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Thermogravimetric Study of the *M*–Ni–O System. I. *M* = Ta and Nb

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Phase equilibria in the Ta–Ni–O and Nb–Ni–O systems were studied at 1200°C at oxygen partial pressures ranging from 1 to $10^{-12.00}$ atm in the Ta–Ni–O system and from 1 to $10^{-14.50}$ atm in the Nb–Ni–O system. The Ni–O system was reinvestigated to confirm the previous data and to check the experimental method. In both systems Ta_2NiO_6 and Nb_2NiO_6 are stable ternary compounds under the present experimental conditions; the former has a small compositional width and the latter is almost stoichiometric. $Nb_2Ni_3O_8$ and $Nb_2Ni_4O_9$ are not stable. Lattice constants of the ternary compounds were obtained for the quenched samples. The standard Gibbs energies of the reaction $M_2O_5 + Ni + \frac{1}{2} O_2 = M_2NiO_6$ were also determined from the oxygen partial pressures in equilibrium with three solids.

The similarity between the elements niobium and tantalum is well known. They frequently occur together in nature because of their similar chemical behavior. Both elements have a valence of 5+ in the fully oxidized state. Also, their ionic radii are virtually the same, 0.64 Å, in six coordination (*1*); compounds containing either niobium or tantalum would be expected to have similar compositions.

In this paper NiO is selected as the other constituent because the Ni–O system is well studied and simple. NiO has the rock-salt structure; it is the only oxide in the system and tends to contain excess oxygen. As a result, Ni^{2+} is oxidized to Ni^{3+} in the presence of excess oxygens (*2*).

In the Ta–Ni–O and Nb–Ni–O systems, Ta_2NiO_6, Nb_2NiO_6, $Nb_2Ni_3O_8$, and $Nb_2Ni_4O_9$ are well known and their crystallographic and physical properties have been reported. $Nb_2Ni_4O_9$ has been prepared in air and its lattice constants have been reported by Bertaut *et al.* (*3*). The atomic parameters of the columbite Nb_2NiO_6 were refined by means of neutron diffraction powder diagrams (*4*). The preparation of $Nb_2Ni_3O_8$ with deep yellow was accomplished and X-ray powder pattern data for it was presented by Wanklyn *et al.* (*5*).

In neutron and X-ray diffraction studies, Ta_2NiO_6 was found to be an ideally ordered trirutile structure (*6*); susceptibility measurements showed it to be antiferromagnetic with a Néel temperature of 26 K (*7*).

A phase analysis of the NiO–Nb_2O_5 system has been performed in the composition range $1 > X_{Nb_2O_5} > \frac{1}{2}$ at temperatures between 1200° and 1500°C (*8*). Three phases, $Ni_{2/3}Nb_{34/3}O_{29}$ (o–rh), $Ni_{2/3}Nb_{34/3}O_{29}$ (mon), and $Ni_{1/3}Nb_{74/3}O_{62}$ (mon), have been observed and crystallographic data of these compounds have been reported. In the Ta_2O_5–NiO system Ta_2NiO_6, trirutile, was

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found in the temperature range from 1200° to 1600°C in samples for which $Ta_2O_5/NiO = 95/5$ and 90/10 (*9*).

As described above, the interest in the systems seems to have been focused on the crystallographic and physical properties of the compounds which were generated in the systems. Many compounds are stable in the $NiO-Nb_2O_5$ system, but reliable information on the stability of these compounds is still limited.

The objectives of the present study were: (1) to establish the detailed phase equilibria in these systems at 1200°C as a function of the oxygen partial pressure, including the well-known Ni–O system, and (2) to calculate the thermochemical properties based upon the phase equilibria.

Experimental

Analytical-grade Ta_2O_5 (99.9%), Nb_2O_5 (99.9%), and NiO (99.9%) were used as starting materials. These oxides were dried at 1200°C by firing in the air before use. Mixtures with desired molar ratios of Ta_2O_5/NiO and Nb_2O_5/NiO were obtained by mixing calculated amounts of constituent binary oxides thoroughly in an agate mortar. The mixtures thus obtained were heated at 1200°C several times under repeated mixing and were used in the thermogravimetric analysis following the same procedures described previously (*10*).

The apparatus and means of controlling the oxygen partial pressures and of keeping a constant temperature, the method of thermogravimetry, and the criterion for the establishment of equilibrium have been described previously (*10, 11*). To characterize the phases in the quenched samples in both systems, X-ray powder diffractometry was used, employing Ni-filtered Cu*Kα* radiation. Lattice constants were also determined on the mixed quenched samples by the powder X-ray method with a slow scanning speed of 0.5° 2θ/min. A standard specimen of an external silicon was used as the 2θ calibrant. Mixed gases of CO_2 and H_2 and of CO_2 and O_2 were used to achieve the required oxygen partial pressures. The actual oxygen partial pressures were measured by means of a solid electrolytic cell, $(ZrO_2)_{0.85}(CaO)_{0.15}$ (*12*).

Results and Discussion

1. *Phase Equilibrium*

a. Ni–O system. Before the experiments were carried out, the Ni–O system was reinvestigated in order to confirm the previous data and to check the operation of the apparatus in the laboratory. In Fig. 1 the relationship between the oxygen partial pressure, $-\log(P_{O_2}/\text{atm})$, and the mass change, W_{O_2}/W_T, was shown. Here, W_{O_2} is

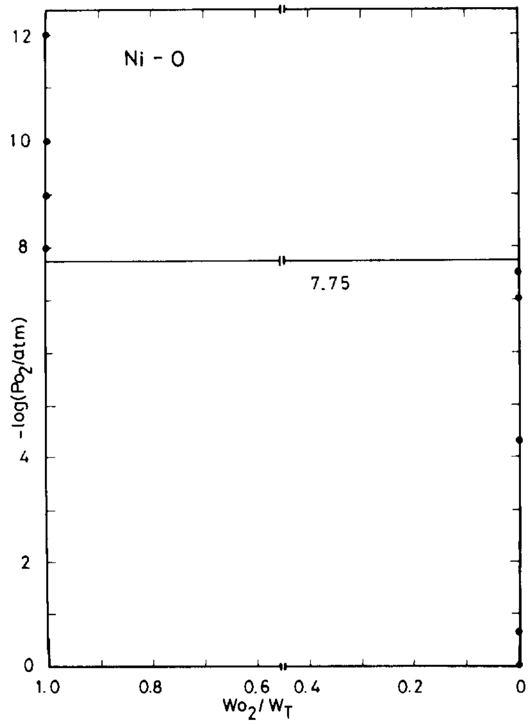

FIG. 1. The relationship between the composition W_{O_2}/W_T and the oxygen partial pressures in the system Ni–O at 1200°C.

the mass decrease of the samples relative to the reference mass at 1 atm O_2, and W_T is the total mass decrease as calculated from the reaction $NiO = Ni + \frac{1}{2} O_2$. NiO exhibits a small degree of nonstoichiometry, although Fig. 1 does not show this property because of the small changes in mass. For example, the mass of 6.4836 g NiO at 1 atm O_2 decreased by 3.2 mg at $10^{-7.50}$ atm O_2, which corresponds to the composition $NiO_{0.9977}$; it showed a 1.3888-g decrease in weight at $10^{-12.00}$ atm O_2, which just matches the mass decrease as calculated from the above reaction. These data also indicate that nickel oxide has the stoichiometric composition NiO only in an O_2 atmosphere; at oxygen partial pressures lower than 1 atm the oxygen content decreases. The relationship $N_O/N_{NiO} = 3.067 \times 10^{-4} \log P_{O_2}$ holds for NiO solid solutions, where N_O and N_{NiO} indicate the mole fraction of the subscripts for the solid solution.

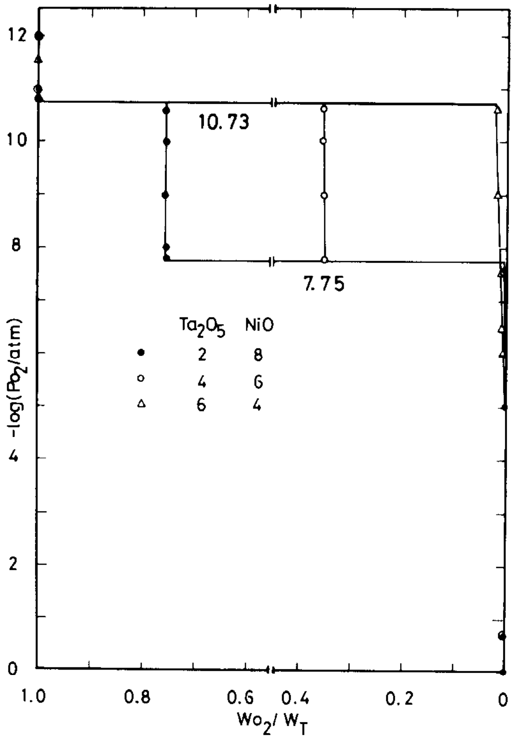

FIG. 2. The relationships between the composition W_{O_2}/W_T and the oxygen partial pressure in the Ta_2O_5–NiO–Ni system at 1200°C with Ta_2O_5/NiO ratios of (●) 2/8, (○) 4/6, and (△) 6/4.

Thermogravimetric measurements were made on NiO from 800° to 1100°C in the range 10^{-1} to 10^{-4} O_2 atm to determine the defect concentrations (*13*). However, the relative mass change (μg) relative to the reference state remains uncertain.

At $\log P_{O_2} = -7.75$ a sudden mass decrease is observed which continues to the point where $W_{O_2}/W_T = 1.000$, at which only Ni metal is stable. The corresponding value, $\log P_{O_2} = -7.75$, is in good agreement with values of -7.70, -7.82, and -7.76, which have been calculated from $\Delta G°$ values by Kubaschewskii *et al.* (*14*), Elliott and Gleiser (*15*), and Kemori *et al.* (*16*), respectively. Sockel and Schmalzried (*17*) also cited a value of -7.79 based on a coulometric titration method.

b. Ta_2O_5–Ni–NiO system. Three mixtures with Ta_2O_3/NiO mole ratios of 6/4, 4/6, and 2/8 were prepared and used in thermogravimetric experiments.

In Fig. 2 are shown the relationships between the oxygen partial pressure (ordinate) and the mass change (abscissa) for the three samples. The mass at 1 atm O_2 was used as the reference as in the case of the Ni–O system. As is shown in Fig. 2, abrupt mass changes are encountered at $\log P_{O_2} = -7.75$ and -10.73. The former is identical with that of the Ni–O system and therefore reflects the oxygen partial pressure in equilibrium with Ni and NiO. The latter corresponds to the oxygen partial pressure in equilibrium with three solid phases, Ta_2O_5, Ni, and Ta_2NiO_6.

The identification of the phases was carried out with samples which were quenched under different oxygen partial pressures. The results are shown in Table I in terms of two-phase combinations.

Based upon the thermogravimetric

TABLE I

IDENTIFICATION OF PHASE

M_2O_5	NiO	$-\log P_{O_2}$	Time	
(mol%)		(atm)	(hr)	Phase
Ta_2O_5				
60	40	0.68	8	$Ta_2O_5 + Ta_2NiO_6$
		10.50	8	$Ta_2O_5 + Ta_2NiO_6$
		11.00	8	$Ni + Ta_2O_5$
40	60	0.68	8	$NiO + Ta_2NiO_6$
		8.00	16	$Ni + Ta_2NiO_6$
		12.00	8	$Ni + Ta_2O_5$
20	80	7.50	16	$NiO + Ta_2NiO_6$
		10.50	8	$Ni + Ta_2NiO_6$
		11.00	8	$Ni + Ta_2O_5$
Nb_2O_5				
60	40	0.68	8	$Nb_2O_5 + Nb_2NiO_6$
		7.60	15	$Nb_2O_5 + Nb_2NiO_6$
		10.00	8.5	$Nb_2O_5 + Nb_2NiO_6$
		11.00	8	$Ni + Nb_2O_5$
		13.00	9	$Ni + Nb_2O_5$
		13.75	8	$Ni + NbO_{2.42}$[a]
		14.00	8	$Ni + NbO_2$
40	60	0.68	8	$NiO + Nb_2NiO_6$
		7.60	15	$NiO + Nb_2NiO_6$
		8.00	15	$Ni + Nb_2NiO_6$
		10.00	8.5	$Ni + Nb_2NiO_6$
		11.00	8	$Ni + Nb_2O_5$
		13.75	8	$Ni + NbO_{2.42}$
20	80	7.60	15	$NiO + Nb_2NiO_6$
		8.00	15	$Ni + Nb_2NiO_6$
		11.00	8	$Ni + Nb_2O_5$
		13.75	8	$Ni + NbO_{2.42}$
		14.00	8	$Ni + NbO_2$

[a] JCPDS Card No. 19-861.

results and the phase identifications, a phase diagram was drawn as shown in Fig. 3 for the Ta_2O_5–Ni–NiO system. The diagram is very simple and is depicted with a ternary compound, Ta_2NiO_6. Four phases, Ta_2O_5, Ni, NiO, and Ta_2NiO_6 (*A*) are stable in the diagram. The numerical values in the three solid fields in Fig. 3 are the two values in $-\log P_{O_2}$ described above. Ta_2NiO_6 exhibits a small degree of nonstoichiometry. The compositional range is, however, too small to permit evaluation of the deviation from stoichiometry as a function of the oxygen partial pressure. The lattice constants of Ta_2NiO_6 were determined with two quenched samples containing Ta_2O_5 and NiO. Both values are identical and are in good agreement with those of Heidenstam (*6*). This fact suggests that the formation of solid solutions with Ta_2O_5 and NiO might be very small.

c. NbO_2–Ni–O system. In the previous paper (*18*), the phase equilibria in the NbO_2–Nb_2O_5 system were reinvestigated in

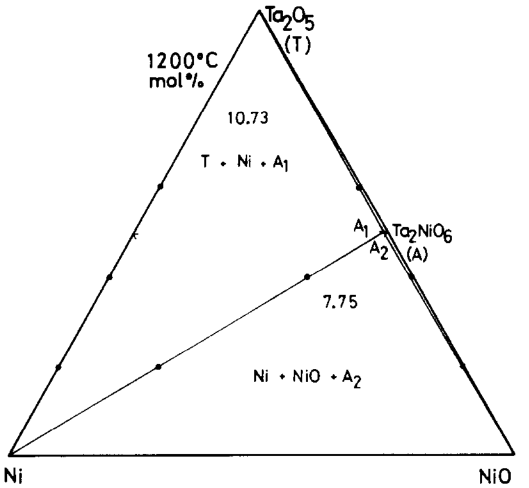

FIG. 3. Phase equilibria in the Ta_2O_5–NiO–Ni system at 1200°C. Numerical values in the three-phase regions are the oxygen partial pressures in $-\log(P_{O_2}/\text{atm})$ in equilibrium with the three solid phases. Symbols are the same as those in the text. The solid solution range of Ta_2NiO_6 is somewhat exaggerated.

the study of the phase equilibria of the Fe–Nb–O system. According to these results, the Nb_2O_5 phase displays nonstoichiometric compositions in the range 0 to −13.40 in $\log(P_{O_2}/\text{atm})$; from −13.40 to −13.90 in $\log(P_{O_2}/\text{atm})$ the intermediate phase, $Nb_2O_{4.84}$, is stable. The intermediate phase and stoichiometric NbO_2 are in equilibrium at an oxygen partial pressure of $\log P_{O_2} = -13.90$.

Five samples, Nb_2O_5/NiO = 9/1, 8/2, 6/4, 4/6, and 2/8, were prepared for thermogravimetry. In Fig. 4 the relationships between the oxygen partial pressure and the mass decrease in the samples are shown for two samples with Nb_2O_5/NiO = 4/6 and 8/2. The mass at 1 atm O_2 was again chosen as a reference. In the oxygen partial pressure ranges used, four abrupt mass changes were encountered at $\log P_{O_2} = -7.75$, −10.57, −13.40, and −13.90. These values, except for −10.57, are common to the Ni–O and Nb_2O_5–NbO_2 systems. The $\log P_{O_2} = -10.57$ value reflects the equilibrium with Nb_2O_5 (D_1), Nb_2NiO_6, and Ni. Because NbO_2 had been considered to be stoichiometric in the oxygen partial pressure range from $10^{-13.90}$ to $10^{-16.60}$ (*18*), it was expected that in the same oxygen partial pressure range no mass change would be observed. Contrary to expectations, mass changes with oxygen pressures were encountered, as shown in Fig. 4. The Nb_2O_5–NbO_2 system was, therefore, reinvestigated and the previous results were confirmed. That is, two W_{O_2}/W_T mass and O/Nb mole ratios change from 0.993 to 1.006 and from 2.003 to 1.997 in an oxygen partial pressure range from $10^{-14.00}$ to $10^{-15.75}$ atm, respectively. Here, W_{O_2} is the mass decrease of Nb_2O_5 and W_T is the calculated total mass decrease of the samples in the reaction $Nb_2O_5 = 2NbO_2 + \frac{1}{2}O_2$. In Ref. (*18*) these differ-

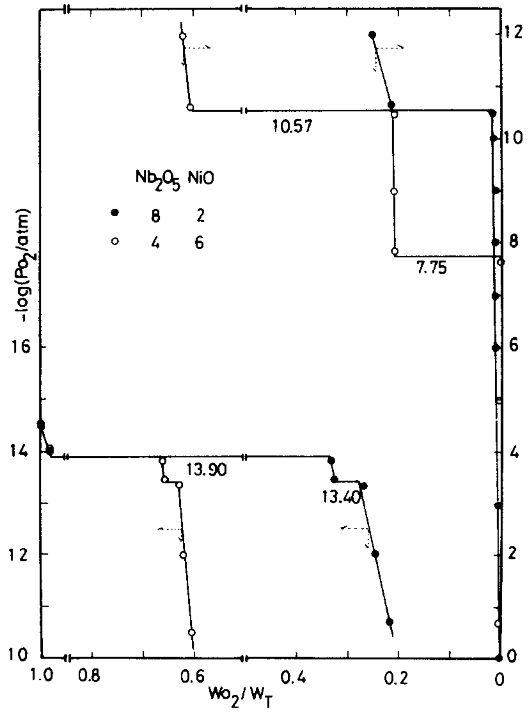

FIG. 4. The relationships between the composition W_{O_2}/W_T and the oxygen partial pressure in the NbO_2–Ni–O system at 1200°C with ratios of Nb_2O_5/NiO of (●) 8/2 and (○) 4/6.

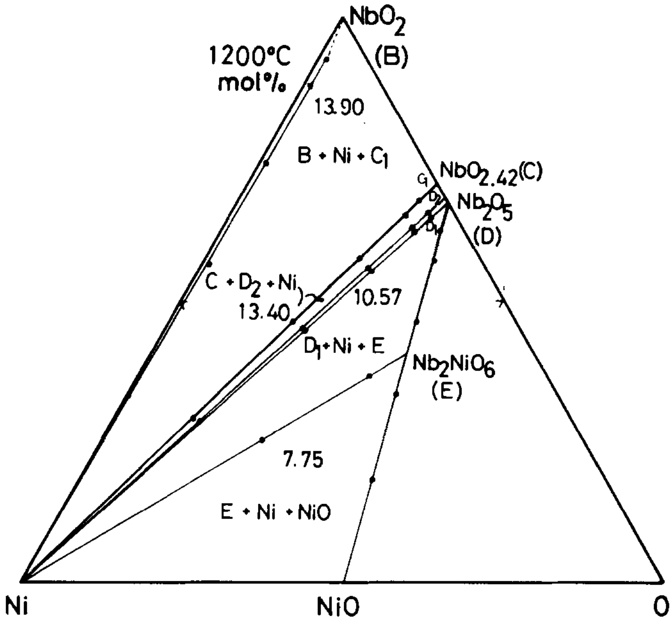

FIG. 5. Phase equilibria in the NbO_2–Ni–O system at 1200°C. Numerical values in the three-phase regions are the oxygen partial pressures in $-\log(P_{O_2}/\text{atm})$ in equilibrium with the three solid phases. Symbols are the same as those in the text.

ences were regarded as lying within the experimental error, indicating that NbO_2 exhibits only a small degree of nonstoichiometry.

The identification of the phases was carried out on samples which were quenched at different oxygen partial pressures. A part of these results is shown in Table I as two-phase combinations, together with those of the Ta_2O_5–Ni–NiO system.

Based upon the thermogravimetric results and the phase identification, a phase diagram was drawn up with the apices representing NbO_2, Ni, and O as shown in Fig.

TABLE II

LATTICE CONSTANTS OF TERNARY COMPOUNDS

Compound	$-\log P_{O_2}$ (atm)	Other phases	a (Å)	b (Å)	c (Å)	V (Å^3)	Ref.
Ta_2NiO_6	0.68	Ta_2O_5	4.716 ± 0.001		9.117 ± 0.001	202.8 ± 0.1	This work
	0.68	NiO	4.716 ± 0.001		9.117 ± 0.001	202.8 ± 0.1	This work
			4.7173 ± 0.0004		9.127 ± 0.001		(5)
Nb_2NiO_6	0.68	Nb_2O_5	14.011 ± 0.004	5.676 ± 0.002	5.018 ± 0.002	399.1 ± 0.2	This work
	0.68	NiO	14.026 ± 0.003	5.681 ± 0.001	5.023 ± 0.001	400.2 ± 0.1	This work
			14.044 ± 0.016	5.670 ± 0.006	5.020 ± 0.005		(17)
			14.018 ± 0.004	5.678 ± 0.002	5.021 ± 0.002		(16)

TABLE III

The Standard Gibbs Energy of Reaction at 1200°C

Reaction	$-\log P_{O_2}$ (atm)	$-\Delta G^\circ$ (kJ)	$-\Delta G^\circ$ (kJ)
1. $Ni + \frac{1}{2} O_2 = NiO$	7.75 ± 0.05	109.3 ± 1.0	108.8 ± 8.4 (*14*), 110.3 (*15*) 109.4 (*16*)
2. $Ni + Ta_2O_5 + \frac{1}{2} O_2 = Ta_2NiO_6$	10.73 ± 0.05	151.3 ± 1.0	
3. $Ni + Nb_2O_5 + \frac{1}{2} O_2 = Nb_2NiO_6$	10.57 ± 0.05	150.4 ± 1.0	

5. Numerical values in the three solid fields indicate four equilibrium oxygen partial pressures in $-\log P_{O_2}$. In order to be consistent with the previous data, the boundary curve near NbO_2 was drawn as a dotted line. Six phases, NbO_2 (*B*), $NbO_{2.42}$ (*C*), Nb_2O_5 (*D*), Ni, NiO, and Nb_2NiO_6 (*E*) are stable. $Nb_2Ni_3O_8$, $Nb_2Ni_4O_9$, and three other reported phases (*8*) were not found. $Nb_2Ni_3O_8$ and $Nb_2Ni_4O_9$ might be stable at temperatures lower than 1200°C, judging from the results of a previous study (*5*). In order to assure the stability conditions of these compounds, an experiment at lower temperatures would be desirable. Nb_2NiO_6 is stoichiometric. Numerous phases were reported in the NbO_2–Nb_2O_5 system, but the $NbO_{2.42}$ phase seems to be the only definite reported oxide phase in the system (*18*).

2. Lattice Constants and the Standard Gibbs Energy of Reaction

According to the previous reports, Ta_2NiO_6 is of the trirutile type (*6, 19*), and Nb_2NiO_6 exhibits two types of crystal system, columbite (*20, 21*) and rutile (*20*). The crystal system of Nb_2NiO_6 prepared by the quenching technique crystallized as columbite-type. The lattice constants obtained are listed in Table II. Values of both compounds are in good agreement with previous values and would not change under conditions of coexistence with other phases. This might indicate that the width of the nonstoichiometric composition toward the apex compounds are negligible or zero as shown in Figs. 3 and 5.

On the basis of the established phase diagrams, the standard Gibbs energies of reactions, which appear in the diagrams and are shown in Table III, are determined from the relation $\Delta G^\circ = -RT \ln K$. Here, *R* is the gas constant, *T* the absolute temperature, and *K* the equilibrium constant of the reaction. The activity of the component Ta_2NiO_6 in the solid solution is assumed to be unity, although a small degree of nonstoichiometry is observed. The activity of the Nb_2O_5 component at $\log P_{O_2} = -10.57$ was calculated to be 0.894 from previous data (*18*). The present value −109.3 kJ for reaction (1) in Table III is in good agreement with three values reported previously (*14–16*).

Acknowledgment

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