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Proposed Phase Diagram for the System Vanadium Pentoxide – Zinc Oxide

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U.S. NAVAL RESEARCH LABORATORY
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The liquidus-solidus regions of the system V_2O_5-ZnO were investigated over the entire composition range, with the following principal findings. There are three congruently melting compounds: $ZnO \cdot V_2O_5$ melting at 665°C, $2ZnO \cdot V_2O_5$ melting at 880°C, and $3ZnO \cdot V_2O_5$ melting at 897°C. There are four eutectics, one at 23 mole percent V_2O_5 melting at 895°C, one at 27 mole percent V_2O_5 melting at 866°C, one at 46 mole percent V_2O_5 melting at 645°C, and one at 64 mole percent V_2O_5 melting at 634°C.

INTRODUCTION

During experiments involving the melting of mixtures of zinc oxide and certain sodium-vanadium oxides which had been isolated from oil-ash deposits taken from naval boilers (1), a new crystalline phase appeared but remained unidentified for lack of comparable x-ray diffraction data in the literature. Since the data for the systems Na_2O-V_2O_5 and Na_2O-ZnO were already at hand, an investigation of the system V_2O_5-ZnO was initiated.

A liquidus curve for this system had been determined by Lucas (2), who used the deformation characteristics of pyrometric cones as a means of detecting the appearance of liquid and the disappearance of solids when mixtures of vanadium pentoxide and zinc oxide were heated. Temperatures were estimated by means of a thermocouple placed next to the cones. From undulations of this curve Lucas concluded that there are three compounds in the system, these being $ZnO \cdot V_2O_5$, $2ZnO \cdot V_2O_5$, and $3ZnO \cdot V_2O_5$. The presence of only $2ZnO \cdot V_2O_5$ was said to have been verified by x-ray diffraction techniques. The temperature at which an equimolar mixture of zinc oxide and vanadium oxide begin to react was reported to be 550°C by Tammann (3), who found that a color change and sintering occurred after a specimen had been at a temperature of 600°C for ten minutes.

A compound having the formula $7ZnO \cdot 2V_2O_5$ precipitates at room temperature from water solutions (4). In addition to these references to pentavalent vanadium compounds with zinc, there have been several references to zinc-vanadium spinels containing trivalent vanadium (5-8). The use of compounds of zinc as fuel-oil additives has been the basis of at least three recent patents (9-11).

LABORATORY METHODS

The characteristics of the system V_2O_5-ZnO were determined by means of heating and cooling curves, x-ray diffraction analysis of crystallized melts, x-ray diffraction analysis of mixtures reacted in the solid state at temperatures below the melting point of the lowest melting eutectic mixtures, and by a visual method for the detection of solidus and liquidus temperatures which has found use in this laboratory on other occasions (1,12).

A typical series of experiments was performed as follows. Portions of zinc oxide and of vanadium pentoxide reagents which had been dried by being heated to a temperature above 150°C were weighed to the nearest milligram, blended, wet with trichloroethylene, and mulled by hand with mortar and pestle until dry. The final weight of each mix was of the order of three grams.

Small portions of the mixed oxides were pressed into 1/4-inch-round pellets under a pressure of 12,500 psi in a die made from a tool-steel plate and with a drill-rod plunger. These pellets weighed about 0.2 gram and required a pressure of 1000 psi to be crushed.

The solidus and liquidus temperatures were determined as follows. Each pellet composed of mixed oxides was supported by a small thermocouple bead in such a manner that it appeared silhouetted against a lamp on the opposite side of a tube furnace. The specimen served to shield

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the thermocouple from direct radiation. Small squares of platinum foil collected liquid as it formed and permitted the first material to melt to act as a solvent for more refractory portions of the mix. The initial melting temperature (solidus) was taken as the temperature at which, with the temperature of the specimen rising at a rate of 2°C per minute, the corners of the specimen became less sharp and the sides began to bulge. The liquidus was taken as the point at which the profile of the partially melted specimen flattened.

Mixtures approaching eutectic or compound composition, melted sharply, even though the mixed oxides had not previously been heated to the melting temperature, but the time of melting became quite long at points far removed from these unique compositions. Consequently, the melting points of some mixtures are vague as determined by this method, while others are sufficiently well defined that duplicate runs give melting points within three degrees of one another, even at temperatures above 1000°C.

The melted specimens were cooled slowly through the solidification point and then air cooled to room temperature. Crystalline material was examined by x-ray powder-diffraction techniques using a spectrometer, copper Kα radiation, and a scanning speed of two degrees per minute.

When it was noticed that on cooling some of the crystallized melts suddenly changed color from red to tan and that during the change small particles were expelled, the thermocouple which had initially been used to record the melting temperature was connected to a potentiometric recorder. It was possible with this setup to detect the presence of thermal effects in the small amount of solid material adhering to the thermocouple wires, although the exact temperatures could not always be determined due to the fact that the semiconducting solid mixtures short circuited the thermocouple wires, causing the recorded temperature to be the temperature at the point of short circuiting, rather than that of the sample as a whole.

As a result of the thermal studies it was found that the color change was accompanied by evolution of heat and occurred at temperatures about 600°C, but that the effect occurred only on cooling the crystallized melts for the first time and was neither reproducible nor reversible. It occurred even under conditions of slow cooling. Examination of the powders with a polarizing microscope revealed the presence of highly strained crystals exhibiting anomalous interference colors. For this reason portions of each of the unreacted original mixes were heated to 550°C, a temperature below the "transition" temperature, and also below the lowest melting temperature detected in the system, in an attempt to prepare the equilibrium phases by diffusion in the solid state.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The liquidus and solidus lines of the proposed phase diagram (Fig. 1)* were based entirely on temperatures determined by the visual method for detecting melting points (Table 1). The presence of compounds at 33.4 and 50 mole percent V_2O_5 was clearly suggested by the maxima in the liquidus line (Fig. 1). The compound at 25 mole percent was not as well defined, since mixtures with compositions of 22.0, 24.2, and 25.0 mole percent V_2O_5 melted within three degrees of one another. In each of these cases the initial melting was obscured by the fact that three eutectics had already formed and had been reassimilated prior to the time at which the specimens reached the melting point, and considerable distortion of the specimen pellet had already occurred before initial melting began. The abrupt change in slope at 25 mole percent V_2O_5 indicated the probable existence of a compound having approximately this composition.

The x-ray diffraction patterns for the specimens crystallized from the melts verified the existence of the three compounds between zinc and vanadium oxides which had been suggested by the shape of the liquidus curve (Table 2, Fig. 2). The pattern of $3ZnO{\cdot}V_2O_5$ was reproducible, however, only when preparations were cooled very slowly. Since a vague, reversible, exothermic effect had been detected at 860°C when compositions containing this compound were cooled and heated, it is probable that a transition occurs at this temperature and that a certain amount of the high-temperature crystalline modification persists to room temperature unless cooling is very slow.

Additional information was obtained from reactions between ZnO and V_2O_5 occurring in the solid state. After portions of mixed oxides had

*All figures and tables appear consecutively at the end of this report.

been heated at 575°C for a period of one-hundred hours, the reactions of many mixtures were completed, although it is probable that some mixtures reached equilibrium in a much shorter time (Table 3, Fig. 3). Further treatment of the higher-melting compositions for an additional 24 hours at 675°C, a temperature higher than that at which the color change had been observed in cooling of melts, had little effect on the nature of the room-temperature x-ray diffraction patterns, but with one exception; a specimen having a composition of 17 mole percent V_2O_5 was less well crystallized after having been reheated to 675°C.

A new series of diffraction lines appeared in compositions less than 30 mole percent V_2O_5, and these were probably due to the presence of another compound between ZnO and V_2O_5 which is stable only at relatively low temperatures. Lines for this compound were most intense at a composition of 22.0 mole percent V_2O_5. It should be noted that the compound $7ZnO{\cdot}2V_2O_5$, which is reported to crystallize from water at room temperature, has a composition of 22.2 mole percent V_2O_5.

The x-ray diffraction pattern of the compound $2ZnO{\cdot}V_2O_5$ taken from material cooled slowly from the melt was identical with that of material reacted in the solid state, but different from the pattern of rapidly quenched crystals. It is probable, therefore, that this compound does indeed undergo a transition at some elevated temperature.

The color change at about 600°C, which had been accompanied by the evolution of heat and by violent decrepitation of the specimens, but which was neither reproducible nor reversible, may have been due to the escape of occluded gases trapped in the solid material during crystallization from the melt. The extraordinary solubility of oxygen in melts containing pentavalent vanadium is a well-known phenomenon (13).

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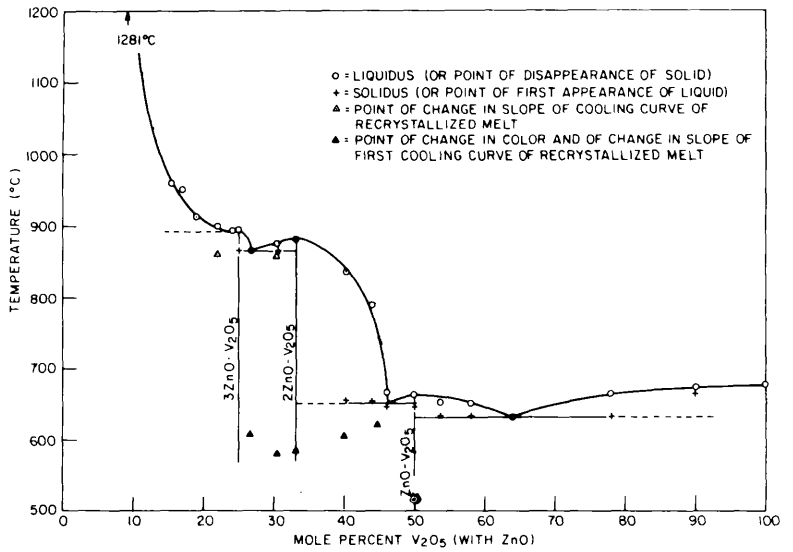

Fig. 1 - Suggested phase diagram for the liquidus-solidus regions of the system V_2O_5-ZnO

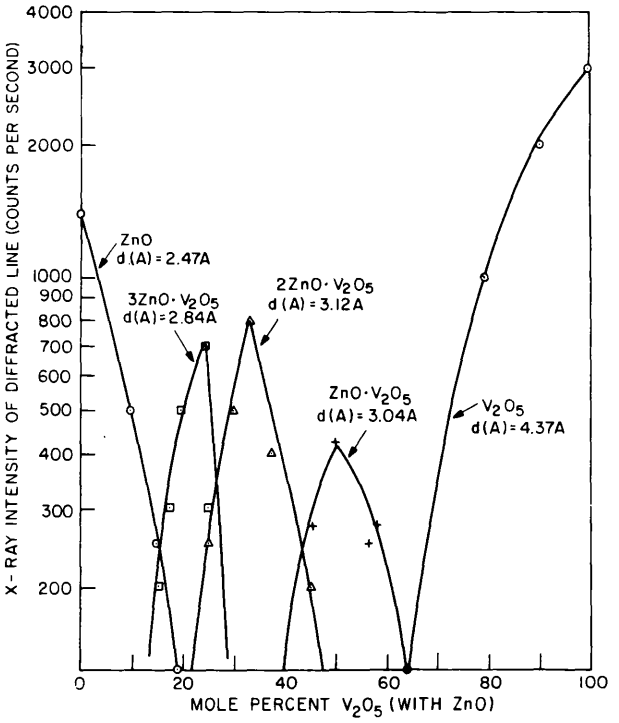

Fig. 2 - Changes in intensity of x-ray lines as a function of melt composition

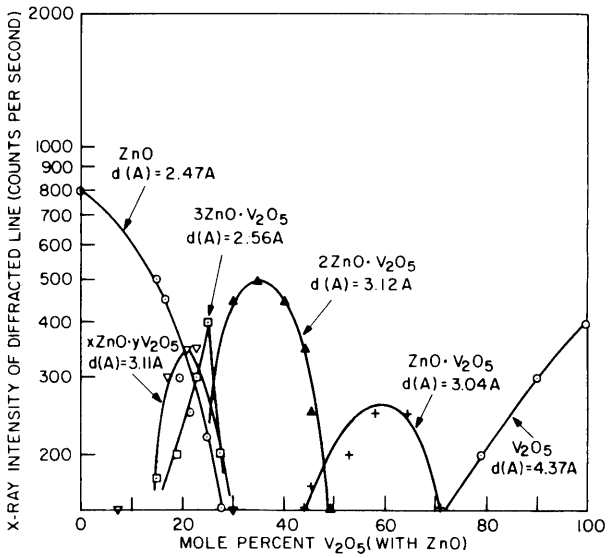

Fig. 3 - Changes in intensity of x-ray lines as a function of composition after sintering of mixed oxides at 575°C

TABLE 1
Melting-Point Data for the System ZnO-V_2O_5 Obtained from Visual Observation of Heated Pellets

Sample Number	Mole Percent V_2O_5	Solidus (°C)	Liquidus (°C)
14	9.4	*	1281
8	15.4	*	960
19	17.0	*	951
21	19.3	*	911
7	22.0	*	899
22	24.2	*	896
20	25.0	864	897
2	26.6	866	866
6	30.5	862	874
12	33.5	880	881
5	40.3	654	834
13	43.9	650	787
10	46.1	644	665
9	50.5	644	661
17	53.9	633	651
4	58.0	633	650
3	64.0	633	634
1	77.8	633	663
11	90.1	663	670

*Obscure.

TABLE 2

X-Ray Diffraction Data for Compound Compositions in the System V_2O_5-ZnO (Copper Kα Radiation)*
(Compounds Containing Vanadium Were Crystallized from Melts)

ZnO Reagent		$3ZnO \cdot V_2O_5$		$2ZnO \cdot V_2O_5$		$ZnO \cdot V_2O_5$		V_2O_5	
d(A)†	I/I_o‡	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)†	I/I_o‡
2.820	70	8.5	1	5.30	5	5.75	5	5.78	3
2.608	50	5.9	1	4.69	10	5.32	20	4.87	2
2.479	100	5.34	5	4.15	5	4.34	30	4.38	100
1.916	25	4.62	1	3.80	10	4.09	5	4.11	10
1.629	40	4.26	15	3.45	25	3.45	60	3.50	1
		4.18	5	3.11	100	3.26	5	3.42	1
		3.45	20	2.77	5	3.12	55	2.89	3
		3.19	5	2.66	5	3.08	35	2.77	1
		3.12	45	2.57	20	3.04	100	2.189	20
		3.052	15	2.40	10	2.88	15	2.152	3
		2.95	1	2.35	1	2.77	5	1.920	1
		2.838	100	2.215	5	2.39	3	1.902	1
		2.77	1	2.135	15	2.31	15	1.865	1
		2.65	5	2.070	5	2.22	1	1.447	1
		2.60	1	1.951	1	2.149	10		
		2.58	5	1.901	15	2.074	1		
		2.52	3						
		2.47	3						
		2.30	5						
		2.24	15						
		2.174	1						
		2.138	1						
		2.074	1						
		2.047	1						
		2.004	1						
		1.905	1						
		1.812	1						
		1.663	10						
		1.630	5						
		1.596	15						
		1.572	3						

*Maximum $2\theta = 60$ degrees.
†Lattice spacing in angstroms.
‡Line intensity relative to the strongest line.

TABLE 3
X-Ray Powder Diffraction Data for Mixtures of Oxides Sintered 100 Hours at 575°C

0 Mole Percent V_2O_5		7.2 Mole Percent V_2O_5		15.4 Mole Percent V_2O_5		17.0 Mole Percent V_2O_5		19.3 Mole Percent V_2O_5		22.0 Mole Percent V_2O_5		24.2 Mole Percent V_2O_5		25.0 Mole Percent V_2O_5		26.6 Mole Percent V_2O_5		30.5 Mole Percent V_2O_5	
d(A)*	I/I_o†	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o
2.82	70	5.7	2	5.7	3	5.8	5	5.8	10	5.8	10	5.8	10	5.8	5	5.8	5	5.3	25
2.61	50	5.3	2	5.3	5	5.3	5	5.3	10	5.3	15	5.3	5	5.3	10	5.3	5	4.7	5
2.48	100	4.7	2	4.7	4	4.7	10	4.7	10	4.7	10	4.7	10	4.7	10	4.7	10	4.3	2
1.91	25	4.2	1	4.1	4	4.2	5	4.1	5	4.1	55	4.2	5	4.2	5	4.2	5	4.1	10
1.63	40	3.45	2	3.44	15	3.45	15	3.44	40	3.45	45	3.44	55	3.46	50	3.46	35	3.44	50
		3.37	2	3.35	6	3.37	15	3.35	10	3.36	15	3.36	20	3.37	10	3.37	20	3.27	5
		3.29	3	3.27	10	3.29	20	3.27	25	3.29	25	3.29	30	3.29	15	3.30	35	3.25	5
		3.11	8	3.11	25	3.12	30	3.11	65	3.12	100	3.11	40	3.12	100	3.12	65	3.11	100
		3.03	11	3.02	20	3.03	35	3.02	45	3.03	50	3.02	60	3.03	25	3.04	65	3.02	10
		2.88	4	2.87	7	2.88	15	2.87	20	2.88	25	2.87	20	2.88	10	2.88	30	2.86	5
		2.81	70	2.80	70	2.81	60	2.80	75	2.81	45	2.80	15	2.81	30	2.81	10	2.80	35
		2.70	1	2.69	3	2.70	5	2.69	5	2.70	10	2.70	5	2.70	5	2.70	5	2.76	10
		2.61	50	2.60	50	2.66	5	2.65	5	2.66	5	2.66	5	2.66	10	2.66	4	2.65	10
		2.57	15	2.56	40	2.61	45	2.60	50	2.60	25	2.60	5	2.61	25	2.60	5	2.59	30
		2.47	100	2.49	5	2.57	60	2.56	70	2.57	80	2.56	100	2.57	50	2.58	100	2.56	15
		2.09b	4	2.47	100	2.49	10	2.49	15	2.49	30	2.49	40	2.49	20	2.49	55	2.49	5
		2.07	2	2.09b	10	2.47	100	2.47	100	2.47	70	2.47	30	2.47b	50	2.48	10	2.47	60
		1.91	25	2.07	5	2.21	2	2.21	5	2.46	5	2.46	30	2.22	10	2.46	15	2.38	10
		1.62	30	1.91	25	2.12	2	2.13	5	2.22	10	2.21	5	2.14	10	2.22	5	2.34	10
				1.62	35	2.09b	20	2.09b	25	2.13	5	2.13	5	2.09b	10	2.14	5	2.21	10
						2.07	10	2.07	15	2.09b	25	2.09b	30	2.07	10	2.09b	30	2.13	10
						1.91	15	1.91	20	2.07	20	2.07	10	1.91	15	2.07	25	2.07	10
						1.87	3	1.87	3	1.91	15	1.91	15	1.87	5	1.91	5	1.95	5
						1.76	2	1.81	3	1.87	5	1.87	5	1.80	5	1.87	5	1.91	15
						1.71	5	1.76	3	1.80	3	1.80	5	1.76	5	1.80	5	1.63	15
						1.62	30	1.71	5	1.77	3	1.76	5	1.71	5	1.72	5	1.62	25
						1.60	10	1.62b	40	1.71	5	1.71	5	1.62b	20	1.62b	10	1.59	25
								1.59	20	1.67	5	1.67	5	1.59	15	1.59	25		
										1.62b	30	1.62	10						
										1.59	20	1.59	10						

*Lattice spacing in angstroms.
†Line intensity relative to the strongest line.
b = broad.
d = double.

(Table continues)

TABLE 3(continued)
X-Ray Powder Diffraction Data for Mixtures of Oxides Sintered 100 Hours at 575°C

33.5 Mole Percent V_2O_5		40.3 Mole Percent V_2O_5		43.9 Mole Percent V_2O_5		46.1 Mole Percent V_2O_5		53.9 Mole Percent V_2O_5		58.0 Mole Percent V_2O_5		64.0 Mole Percent V_2O_5		77.8 Mole Percent V_2O_5		90.1 Mole Percent V_2O_5		100 Mole Percent V_2O_5	
d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o
5.3	25	5.30	25	5.3	25	5.3	20	5.3	10	4.4d	35	5.7	15	5.7	30	5.7	25	5.7	45
4.7	3	4.7	5	4.7	3	4.3	20	4.5d	35	4.1	5	4.4d	45	4.4	100	4.4	100	4.4	100
4.3	3	4.3	5	4.3	10	4.2	5	4.1	5	3.45	5	4.1	10	4.1	25	4.1	30	4.1	30
4.1	10	4.1	5	4.1	5	3.45	55	3.44	20	3.41	15	3.40	30	3.4	70	3.40	55	3.40	95
3.45	45	3.45	45	3.45	55	3.40	5	3.40	10	3.26	80	3.26	65	3.25	50	3.26	15	2.87	65
3.27	5	3.26	15	3.26	35	3.26	35	3.25	80	3.11	20	3.08	60	3.07	50	3.08	10b	2.76	30
3.25	5	3.12	100	3.11	100	3.12	100	3.11	40	3.08	65	3.04	100	3.03	65	3.04	20	2.68	15
3.12	100	3.08	5	3.08	30	3.09	60	3.07	75	3.04	100	2.88	20	2.87	55	2.88	45	2.61	30
3.03	5	3.04	30	3.04	30	3.04	75	3.04	100	2.88	10	2.76	5	2.76	25	2.76	20	2.30	5
2.88	5	2.88	3	2.76	5	2.88	10	2.86	15	2.76	5	2.73	60	2.72	50	2.73	10	2.18	10
2.81	10	2.78	10	2.73	30	2.77	10	2.77	5	2.73	80	2.60	20	2.67	5	2.69	10	2.14	5
2.77	10	2.73	15	2.66	15	2.73	50	2.72	60	2.61	5	2.40	5	2.61	20	2.61	25	1.99	15
2.66	15	2.66	15	2.45	5	2.66	15	2.65	5	2.40	5	2.31	40	2.38	10	2.40	5	1.92	20
2.59	5	2.57	15	2.35	5	2.58	5	2.60	5	2.31	45	2.22	10	2.31	25	2.31	5	1.90	10
2.57	15	2.49	3	2.31	25	2.40	10	2.57	5	2.22	5	2.17	5	2.23	5	2.18	10	1.78	20
2.49	5	2.40	10	2.22	10	2.35	5	2.40	10	2.17	5	2.15	10	2.18	5	2.14	5		
2.47	15	2.35	10	2.14	5	2.31	35	2.31	55	2.15	5	2.10	5	2.15	5	2.04	5		
2.39	5	2.31	5	2.07	5	2.20	10	2.22	10	2.10	5	2.04	20	2.10	5	1.99	10		
2.35	5	2.22	15	2.04	10	2.15	10	2.16	5	2.04	20	1.92	5	2.04	10	1.92	15		
2.21	10	2.14	10	1.90	5	2.06	5	2.15	5	1.92	15	1.85d	20	1.99	10	1.90	10		
2.14	10	2.07	10	1.77	20	2.04	15	2.10	5	1.85d	25	1.76	20	1.92	15	1.86	5		
2.07	15	2.04	5	1.63	20	1.92	5	2.04	20	1.76	30	1.63	15	1.90	10	1.78	10		
1.95	3	1.90	5			1.90	5	1.92	15	1.63	10	1.60	10	1.85d	5				
1.90	5	1.63	20			1.85d	10	1.85d	20	1.60	5			1.78d	10				
1.63	20					1.76	20	1.76	20										
1.59	5					1.63	20	1.63	15										
						1.60	10	1.60	10										

*Lattice spacing in angstroms.
†Line intensity relative to the strongest line.
b = broad.
d = double.

* * *