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Thermodynamic Study of the System NbO_2–Nb_2O_5 at High Temperature

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The partial pressure of oxygen in equilibrium with niobium oxides was determined from thermogravimetric gas-equilibrium measurements over the range 1000–1100°C. Hysteresis phenomena were shown, and a method has been perfected to eliminate these phenomena. Two nonstoichiometric stable phases, $NbO_{2.42}$ and $NbO_{2.47}$, were found. A new partial phase diagram is proposed.

Introduction

Since the investigations of Brauer (*1*), niobium pentoxide, Nb_2O_5, has been considered as nonstoichiometric. According to him, the examination by X-ray diffraction of samples heated to 1350°C and quenched, indicated a single phase region between $NbO_{2.40}$ and $NbO_{2.50}$. This result was confirmed by Blumenthal, Moser, and Whitmore (*2*), who determined the partial pressure of oxygen in equilibrium with a niobium dioxide/niobium pentoxide mixture from electrochemical cell measurements over the range 800–1070°C and from thermogravimetric gas-equilibrium measurements at 1000 and 1200°C. On the other hand, Norin and Magneli (*3*) showed that three additional individual oxides, $NbO_{2.40}$, $NbO_{2.46}$, and $NbO_{2.48}$, exist within the same composition range at 1150°C. Schafer, Bergner, and Gruehn (*4*) studied the thermodynamic stability of niobium oxides and found five phases by reaction between NbO_2 or Nb_2O_5 and H_2O/H_2 mixtures. The quenched samples were investigated by X-ray diffraction and chemically analysed. Three of these phases are stoichiometric oxides, $Nb_{2.417}$, $NbO_{2.453}$, and $NbO_{2.483}$. The other two have an homogeneity range from $NbO_{2.464}$ to $NbO_{2.467}$ and from $NbO_{2.472}$ to $NbO_{2.478}$. Kovba, Trunov, and Pol'shchikova (*5*) noticed the existence of a single phase between $NbO_{2.454}$ and $NbO_{2.474}$ at 1100–1200°C. Kofstad and Anderson (*6*) measured the partial pressure of oxygen in equilibrium with Nb_2O_5 without giving boundaries of the homogeneity range. Gatehouse and Wadsley (*7*) have proposed that an homologous series of oxides with the general formula $Nb_{2n+1}O_{8n-2}$ is formed in this region. The composition $NbO_{2.50}$ corresponds to a value of $n = 9$, and the oxides corresponding to $n = 8$ ($NbO_{2.48}$) and $n = 7$ ($NbO_{2.457}$) are known. According to Roth and Wadsley (*8*) these oxides have a shear structure.

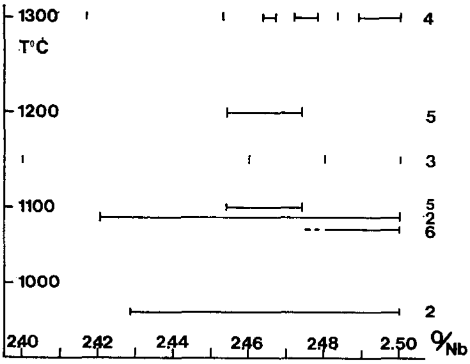

FIG. 1. Phases reported for the system NbO_2–Nb_2O_5. Numbers indicate the references.

The results that we summarized are incomplete and inconsistent, as it is shown in Fig. 1 where the different phase boundaries are collected. To explain these discrepancies, we might point to the very different sensitivities of the methods used. But we think that they may be ascribed to the lack of verification of supposed equilibrium states and to the difficulty of keeping the structures unchanged when quenching.

That has moved us to study again the system NbO_2–Nb_2O_5 by the method of equilibration between oxides and buffer gaseous mixtures, which is the most reliable.

Experimental Procedure

The experimental apparatus has been previously described (*9*). It consisted of:

(a) A Ugine-Eyraud B60 Thermobalance which had a useful sensitivity of 0.015 mg corresponding to $\delta x = 0.0001$ for a sample of Nb_2O_{5-x} weighing 1.5 g.

(b) A Chevenard furnace.

(c) Wosthöff pumps which proportioned and moved the gas mixture in the apparatus.

The accuracy of the experimental measures made with this device has been previously discussed (*9*). The gases are carbon dioxide, nitrogen, and argon purified as was mentioned before (*10*), and carbon monoxide containing these impurities: O_2, 0.004%; H_2, 0.2%; and nitrogen, 0.2%. It was not purified, and H_2 was likened to CO for the calculation of partial pressure of oxygen. The oxide used was Johnson Matthey Nb_2O_5, quality specpure. The impurities were Fe, 0.0002%; Mg < 0.0001%; and Ta < 0.01%.

Nb_2O_5 powder was sintered in air at 1380°C, in the shape of plates or cylindrical rods. The samples had a density between 80 and 90% of the theoretical density. The recrystallized alumina Morgan crucibles containing Nb_2O_5 were heated to and maintained at 1100°C in air during 24 hr. After a month of experimenting at 1100°C, the respective weights of the crucible and the sample of Nb_2O_5 had not changed, and the good reproducibility of our measurements proved the inertia of the crucibles.

Procedure. One and a half gram of Nb_2O_5 was heated in a dry air flow in the thermobalance. We ascertained that the weight corresponding to stoichiometric Nb_2O_5 remained constant during 24 hr. The air was replaced by a CO_2/CO mixture with a constant and known composition, and the oxide slowly reached equilibrium with the gaseous phase. We recorded the weight variations in the solid phase, and we assumed that the equilibrium was reached when the weight remained constant to 0.015 mg during 24 hr. During each experiment, we verified the constancy of the indication corresponding to Nb_2O_5 by periodical oxidations of the sample in dry air. The composition of an oxide was calculated by the difference of weight with Nb_2O_5.

Preliminary Study at 1100°C

We started with reduction. More and more reducing gaseous mixtures were blown on the oxide. For each value of the partial pressure of oxygen P_{O_2}, we noticed a decrease of weight, ending after 2 hr of reaction. The isotherm obtained is plotted in Fig. 2 (curve A). The values of P_{O_2} were calculated from the thermodynamic data of the Bureau of Mines (*11*) and the National Bureau of Standards (*12*)

With $\log P_{O_2} = -15.350$, we observed a continuous decrease of weight, first very fast then becoming slower and slower pointing out the reduction of Nb_2O_5 into NbO_2. The solid phase having reached the composition

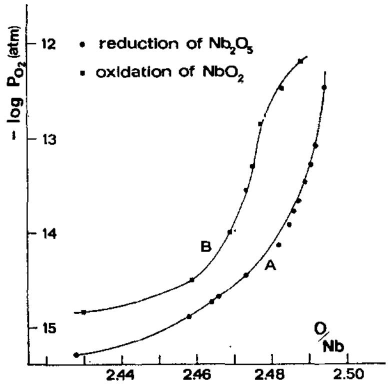

FIG. 2. Oxygen pressure as a function of the composition O/Nb. Preliminary results at 1100°C.

$NbO_{2.12}$, we oxidized it again by a gaseous mixture such as $\log P_{O_2} = -14.822$. When the weight had become constant, we noticed that the obtained composition $NbO_{2.43}$ was very different from $NbO_{2.46}$ marked on curve A for the same value of P_{O_2}. We continued the oxidation of the solid phase, gradually increasing the percentage of CO_2 in the gaseous mixture. The isotherm obtained by oxidation (curve B) was very different from the curve obtained by reduction (curve A). This phenomenon of hysteresis is similar to those observed with PrO_x (*13*) and TiO_x (*14*).

However, unlike isotherms obtained with titanium oxides, which show a stair shape (*14*), suggesting the existence of discrete phases, our isotherms do not show discontinuities and seem to indicate a single phase for a wide field of composition; that would corroborate the results of Refs. (*1*) and (*2*).

It is impossible to obtain the isotherms (B) by reduction and the isotherms (A) by oxidation, and it seems that these isotherms correspond to metastable states.

To confirm the existence of this single phase, we measured the electrical resistance R of the solid phase and plotted the curve $\log R$ vs $\log P_{O_2}$. This very sensitive method allows the detection of changes of phases, by the appearance of discontinuities in the curve $\log R$ vs $\log P_{O_2}$. But the hysteresis phenomenon compelled us to know also the composition of the solid phase, and, for this purpose, we have modified our thermobalance so that we measured the weight and resistance variations of the same sample. This one was a Nb_2O_5 plate sintered at 1400°C, the density of which was 86% of the theoretical density.

The sample, tightened between two Pt/10% Rh sheets used as electrodes, was hung on a stirrup by measuring wires, also made of Pt/10% Rh. The bottom ends of these wires were joined to electrodes; the upper ends were joined to silver contacts, fixed on an insulator at the upper part of the stirrup (Fig. 3a). The stirrup was dependent on the thermobalance beam only for a weight measure (Fig. 3b); during one measure of electrical resistance the beam and the stirrup were no longer dependent, and a mechanical device allowed to clamp the stirrup against a settled piece so that the contact was made between the hanging wires and the external circuit of measure (Fig. 3b).

The excellent reproducibility of our measurements proved the perfection of the various contacts. The resistance was measured by the two points method. Two wires conducted the current, the intensity of which was

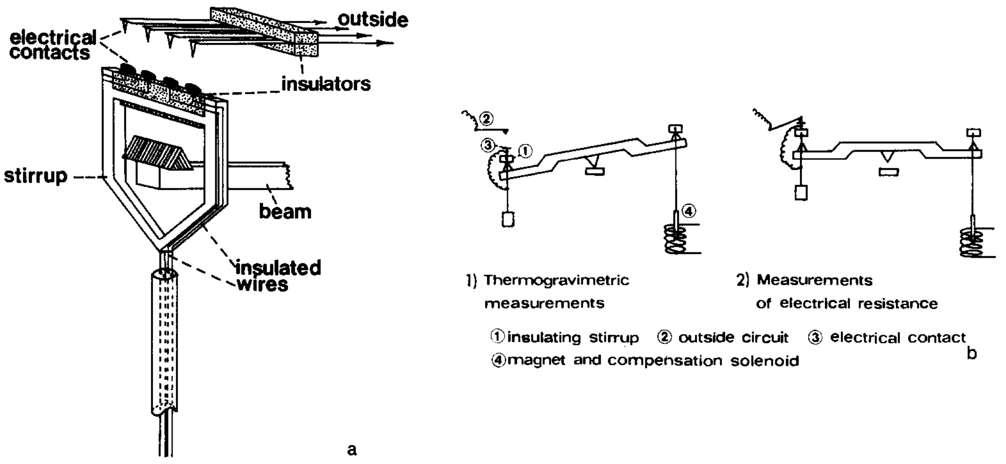

FIG. 3. (a) Schematic diagram of the stirrup. The mechanical device allowing us to clamp the stirrup is not represented. (b) Schematic diagram of the changed balance. (1) Thermogravimetric measurement: there is no contact between the outside circuit and the hanging wires. (2) Measurement of electrical resistance: the stirrup is clamped.

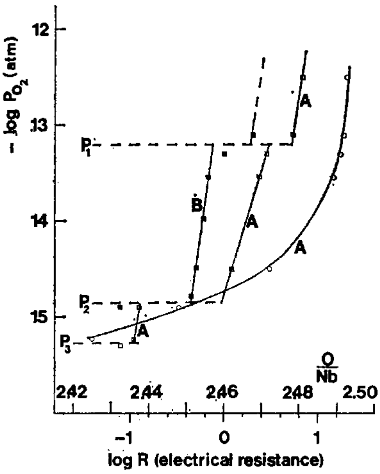

FIG. 4. Oxygen pressure as a function of the electrical resistance and the composition. The curves A are the curves of reduction. The curve B is a curve of oxidation.

obtained by measuring the potential drop across a standard resistance. Two other wires allowed the measurements of the potential drop across the sample with a Tinsley type 5590 potentiometer. To avoid any contribution to the measured potential from thermally generated electromotive forces, readings were taken in both forward and reverse directions and averaged. The resistance was evaluated at several different potentials to be certain that the sample behaved ohmically. We also checked that the value of the electrical resistance R did not change when we substituted CO/CO_2 mixtures with nitrogen, argon, or by creating a vacuum. Then, the resistance depended only on the composition of the oxide.

We repeated our experiments of reduction and oxidation. The results are plotted in Fig. 4. The curve $\log P_{O_2}$ (O/Nb) for the oxidation, which is similar to the one in Fig. 2, is not plotted. The isotherms are different according to whether we reduced Nb_2O_5 (A) or oxidized NbO_2 (B). But, contrary to the isotherms $\log P_{O_2}$ (O/Nb), the curves $\log R$ vs $\log P_{O_2}$ show discontinuities of $\log R$ for values of $P_{O_2} = p_1$, p_2, and p_3, which are the same on the curves (A) and (B). We obtained:

$$-13.300 < \log p_1 < -13.100,$$
$$-14.890 < \log p_2 < -14.830,$$
$$-15.300 < \log p_3 < -15.250.$$

Then, we supposed that each discontinuity characterized the formation of a new phase and distinct phase squared with each of the intervals p_1–p_2 and p_2–p_3. To confirm this assumption, we carried out the following experiments (Fig. 5):

(a) Nb_2O_5 was reduced by gaseous mixtures corresponding to different values of $p_{O_2} \geqslant p_1$ so that we drew the segment (m–n) of the isotherm (A). The oxide n ($NbO_{2.4908}$) prepared

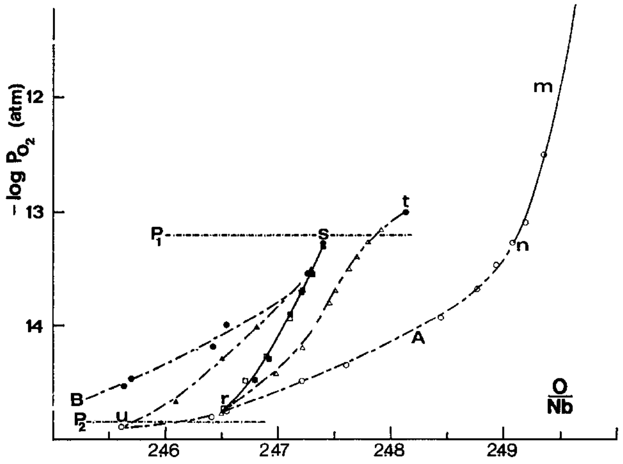

FIG. 5. Preliminary study. (○) Reduction of Nb_2O_5, (●) oxidation of NbO_2, (▲) oxidation of u, (■) oxidation of r, (□) reduction of s, (△) reduction of t.

under $p_{O_2} = 10^{-13.286}$ atm $\simeq p_1$ was oxidized. For each value of p_{O_2}, the compositions obtained by reduction and oxidation of the solid phase were the same. Therefore, (*m–n*) belonged to an isotherm corresponding to true equilibrium states.

(b) Nb_2O_5 was reduced by gaseous mixtures such as $p_2 \leqslant p_{O_2} \leqslant p_1$ until the composition $NbO_{2.4640}$ (point *r*, curve A) under $p_{O_2} = 10^{-14.820}$ atm $\simeq p_2$ was obtained. Then, *r* was oxidized, but contrary to what was observed for $p_{O_2} \geqslant p_1$, for each value of p_{O_2} the oxide prepared by reduction of *n* (segment *n–r*) had a different composition from the oxide obtained by oxidation of *r* (segment *r–s*). For $p_{O_2} = 10^{-13.286}$ atm $\simeq p_1$, the oxide was not *n* but *s* with a composition $NbO_{2.4740}$.

(c) We oxidized the compound *u* ($NbO_{2.4560}$) of the isotherm (A) prepared by reduction of Nb_2O_5 under $p_{O_2} = 10^{-14.900}$ atm. The curve of oxidation of *u* also goes through the point *s*. The oxidation of NbO_2 and the oxides prepared by reduction of Nb_2O_5 under $p_{O_2} \leqslant p_2$ gave different isotherms which all go through *s*.

(d) The reduction of the oxides belonging to the curve B and prepared by oxidation of NbO_2 under $p_{O_2} \geqslant p_1$ is represented by distinct isotherms going all through point *r*. It is the case with the oxide *t* ($NbO_{2.4815}$) obtained by oxidation of NbO_2 under $p_{O_2} = 10^{-12.900}$ atm. Therefore, the reduction of Nb_2O_5 and the oxides prepared by oxidation of NbO_2 under $p_{O_2} \geqslant p_1$, is represented by isotherms all going through *r*.

Among these isotherms, there is one very characteristic (*r–s*) which belongs to both groups of isotherms; it was obtained by reduction as well as by oxidation. It characterizes true equilibrium states: therefore, a stable phase. Then we prepared an oxide of the phase (*r–s*) and checked that every point might be obtained by reduction or oxidation.

We have shown that the range p_2–p_3 corresponds to a third phase.

Method to Obtain the Stable Phases of the System NbO_2–Nb_2O_5

From the preliminary study, it was possible to obtain the isotherms $\log p_{O_2}$ $(O/Nb)_T$ excluding the hysteresis phenomena and the metastable phases at various temperatures. For this purpose, we did as follows: we drew $\log R$ versus $\log p_{O_2}$, on which the discontinuities gave us the values of p_{O_2} in equilibrium with the diphasic systems. Then to prepare an oxide of the phase (*r–s*), the stability range of which is between p_1 and p_2, it was sufficient to reduce Nb_2O_5 under $p_{O_2} = p_2$ or to oxidize NbO_2 under $p_{O_2} = p_1$. In these conditions, only an oxide of the phase (*r–s*) was prepared. We did the same for the other phase.

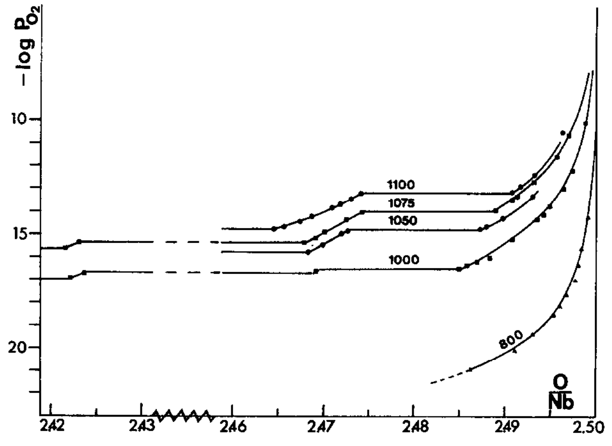

FIG. 6. Isotherms: oxygen pressure as a function of the composition corresponding to stable phases.

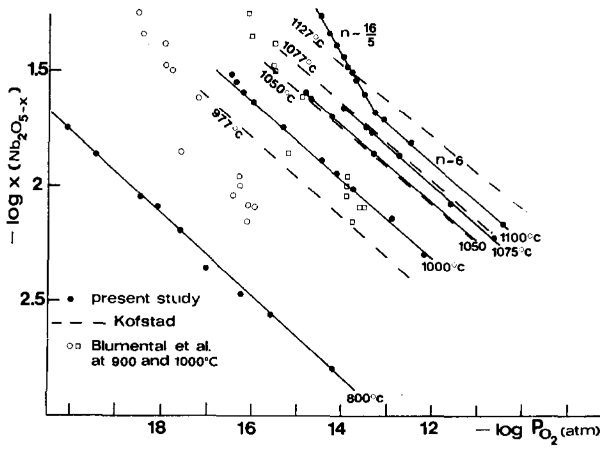

FIG. 7. The deviation from stoichiometry in Nb_2O_5 as a function of the partial pressure of oxygen at 800, 1000, 1050, 1075, and 1100°C. (●) This investigation. (○□) Results of Blumenthal, Moser, and Whitmore according to Table IV in Ref. (*2*). (— —) Results of Kofstad and Anderson according to Fig. 3 in Ref. (*6*).

Results

The isotherms $\log p_{O_2}$ (O/Nb) at 800, 1000, 1050, and 1100°C are plotted in Fig. 6. All the points of these curves have been obtained by reduction and oxidation.

The whole of our measurements shows that there are two phases between NbO_2 and Nb_2O_5, the composition of which is close to $NbO_{2.42}$ and $NbO_{2.47}$, between 1000 and 1100°C. The shape of the isotherms shows that the phases Nb_2O_5, $NbO_{2.47}$, and $NbO_{2.42}$ are nonstoichiometric, and at 1100°C the first two of them have a rather important homogeneity range. This allows us to assert that, in the investigated temperature range, there are not stable discrete phases between NbO_2 and Nb_2O_5, but two monophasic regions.

Phase Nb_2O_{5-x}

Our thermogravimetric measurements show that this oxygen deficient phase has an homogeneity range much narrower than it was assumed by Brauer and by Blumenthal, but in good agreement with the studies of Schafer. The isotherms $\log x$ vs $\log p_{O_2}$ are plotted in Fig. 7; x is the deviation from stoichiometry in Nb_2O_{5-x}. The points of the metastable isotherm obtained by reduction at 1100°C (part *n–r*, Fig. 5) are also plotted. We can see that for the thermodynamically stable phase, the isotherms are straight lines, the slope of which is $-1/n$ with $n = 5.85 \pm 0.15$, average value of the slopes for five isotherms, in good agreement with the results of Kofstad. This value is close to $n = 6$, a value which would correspond to a defect of structure involving doubly ionized oxygen vacancies. For the metastable isotherm, we obtained another straight line with a slope such as $n = 3.1$; this value is close to $n = 16/5 = 3.2$, which would correspond to a defect of structure with triply ionized niobium interstitials.

We also notice that our measurements of

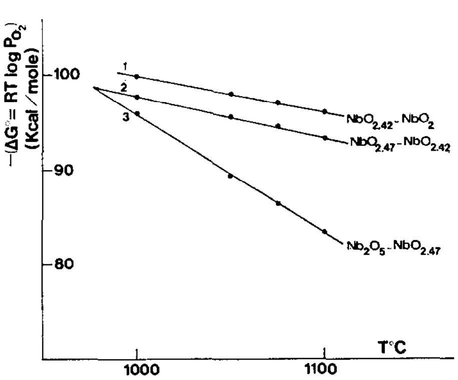

FIG. 8. Free standard energies for the reactions (1), (2), and (3).

TABLE I

T(°C)	$\Delta G° = RT\,\mathrm{Log}_e p_{O_2}$ (cal/mole)		
	Réaction 1	Réaction 2	Réaction 3
1000	−99,980 ± 190	−97,800 ± 210	−96,000 ± 220
1050	−98,000 ± 220	−95,600 ± 190	−89,400 ± 200
1075	−97,200 ± 200	−94,500 ± 400	−86,400 ± 140
1100	−95,960 ± 130	−93,340 ± 190	−83,380 ± 160

TABLE II

T(°C)	O/Nb in $NbL_{2.42}$	O/Nb in $NbO_{2.47}$	O/Nb in Nb_2O_5
1000	2.4219–2.4236	2.4688	2.4846–2.5000
1050	—	2.4680–2.4722	2.4875–2.5000
1075	2.4215–2.4230	2.4678–2.4745	2.4893–2.5000
1100	—	2.4640–2.4740	2.4905–2.5000

resistivity are in perfect agreement with the results of Kofstad (*15*).

Phase $NbO_{2.47}$

The width of its homogeneity range increases with the temperature, and at 1000°C it is very narrow. Its composition $NbO_{2.4688}$ corresponds to the $Nb_{32}O_{79}$ ($NbO_{2.4687}$) phase proposed by Wadsley (*8*). The curves log R vs $\log p_{O_2}$ show that R is proportional to $p_{O_2}{}^{1/6}$ as for Nb_2O_5, and we suppose that $NbO_{2.47}$ is also an n-type conductor.

Phase $NbO_{2.42}$

It has a narrow homogeneity range. It corresponds to the phase $Nb_{12}O_{29}$ as it is confirmed by X-ray diffraction from the Norin's data (*16*).

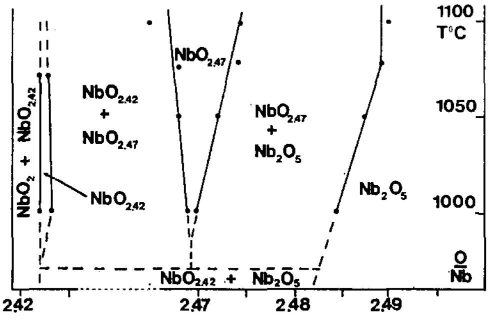

FIG. 9. Partial phase diagram for the system NbO_2–Nb_2O_5.

To specify the stability ranges of these various oxides, the free standard energies $\Delta G°$ for the following reactions are plotted in Fig. 8 and given in Table I:

$$(100/21)\ NbO_2 + O_2 = (100/21)\ NbO_{2.42} \quad (1)$$

$$40\ Nb_{2.42} + O_2 = 40\ NbO_{2.47} \quad (2)$$

$$200/3\ Nb_{2.47} + O_2 = (200/3)\ NbO_{2.50} \quad (3)$$

We obtained three straight lines, and the intersection of curves (2) and (3) leads to the conclusion that $NbO_{2.47}$ is metastable below 970°C. The whole of these results suggests a partial phase diagram of the Nb–O systems which is plotted in Fig. 9. The homogeneity field boundaries of the different oxides are collected in Table II.

Summary

The thermogravimetric study of the Nb–O system within the composition range NbO_2–Nb_2O_5, between 800 and 1100°C, shows that there are hysteresis phenomena. A thermobalance was changed in order to measure both the weight and the electrical resistance of a sample. This device permitted us to differentiate stable phases from metastable phases, and we perfected a method to prepare

only stable phases. Two monophasic regions, $NbO_{2.42}$ and $NbO_{2.47}$, were found between 800 and 1100°C in the studied composition range. This method may be applied to the metal–oxygen systems showing such anomalies.

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