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On the Phase Composition of the $NiO-Nb_2O_5$ System

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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. The three phases $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(o-rh), $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(mon), and $Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$ have been observed.

In their paper on phases in the $NiO-Nb_2O_5$-system, Burdese *et al.*[1] reported the existence of $NiO\cdot 7Nb_2O_5$, $NiO\cdot 18Nb_2O_5$, and $NiO\cdot 34Nb_2O_5$ in the niobium-rich half of the system. They considered these three phases to be isostructural with $NbO_{2.40}$, $NbO_{2.46}$, and $NbO_{2.48}$,[2] respectively. Subsequent investigations[3–8] have shown the existence of six intermediate phases in the NbO_2-Nb_2O_5-system, the crystal structures of which have all been determined. In order to determine the crystal structures of the three nickel-niobium phases mentioned above, the preparation of these three oxides was attempted.

Samples were prepared in three different ways:

Method 1. Intimate mixtures of high purity Nb_2O_5 and NiO were pressed into small tablets. The tablets were melted and quenched, or melted and tempered in air at 1250 – 1400°C for 1 – 15 days. Some of the samples were prepared in a stream of oxygen.

Method 2. Intimate mixtures of Nb_2O_5 and $NiCO_3$ were pressed into small tablets which were subsequently tempered at 1300 – 1400°C for 1 – 15 days.

Method 3. Nb_2O_5 was dissolved in a heated mixture of $(NH_4)_2SO_4$ and H_2SO_4 and $Nb_2O_5(H_2O)_x$ was precipitated with dilute ammonia from the cooled solution, filtered, washed and dried at 80°C. Intimate mixtures of $Ni(OH)_2$ and this hydrated form of Nb_2O_5 were pressed into small tablets and tempered at 1300 – 1400°C for 1 – 7 days.

All the samples were investigated with powder photographs using the Guinier method. Weissenberg photographs $h0l-h2l$ were also taken from a single crystal found in a sample with the molar ratio Ni/Nb = 1/14, prepared by Method 1. The result of the phase analysis is given in Table 1.

Powder patterns of phases *A* and *B* show that these oxides are isostructural with $Ti_2Nb_{10}O_{29}$(o-rh)[9] and $Nb_{12}O_{29}$(mon).[4] They can thus be assigned the formulae $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(o-rh) and $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(mon), respectively. The powder

Table 1. Experimental data from the preparation of phases in the $NiO-Nb_2O_5$-system. The phases found in the different samples are denoted: $A = Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(o-rh), $B = Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(mon), and $C = Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$.

Ni/Nb molar ratio	Prepared by method No.	Heat treatment	Phases found
1/14	1	Melted	H-$Nb_2O_5 + B$
1/14	1	Melted and tempered in O_2 at 1400°C for 4 d	H-$Nb_2O_5 + A$
1/14	1	Melted and tempered at 1250°C for 2 d	H-$Nb_2O_5 + NiNb_2O_6$
1/14	2	Tempered at 1400°C for 3 h	H-$Nb_2O_5 + B$
1/34	3	Tempered at 1400°C for 2 h	H-$Nb_2O_5 + C$
1/34	3	Tempered at 1400°C for 26 h	H-$Nb_2O_5 + NiNb_2O_6$

Table 2. Crystallographic data for $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(o-rh). Unit cell dimensions: $a = 28.71 \pm 0.02$ Å; $b = 3.837 \pm 0.002$ Å; $c = 20.65 \pm 0.01$ Å.
Systematically absent reflexions: hkl with $k+l=$ odd, $h0l$ with $h=$ odd.
Possible space groups: No. 63 *Amma*, No. 40 *Am2a*, and No. 36 $A2_1ma$.
$Z = 4$.
Powder pattern data. $CuK\alpha_1$ radiation. $\lambda(CuK\alpha_1) = 1.5405$ Å.

I obs	$\sin^2\theta \times 10^5$ obs	d obs	$h\,k\,l$	$\sin^2\theta \times 10^5$ calc	d calc
w	289	14.33	2 0 0	288	14.36
w	630	9.704	1 0 2	629	9.714
w	1153	7.173	4 0 0	1152	7.177
s	2232	5.156	0 0 4	2227	5.161
vvw	2305	5.073	1 0 4	2299	5.080
s	2593	4.783	6 0 0	2591	4.785
vs	4174	3.770	0 1 1	4168	3.773
vs	4239	3.741	1 1 1	4240	3.740
vvs	4607	3.589	8 0 0	4607	3.589
vs	5011	3.441	0 0 6	5011	3.441
m	5080	3.417	1 0 6	5083	3.416
s	5283	3.351	0 1 3	5282	3.351
vvw	7200	2.871	10 0 0	7198	2.871
vvs	7580	2.798	1 1 5	7581	2.797
vw	8160	2.696	3 1 5	8157	2.697
vvw	8534	2.637	7 0 6	8538	2.636
vvw	8755	2.603	8 1 1	8775	2.600
vw	9319	2.523	5 1 5	9309	2.525
vvw	9901	2.448	8 1 3	9889	2.449
vvw	10370	2.392	12 0 0	10365	2.392
vvw	10852	2.338	0 1 7	10849	2.338
m	11039	2.318	7 1 5	11036	2.319
vvw	13343	2.109	9 1 5	13340	2.109
s	13919	2.065	0 0 10	13919	2.065
s	14110	2.051	14 0 0	14108	2.051
vs	16118	1.919	0 2 0	16117	1.919

Table 3. Crystallographic data for $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(mon). Unit cell dimensions: $a = 31.19 \pm 0.05$ Å; $b = 3.836 \pm 0.005$ Å; $c = 20.65 \pm 0.02$ Å; $\beta = 113.1 \pm 0.1°$.
$Z = 4$.
Powder pattern data. $CuK\alpha_1$ radiation. $\lambda(CuK\alpha_1) = 1.5405$ Å.

I obs	$\sin^2\theta \times 10^5$ obs	d obs	$h\,k\,l$	$\sin^2\theta \times 10^5$ calc	d calc
vw	291	14.28	2 0 0	288	14.35
vw	613	9.838	2 0 −2	605	9.906
vvw	662	9.467	0 0 2	657	9.500
vw	1159	7.155	4 0 0	1152	7.175
m	2242	5.144	2 0 −4	2236	5.151
m	2601	4.776	6 0 0	2593	4.783
vvs	4204	3.757	0 1 1	4196	3.760
w	4313	3.709	2 1 −1	4314	3.709
vs	4612	3.587	8 0 0	4610	3.588
vvw	4660	3.568	2 1 1	4654	3.570
vs	5033	3.433	4 0 −6	5024	3.436
vvw	5188	3.382	2 0 −6	5183	3.383
m	5288	3.350	2 1 −3	5288	3.350
vvw	5457	3.297	6 0 −6	5442	3.302
vw	5693	3.228	4 1 1	5689	3.229
vw	8006	2.722	10 0 −6	8007	2.722
m	8139	2.700	8 1 −1	8124	2.702
vw	8954	2.574	4 0 −8	8945	2.575
w	9112	2.552	4 0 6	9115	2.551
vw	9289	2.527	2 1 5	9281	2.528
vw	9340	2.520	8 1 −5	9342	2.520
vvw	9498	2.499	8 1 1	9487	2.501
vvw	9645	2.480	6 1 3	9638	2.481

pattern of $NiO \cdot 7Nb_2O_5$[1] shows that this oxide is identical with one of the forms of $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$. As the powder patterns of our two modifications are very similar, and only relatively few reflexions have been obtained by Burdese *et al.*[1] for $NiO \cdot 7Nb_2O_5$, nothing definite can be said if this substance is the orthorhombic or the monoclinic form. Crystallographic data for the two oxides are given in Tables 2 and 3. The powder pattern of $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$(mon) was registered from a sample prepared by Dr. Emmenegger (Zürich),[12] who used a transport reaction. It was kindly placed at our disposal through Dr. Gruehn. The cell dimensions have been refined with a program written by Lindqvist and Wengelin[10] for the computer IBM 360/65.

Phase *C* appeared only in samples prepared by Method 3. It could not be prepared in a pure form and tended to decompose when tempered at high temperatures. The powder pattern of this phase shows it to be isostructural with $TiNb_{24}O_{62}$[11] and it may thus be assigned the formula $Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$. Its powder pattern agrees with that of $NiO \cdot 18Nb_2O_5$,[1] the agreement being, however, rather poor. As $Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$ always occurred together with H-Nb_2O_5 in our samples and the powder patterns of these compounds are extremely similar with a large number of coincident reflexions, it was not possible to refine the unit cell parameters of this nickel-niobium oxide. The crystallographic data proposed for this compound, given in Table 4, are based on the assumption that this compound is isostructural with $TiNb_{24}O_{62}$.

Table 4. Crystallographic data for $Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$.

Unit cell dimensions: $a = 29.85 \pm 0.08$ Å; $b = 3.82 \pm 0.02$ Å; $c = 21.20 \pm 0.07$ Å; $\beta = 95.0 \pm 0.2°$ $Z = 2$.

Powder pattern data of a mixed H-$Nb_2O_5 - Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$ sample with the approximate molar ratio H-$Nb_2O_5/Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62} = 3/2$. $CuK\alpha_1$ radiation. $\lambda(CuK\alpha_1) = 1.5405$ Å.

I obs	$\sin^2\theta \times 10^5$ obs	d obs	$h\,k\,l$	$\sin^2\theta \times 10^5$ calc	d calc
*w	531	10.57	0 0 2	532	10.56
*vvw	706	9.167	2 0 −2	735	8.983
*vvw	2125	5.284	0 0 4	2129	5.279
*m	2264	5.119	2 0 −4	2267	5.116
vvw	2651	4.731	6 0 1	2647	4.735
*vvs	4241	3.740	1 1 −1	4244	3.739
w	4550	3.611	8 0 1	4558	3.608
*vvs	4885	3.485	2 0 −6	4862	3.493
*s	5285	3.351	1 1 −3	5276	3.353
vvw	5713	3.223	3 1 −3	5715	3.222
*vvw	6216	3.089	6 0 5	6232	3.086
*vs	7394	2.833	1 1 −5	7372	2.837
*s	7726	2.771	3 1 −5	7745	2.768
*vvw	9057	2.559	4 0 −8	9066	2.558
*m	9205	2.539	10 0 −5	9220	2.537
*vvw	9904	2.448	7 1 4	9934	2.444
w	10604	2.365	12 0 2	10587	2.367

* Overlap with a H-Nb_2O_5 reflexion.

All attempts to prepare the third phase reported by Burdese *et al.*,[1] $NiO \cdot 34Nb_2O_5$, have proved unsuccessful. The powder pattern reported has similarities with that of $Nb_{53}O_{132}$[6] indicating that this nickel-niobium phase might be isostructural with $Nb_{53}O_{132}$. If this were the case, its formula would be $Ni_{\frac{1}{3}}Nb_{52\frac{2}{3}}O_{132}$.

The occurrence of the dimorphous $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ agrees with corresponding observations in other binary oxide systems[13,14] in which Nb_2O_5 is one of the components. The monoclinic modification is formed when a melt is quenched, while the orthorhombic phase seems to be stable at temperatures below the melting point, at least down to about 1400°C, in agreement with observations for some other similar binary oxide systems.[13,14] Other phases isostructural with $Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$ have also been observed in some systems[11,14–16] of this type. Both $Ni_{\frac{2}{3}}Nb_{11\frac{1}{3}}O_{29}$ and $Ni_{\frac{1}{3}}Nb_{24\frac{2}{3}}O_{62}$ decompose to H-Nb_2O_5 and $NiNb_2O_6$ when tempered at 1200 − 1300°C which is not the case for corresponding phases in the systems mentioned.

It is remarkable that the rate of reaction in the solid state seems to be much lower in the $NiO - Nb_2O_5$-system than in most other related systems investigated. It has proved difficult to prepare intermediate nickel-niobium oxides and the reactions have not normally reached equilibrium.

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