed in **Table 3**. The oxygen concentrations in Nb after the experiments were about 30 mass ppm. The nitrogen and carbon concentrations did not increase, and they were close to those of the initial specimens. The existence of Ti in the reaction vessel does not disturb the Nb-Ca-O-Cl equilibrium, and the oxygen in Ti simply acts as p_{O_2} sensor [9].

Fig. 4 shows the oxygen concentrations in the Ti specimens heated with the Nb specimens. The oxygen concentrations under the equilibrium of Ti-Ca-CaO, Ti-Nb-Ca-CaO and Ti-Nb-Ca-CaO- CaCl_2 were very close, i.e., 481 ± 63 ppm, 465 ± 23 ppm and 464 ± 15 ppm, respectively. The existence of Nb did not interfere with the Ca deoxidation of Ti, because the oxygen affinity of Nb is weaker than that of Ti and Ca. The oxygen concentrations in Ti were well coincident with recent results for Ti-Ca-CaO and Ti-Ca-CaO- CaCl_2 [8,9,20-22]. These coincidences indicate that the other thermodynamic properties such as p_{O_2} and a_{Ca} should be the same for these equilibria, and that the deoxidation capacity of Ca was not affected by CaCl_2 . This result simultaneously verifies the previous assumption that the Ca vapor can saturate the molten CaCl_2 .

By reducing the CaO fraction in the CaCl_2 melt, the oxygen concentration in Ti decreased as shown in Fig. 4, and approached to the 60-70 ppm level when CaO had not been added initially. The previous studies reported that the scatter in the range of 16-90 ppm depended on the amount of CaO derived from deoxidation [8,9]. Fig. 4 shows clearly that the dissolution of CaO into the halide flux is not effective for the deoxidation of Ti. Therefore, it is essential for the halide flux deoxidation to remove CaO from the halide flux supplied for deoxidation.

(b) Activity of Oxygen and CaO

The oxygen equilibrium in Ti can be written as,



$$\Delta G^\circ_6 = -RT \ln \frac{f_{\text{O in Ti}} \cdot [\text{mass\% O in Ti}]}{\sqrt{P_{\text{O}_2}}}, \quad (5)$$

where $f_{\text{O in Ti}}$ is the Henrian activity coefficient of oxygen in Ti, and constant at our conditions [22]. Supposing that $f_{\text{O in Ti}}$ in Eq.(5) was the same in the Nb-Ti-Ca-CaO-CaCl₂ system, P_{O_2} can be evaluated by the thermodynamic data for the Ti-O binary system [22] and the analyzed concentration of oxygen (mass%) in Ti, [mass% O in Ti].

$$\ln [\text{mass\% O in Ti}] = \frac{\Delta G^\circ_f (\text{CaO}) - \Delta G^\circ_6}{RT} + \ln \frac{a_{\text{CaO}}}{a_{\text{Ca}} \cdot f_{\text{O in Ti}}}. \quad (6)$$

We may assume that the activities a_{Ca} for the three equilibria (Ti-Nb-Ca-CaO-CaCl₂(B), Ti-Nb-Ca-CaO(A), Ti-Ca-CaO(A)) are commonly 0.991, because the oxygen concentrations in Ti under these equilibria were identical. Then Eq. (6) shows that a_{CaO} is proportional with [mass% O in Ti]. The right scale of Fig. 4 for a_{CaO} was thus calculated. Tago *et al.* [23] reported a_{CaO} in the CaO-CaCl₂ flux in equilibrium with Ca-Ag alloys at 1673 K. Although temperatures were different, the compositional dependency was common.

4.4 Electric resistivity

The residual amounts of interstitial elements affect the electric resistivity, $\rho(T)$, which is a good measure to evaluate the purity. The residual resistivity ratio (RRR) was commonly used for purity evaluation of the highly purified niobium [1,2,4,7,24-26]. Here it is defined as,

$$\text{RRR} = \frac{\rho(273\text{K})}{\rho(4.2\text{K})} = \frac{R(273\text{K})}{R(4.2\text{K})} \quad (7)$$

where $R(273\text{K})$ and $R(4.2\text{K})$ are the measured resistance at 273 K and 4.2 K, respectively.

Assuming that the impurities in our sample were oxygen, nitrogen, carbon and tantalum, $\rho(4.2\text{K})$ is expressed as,

$$\begin{aligned} \rho(4.2\text{K}) &= \rho_0(4.2\text{K}) + \Delta\rho_{\text{O}} + \Delta\rho_{\text{N}} + \Delta\rho_{\text{C}} + \Delta\rho_{\text{Ta}} \\ &= 4.5 \times 10^{-4} + 450 X_{\text{O}} + 520 X_{\text{N}} + 430 X_{\text{C}} + 25 X_{\text{Ta}} \text{ (}\mu\Omega\text{cm)} \end{aligned} \quad (8)$$

where $\rho_0(4.2\text{K})$ is the intrinsic value related with lattice vibration, and $\Delta\rho_i$ is the contribution of electron scattering by an interstitial impurity i [4]. The latter is proportional with the solute molar fraction, X_i [4,27].

Table 4 shows $\rho(4.2\text{K})$ and RRR for the Nb wires that were deoxidized at 1273 K with CaCl_2 and CaO . Applying Eq.(8) with the measured $\rho(4.2\text{K})$, X_{N} , X_{C} and X_{Ta} , X_{O} were calculated. This evaluation gave 72 ± 6 mass ppm oxygen for the starting Nb wire after annealing in vacuum, and not far from the analytical value (90 ± 20 ppm) [26]. RRR increased as the decrease of p_{O_2} that was deduced by the oxygen concentration in Ti [22]. The evaluated oxygen concentrations in the deoxidized samples were of a single ppm level or even negative values. This result supports the thermodynamic extrapolation from the Nb-O assessed dataset. The final judgment for the equilibrium oxygen concentration in Ca-saturated CaCl_2 molten salt should be based on more reliable characterization techniques [4]

For the external gettering, higher optimized values of RRR were reported as in Table 4 [17,27]. The RRR obtained in the present study was satisfactorily high, considering that a commercial wire was used as the starting material. We believe that our method may still hold the potential for higher values of RRR, for example, by reducing the impurity contamination such as nitrogen and carbon.

5. Conclusions

When Ca was supplied as vapor into CaO-saturated CaCl_2 melt in case (B) of Fig. 1, both Nb and Ti were simultaneously deoxidized. Because the oxygen concentration in Ti was the same as that under Ca-CaO equilibrium (A), it was found that Ca could saturate in CaCl_2 melt and that the Ca-saturated molten salt could act as an efficient media for deoxidation. Nb was deoxidized below the lower limit of quantitative chemical analysis, 50 ppm, and the contamination of carbon and nitrogen was suppressed when the molten salt was applied.

The Ca-halide flux deoxidation was studied in the compositional range of (C). Oxygen was removed from Ti to below 100 ppm as reported previously, and the activity of CaO in the Ca-saturated CaCl_2 melt was evaluated using the oxygen concentration in Ti. The oxygen content in Nb was again below the lower limit of quantitative analysis. However, it was estimated to be smaller than a single ppm, using the electric resistivity at 4.2K. The residual resistivity ratio, RRR, of Nb increased to 516 from 61 of the commercial Nb wire.

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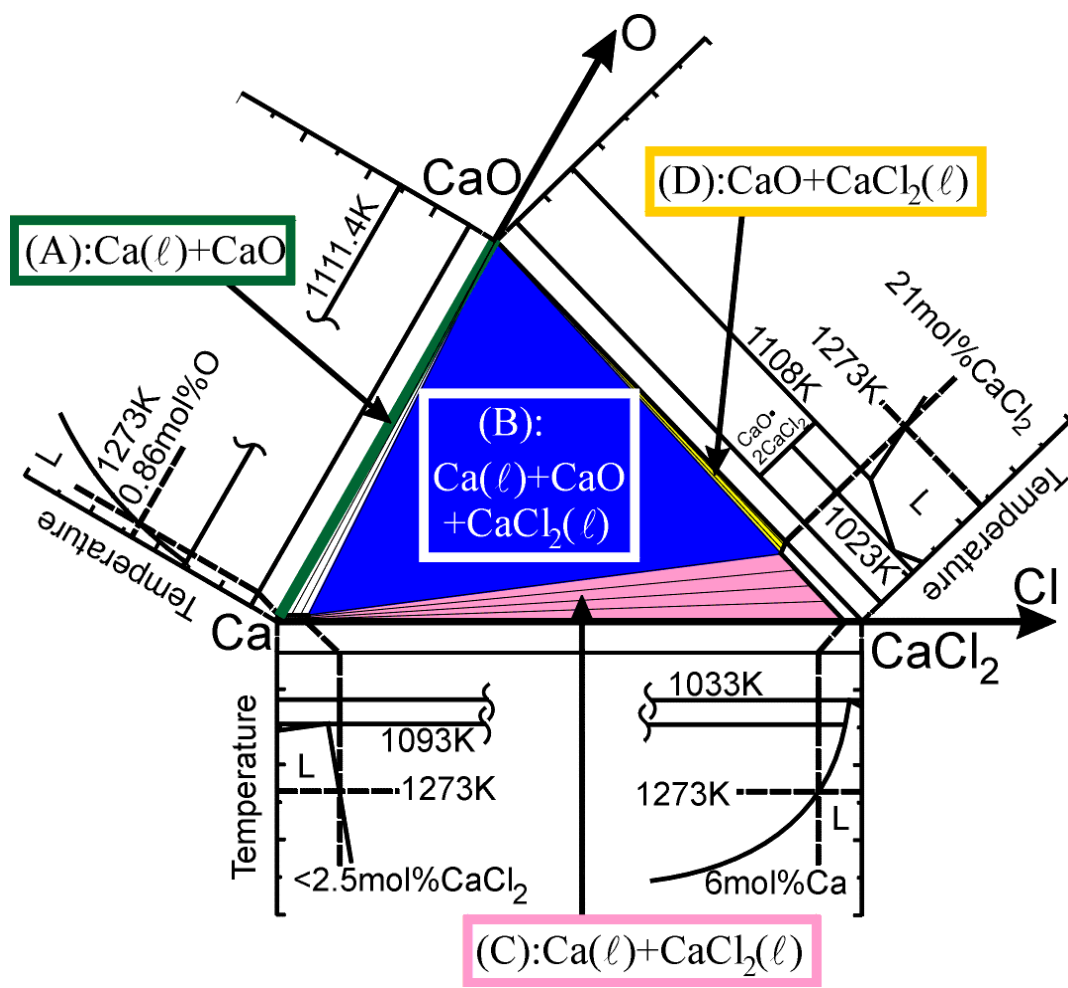


Fig. 1 Binary phase diagrams [7,12,13,18,19] and the isothermal section of the ternary system illustrated at 1273 K. The studied phase equilibria (A), (B) and (C) are hatched.

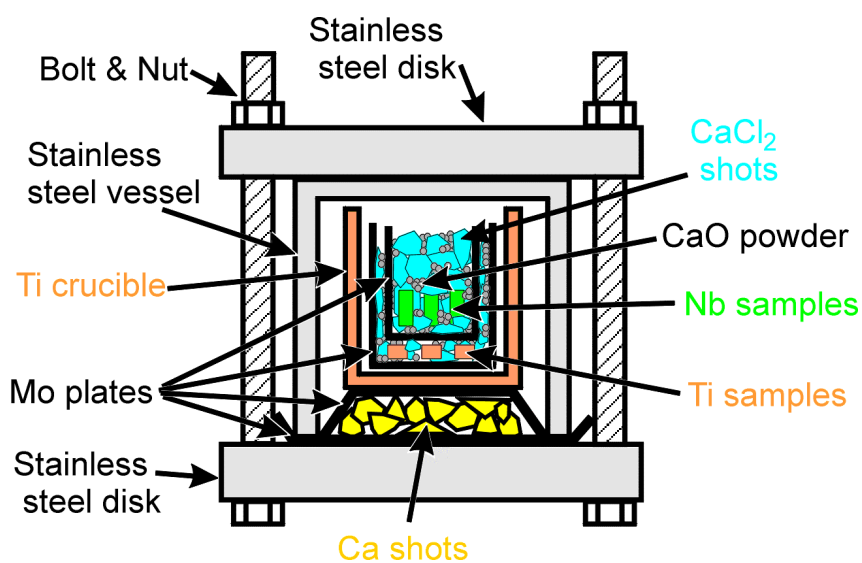


Fig. 2 Schematic illustration of reaction vessel for the equilibria of $\text{Ca}(\ell) + \text{CaCl}_2(\ell) + \text{CaO}$ and of $\text{Ca}(\ell) + \text{CaCl}_2(\ell)$.

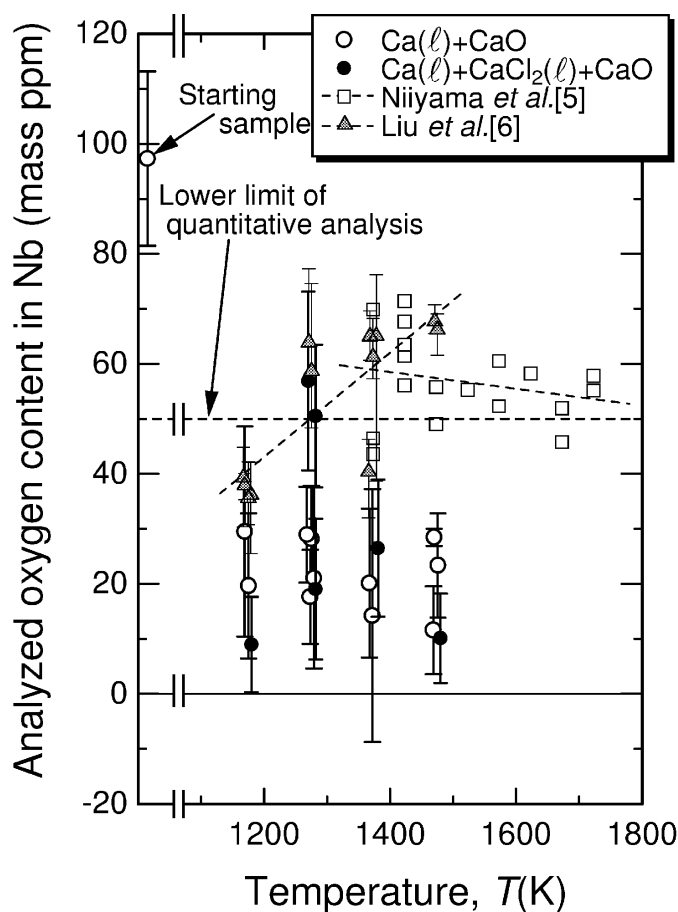


Fig. 3 Oxygen content in Nb at the $\text{Ca}(\ell) + \text{CaO}$ coexistence.

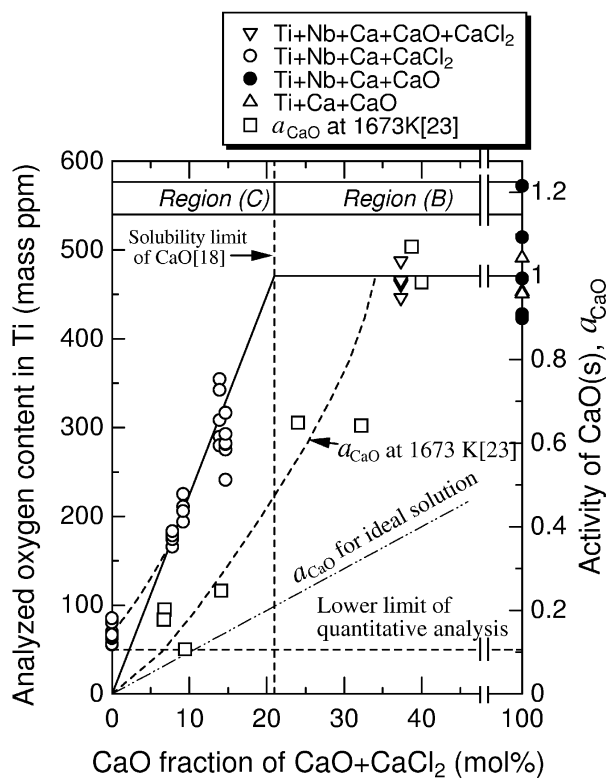


Fig. 4 Oxygen content in Ti at 1273 K and the activity of CaO.

Table 1 Impurity concentrations in Nb after annealing with Ca and CaO. Analytical data smaller than the lower limit of quantitative analysis are given in parentheses.

Run No.	Temperature (K)	Time (ks)	Analyzed concentration (mass ppm)				Remarks
			Oxygen	Nitrogen	Carbon	Calcium	
Starting Nb wire			97±16	8±7	3.1±1	<1	
Starting Nb sheet			(30±19)	13±6	-	-	
#O0806	1173	345.6	(20±13)	8±4	-	-	Nb sheets were used.
#H0806	1173	345.6	(29±19)	13±6	-	<1	
#W0518	1273	241.2	(28±10)	16±4	41±5	-	
#WT0518	1273	241.2	(18±9)	26±8	-	<1	Ti wires were added.
#M0518	1273	241.2	(21±16)	13±9	1300±50	-	Not etched.
#MT0518	1273	241.2	(29±9)	26±26	-	<1	Ti wires were added. Not etched
#P0620	1373	86.4	(20±13)	20±23	75±1	-	
#T0702	1373	86.4	(14±23)	18±8	-	<1	Ti wires were added.
#K0806	1473	82.8	(23±10)	31±1	-	-	Nb sheets were used.
#S0806	1473	82.8	(28±2)	58±17	-	<1	Nb sheets were used.
#N0806	1473	82.8	(12±8)	86±49	-	-	

Table 2 Impurity concentrations in Nb after annealing with 37.3 mol%CaO and 62.7 mol%CaCl₂ under gaseous Ca. Analytical data smaller than the lower limit of quantitative analysis are given in parentheses.

Run	Temperature	Time	Analyzed concentration (mass ppm)		
No.	(K)	(ks)	Oxygen	Nitrogen	Carbon
Starting Nb wire			97±16	8±7	3.1±1
#D0112	1173	324.0	(9±9)	15±19	4±2
#A1210	1273	172.8	51±13	25±2	8±2
#B1208	1273	172.8	57±16	23±2	-
#F1104	1273	172.8	(19±13)	(3±2)	-
#E1012	1373	86.4	(27±12)	30±15	10±2
#G1012	1473	86.4	(10±8)	11±10	5±2

*: Ti wire was added.

Table 3 Impurity concentrations in Nb after annealing with Ca, Ti, CaO and CaCl₂ at 1273 K for 172.8 ks. Analytical data smaller than the lower limit of quantitative analysis are given in parentheses.

Run No.	Salt concentration (mol%CaO)	Concentration in Nb (mass ppm)			Concentration in Ti (mass ppm)	
		Oxygen	Nitrogen	Carbon	Oxygen	Nitrogen
Starting Nb wire		97±16	8±7	3.1±1	-	-
Starting Nb sheet		(30±19)	13±6	-	-	-
Starting Ti wire		-	-	-	474±20	32±15
Starting Ti sheet		-	-	-	834±10	47±4
#0C	0	(10±11)	9±2	-	72±10	93±9
#0D	0	(30±3)	11±3	3±1	61±8	71±43
#2	7.8	(12±9)	9±5	-	175±7	68±9
#3	9.2	(28±7)	11±3	3±1	209±13	93±23
#41	13.9	(30±10)	13±3	-	315±32	44±5
#42	14.7	(20±11)	10±3	-	281±25	75±7
#A1210	37.3	51±13	25±2	8±2	464±15	146±62

*: Nb sheets were used.

Table 4 Electrical resistivity at 4.2 K, $\rho(4.2\text{K})$, and residual resistivity ratio, RRR, of the Nb samples after the heat treatment.

Run No. or Ref. No.	Heat treatment	$\text{Log}_{10}P_{\text{O}_2}$ (atm)	$\rho(4.2\text{K})$ ($\mu\Omega\text{cm}$)	RRR	Oxygen concentration (mass ppm)	
					Calculated	Analyzed
Starting Nb wire [26]	at 1473 K for 64.8 ks in vacuum	< -9	0.2228	60.7	72±6	90±20
#A1210	at 1273 K for 172.8 ks in 37.3 mol%CaO-CaCl ₂	-41.3* ¹	0.1021	130.2	0.1±4.2	51±13
#3	at 1273 K for 172.8 ks in 9.2 mol%CaO-CaCl ₂	-42.0* ¹	0.0329	404.5	-5.3±4.3	(28±7)
#0B	at 1273 K for 172.8 ks in 100 mol% CaCl ₂	-43.1* ¹	0.0258	515.8	-8.6±4.5	(30±3)
[17]	Ti external gettering at 1463 K for 144 ks in vacuum	< -34.6* ²	0.0165	777	< 3.8* ³ < 50* ⁴	-
[27]	Ti external gettering with Optimized heat treatment	< -34.6* ²	-	1940	-	-

*¹: Evaluated by oxygen concentration in Ti [22].

*²: Estimated as $P_{\text{O}_2} < P_{\text{O}_2}(\text{Ti-TiO})$ [15,17].

*³: Estimated by assuming that the impurity was only oxygen.

*⁴: Estimated by $\rho(273\text{K})$ [17].