

# Phase Equilibria in the System Niobium Pentoxide–Boric Acid

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(October 11, 1965)

The phase-equilibrium diagram for the system  $Nb_2O_5-B_2O_3$  was determined experimentally using the quenching technique and examining the samples by optical microscopy and x-ray powder diffractometry. The system contains one binary compound of approximate composition " $3Nb_2O_5 \cdot B_2O_3$ ," which melts incongruently at about 1150 °C to H- $Nb_2O_5$  and  $B_2O_3$ -rich liquid. A large region of liquid immiscibility extends, at 1352 °C, from 10 mole percent  $Nb_2O_5$  to 65.7 mole percent  $Nb_2O_5$ . The theoretically calculated extent of immiscibility is in reasonable agreement with the experimentally determined value.

Key Words: Boric oxide, immiscibility, niobium pentoxide, oxides, phase equilibria.

## 1. Introduction

Consistent with the objective expressed in the Introduction to the preceding paper on the system  $Nb_2O_5-GeO_2$  [1],<sup>1</sup> the systematic study of immiscibility was extended to include the phase relations in the system  $Nb_2O_5-B_2O_3$ . The  $Nb^{5+}$  cation has a high charge and moderate ionic radius, 0.69 Å; and, consequently, a high ionic field strength. Notwithstanding the high field strength, the  $Nb_2O_5-GeO_2$  system does not show liquid immiscibility. However, the  $Nb_2O_5-SiO_2$  system was found to contain a large region of immiscibility [2]. Based on the observation that no case has been reported in which liquid immiscibility exists for the silicate system but not for the corresponding borate system, immiscibility in the  $Nb_2O_5-B_2O_3$  system was to be expected. Furthermore, the system offered a possible opportunity to apply and to extend the principles of immiscibility developed mainly from systems of borates with the oxides of divalent cations.

## 2. Sample Preparation and Test Methods

Starting materials for the preparation of mixtures consisted of high-purity niobium pentoxide and reagent grade boric acid powder. The  $Nb_2O_5$  contained the following impurities when examined by the general qualitative spectrochemical method: Si—less than 0.1 percent; Fe, Sn, Ti—0.001 to 0.01 percent; Ca, Mg—0.0001 to 0.001 percent; Cu—? The boric acid was of especially high purity, containing only faint traces (0.0001 to 0.001%) of Mg and Si.

Three-gram batches, on an ignited basis, of the starting materials were formulated by mixing or grinding, pressing, and heating for 4 hr, at three successively higher temperatures: 700, 800, and about 900 °C. Phase equilibrium relations were studied by the well-established quenching technique. Samples were heated in sealed Pt tubes for periods of 1 to 336 hr.

Temperatures were measured with a calibrated Pt-90Pt:10 Rh thermocouple. Quenched samples were examined with the binocular and polarizing microscopes and by x-ray powder diffractometry (Ni-filtered  $CuK\alpha$  radiation) using a high-angle Geiger-counter diffractometer. The technique and details of sample preparation, apparatus, and method have been described in previous publications [3] and were the same as for the study of the  $Nb_2O_5-GeO_2$  system [1]. The overall maximum uncertainty of the liquidus temperatures reported are estimated to be within  $\pm 10$  °C.

It should be noted that the polarizing microscope was of limited value because clear homogeneous glass was not observed, even for the compositions richest in  $B_2O_3$ . Quenched liquid devitrified, to lesser or greater extent, and the grains appeared brownish, finely mottled, and very weakly birefringent, when viewed under the microscope.

## 3. Chemical Analysis

Formulated compositions were analyzed by the Analytical Chemistry Division. For most of the compositions only the  $Nb_2O_5$  content was determined, by titration of an unbuffered solution at pH 4.5 with standard EDTA solution. Percent  $B_2O_3$  was estimated by difference from 100 percent. Analyses of three compositions (formulated at 25, 50, and 66.7 mole percent  $Nb_2O_5$ ) as well as analysis of the mechanically separated heavy and light devitrified liquids in the immiscibility region were made for both  $Nb_2O_5$  and  $B_2O_3$ .  $B_2O_3$  was determined by titration of a neutral solution (pH 7.00) with standard NaOH solution, after the additions of manitol.  $Nb_2O_5$  was determined from the weight of the ignited residue. Analyzed values were used in constructing the phase diagram. Those compositions for which one of the components was determined by difference have an estimated uncertainty of about 2 mole percent. Those for which both components were analyzed have an estimated accuracy of better than 1 mole percent.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

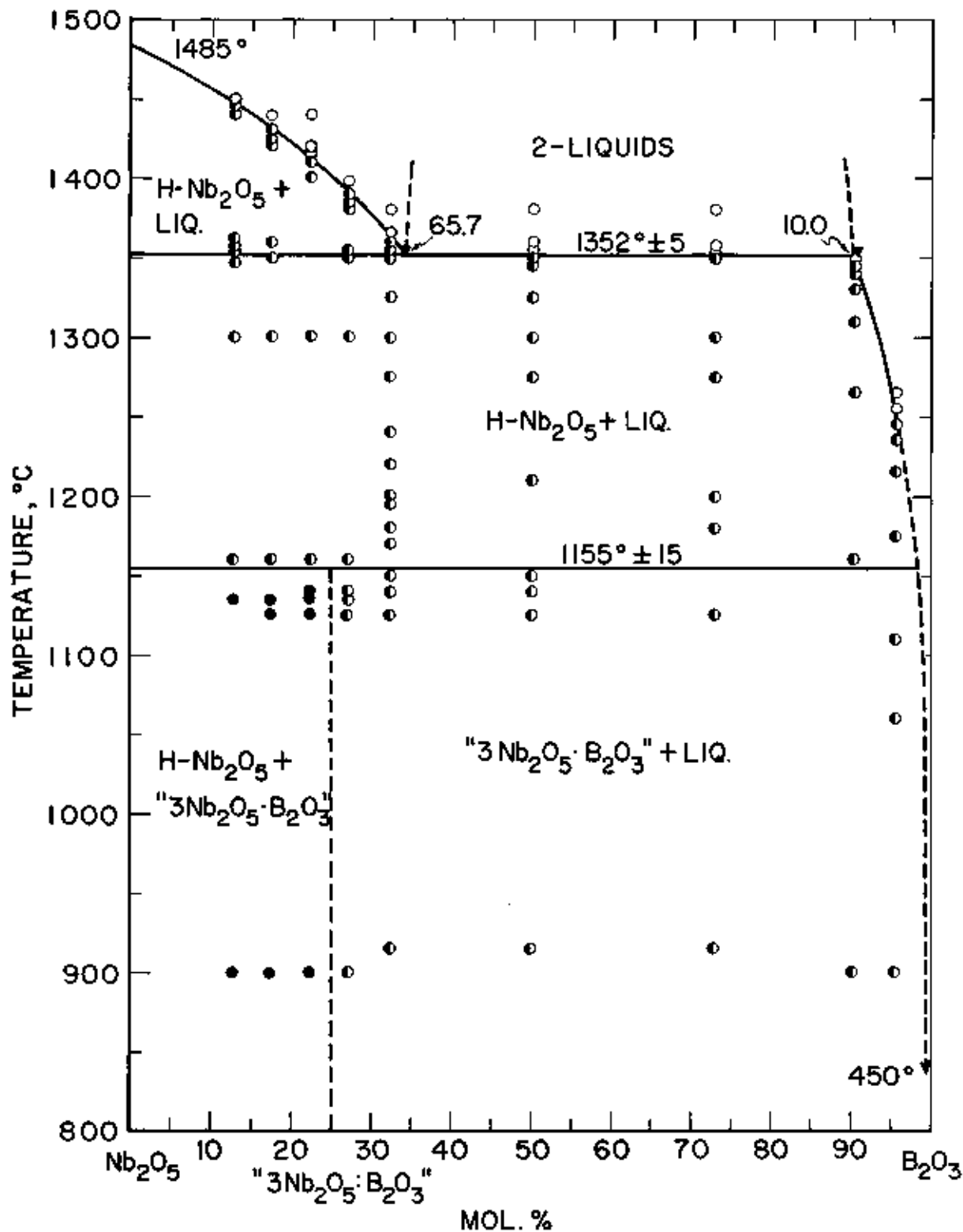


FIGURE 1. Phase diagram for the system  $\text{Nb}_2\text{O}_5$ - $\text{B}_2\text{O}_3$ .  
 ●—No melting; ◐—partial melting; ○—complete melting.  
 ▼—chemically analyzed values of mechanically separated phases in two liquid regions.

## 4. Results and Discussion

### 4.1. Nb<sub>2</sub>O<sub>5</sub> and B<sub>2</sub>O<sub>3</sub> Components

No quenching experiments were made with the components, as they were the same materials that had been used previously in phase equilibrium studies originating in this laboratory [3, 4]. As regards the Nb<sub>2</sub>O<sub>5</sub> component, the same remarks pertain as for the Nb<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub> system [1]. For purposes of consistency with previous publications the indicated melting temperature of B<sub>2</sub>O<sub>3</sub> is given as 450°C, although this value may be 5° to 10° low [5].

### 4.2. Phase Diagram

The phase diagram for the system is shown in figure 1, and table 1 lists the compositions studied, heat treatments, and phases identified. The system is characterized by a large region of liquid immiscibility, extending from about 10 mole percent to 65.7 mole percent Nb<sub>2</sub>O<sub>5</sub>, and by a binary compound, "3Nb<sub>2</sub>O<sub>5</sub>·B<sub>2</sub>O<sub>3</sub>" melting incongruently at 1150°C, some 200° below the monotectic.

The two triangles in figure 1 designate the chemically analyzed values for the B<sub>2</sub>O<sub>3</sub>-rich and the Nb<sub>2</sub>O<sub>5</sub>-

TABLE 1. Experimental data for compositions in the binary system Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>

Composition <sup>1</sup>		Heat treatment <sup>2</sup>		Results		Notes			
Nb <sub>2</sub> O <sub>5</sub>	B <sub>2</sub> O <sub>3</sub>	Temp.	Time	Physical observation	X-ray diffraction analyses <sup>3</sup>				
Mole %	Mole %	°C	hour						
4.3	95.6	900	3	Considerable melting.	3:1 + glass hump + (H <sub>2</sub> BO <sub>3</sub> )	No H-Nb <sub>2</sub> O <sub>5</sub> detected. Tube leaked.			
		1061	1	Considerable melting.	3:1 + glass hump + (L-Nb <sub>2</sub> O <sub>5</sub> )				
		1109	1.5	Considerable melting.	3:1 + glass hump + (L-Nb <sub>2</sub> O <sub>5</sub> )				
		1175	1	Considerable melting.	[H <sub>2</sub> BO <sub>3</sub> ] + 3:1 + (L-Nb <sub>2</sub> O <sub>5</sub> ) + H-Nb <sub>2</sub> O <sub>5</sub>				
		1216	1	Considerable melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + 3:1 + [H <sub>2</sub> BO <sub>3</sub> ] + H-Nb <sub>2</sub> O <sub>5</sub>				
		1235	2	Considerable melting.	3:1 + (H <sub>2</sub> BO <sub>3</sub> ) + (L-Nb <sub>2</sub> O <sub>5</sub> ) + H-Nb <sub>2</sub> O <sub>5</sub>				
		1246	2	Near complete melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + [3:1]				
		1256	2	Complete melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + [3:1]				
		1265	2	Complete melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + [3:1]				
		9.7	90.3	900	3		Some melting.	3:1 + glass hump	Above decomp. 3:1. Very weak x-ray pattern. Tube leaked. One liquid.
1161	68			Considerable melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
1265	2			Considerable melting.	(L-Nb <sub>2</sub> O <sub>5</sub> ) + 3:1				
1310	1.5			Considerable melting.	3:1 + (L-Nb <sub>2</sub> O <sub>5</sub> ) + H-Nb <sub>2</sub> O <sub>5</sub>				
1331	1.5			Considerable melting.	5:1 + (L-Nb <sub>2</sub> O <sub>5</sub> ) + H-Nb <sub>2</sub> O <sub>5</sub>				
1339	1.5			Considerable melting.	3:1 + (L-Nb <sub>2</sub> O <sub>5</sub> ) + (H <sub>2</sub> BO <sub>3</sub> )				
1345	1.5			Near complete melting.	(L-Nb <sub>2</sub> O <sub>5</sub> ) + 3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
1350	1.5			Complete melting.	(L-Nb <sub>2</sub> O <sub>5</sub> )				
27.2	72.8			915	4	Slight melting.	5:1	B <sub>2</sub> O <sub>3</sub> -rich glass present. Above decomp. 3:1. [Shows reversibility: 3:1 ↔ H-Nb <sub>2</sub> O <sub>5</sub> + liquid. Above monotectic. Chem. Analysis of each phase.	
				1180	53.5	Some melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>		
		1200	66.5	Some melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1275	15	Some melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1300	18	Some melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 + (L-Nb <sub>2</sub> O <sub>5</sub> )				
		1300	18		3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1125	117		H-Nb <sub>2</sub> O <sub>5</sub> + (L-Nb <sub>2</sub> O <sub>5</sub> ) + 3:1				
		1349	2	Some melting.	(L-Nb <sub>2</sub> O <sub>5</sub> ) + (H-Nb <sub>2</sub> O <sub>5</sub> )				
		1354	1.5	Complete melting.					
		1357	1	Complete melting.					
50.2	49.8	915	4	Slight melting.	3:1	Above decomp. 3:1. [Shows reversibility: 3:1 ↔ H-Nb <sub>2</sub> O <sub>5</sub> + liquid. Decomp. 3:1 sluggish. Above monotectic. For chem. analysis. Above monotectic.			
		1140	69	Slight melting.	3:1 + (H <sub>2</sub> BO <sub>3</sub> )				
		1150	45	Some melting.	5:1				
		1210	40	Some melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1275	15	Some melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1300	18	Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1300	18		3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1125	117		3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1325	1	Considerable melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1345	1.25	Considerable melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
67.8	32.2	915	4	Slight melting.	3:1	B <sub>2</sub> O <sub>3</sub> -rich glass present. Decomp. 3:1 sluggish. [Shows reversibility: 3:1 ↔ H-Nb <sub>2</sub> O <sub>5</sub> + liquid. Above monotectic.			
		1140	69	Slight melting.	3:1				
		1150	45	Slight melting.	3:1				
		1170	20	Melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub> (?)				
		1180	53.5	Melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1194	1.75	Melting.	3:1				
		1200	66.5	Melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1220	8.5	Melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1240	1.5	Melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1275	1.5	Melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
1300	18	Melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)						
1300	18		3:1 + H-Nb <sub>2</sub> O <sub>5</sub>						
1125	117		3:1 + H-Nb <sub>2</sub> O <sub>5</sub>						
1325	1		H-Nb <sub>2</sub> O <sub>5</sub> + (L-Nb <sub>2</sub> O <sub>5</sub> )						
1350	1		H-Nb <sub>2</sub> O <sub>5</sub>						
1356	1	Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub>						
1361	1.5	Near complete melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [3:1]						
1367	1	Complete melting.	(L-Nb <sub>2</sub> O <sub>5</sub> ) + [3:1]						
1380	2	Complete melting.	(L-Nb <sub>2</sub> O <sub>5</sub> ) + [3:1]						

TABLE 1. Experimental data for compositions in the binary system Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub>-Continued

Composition <sup>1</sup>		Heat treatment <sup>2</sup>		Physical observation	Results	Notes			
Nb <sub>2</sub> O <sub>5</sub>	B <sub>2</sub> O <sub>3</sub>	Temp.	Time				X-ray diffraction analyses <sup>3</sup>		
Mole %	Mole %	°C	Hour						
73.0	27.0	900	3	Opalescent.	3:1	Above decomp. 3:1. {Shows reversibility: {3:1 ↔ H-Nb <sub>2</sub> O <sub>5</sub> + liquid. Above monotectic. All devitrify from liquid.			
		1125	336	Opalescent.	3:1				
		1140	69	Opalescent.	3:1				
		1161	68	Opalescent.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
		1300	18	Opalescent.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)				
		1300	18		H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1125	117		H-Nb <sub>2</sub> O <sub>5</sub>				
		1351	1.5	Slight melting.	H-Nb <sub>2</sub> O <sub>5</sub>				
		1355	1.5	Melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1380	1.5	Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1385	1.5	Near complete melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ] + 3:1				
		1390	1.5	Near complete melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1398	1.5	Complete melting.	[H-Nb <sub>2</sub> O <sub>5</sub> ] + [L-Nb <sub>2</sub> O <sub>5</sub> ] + {3:1}				
		77.8	22.2	900	3		No melting.	3:1	Above decomp. 3:1. {Shows reversibility: {3:1 ↔ H-Nb <sub>2</sub> O <sub>5</sub> + liquid.
				1135	336		No melting.	3:1	
1140	69			No melting.	3:1				
1161	68			Slight melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>				
1300	18			Opalescent.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)				
1300	18				H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
1125	117				H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ] + 3:1				
1401	1			Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ] + 3:1				
1409	2.5			Near complete melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ] + 3:1				
1415	1.5			Complete melting.	[H-Nb <sub>2</sub> O <sub>5</sub> ] + [L-Nb <sub>2</sub> O <sub>5</sub> ] + {3:1}				
1420	1			Complete melting.	{[L-Nb <sub>2</sub> O <sub>5</sub> ] + [L-Nb <sub>2</sub> O <sub>5</sub> ]				
1440	1			Complete melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + [H-Nb <sub>2</sub> O <sub>5</sub> ]				
82.9	17.1			900	3	No melting.	3:1	Above decomp. 3:1. Reversibility sluggish. Below monotectic. Above monotectic.	
				1135	336	No melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>		
				1161	68	Slight melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>		
		1300	18	Melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)				
		1300	18		H-Nb <sub>2</sub> O <sub>5</sub> + 3:1				
		1125	117		H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ]				
		1349	3	Melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ]				
		1359	3	Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ]				
		1420	1	Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ] + 3:1				
		1425	1.5	Near complete melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)				
		1430	1	At liquidus.	[H-Nb <sub>2</sub> O <sub>5</sub> ] + [L-Nb <sub>2</sub> O <sub>5</sub> ] + {3:1 (?)}				
		1440	1	Complete melting.	[H-Nb <sub>2</sub> O <sub>5</sub> ] + [L-Nb <sub>2</sub> O <sub>5</sub> ]				
		87.2	12.8	900	3	No melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub> (?)		Above decomp. 3:1. N <sub>pl</sub> < 1.47, below monotectic. Above monotectic.
				1135	336	No melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>		
				1161	68	Melting.	3:1 + H-Nb <sub>2</sub> O <sub>5</sub>		
1300	18			Melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)				
1348	2			Melting.	H-Nb <sub>2</sub> O <sub>5</sub>				
1356	2			Moderate melting.	H-Nb <sub>2</sub> O <sub>5</sub>				
1358	1.5			Moderate melting.	H-Nb <sub>2</sub> O <sub>5</sub>				
1362	1.5			Moderate melting.	H-Nb <sub>2</sub> O <sub>5</sub>				
1440	1			Considerable melting.	H-Nb <sub>2</sub> O <sub>5</sub> + 3:1 (?)				
1445	1			Near complete melting.	H-Nb <sub>2</sub> O <sub>5</sub> + [L-Nb <sub>2</sub> O <sub>5</sub> ] + {3:1}				
1450	1			Complete melting.	[L-Nb <sub>2</sub> O <sub>5</sub> ] + [H-Nb <sub>2</sub> O <sub>5</sub> ]				

<sup>1</sup> Analyzed value for Nb<sub>2</sub>O<sub>5</sub>; B<sub>2</sub>O<sub>3</sub> by difference.

<sup>2</sup> Specimens quenched in sealed Pt tubes.

<sup>3</sup> Phases identified are listed in order of amount present at room temperature. Phases not necessarily present at the elevated temperatures are enclosed in brackets. 3:1 refers to 3Nb<sub>2</sub>O<sub>5</sub>·B<sub>2</sub>O<sub>3</sub>, the most likely composition of the binary compound.

rich devitrified liquids which were mechanically separated from samples quenched from above the monotectic. When the Pt was removed from the quenched specimens, two distinct layers were clearly visible. The top layer appeared opalescent white and was found to be hard and glassy when ground. An index of refraction of approximately  $1.51 \pm 0.01$  was determined for clear portions of some of the grains. The lower layer appeared crystalline, metallic grey in color. Under the microscope the grains were dark and very weakly birefringent. The x-ray powder patterns showed that the top layer (B<sub>2</sub>O<sub>3</sub>-rich) contained low-Nb<sub>2</sub>O<sub>5</sub> with a trace of high-Nb<sub>2</sub>O<sub>5</sub>, whereas

the lower layer (Nb<sub>2</sub>O<sub>5</sub>-rich) contained appreciable high-Nb<sub>2</sub>O<sub>5</sub>, low-Nb<sub>2</sub>O<sub>5</sub>, and a small amount of "3Nb<sub>2</sub>O<sub>5</sub>·B<sub>2</sub>O<sub>3</sub>."

Homogeneous glasses were never obtained for any composition as the liquids devitrified on quenching. X-ray examination showed either low-Nb<sub>2</sub>O<sub>5</sub>, high-Nb<sub>2</sub>O<sub>5</sub>, "3Nb<sub>2</sub>O<sub>5</sub>·B<sub>2</sub>O<sub>3</sub>", or combinations. The low-Nb<sub>2</sub>O<sub>5</sub> phase corresponded to the pseudo-orthorhombic subcell of low-Nb<sub>2</sub>O<sub>5</sub> found for some of the quenched liquids in the Nb<sub>2</sub>O<sub>5</sub>-GeO<sub>2</sub> system. It had the same unit cell dimensions [1]. The metastable low-temperature niobia-type phase of hexagonal symmetry occurring in the GeO<sub>2</sub> system was not found.

### 4.3. Compound "3Nb<sub>2</sub>O<sub>5</sub> · B<sub>2</sub>O<sub>3</sub>"

The exact composition of this compound could not be determined because of insufficient sensitivity, in this instance, of the microscopic and x-ray methods together with some uncertainty in the chemical analyses. Therefore, the 3:1 ratio of oxides is given as the most probable.

The compound formed readily for all compositions in the system. It melted incongruently at about 1150 °C to liquid and H-Nb<sub>2</sub>O<sub>5</sub>. However, disappearance of the compound above the melting point was extremely sluggish. The compound could be detected in diminishing amounts up to the monotectic and liquidus temperatures (see table 1). Even compositions heated at 1161 °C for 68 hr showed appreciable amounts of the compound, but the appearance of H-Nb<sub>2</sub>O<sub>5</sub> indicated that the temperature was above the incongruent melting point. X-ray powder diffraction data suitable for identification is given in table 2. The pattern is of low symmetry with regions of closely spaced low-intensity peaks and could not be indexed.

TABLE 2. X-ray powder diffraction data (CuK<sub>α</sub> radiation) for the compound "3Nb<sub>2</sub>O<sub>5</sub> · B<sub>2</sub>O<sub>3</sub>"

(Pattern of low symmetry and could not be indexed)

<i>d</i>	<i>h</i> <sub>k</sub>	<i>d</i>	<i>h</i> <sub>k</sub>
Å	%	Å	%
*14.4(b)	3	2.434	3
7.16	7	2.389	7
6.93	6	2.369	4
4.774	34	2.337	3
4.741	27	2.302	17
3.770	71	*2.094(b)	3
3.584	90	2.049	26
3.553	100	2.043	27
3.170	12	1.9125	33
2.864	6	*1.7918(b)	5
2.833	10	1.7745	10
2.773	57	1.7697	10
*2.730(b)	7	1.6995	22
2.575	9	1.6874	21
2.570	6	1.6842	23
2.520	7	*1.5838(b)	6
2.506	9	1.5769	16
2.473	4		

\*b = broad peak.

### 4.4. Application to Liquid Immiscibility Theory

The niobium borate and niobium silicate systems both contain large regions of immiscibility, whereas the niobium germanate system shows complete liquid miscibility. Thus, as previously discussed [1], the niobium cation possesses a critical ionic field strength for the formation of two liquids with the glass-forming cations.

With data on immiscibility in the niobium borate and silicate systems, it is possible to test and to extend the principles of immiscibility developed mostly from data on the divalent cations to the cations of high charge. A fundamental consideration in the structural approach is the average number of oxygens associated with a modifier cation, in the modifier-rich

liquid. Once this value is known, statement of the nominal composition is a routine calculation. The oxygen-volume method, discussed in previous publications [3, 6] is an attempt to make a reasonable estimate of this number.

TABLE 3. Calculated composition of modifier-rich liquids, in #O/Nb and in mole percent Nb<sub>2</sub>O<sub>5</sub>, based on the oxygen-volume method [6] and two values both for the niobium separation and the volume of space occupied by O<sup>-2</sup> (V<sub>0</sub>).

System	Experimental		Calculated from Nb-Nb separation:					
			of 4.18 Å (2(1.40 + 0.69)), and			of 4.08 Å, and		
			V <sub>0</sub> = 17 Å <sup>3</sup>		V <sub>0</sub> = 19 Å <sup>3</sup>		V <sub>0</sub> = 19 Å <sup>3</sup>	
Nb <sub>2</sub> O <sub>5</sub>	#O/Nb	#O/Nb	Nb <sub>2</sub> O <sub>5</sub>	#O/Nb	Nb <sub>2</sub> O <sub>5</sub>	#O/Nb	Nb <sub>2</sub> O <sub>5</sub>	
Nb <sub>2</sub> O <sub>5</sub> -B <sub>2</sub> O <sub>3</sub>	Mole % 65.7	3.28	4.18	Mole % 47.2	3.72	Mole % 55.1	3.45	Mole % 61.1
Nb <sub>2</sub> O <sub>5</sub> -SiO <sub>2</sub> [2]	47.5	3.61	4.18	37.4	3.72	45.0	3.45	51.2

Table 3, column 3 gives the number of oxygens per modifier cation calculated directly from the experimentally determined composition of the modifier-rich liquid. For example, in the Nb<sub>2</sub>O<sub>5</sub>-B<sub>2</sub>O<sub>3</sub> system:

$$\#O/Nb = \frac{5 \times 0.657 + 3(1.00 - 0.657)}{2 \times 0.657} = 3.28.$$

Similarly, in the Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> system:

$$\#O/Nb = \frac{5 \times 0.475 + 2(1.00 - 0.475)}{2 \times 0.475} = 3.61.$$

As a first approximation the number of oxygens per cation may be considered independent of the glass-forming cation. Using the data in column 3 for one of the systems, it is possible to calculate the composition of the modifier-rich liquid in the other system. The calculation yields 57.5 mole percent Nb<sub>2</sub>O<sub>5</sub> in the borate system,<sup>2</sup> using the 3.61 value, and 56.2 mole percent Nb<sub>2</sub>O<sub>5</sub> in the silicate system, using the 3.28 value. The calculated value in the borate system is about 8 mole percent low, that in the silicate system about 9 mole percent high. As will be shown later, this seemingly large discrepancy is due to the sensitivity of the calculations in the niobium oxide systems.

Table 3 (columns 4-7) lists the calculated #O/Nb and the corresponding mole percent Nb<sub>2</sub>O<sub>5</sub>, based on the oxygen-volume method using a Nb-O-Nb bond angle of 180° and Ahrens' ionic radii for Nb<sup>+5</sup> and O<sup>-2</sup>. In the original papers on immiscibility the value of 17 Å<sup>3</sup> was taken as the average volume of space occupied by an oxygen atom in the modifier-rich liquid.

<sup>2</sup> Nominal oxide formula  $\frac{Nb_2O_5 \cdot (2 \times 3.61 \cdot 5)}{3} B_2O_3 = Nb_2O_5 \cdot 0.748B_2O_3$  (57.5 mole % Nb<sub>2</sub>O<sub>5</sub>).

An analysis of the experimental data in about 40 borate and silicate systems showing immiscibility [7] gives an empirical value of about  $19 \text{ \AA}^3$ . Therefore, in table 3 calculations are given for both oxygen values. It may be seen that for the  $19 \text{ \AA}^3$  value in the silica case agreement is good between the calculated mole percent  $\text{Nb}_2\text{O}_5$  (45.0) and the experimental one (47.5). In the borate case the calculated value is 11 mole percent low.

For the case of small highly charged modifier cations, such as niobium, the calculations are very sensitive to cationic radius because a small difference in separation has a large effect on the calculated number of oxygen per cation. For example, using a separation of only 0.1  $\text{ \AA}$  less than 4.18, will increase the calculated value by about 6 mole percent (column 9); and the calculated number of oxygens per niobium (column 8) is intermediate between 3.28 and 3.61, the experimentally determined values for the borate and silicate systems, respectively. Gatehouse and Wadsley [8], from a crystal structure determination of high- $\text{Nb}_2\text{O}_5$ , have concluded that in  $\text{Nb}_2\text{O}_5$  the average ionic radius of  $\text{O}^{2-}$  is 1.40  $\text{ \AA}$  and that of  $\text{Nb}^{5+}$ , 0.59  $\text{ \AA}$ . The latter value is 0.1  $\text{ \AA}$  less than Ahrens' ionic radius.

### 5. Summary

The phase equilibrium diagram for the system  $\text{Nb}_2\text{O}_5\text{-B}_2\text{O}_3$  was constructed from "quenching" data on nine selected compositions. Solidus and liquidus values were determined by examination of the samples with the binocular and polarizing microscopes and x-ray powder diffractometry.

The system was found to contain one binary compound, " $3\text{Nb}_2\text{O}_5 \cdot \text{B}_2\text{O}_3$ ", which melts incongruently at about 1150  $^\circ\text{C}$ , some 200 below a monotectic. The liquidus is characterized by a large two-liquid region, at 1352  $^\circ\text{C}$ , extending from about 10 mole percent  $\text{Nb}_2\text{O}_5$  to 65.7 mole percent  $\text{Nb}_2\text{O}_5$ .

Experimental limitations precluded an unequivocal statement of the composition of the " $3\text{Nb}_2\text{O}_5 \cdot \text{B}_2\text{O}_3$ " compound. Above the incongruent melting point its decomposition to  $\text{H-Nb}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$ -rich liquid is sluggish. X-ray powder data suitable for identification is listed.

In the modifier-rich liquid in the immiscibility region, an average of 3.28 oxygen are associated with each Nb atom, as compared to 3.61 for the corresponding silicate system. Calculation of the composition of the modifier-rich liquid, by the oxygen-volume method, gives acceptable agreement with the experimentally determined value, considering that for cations of large valence the calculation is sensitive to small changes in the parameters.

### 6. References

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(Paper 70A1-382)