JOURNAL OF SOLID STATE CHEMISTRY 6, 438–449 (1973)

Phase Equilibria in the System NbO_2–Nb_2O_5: Phase Relations at 1300 and 1400°C and Related Thermodynamic Treatment

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Received July 11, 1972

Phase equilibria in the system NbO_2–Nb_2O_5 at 1300 and 1400°C were studied and the variations of composition of solid oxide phases with oxygen pressure in the atmosphere were determined by using CO_2/H_2 gas mixture. Five discrete compounds, $Nb_{12}O_{29}$, $Nb_{22}O_{54}$, $Nb_{47}O_{116}$, $Nb_{25}O_{62}$, and $Nb_{53}O_{132}$ were observed to exist between NbO_2 and Nb_2O_5 at both temperatures. No appreciable tendency of increase of existence region was found for any of the studied compounds at higher temperatures. A mean for thermodynamic treatment of crystallographic shear planes including Wadsley intergrowth defects is proposed and, as a consequence, it was shown that Wadsley intergrowth defects in the studied compounds are probably of nonequilibrium nature.

Introduction

Since Brauer's study (*1*) of subsolidus phase equilibria in the system Nb–O, it has been widely accepted that the stable oxide phases present in the system are NbO, NbO_2, and Nb_2O_5. The phase equilibrium study including the liquid phase by Elliott (*2*) confirmed the above-stated information. The former study indicated that the Nb_2O_5 phase shows a solid solution region extended toward NbO_2 with the composition limit represented by $NbO_{2.40}$. However, the detailed study of this solid solution region by Norin and Magnéli (*3*) revealed it to consist of several discrete compounds which are very similar to each other in structure. These compounds are crystallographically in the same category as those called "homologous series compounds," which were found among the oxides of Mo, W, and Ti by Magnéli (*4*), Magnéli, Andersson and Sundkvist (*5*) and Andersson and Magnéli (*6*). Five compounds, namely $Nb_{12}O_{29}$, $Nb_{22}O_{54}$, $Nb_{47}O_{116}$, $Nb_{25}O_{62}$, and $Nb_{53}O_{132}$ have been hitherto found to exist in the composition range between NbO_2 and Nb_2O_5 and the conditions for the stable existence of these compounds at 1300°C were studied by Schäfer, Bergner and Gruehn (*7*) who controlled the oxygen pressure by using H_2/H_2O gas mixture.

According to Schäfer, Bergner and Gruehn (*7*), the real compositions of the above-listed five solid phases are all deviated toward the oxygen-deficient side from those expected with the formulas, although the X-ray diffraction patterns indicate the crystal structures corresponding to the formulas, the crystal structures of these compounds having been studied by Norin (*8*, *9*), Gruehn and Norin (*10*, *11*), and Roth and Wadsley (*12*). It was also reported that $Nb_{47}O_{116}$ and $Nb_{25}O_{62}$ have considerably extended composition regions (*7*).

Meanwhile, the phase equilibrium study by Elliott (*2*) showed that the melting temperature of Nb_2O_5 becomes higher as it loses small amounts of oxygen and the melting relation in the composition region is characterized to be peritectic, thus suggesting that five homologous series compounds are incorporated into a single solid solution system extended from Nb_2O_5.

During the past few years, the study of crystallographic shear planes and Wadsley intergrowth defects (or Wadsley defects[1]) in compounds

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[1] This name was proposed by Dr. Sten Andersson at the conference on "The Chemistry of Extended Defects in Nonmetallic Solids," held at Scottsdale, Arizona, in Apr. 1969, and was simplified to "Wadsley defects" by Allpress and Roth (*15*), Allpress, Tilley and Sienko (*16*).

related to those presently studied has been intensively carried out by Allpress (*13*, *14*), Allpress and Roth (*15*) and Allpress, Tilley and Sienko (*16*) by the technique of electron microscopy. Wadsley defects are coherent intergrowths of one member of the homologous series compounds in a matrix of another. If Wadsley defects were of equilibrium nature and a thermodynamic quantitative treatment of these defects were possible, the information to be obtained through it would be of some interest in relation to the role of Wadsley defects in the homologous series compounds and the behavior of these compounds at different temperatures. No thermodynamic treatment has yet been carried out on the crystallographic shear planes, while various types of point defects have been treated thermodynamically to give information for various inorganic compounds (*17*).

In the present study, the phase equilibria in the system NbO_2–Nb_2O_5 at 1300 and 1400°C were observed in terms of the variations of composition of oxide phases with oxygen pressure in the atmosphere by using CO_2/H_2 gas mixture, and a mean for thermodynamic treatment of crystallographic shear planes including Wadsley defects is proposed and, as a consequence, it was shown that Wadsley defects in the studied compounds are probably of nonequilibrium nature.

Experimental Procedure

General Procedure

Spec-pure grade Nb_2O_5 powder (Johnson and Matthey Co., 99.97% pure) was sintered at 1450°C in a platinum crucible in air for 2 hr. A part of the sintered Nb_2O_5 was then reduced to NbO_2 at 1450°C in an atmosphere of CO_2/H_2 gas mixture with the ratio $CO_2/H_2 = 0.1$. A disc-shaped lump of approximately 1.5 g was taken from each of the sintered Nb_2O_5 and NbO_2 and suspended side by side with thin platinum wire (0.1 mm diam) in a molybdenum wound vertical quench furnace in which the temperature and the oxygen pressure had been preadjusted. The running duration of 15–70 hr was given for equilibration and the specimens were quenched on the cold brass bottom of the furnace. The specimens were then analyzed chemically and by X-ray.

Temperature Control

The furnace temperature was controlled by using a W–W26%Re thermocouple as the detector. The temperature at the specimen-setting position was measured before and after the run by using a Pt–Pt13%Rh thermocouple. The measuring thermocouple was standardized from time to time at the melting points of Pd (1552°C) and Au (1063°C) and the temperature measurement was always made after the atmosphere of CO_2/H_2 mixture had been replaced with air of the similar flow rate to prevent the deterioration of the thermocouple. The temperature fluctuation during the run was monitored with a recorder. The estimated error in the measured temperature is ± 3°C.

Atmosphere Control

Mixture of CO_2 and H_2 was employed to control the oxygen pressure in the furnace. The procedures for preparation of gas mixtures and calculation of the oxygen pressures are shown elsewhere (*18*). The estimated error in the mixing ratio is ± 1%.

Analysis of Specimens

The oxygen content of each of the specimens was determined by observing the weight gain when heated to Nb_2O_5 in air at 1000°C for 3 hr. The estimated error in this analysis is ± 0.002 or smaller in terms of atom oxygen per atom niobium. The specimens were also studied by X-ray diffraction technique, when judged to be necessary, and the attention was particularly focused on the low angle diffractions to determine the phases present.

Experimental Results

No appreciable difference between the rates of equilibration reactions at two different temperatures was observed. The running conditions, however, were found to influence the durations of completion of equilibrium reactions. When the running condition is close to that for a two-solid-phase equilibrium, the equilibrium reaction was found to be considerably sluggish. Therefore, the running duration for the present experiment ranged from 15 to 70 hr. It was also observed in some runs that the compositions reached from two sides, one being Nb_2O_5 and the other NbO_2, cross over each other. The composition reached from Nb_2O_5 was often more reduced than that reached from NbO_2. This situation is unusual and was a difficulty in the determination of equilibrium compositions. Tentatively, the equilibrium composition was understood to lie

TABLE I
EQUILIBRATION RESULTS AT 1300°C

Specimen no.	CO_2/H_2	$\mathrm{Log}P_{O_2}$	Final composition		Phases identified by X-ray
			From Nb_2O_5	From NbO_2	
87	0.148	−12.22	—	—	$Nb_{12}O_{29}$, NbO_2
85	0.151	−12.20	2.418	2.417	
83	0.154	−12.18	2.416	2.417	
81	0.157	−12.16	2.424	2.419	
95	0.161	−12.14	2.418	2.418	$Nb_{12}O_{29}$
80	0.164	−12.12	2.443	2.444	$Nb_{12}O_{29}$, $Nb_{22}O_{54}$
89-1	0.171	−12.08	2.448		$Nb_{22}O_{54}$
89-2	0.171	−12.08		2.446	$Nb_{22}O_{54}$, trace $Nb_{12}O_{29}$
69	0.182	−12.02	2.448	2.449	
71	0.219	−11.84	2.450	2.450	
70	0.258	−11.67	2.451	2.452	
62	0.279	−11.60	2.454	2.454	
102	0.319	−11.46	2.453	2.454	
99-1	0.325	−11.44	2.455		$Nb_{22}O_{54}$, $Nb_{47}O_{116}$
99-2	0.325	−11.44		2.457	$Nb_{22}O_{54}$, minor $Nb_{47}O_{116}$
93	0.337	−11.40	2.463	2.395	
92-1	0.385	−11.26	2.463		$Nb_{47}O_{116}$, trace $Nb_{22}O_{54}$
92-2	0.385	−11.26		2.460	$Nb_{47}O_{116}$, minor $Nb_{22}O_{54}$
88	0.481	−11.02	2.463	2.462	
98-1	0.499	−10.98	2.465		$Nb_{47}O_{116}$, minor $Nb_{25}O_{62}$
98-2	0.499	−10.98		2.464	$Nb_{25}O_{62}$, minor $Nb_{47}O_{116}$
86-1	0.517	−10.94	2.467		
86-2	0.517	−10.94		2.469	$Nb_{25}O_{62}$, trace $Nb_{47}O_{116}$
82	0.565	−10.84	2.468	2.469	
96-1	0.791	−10.46	2.472		$Nb_{25}O_{62}$
96-2	0.791	−10.46		2.472	
90	1.25	−9.92	2.475	—	
94	1.30	−9.88	2.478	2.477	
100-1	1.32	−9.86	2.475		$Nb_{25}O_{62}$, trace $Nn_{53}O_{132}$
100-2	1.32	−9.86		2.475	
105-1	1.34	−9.84	2.487		Nb_2O_5, minor $Nb_{25}O_{62}$
105-2	1.34	−9.84		2.481	$Nb_{53}O_{132}$, minor $Nb_{25}O_{62}$
107-1	1.39	−9.80	2.487		$Nb_{53}O_{132}$, Nb_2O_5, $Nb_{25}O_{62}$
107-2	1.39	−9.80		2.481	$Nb_{53}O_{132}$, $Nb_{25}O_{62}$
108-1	1.50	−9.71	2.483		$Nb_{53}O_{132}$, trace Nb_2O_5, trace $Nb_{25}O_{62}$
108-2	1.50	−9.71		2.481	$Nb_{53}O_{132}$, trace $Nb_{25}O_{62}$
106-1	1.66	−9.60	2.490		Nb_2O_5
106-2	1.66	−9.60		2.486	$Nb_{53}O_{132}$
103-1	1.81	−9.50	2.490		Nb_2O_5, trace $Nb_{53}O_{132}$
103-2	1.81	−9.50		2.487	$Nb_{53}O_{132}$, trace Nb_2O_5
78	1.86	−9.47	2.488	2.484	
68-1	1.94	−9.42	2.491		Nb_2O_5
68-2	1.94	−9.42		2.489	
101-1	1.91	−9.44	2.486		$Nb_{53}O_{132}$, Nb_2O_5
101-2	1.91	9.44		2.485	
104-1	1.98	−9.40	2.489		Nb_2O_5, trace $Nb_{53}O_{132}$
104-2	1.98	−9.40		2.486	$Nb_{53}O_{132}$, trace Nb_2O_5
109	2.02	−9.38	2.486	2.486	$Nb_{53}O_{132}$, Nb_2O_5
57	2.55	−9.13	2.492	2.490	
49	4.94	−8.45	2.492	—	
50	10.05	−7.78	2.495	—	
51	17.4	−7.28	2.496	—	

TABLE II

EQUILIBRATION RESULTS AT 1400°C

			Final composition		
Specimen no.	CO_2/H_2	$\mathrm{Log}P_{O_2}$	From Nb_2O_5	From NbO_2	Phases identified by X-ray
419	0.190	−10.97	—	—	NbO_2, $Nb_{12}O_{29}$
411-1	0.200	−10.92	2.421		
411-2	0.200	−10.92		2.418	$Nb_{12}O_{29}$
423-1	0.219	−10.83	2.444		$Nb_{22}O_{54}$, minor $Nb_{12}O_{29}$
423-2	0.219	−10.83		2.419	$Nb_{12}O_{29}$
417	0.230	−10.78	2.441	2.422	
425-1	0.240	−10.74	2.446		$Nb_{22}O_{54}$
425-2	0.240	−10.74		2.429	
413	0.260	−10.66	2.445	2.446	
421	0.300	−10.51	2.449	2.449	
401	0.350	−10.35	2.450	2.450	
402	0.400	−10.21	2.451	2.451	
403-1	0.456	−10.06	2.451		
403-2	0.456	−10.06		2.452	$Nb_{22}O_{54}$
430	0.480	−10.00	2.451	—	
405-1	0.500	−9.96	2.455		$Nb_{22}O_{54}$
405-2	0.500	−9.96		2.460	$Nb_{22}O_{54}$, trace $Nb_{47}O_{116}$
427-1	0.525	−9.90	2.460		
427-2	0.525	−9.90		2.461	$Nb_{47}O_{116}$, trace $Nb_{22}O_{54}$
412-1	0.550	−9.85	2.463		$Nb_{47}O_{116}$, trace $Nb_{22}O_{54}$
412-2	0.550	−9.85		2.462	
404-1	0.608	−9.73	2.463		$Nb_{47}O_{116}$,
404-2	0.608	−9.73		2.466	$Nb_{47}O_{116}$, $Nb_{25}O_{62}$
432	0.670	−9.62	2.466	2.467	
407-1	0.750	−9.48	2.467		
407-2	0.750	−9.48		2.469	$Nb_{25}O_{62}$
420-1	0.870	−9.30	2.471		$Nb_{25}O_{62}$
420-2	0.870	−9.30		2.473	
424	1.00	−9.13	2.473	2.473	
418	1.20	−8.91	2.473	2.472	
414	1.40	−8.72	2.475	2.474	
408	1.50	−8.64	2.477	2.477	
426-1	1.62	−8.55	2.477		
426-2	1.62	−8.55		2.476	$Nb_{25}O_{62}$
435-1	1.74	−8.47	2.484		$Nb_{53}O_{132}$
435-2	1.74	−8.47		2.483	$Nb_{53}O_{132}$
433-1	1.75	−8.46	2.481		$Nb_{53}O_{132}$, $Nb_{25}O_{62}$
433-2	1.75	−8.46		2.482	$Nb_{53}O_{132}$, $Nb_{25}O_{62}$
416	1.80	−8.43	2.481	2.482	
431	2.00	−8.31	2.483	2.483	
434	2.11	−8.25	2.485	2.483	
406	2.24	−8.18	2.484	2.488	
429-1	2.34	−8.13	2.483		$Nb_{53}O_{132}$, $Nb_{25}O_{62}$, Nb_2O_5
429-2	2.34	−8.13		2.486	$Nb_{53}O_{132}$, trace Nb_2O_5
436-1	2.46	−8.08	2.488		Nb_2O_5, $Nb_{53}O_{132}$
436-2	2.46	−8.08		2.487	Nb_2O_5, $Nb_{53}O_{532}$
422	3.00	−7.86	2.489	2.490	Nb_2O_5
428	5.00	−7.34	2.493	2.493	Nb_2O_5

between the compositions reached from both sides, the criterion for determination being the same as when they are not crossed over by each other. The results of the equilibration runs are tabulated in Tables I and II.

Phase identification with Cu:$K\alpha$ radiation of the studied oxides was found to be relatively easy when the peaks of $2\theta = 17$–$20°$ were studied, while otherwise difficult. The results of phase identification for some of the specimens are also listed in Tables I and II.

In some specimens, the equilibration reaction was found to have ceased in a two-solid-phase region. This situation may be due to either exsolution during quenching or incomplete equilibration reactions. Exsolution during quenching is, however, believed to be negligible, for the slow equilibration reactions under the corresponding conditions. Thus the equilibration reactions are incomplete for some reason. In order to estimate the real compositions of $Nb_{12}O_{29}$, $Nb_{47}O_{116}$, and $Nb_{53}O_{132}$ or of the end members of solid solution series of $Nb_{22}O_{54}$, $Nb_{25}O_{62}$, and Nb_2O_5 by using data including those from probably incomplete equilibration reactions, the compositions of, and the identified phases in the specimens were both carefully checked.

The specimens of the compositions falling in the existence region of $Nb_{22}O_{54}$ or $Nb_{25}O_{62}$ did not show an appreciable variation in diffraction pattern with composition.

For better understanding the experimental results, the data in Tables I and II are plotted in Figs. 1 and 2 in terms of the composition of the solid phase in atom oxygen per atom niobium ($x = \mathrm{O/Nb}$) versus the oxygen pressure (atm) in logarithmic scale ($\log P_{O_2}$). The data of phase identification being combined, the overall composition–P_{O_2} relation may be found to be represented by the solid curve in each of Figs. 1 and 2. Five intermediate phases are present in addition to NbO_2 and Nb_2O_5, the former of which is not shown in the Figs. 1 and 2 for the scale of these figures is so expanded and the shown composition range is so close to the Nb_2O_5 apex. The chemical composition of the crystallographically assigned formulas is shown by open circles in the figures. For comparison, the data by Schäfer, Bergner and Gruehn (7) are also shown in Fig. 1 (broken line).

The detailed description of five intermediate compounds and Nb_2O_5 are shown in Table III. The variation in the width of existence region for

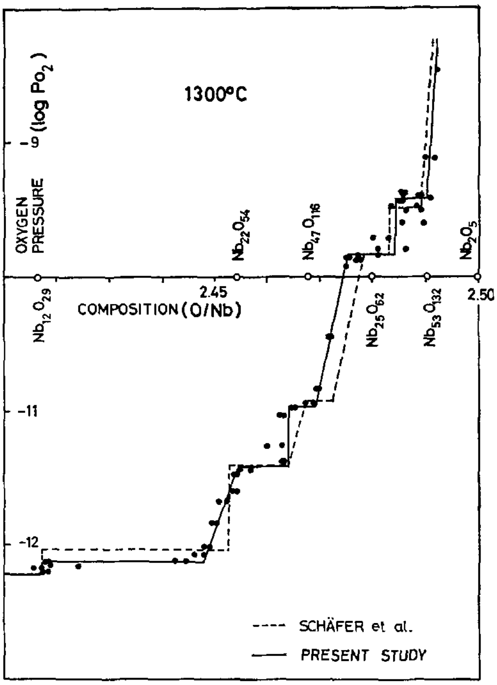

FIG. 1. Relation between the composition of the solid phase and the equilibrium oxygen pressure in the system NbO_2–Nb_2O_5 at 1300°C. The broken curve is the result of the work by Schäfer, Bergner, and Gruehn (7).

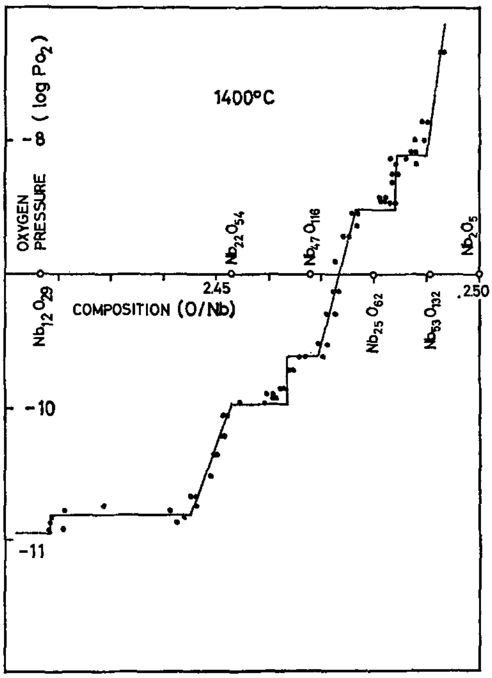

FIG. 2. Relation between the composition of the solid phase and the equilibrium oxygen pressure in the system NbO_2–Nb_2O_5 at 1400°C.

TABLE III

DESCRIPTION OF THE OXIDE PHASES

Formula		At 1300°C	At 1400°C
$Nb_{12}O_{29}$	Chemical composition	$NbO_{2.417}$	$NbO_{2.418}$
	LogP_{O_2} range	−12.21 ~ −12.13	−10.94 ~ −10.81
$Nb_{22}O_{54}$	Chemical composition	$NbO_{2.448-2.454}$	$NbO_{2.446-2.453}$
	LogP_{O_2} range	−12.13 ~ −11.42	−10.91 ~ −9.98
$Nb_{47}O_{116}$	Chemical composition	$NbO_{2.464}$	$NbO_{2.463}$
	LogP_{O_2} range	−11.42 ~ −10.98	−9.98 ~ −9.63
$Nb_{25}O_{62}$	Chemical composition	$NbO_{2.469-2.475}$	$NbO_{2.470-2.476}$
	LogP_{O_2} range	−10.98 ~ −9.84	−9.63 ~ −8.52
$Nb_{53}O_{132}$	Chemical composition	$NbO_{2.484-2.485}$	$NbO_{2.483-2.484}$
	LogP_{O_2} range	−9.84 ~ −9.40	−8.52 ~ −8.11
Nb_2O_5	Chemical composition	$NbO_{2.490-2.500}$	$NbO_{2.490-2.500}$
	LogP_{O_2} range	−9.40 ~	−8.11 ~

any of these compounds with increase of temperature is indicated to be within the experimental error. The present results seem to be incompatible with Elliott's findings (*2*).

Thermodynamic Approach to Crystallographic Shear Planes and Wadsley Defects

It is known to be successful in study of nonstoichiometry of many inorganic compounds to use the mass action relations by treating lattice and electronic defects as chemical entities. The mass action law is applicable to any equilibrium reaction, provided that each of the involved chemical entities is characterized with a fixed chemical potential. To reactions among the crystals containing the crystallographic shear planes as the essential structural constituent, the mass action law may be applicable by grouping the constituent chemical entities as few as possible.

By a careful analysis of the crystal structures of the presently studied homologous series compounds, which are available in the literature either as the result of direct structure analysis or as a convincing postulation (*8–12*), it was found that oxygen ions on the lattice are classified into four major groups. The basis for the classification is the number of directly neighboring Nb ions. The oxygen ions in the first group have two directly neighboring niobium ions each, those in the second group have three each and those in the third have four each. Structurally, those in the first group are located in the part intact from the shear planes, those in the second group are along the shear planes, and those in the third are at the intersections of the shear planes developed in two directions. The niobium ions neighboring the oxygen ions in the first three groups are all at the octahedral coordination site. On the other hand, the oxygen ion in the fourth group is characterized by two directly neighboring niobium ions, one of which is at the tetrahedral coordination site.

The classification of oxygen ions may be better understood in reference to Fig. 3, in which the crystal structure of $Nb_{22}O_{54}$, as determined by Norin (*9*), is shown in the same way as generally found in the literature [see, for example, Wadsley and Andersson (*19*)]. The octahedrons viewed from top to bottom represent niobium ions surrounded by six oxygen ions each. The illustrated arrangement of ions should be understood to be repeated infinitely along the perpendicular direction to the page plane. For convenience, the oxygen ion in each group is

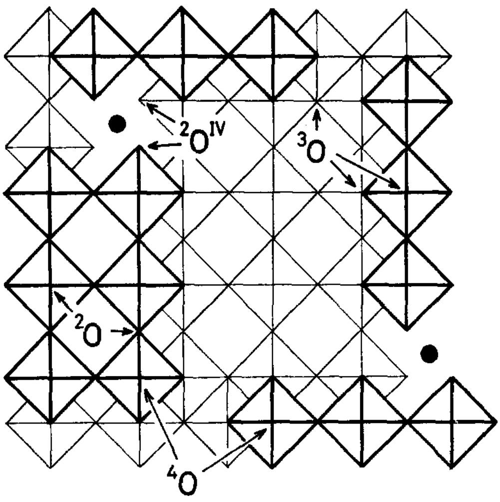

FIG. 3. The crystal structure of $Nb_{22}O_{54}$ as determined by Norin (9), schematically presented in order to show where and how ^2O, ^3O, ^4O, and $^2O^{IV}$ are located.

expressed by ^2O, ^3O, ^4O, or $^2O^{IV}$, indicating the number of the closest neighbor cations by the superscript. The Roman letter IV of $^2O^{IV}$ indicates the coordination condition of one of the closest neighbor cations which is shown by dots in the illustrated crystal structure in Fig. 3. The positions of ^2O, ^3O, ^4O, and $^2O^{IV}$ are easily found in the figure and it is understood that every oxygen ion belongs to one of the four groups. This situation is true in all of the presently studied homologous series compounds including Nb_2O_5 (*20*), although $Nb_{12}O_{29}$ does not contain $^2O^{IV}$. The distribution of oxygen ions in each of the studied compounds may be found by checking the crystal structure and is shown in Table IV, assuming that the assigned formulas represent the real compositions of these compounds. These four groups of oxygen ions being chosen as the chemical entities to influence the oxygen pressure in the environment, the mass action law may be applied. Thus the oxygen pressure is understood to be an indicator of what really takes place in the solid phase. In a precise discussion, all of the oxygen ions belonging to a specific group may not be characterized by the same chemical potential, for the crystal structures under consideration are known to deviate from the ideal ones (*19*). As an approximation, however, the chemical potentials of oxygen ions in the same group are presently taken to be the same.

For application of the mass action law, the contributions of chosen chemical entities to

TABLE IV

CONCENTRATIONS OF VARIOUS OXYGEN IONS IN THE OXIDE PHASES OF IDEAL FORMULAS AND THE CALCULATED EQUILIBRIUM CONSTANTS FOR THE TWO-SOLID-PHASE EQUILIBRIA

Phase	$Nb_{12}O_{29}$		$Nb_{22}O_{54}$		$Nb_{47}O_{116}$		$Nb_{25}O_{62}$		$Nb_{53}O_{132}$		Nb_2O_5
$[^2O]$	1.417		1.364		1.404		1.440		1.472		1.500
$[^3O]$	0.833		0.818		0.809		0.800		0.792		0.786
$[^4O]$	0.167		0.091		0.085		0.080		0.076		0.071
$[^2O^{IV}]$	—		0.182		0.170		0.160		0.151		0.143
$[Nb^{4+}]$	0.166		0.090		0.064		0.040		0.018		0.000
$[Nb^{5+}]$	0.834		0.910		0.936		0.960		0.982		1.000
$\mathrm{Log}P_{O_2}$											
(1300°C)		−12.13		−11.42		−10.98		−9.84		−9.40	
(1400°C)		−10.81		−9.98		−9.63		−8.52		−8.11	
$\mathrm{Log}K_3$											
(1300°C)		−8.11		−8.36		−8.50		−8.45		−8.92	
(1400°C)		−7.45		−7.46		−7.83		−7.74		−8.28	
$\mathrm{Log}K_4$											
(1300°C)		−8.60		−9.08		−9.23		−9.81		−9.66	
(1400°C)		−7.94		−8.36		−8.56		−8.47		−9.02	
$\mathrm{Log}K_5$											
(1300°C)		—		−11.44		−11.71		−11.77		−12.36	
(1400°C)		—		−10.72		−11.04		−11.06		−11.72	

equilibrium reactions have to be considered. The formation of additional shear planes introduces extra numbers of ^3O, ^4O, or $^2O^{IV}$ into the structure in sacrifice of ^2O. This is clearly demonstrated by the change of the distribution of oxygen ions from one compound to another (see Table IV). For the amount of these four types of oxygen ions, the following relation is found to exist:

$$4[^2O] + 6[^3O] + 8[^4O] + 5[^2O^{IV}] = 12, \quad (1)$$

where [ ] represents the number of the indicated oxygen ions per niobium ion. The derivation of Eq. (1) is described in the Appendix. The basis of deriving Eq. (1) is such that it is applicable to any reactions involving the formation or the destruction of shear planes of the presently discussed type.

In order to find the appearance–disappearance reactions among various oxygen ions during the reaction, Eq. (1) is differentiated to give

$$4d[^2O] + 6d[^3O] + 8d[^4O] + 5d[^2O^{IV}] = 0. \quad (2)$$

In Eq. (2), one may find the indication that three elementary equilibrium reactions exist in maintaining the relation shown by Eq. (1). These reactions are,

$$3(^2O)^{2-} + 2Nb^{5+} = 2(^3O)^{2-} + 2Nb^{4+} + 1/2O_2(g), \quad (3)$$

$$2(^2O)^{2-} + 2Nb^{5+} = (^4O)^{2-} + 2Nb^{4+} + 1/2O_2(g), \quad (4)$$

$$5(^2O)^{2-} + 2Nb^{5+} = 4(^2O^{IV})^{2-} + 2Nb^{4+} + 1/2O_2(g). \quad (5)$$

Equations (3), (4), and (5) are derived by considering: (i) ^2O is always consumed for the formation of other oxygen ions, (ii) the coefficients should be determined by keeping constant the amounts of the species other than those involved, and (iii) the electrical neutrality should be kept for each reaction.[2]

The mass action law should apply to each of the equilibrium reactions (3), (4), and (5). Since these three equations are elementary and independent of each other, calculations of the apparent equilibrium constants K_3, K_4, and K_5 for the reactions (3), (4), and (5), respectively, can be carried out independently as shown below:

$$K_3 = \frac{[^3O]^2 \cdot [Nb^{4+}]^2}{[^2O]^3 \cdot [Nb^{5+}]^2} \cdot P_{O_2}^{1/2}, \quad (6)$$

$$K_4 = \frac{[^4O] \cdot [Nb^{4+}]^2}{[^2O]^2 \cdot [Nb^{5+}]^2} \cdot P_{O_2}^{1/2}, \quad (7)$$

$$K_5 = \frac{[^2O^{IV}]^4 \cdot [Nb^{4+}]^2}{[^2O]^5 \cdot [Nb^{5+}]^2} \cdot P_{O_2}^{1/2}. \quad (8)$$

A typical reaction of the formation and the destruction of the crystallographic shear planes is seen in a two-solid-phase equilibrium. Thus the above derived relations may be applied to the two-solid-phase equilibria observed in the present study. The measured oxygen pressures and the calculated values of $\log K_3$, $\log K_4$, and $\log K_5$ for the observed equilibria are listed in Table IV. They are found to be notably scattered.

In the above calculation, the equilibrium oxygen pressures are the only data that have been used. As shown in Table III, however, the composition of the solid phases deviates from those indicated by the ideal formulas. The observed composition deviations may also have to be considered to proceed in the calculation. For obtaining the concentrations of various oxygen ions in the solid phases of the deviated compositions, it was assumed that the observed composition deviations are due to the formation of vacant sites of oxygen and the vacancy is evenly distributed among ^2O, ^3O, ^4O, and $^2O^{IV}$. Table V lists the concentrations of each ion in the solid phases in the same manner as in Table IV.

Again, the calculations of $\log K_3$, $\log K_4$, and $\log K_5$ were carried out and the results are also shown in Table V. The obtained values of $\log K_3$, $\log K_4$, and $\log K_5$ seem to suggest well the applicability of Eqs. (6), (7), and (8). Except for the equilibria between $Nb_{12}O_{29}$ and $Nb_{22}O_{54}$ and between $Nb_{53}O_{132}$ and Nb_2O_5, each of $\log K_3$, $\log K_4$, and $\log K_5$ is essentially constant.

The fact that the calculated values of $\log K_3$, $\log K_4$, and $\log K_5$ for the $Nb_{12}O_{29}$–$Nb_{22}O_{54}$ equilibrium are different from those for other equilibria may be understood as the result of the difference in structure series of the involved two compounds. Only $Nb_{12}O_{29}$ belongs to the $Nb_{3n}O_{8n-3}$ series while all other presently studied compounds are in the $Nb_{3n+1}O_{8n-2}$ series (*19*). As shown in Tables IV and V, the $Nb_{12}O_{29}$ phase has no $^2O^{IV}$ ions. It may be rather general that the chemical potentials of oxygen ions of the same

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[2] The electrical neutrality is understood to be kept by the change of the valence state of proper amounts of niobium ions. The distribution of cations was assumed to be homogeneous in consideration of the experimental evidences reported by Roth and Wadsley (*12*), who found no sign of cation ordering in $TiNb_{24}O_{62}$.

TABLE V

CONCENTRATIONS OF VARIOUS OXYGEN IONS IN THE REAL OXIDE PHASES AND THE CALCULATED EQUILIBRIUM CONSTANTS FOR THE TWO-SOLID-PHASE EQUILIBRIA

Phase	$Nb_{12}O_{29}$		$Nb_{22}O_{54}$			$Nb_{47}O_{116}$		$Nb_{25}O_{62}$			$Nb_{53}O_{132}$		Nb_2O_5
[^{2}O]	1.417		1.360	1.362		1.401		1.434	1.437		1.468		1.494
[^{3}O]	0.833		0.817	0.816		0.807		0.798	0.797		0.791		0.783
[^{4}O]	0.167		0.091			0.085		0.080			0.075		0.071
[$^2O^{IV}$]	—		0.182	0.181		0.170		0.160	0.159		0.150		0.142
[Nb^{4+}]													
(1300°C)	0.166		0.104	0.092		0.082		0.062	0.050		0.031		0.020
(1400°C)	0.164		0.108	0.094		0.084		0.060	0.048		0.033		0.020
[Nb^{5+}]													
(1300°C)	0.834		0.896	0.908		0.918		0.938	0.950		0.969		0.980
(1400°C)	0.836		0.892	0.906		0.916		0.940	0.952		0.967		0.980
$\log P_{O_2}$													
(1300°C)		−12.13			−11.42		−10.98			−9.84		−9.40	
(1400°C)		−10.81			−9.98		−9.63			−8.52		−8.11	
$\log K_3$													
(1300°C)		−8.09			−8.32		−8.26			−8.26		−8.45	
(1400°C)		−7.44			−7.58		−7.57			−7.56		−7.76	
$\log K_4$													
(1300°C)		−8.58			−9.04		−8.99			−8.93		−9.20	
(1400°C)		−7.92			−8.30		−8.30			−8.30		−8.50	
$\log K_5$													
(1300°C)		—			−11.40		−11.47			−11.51		−11.89	
(1400°C)		—			−10.66		−10.78			−10.88		−11.20	

type are different in the structures of two different series. Obviously, a different equilibrium constant corresponds to a combination of species of different chemical potentials. This may be the situation in the $Nb_{12}O_{29}$–$Nb_{22}O_{54}$ equilibrium.

The calculated values of $\log K_3$, $\log K_4$, and $\log K_5$ for the equilibrium $Nb_{53}O_{132}$–Nb_2O_5 ($Nb_{28}O_{70}$, when expressed as a member of the $Nb_{3n+1}O_{8n-2}$ (*20*)) are also considerably different from those for other equilibria. The concentration of Nb^{4+} is small in the involved solid phases and has a significant influence to the values of $\log K_3$, $\log K_4$, and $\log K_5$ when varied even slightly. When the composition $NbO_{2.483}$, which was given by Schäfer, Bergner and Gruehn (*7*) as the real composition of the phase $Nb_{53}O_{132}$, was applied for calculations of $\log K_3$, $\log K_4$, and $\log K_5$, the difference from the corresponding value for other equilibria was found to be considerably reduced, although still notable. The real composition of the phase $Nb_{53}O_{132}$ is in the region where the composition determination is difficult due to the sluggish reactions and the small content of Nb^{4+}. It may be tentatively concluded that the calculated values of $\log K_3$, $\log K_4$, and $\log K_5$ for the $Nb_{53}O_{132}$–Nb_2O_5 equilibrium are less reliable than those for other equilibria.

In consideration of above presumptions, the data for the $Nb_{12}O_{29}$–$Nb_{22}O_{54}$ and the $Nb_{53}O_{132}$–Nb_2O_5 equilibria were excluded and other three values for each of $\log K_3$, $\log K_4$, and $\log K_5$ were algebraically averaged and are shown below:

	(°C)	
$(\log K_3)_{av}$	1300	−8.26
	1400	−7.57
$(\log K_4)_{av}$	1300	−8.99
	1400	−8.30
$(\log K_5)_{av}$	1300	−11.46
	1400	−10.77

The mean values of $\log K_3$, $\log K_4$ and $\log K_5$ are applied in turn to Eqs. (6), (7), and (8) for calculating the equilibrium oxygen pressures, thus for obtaining the "calculated" relations between the oxygen pressure and the chemical composition of the solid phase. The result is shown in Figs. 4 and 5.

The application of the mass action law to the crystals containing the crystallographic shear planes as the essential structural constituent has not been done and is tried here as a proposal for the first time. The application itself may be crude and should be repeatedly and critically rechecked, but the present result seems to be significant. The results in Figs. 4 and 5 indicate that the reactions (3), (4), and (5) very probably take place under the conditions of the two-solid-phase equilibria. This indication is important, for it may allow a further presumption that the reactions (3), (4), and (5) take place wherever the destruction and the redistribution of crystallographic shear planes are carried out reversibly. Thus, the Wadsley defects, which are understood to be the result of the destruction and the redistribution of crystallographic shear planes within a solid oxide phase, may be studied by a similar treatment to one carried out presently.

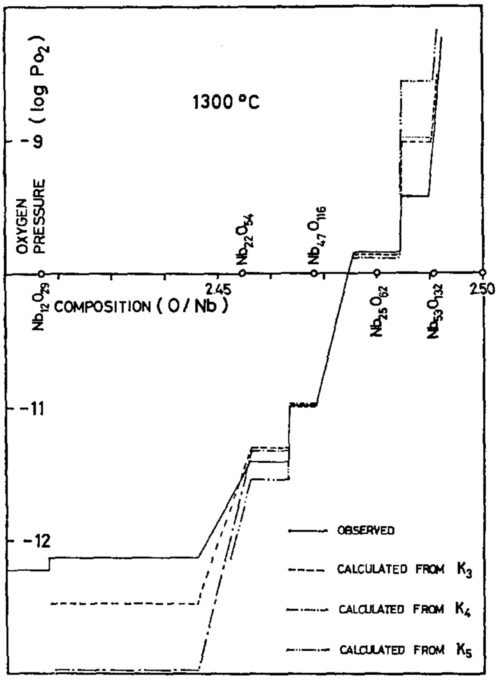

FIG. 4. Comparison of the experimental result with the "calculated" one for relation between the composition of the solid phase and the equilibrium oxygen pressure in the system NbO_2-Nb_2O_5 at 1300°C.

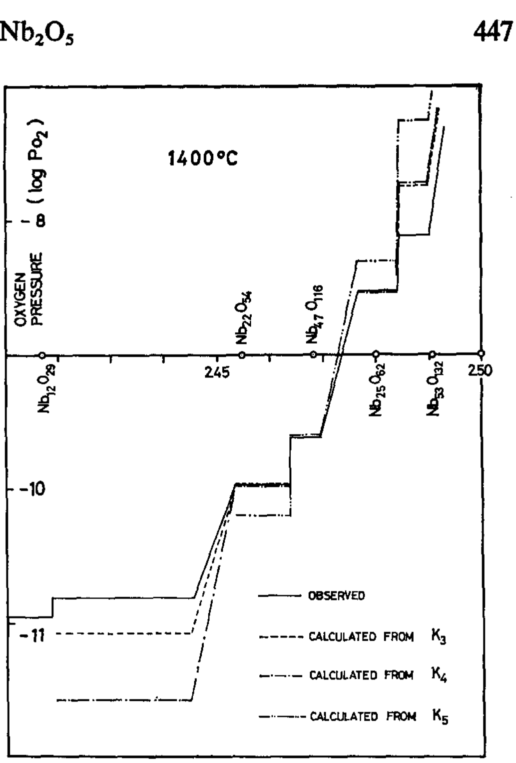

FIG. 5. Comparison of the experimental result with the "calculated" one for relation between the composition of the solid phase and the equilibrium oxygen pressure in the system NbO_2-Nb_2O_5 at 1400°C.

The experimental results show that $Nb_{22}O_{54}$ and $Nb_{25}O_{62}$ have considerable existence regions of composition. The relation between the composition of the solid phase and the corresponding equilibrium oxygen pressure for each of the compounds is shown in terms of $\log[Nb^{4+}]$ versus $\log P_{O_2}$ in Fig. 6.

When the composition variation of the solid phase is limited in a small region, Eqs. (6), (7), and (8) indicate the relation shown below:

$$P_{O_2} \propto [Nb^{4+}]^{-4}. \qquad (9)$$

The experimental results shown in Fig. 6 clearly indicate that relation (9) is not applicable to either of the existence regions of $Nb_{22}O_{54}$ and $Nb_{25}O_{62}$. After seeing such a nice agreement between the experimental data and the assumption in Figs. 4 and 5, it may be postulated that the lack of applicability of Eqs. (6), (7), and (8) denies the presence of Wadsley defects as a predominant equilibrium defect.

Allpress (*14*) once had suspected whether Wadsley defects give an appreciable contribution to the nonstoichiometry of compounds containing crystallographic shear planes. Later, however,

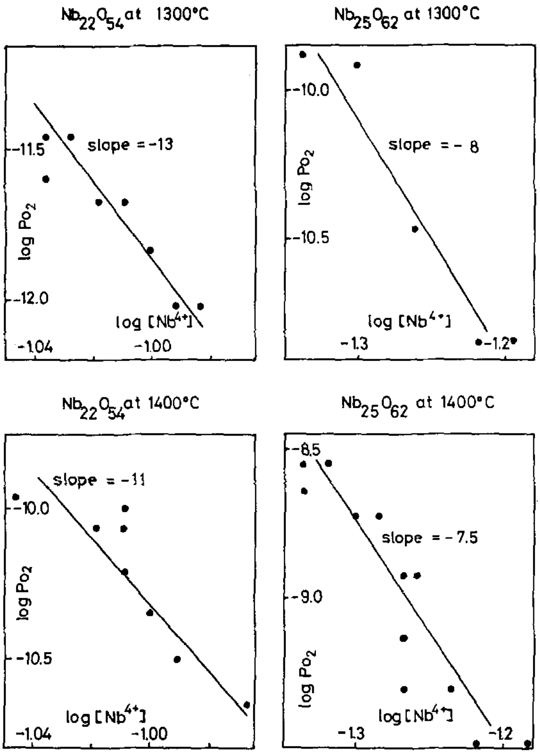

FIG. 6. Relation between the composition of the solid phase and the equilibrium oxygen pressure within the existence regions of $Nb_{22}O_{54}$ and $Nb_{25}O_{62}$ at 1300 and 1400°C.

Allpress and Roth (*15*) observed that Wadsley defects disappear during a prolonged annealing. The present result of the thermodynamic calculation may give support to their observation.

Appendix. Derivation of Eq. (1)

As shown by Wadsley and Andersson (*19*), the homologous series compounds in the Nb–O system are constructed exclusively with the octahedrons of NbO_6 and, as a minor part, the tetrahedrons of NbO_4. The constituent oxygen ions of the octahedrons and the tetrahedrons are shared by two, three, or four niobium ions, as described in the text, yielding four different species among them, presently expressed by ^2O, ^3O, ^4O, and $^2O^{IV}$.

If the oxygen sharing were totally absent, the number of oxygen ions should be expressed by $6N_{Nb^{VI}} + 4N_{Nb^{IV}}$, where N represents the total number of the indicated species. In order to find the relation between the total number of niobium and the numbers of four different types of oxygen, the easiest way seems to be to observe how the hypothetical situation of no oxygen sharing may be attained by starting from the real situation with variously shared oxygen ions. The hypothetical situation is attained by assuming the double numbers of ^2O and $^2O^{IV}$, the triple numbers of ^3O, and the quadruple numbers of ^4O. By carefully checking to which of the octahedrons and the tetrahedrons each oxygen species is bound, one may easily obtain the relations written below:

$$N_{^2O^{VI}} = 4N_{Nb^{IV}}, \tag{A-1}$$

$$2N_{^2O} + 3N_{^3O} + 4N_{^4O} + N_{^2O^{VI}} = 6N_{Nb^{VI}}. \tag{A-2}$$

The overall relation with respect to the total niobium ion is given in the combination of the above two relations.

$$\begin{aligned} &\tfrac{2}{6}N_{^2O} + \tfrac{3}{6}N_{^3O} + \tfrac{4}{6}N_{^4O} + \tfrac{1}{6}N_{^2O^{IV}} + \tfrac{1}{4}N_{^2O^{IV}} \\ &\quad = N_{Nb^{VI}} + N_{Nb^{IV}} \\ &\quad = N_{Nb} \end{aligned} \tag{A-3}$$

Thus,

$$4\frac{N_{^2O}}{N_{Nb}} + 6\frac{N_{^3O}}{N_{Nb}} + 8\frac{N_{^4O}}{N_{Nb}} + 5\frac{N_{^2O^{IV}}}{N_{Nb}} = 12. \tag{A-4}$$

The total number of a particular type of oxygen ion divided by the total number of niobium ion represents the concentration of the oxygen ion, which is expressed with the brackets, [ ], in the text. Consequently, Eq. (A-4) proves itself to be the same as Eq. (1).

Acknowledgment

The author is greatly indebted to Dr. T. Kikuchi whose suggestion on the classification of oxygen ions in the solid phases was the very start of the present procedure for thermodynamic calculation. Thanks are also extended to Dr. M. Goto and other members of the Nb–O research group in the NIRIM for their continued interest in and suggestions for this work.

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