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On the Crystal Structures of Some Phases in the Al_2O_3-Nb_2O_5-System

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A phase analysis of the Al_2O_3-Nb_2O_5-system has been performed in the composition range $1 > x_{Nb_2O_5} > \frac{1}{2}$ at temperatures between 1100°C and 1500°C. Besides the previously known phases $AlNb_{11}O_{29}$ and $Al_{\frac{1}{3}}Nb_{24\frac{1}{2}}O_{62}$, a new phase "$(Al,Nb)O_{2.283}$", probably $Al_{\frac{1}{3}}Nb_{52\frac{1}{3}}O_{132}$, has been observed.

Two previously unknown phases in the Al_2O_3-Nb_2O_5-system, $Al_2O_3 \cdot 9Nb_2O_5$ and $Al_2O_3 \cdot 25Nb_2O_5$, have been reported by Layden.[1] The first oxide was thought to correspond to $NbO_{2.40}$,[2] which was later shown to consist of two forms of $Nb_{12}O_{29}$,[3,4] and the second oxide to $Nb_{11}O_{27}$.[2] Roth, Wadsley and Gatehouse [5] have pointed out that $AlNb_{11}O_{29}$ is isostructural with the corresponding phase in the TiO_2-Nb_2O_5-system. Waring and Roth [6] agree with the above authors on the correspondence between $Al_2O_3 \cdot 25Nb_2O_5$ and $Nb_{11}O_{27}$. Gruehn and Schäfer [7] have suggested the formulae $(Al,Nb)O_{2.417}$, (corresponding to the monoclinic form of $Nb_{12}O_{29}$ [4]) for $Al_2O_3 \cdot 9Nb_2O_5$ and $(Al,Nb)O_{2.467}$ (corresponding to the lower limit, $NbO_{2.467}$, of $Nb_{25}O_{62}$ [15]) for $Al_2O_3 \cdot 25Nb_2O_5$. In order to ascertain the proposed phase composition a reinvestigation of the Nb_2O_5-rich part of the Al_2O_3-Nb_2O_5-system has been performed.

EXPERIMENTAL

Mixtures of high purity Al_2O_3 and Nb_2O_5 were melted at about 1500°C. Some of the melted samples were tempered at various temperatures in the range 1250–1500°C for 1–11 days. Other intimate mixtures were tempered under the same conditions but without first being melted. The samples were quenched and investigated with Guinier and Weissenberg methods. Experimental data obtained from the phase analysis are given in Table 1. In several samples more than two phases occur, indicating either that equilibrium is not reached or that small amounts of neighbouring phases are formed during the quenching. The densities were determined from the apparent loss of weight in benzene.

Table 1. Experimental data from the phase analysis of samples $(Al,Nb)O_x$ with $2.3<x<2.5$. Reflexions from the following phases were found in Guinier photographs of the quenched samples:

Phase 1 = H-Nb_2O_5; 2 = "$(Al,Nb)O_{2.483}$"; 3 = $Al_{\frac{1}{2}}Nb_{24\frac{1}{2}}O_{62}$; 4 = $AlNb_{11}O_{29}$; 5 = $AlNbO_4$.

Molar ratio Al_2O_3/Nb_2O_5	Heat treatment	Phases found
1/40	melted	1, 2, 3, 4
1/40	melted and tempered at 1400°C for 4 d	1, 3
1/25	melted	1, 2, 3, 4
1/25	melted and tempered at 1400°C for 3 d	3.
1/21	melted	1,[a] 2,[a] 3, 4[a]
1/21	melted and tempered at 1400°C for 4 d	3, 4[a]
1/21	tempered at 1400°C for 1 d	3, 4[a]
1/11	melted and tempered at 1400°C for 1 d	3, 4
1/11	tempered at 1400°C for 1 d	3, 4
1/9	melted	3,[a] 4
1/9	melted and tempered at 1100°C for 11 d	4
1/8.5	tempered at 1400°C for 1 d	4
1/5	melted	4, 5

[a] very little.

RESULTS OF THE X-RAY STUDIES

A comparison of Guinier and single crystal data shows that there is no doubt that $AlNb_{11}O_{29}$ and $Al_{\frac{1}{2}}Nb_{24\frac{1}{2}}O_{62}$ are isostructural with $Nb_{12}O_{29}$(mon)[4] and $TiNb_{24}O_{62}$,[8] respectively. d-Values for the two Al-Nb-oxides agree with those given by Layden [1] for $Al_2O_3 \cdot 9Nb_2O_5$ and $Al_2O_3 \cdot 25Nb_2O_5$. Crystallographic

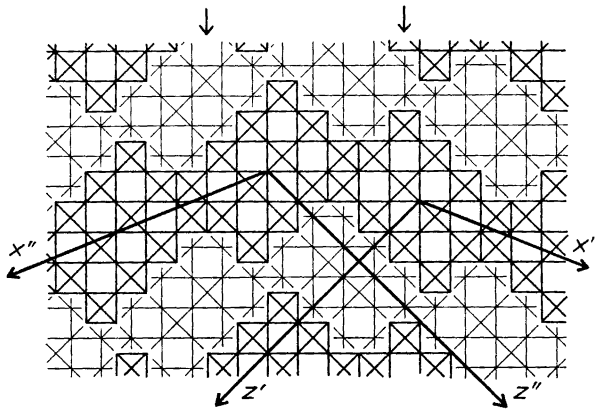

Fig. 1. Idealized projection on the xz-plane showing a plausible mode of twinning of two $AlNb_{11}O_{29}$ crystals along their $20\bar{1}$ planes. Heavy squares with diagonals indicate MeO_6-octahedra (Me=Nb or Al) in $y=0$ and fine squares with diagonals those in $y=\frac{1}{2}$. The axial directions of the two crystals are indicated (*cf.* the idealized picture of $Nb_{12}O_{29}$(mon)[4]). The two small arrows indicate the positions of two planes, parallel to $20\bar{1}$, delimiting those parts of the structure common to both crystals.

data for the two compounds and powder pattern data, refined using a computer program written by Lindqvist,[9] are given in Tables 2 and 3.

All crystals of $AlNb_{11}O_{29}$ hitherto investigated show the same kind of twinning. Examination of the reciprocal lattice of such a twinned crystal shows two lattices with their a^*-axes mutually inclined at an angle of very close to 90° but with their b^*-axes and $20\bar{1}$ directions in common. The crystals must thus be twinned along the $20\bar{1}$ planes with their c-axes inclined at an angle of very close to 90°. A plausible ideal mode of twinning of two $AlNb_{11}O_{29}$-crystals is shown in Fig. 1.

In addition to the powder patterns of H-Nb_2O_5, $Al_{\frac{1}{2}}Nb_{24\frac{1}{2}}O_{62}$, and $AlNb_{11}O_{29}$, lines corresponding to a new phase were observed in Guinier photographs of melted, but not tempered, samples with $x_{Nb_2O_5}>0.95$. Weissenberg photographs $h0l$-$h2l$ for a single crystal found in one of these samples indicated the presence of a phase isostructural with $NbO_{2.483}$.[10] The new phase should therefore be "$(Al,Nb)O_{2.483}$". No analysis has, however, yet been carried out to ascertain its composition. A phase with this composition has been predicted by Gruehn.[11]

Table 2. Crystallographic data for $AlNb_{11}O_{29}$.

Unit cell dimensions: $a=(31.14\pm0.02)$ Å; $b=(3.813\pm0.002)$ Å; $c=(20.55\pm0.02)$ Å; $\beta=(113.26\pm0.04)°$.
Systematically absent reflexions: hkl with $k+l=$odd
$h0l$ with $h=$odd.
Possible space groups: No. 15 $A2/a$ and No. 9 Aa.
$\varrho_{calc}=4.49$ g cm^{-3}; $\varrho_{obs}=(4.47\pm0.02)$ g cm^{-3}.
$Z=4$.
Powder pattern data. Cu$K\alpha_1$ radiation. $\lambda(CuK\alpha_1)=1.5405$ Å.

I obs	$\sin^2\theta\times10^5$ obs	d obs	h	k	l	$\sin^2\theta\times10^5$ calc	d calc
vvw	290	14.30	2	0	0	290	14.30
vw	611	9.85	2	0	$\bar{2}$	608	9.87
vvw	665	9.44	0	0	2	666	9.44
vw	1161	7.149	4	0	0	1160	7.152
m	2257	5.127	2	0	$\bar{4}$	2258	5.126
vvw	2427	4.944	4	0	$\bar{4}$	2434	4.937
m	2609	4.769	6	0	0	2610	4.768
vvw	3639	4.038	2	0	4	3646	4.033
vvst	4244	3.739	0	1	1	4246	3.738
vvw	4307	3.712	6	0	$\bar{2}$	4316	3.708
w	4358	3.690	2	1	$\bar{1}$	4363	3.688
vst	4644	3.574	8	0	0	4639	3.576
vvw	4707	3.550	2	1	1	4710	3.549
vst	5074	3.420	4	0	$\bar{6}$	5067	3.422
vw	5204	3.377	4	0	4	5209	3.375
vvw	5238	3.366	2	0	$\bar{6}$	5238	3.366
m	5341	3.333	2	1	$\bar{3}$	5347	3.331
vvw	5472	3.293	6	0	$\bar{6}$	5477	3.291
vvw	5576	3.262	0	1	3	5577	3.262
vw	5750	3.212	4	1	1	5753	3.211
vvw	6458	3.031	10	0	$\bar{4}$	6442	3.035
vvw	7245	2.862	10	0	0	7249	2.861

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

Unit cell dimensions: $a=(29.78\pm0.02)$ Å; $b=(3.818\pm0.002)$ Å; $c=(21.10+0.02)$ Å; $\beta=(94.94\pm0.04)°$.
Systematically absent reflexions: hkl with $h+k=$odd.
Possible space groups: No. 12 $C2/m$, No. 8 Cm, and No. 5 $C2$.
$\varrho_{calc}=4.56$ g cm^{-3}; $\varrho_{obs}=(4.52+0.02)$ g cm^{-3}.
$Z=2$.
Powder pattern data. Cu$K\alpha_1$ radiation. $\lambda(\mathrm{Cu}K\alpha_1)=1.5405$ Å.

I obs	$\sin^2\theta\times10^5$ obs	d obs	h	k	l	$\sin^2\theta\times10^5$ calc	d calc
vw	269	14.85	2	0	0	269	14.82
vw	534	10.54	0	0	2	537	10.51
vw	739	8.96	2	0	$\bar{2}$	741	8.95
vw	1073	7.44	4	0	0	1078	7.42
vw	1274	6.82	4	0	1	1278	6.81
vvw	2141	5.264	0	0	4	2147	5.257
m	2657	4.725	6	0	1	2658	4.725
w	4129	3.791	1	1	0	4137	3.787
w	4280	3.723	1	1	1	4288	3.720
vvst	4583	3.598	8	0	1	4578	3.600
vw	4660	3.568	3	1	0	4676	3.562
vvst	4905	3.478	2	0	$\bar{6}$	4904	3.478
vvw	5124	3.403	8	0	2	5111	3.407
			8	0	$\bar{3}$	5127	3.402
st	5288	3.349	1	1	$\bar{3}$	5296	3.347
			2	0	6	5297	3.347
vw	5500	3.284	4	0	$\bar{6}$	5516	3.280
w	5748	3.213	5	1	0	5754	3.211
vvw	5957	3.156	5	1	1	5971	3.152
vvw	6275	3.075	6	0	5	6272	3.076
vvw	6296	3.070	4	0	6	6302	3.068
vvw	6619	2.994	3	1	$\bar{4}$	6627	2.992
vvw	6738	2.967	10	0	0	6738	2.967
w	7042	2.903	10	0	1	7036	2.904
st	7412	2.829	1	1	$\bar{5}$	7410	2.830

Since the formula $Nb_{53}O_{132}$ has been proposed for the compound $NbO_{2.483}$,[10] "$(Al,Nb)O_{2.483}$" may be given the corresponding formula $Al_{\frac{1}{2}}Nb_{52\frac{1}{2}}O_{132}$. The following unit cell dimensions have been obtained from Weissenberg photographs:

$$a=63 \text{ Å}; b=3.8 \text{ Å}; c=21 \text{ Å}; \beta=95°$$

Attempts to prepare this phase in a pure state have so far not been successful.

DISCUSSION

It is of interest to compare the phase relations in the Al_2O_3-system with those of the rather well known TiO_2-Nb_2O_5-[8,12-14] and NbO_2-Nb_2O_5-systems.[2-4,10,15,16] Both systems contain the phases $(Me,Nb)_{25}O_{62}$ (Me=Ti, Nb^{IV} or Al) and $(Me,Nb)O_{2.483}$, but the existence of a stability interval for

"$(Al,Nb)O_{2.483}$" has not yet been proved. For Me=Ti,[12,13] Nb(IV),[3,4] Ga, Fe(III), and Ni [14] the oxide $(Me,Nb)_{12}O_{29}$ exists in two modifications, one monoclinic and one orthorhombic, the former observed at low temperatures ($\leq$1100—1200°C) and the latter at high ($\leq$1100—1200°C)[14,16]. No compound $AlNb_{11}O_{29}$(o-rh) has been found in the Al_2O_3-Nb_2O_5-system. The monoclinic oxide $AlNb_{11}O_{29}$ seems to be stable up to its melting point, *i.e.* at temperatures at which the orthorhombic modifications are stable in the other five systems.

Remarkable is the discrepancy between the crystallographic compositions $AlNb_{11}O_{29}$ ($Al_2O_3/Nb_2O_5=1/11$) and $Al_{\frac{1}{2}}Nb_{24\frac{1}{2}}O_{62}$ ($Al_2O_3/Nb_2O_5=1/49$) and the compositions of the corresponding one-phase samples where $Al_2O_3/Nb_2O_5=1/9$ and 1/25, respectively, which agree with the data observed by Layden.[1] The reason for this discrepancy is not yet clearly understood, but an analogous phenomenon is, however, discussed for $NbO_{2.483}$.[10] The composition $Al_2O_3/Nb_2O_5=1/25$ yields a metal/oxygen molar ratio equal to 2.462 which is in good agreement with the value 2.467 given by Gruehn and Schäfer.[7]

Investigations of the related systems, ZnO-Nb_2O_5, NiO-Nb_2O_5, and ZrO_2-Nb_2O_5, are being conducted in order to examine the effect of the ionic radius, electronegativity, and ionic charge of the Me-ion on the formation of Nb_2O_5-rich $(Me,Nb)O_x$-phases.

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