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ABSTRACT

The liquidus-solidus regions of the system $\text{MgO-V}_2\text{O}_5$ were investigated over the entire composition range, with the following principal findings: There are two congruently melting compounds: $2\text{MgO} \cdot \text{V}_2\text{O}_5$ melting at 1128°C , and $3\text{MgO} \cdot \text{V}_2\text{O}_5$ melting at 1210°C . A third compound, $\text{MgO} \cdot \text{V}_2\text{O}_5$, is thought to have an incongruent melting point at 762°C . There are three eutectics: one at approximately 15 mole-percent V_2O_5 melting at 1192°C , one at approximately 30 mole-percent V_2O_5 melting at 1122°C , and one at approximately 75 mole-percent V_2O_5 melting at 658°C .

PROBLEM STATUS

This is a final report on this phase of the problem; work is continuing on other phases.

AUTHORIZATION

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PROPOSED PHASE DIAGRAM FOR THE SYSTEM
MAGNESIUM OXIDE - VANADIUM PENTOXIDE

INTRODUCTION

A recent study on the effects of several pure oxides on the melting point of the compound $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, which is one of the components of troublesome oil-ash deposits in naval boilers (1), was handicapped by the appearance of new compounds for which no diagnostic information was at hand. In an effort to identify these compounds the appropriate two-oxide systems were examined over the entire composition ranges. Although three mixed oxides of vanadium and magnesium were identified, none of these was produced when magnesium oxide was heated with the high-vanadium components of oil ash. However, the investigation resulted in a phase diagram for the system $\text{MgO}-\text{V}_2\text{O}_5$.

In the literature there are numerous references to the system $\text{MgO}-\text{V}_2\text{O}_5$ which are concerned with the effectiveness of foreign oxides for alleviating the oil-ash deposition problem, but there are relatively few instances in which specific physical data have been reported. A liquidus curve for this system was reported by Lucas, Weddle, and Preece (2), who used the deformation characteristics of pyrometric cones as their source of data. They estimated temperatures by placing thermocouples next to the cones, and from undulations in the melting point curves they concluded that there are two compounds in the system, $3\text{MgO} \cdot 2\text{V}_2\text{O}_5$ and $3\text{MgO} \cdot \text{V}_2\text{O}_5$.

This system was also investigated by Zyazev and Esin (3), who identified two compounds, $3\text{MgO} \cdot \text{V}_2\text{O}_5$ and $3\text{MgO} \cdot 2\text{V}_2\text{O}_5$, on the basis of viscosity and density determinations of the melts. They established that melts containing up to 27.7 mole-percent MgO are semiconducting but that greater percentages of MgO lead to ionic conductivity (4,5). This change was thought to be due to a change in short-range order, since it appeared at the approximate composition of the first compound in the system.

Investigations involving compounds prepared by sintering or melting of assumed stoichiometric compositions in the system $\text{MgO}-\text{V}_2\text{O}_5$ have been described in the literature. Durif (6) reported x-ray crystallographic data for the magnesium orthovanadate, $3\text{MgO} \cdot \text{V}_2\text{O}_5$, which was prepared by heating a mixture of vanadium pentoxide and magnesium carbonate slowly to 700°C . King, Koehler, and Adami (7) and Weller and King (8) reported some thermodynamic properties of sintered mixtures with the compositions, $\text{MgO} \cdot \text{V}_2\text{O}_5$ and $2\text{MgO} \cdot \text{V}_2\text{O}_5$.

The reaction of a 1:1 stoichiometric mixture of MgO and V_2O_5 in an oxygen atmosphere and at constant temperatures up to 650°C was studied by Jander and Lorenz (9). They reported that at temperatures between 450°C and 550°C mixtures became yellow-gray, with first signs of compound formation occurring at 530°C . Between 600°C and 650°C the color deepened to yellow-brown as sintering progressed.

By reacting MgO and V_2O_5 (1:1 molar) at a temperature of 650°C , a solid solution of MgO in V_2O_5 was said to have been prepared by King and Suber (10). When the ratio of MgO to V_2O_5 was increased to 3:2 a new compound was observed by petrographic methods.

When used as oil-ash additives, compounds of magnesium are said to form solid solutions between magnesium orthovanadate and magnesium oxide if the ratio of added magnesium to vanadium (from the fuel) was 3:2 or higher (11). Niles and Sanders (12) identified a "low-melting compound," $\text{MgO} \cdot \text{V}_2\text{O}_5$, under similar circumstances. The formation of an unidentified compound containing magnesium was observed in fusion studies involving MgO , V_2O_5 , and Na_2SO_4 (13) and MgO and V_2O_5 (14).

According to Guiter (15), the only magnesium-vanadium oxide crystallizing from aqueous solutions is $5\text{MgO} \cdot \text{V}_2\text{O}_5$. Studies on spinels composed of magnesium and lower valent vanadium combined with oxygen have been reported by several investigators (16-19). Some of these spinels are semiconductors.

LABORATORY METHODS

A visual method for determining the melting characteristics in systems which melt above room temperature has been employed in this laboratory on other occasions (1,20, 21). This method is a modification of techniques used routinely in microscopy at elevated temperatures, in which the specimen is observed in profile as it is heated in a tube furnace. The temperatures at which the liquid first appears and at which the last particles of the solid disappear from view are recorded. From these values, plotted as a function of original composition, approximate liquidus-solidus curves may be constructed.

Until now the opportunity to test the method on a substance having an incongruent melting point has not been met. Such a material forms a compound which is stable at a low temperature but which dissociates into a new compound and a liquid at some definite, elevated temperature. On cooling, the reverse reaction takes place, sometimes very rapidly, and the original compound is again found at the lower temperature. The melting behavior of the system $\text{MgO}-\text{V}_2\text{O}_5$, however, would indicate that at least one compound, $\text{MgO} \cdot \text{V}_2\text{O}_5$, melts incongruently. Direct observation of the melting specimens gave no clue which would serve to indicate the presence of an incongruent melting point. The composition of the compound had to be deduced from x-ray diffraction patterns on mixtures sintered just below the initial melting temperature.

A typical series of experiments was performed as follows: Portions of magnesium 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 milled by hand with mortar and pestle until dry. The final weight of each mix was approximately 3 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 pellet served to shield 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 were vague as determined by this method, while others were so well defined that duplicate runs gave melting points within 2°C 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 $K\alpha$ radiation, and a scanning speed of 2 degrees per minute.

In order to detect thermal effects in the solid state the thermocouple leads were connected to a high-impedance potentiometric recorder during the cooling process. In this way a reversible heat effect, exothermic on cooling, was detected at 910°C for all compositions between 25 and 46 mole-percent V_2O_5 .

EXPERIMENTAL RESULTS AND CONCLUSIONS

The liquidus and solidus lines of the proposed phase diagram (Figs. 1 and 2) were based entirely on temperatures determined by the visual method for detecting melting points (Table 1). The locations of maxima and minima in the liquidus curve are not as obvious as in the system $\text{ZnO}-\text{V}_2\text{O}_5$, which had been investigated earlier (21); but eutectic

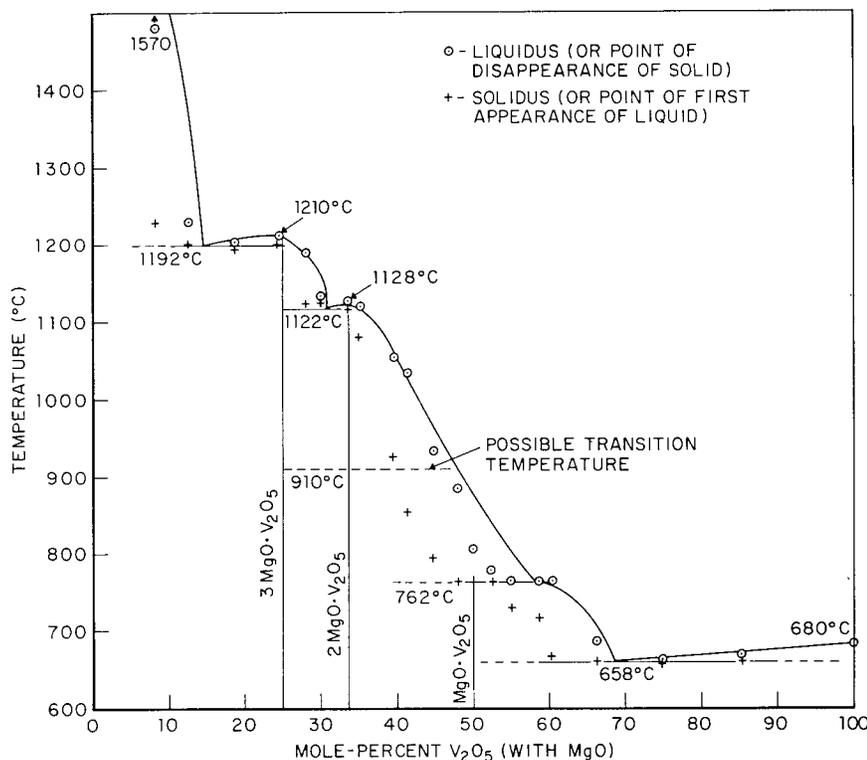


Fig. 1 - Suggested phase diagram for the liquidus-solidus regions of the system $\text{MgO}-\text{V}_2\text{O}_5$ (molar basis)

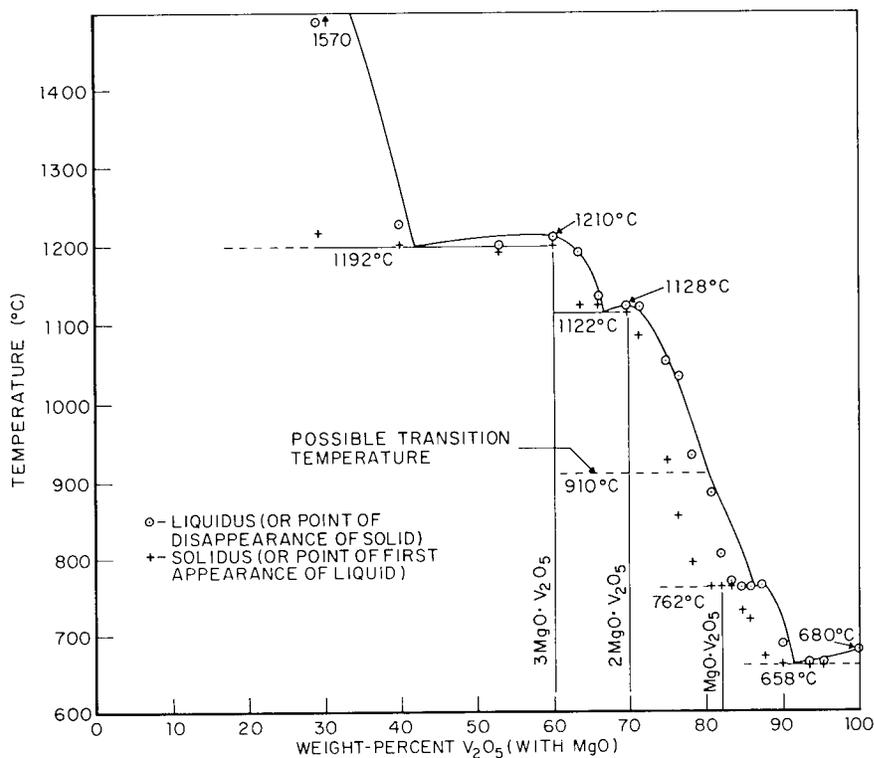


Fig. 2 - Suggested phase diagram for the liquidus-solidus regions of the system $\text{MgO}-\text{V}_2\text{O}_5$ (weight basis)

and peritectic temperatures were readily duplicated, causing the location of the solidus line to be more certain than that of the liquidus line.

The results of x-ray diffraction analysis of specimens either crystallized from their melts or sintered at temperatures below their initial melting temperatures were consistent with predictions based on the proposed phase diagram (Table 2).

The compounds $3\text{MgO}\cdot\text{V}_2\text{O}_5$ and $\text{MgO}\cdot\text{V}_2\text{O}_5$ gave intense x-ray powder patterns, but $2\text{MgO}\cdot\text{V}_2\text{O}_5$ gave poor patterns and was more difficult to characterize. Since a reversible thermal effect had been detected in all specimens which were expected to contain $2\text{MgO}\cdot\text{V}_2\text{O}_5$, it was concluded that a high-temperature modification of $2\text{MgO}\cdot\text{V}_2\text{O}_5$ exists and is stable only at temperatures above 910°C . The x-ray diffraction data are summarized in Table 3.

When the data reported here are compared with those of earlier investigators, it is found that the x-ray data for $3\text{MgO}\cdot\text{V}_2\text{O}_5$ (Table 3) closely matches that of Durif (6). The liquidus curve for this system reported by Lucas (2) parallels that of Fig. 2 but is consistently about 100°C lower over most of its range. The data reported by Greenert (14) for specimens containing MgO and V_2O_5 , initially, but which resulted in unidentified reaction products, can be interpreted on the basis of the present work. His samples Nos. 26 and 27 (18% MgO) gave intense patterns for the compound $\text{MgO}\cdot\text{V}_2\text{O}_5$, but contained a trace of V_2O_5 . His sample No. 28 (33% MgO) matched a specimen prepared in this laboratory which had been cooled rapidly from the elevated sintering temperature and was presumed to represent the metastable high-temperature modification of $2\text{MgO}\cdot\text{V}_2\text{O}_5$. His sample No. 29 (43% MgO) must have been only partly reacted, since it

Table 1
Tabulated Melting Point Data for the System MgO - V₂O₅

Sample	Weight % V ₂ O ₅	Mole % V ₂ O ₅	Initial Melting (°C)	Final Melting (°C)
9	19.5	5.0	Not detected	Not reached
8	29.4	8.4	1218	1570
7	40.0	12.8	1200	1228
6	53.0	19.8	1192	1200
5	60.2	24.9	1202	1209
10	63.8	27.8	1122	1190
18	66.1	30.0	1122	1131
11	69.6	33.4	1111	1116
4	71.3	35.3	1080	1120
1	75.1	39.8	928	1052
3	76.4	41.5	854	1036
17	78.8	44.9	794	934
19	80.6	47.8	764	888
12	82.0	49.9	764	804
20	83.2	52.2	764	768
2	84.8	55.1	730	763
21	86.4	57.8	718	766
16	87.3	60.2	668	768
13	90.0	66.4	660	688
14	93.2	75.0	658	660
15	96.1	85.4	658	662
	100.0	100.0	680	680

Table 2
Compounds Detected by X-Ray Powder Diffraction Methods
After Various Thermal Treatments

Sample	Mole % V_2O_5	Sintered 48 Hours At 575°C	Sintered 24 Hours At 700°C	Sintered At 1000°C	Melted and Slowly Cooled
9	5.0	<u>A</u> + (B weak)	<u>A</u> + (B weak)	<u>A</u> + (B weak)	Not melted
8	8.4	<u>A</u> + (B weak)	<u>A</u> + B	<u>A</u> + B	<u>A</u> + B
7	12.8	<u>A</u> + (B weak)	<u>B</u> + A	<u>B</u> + A	<u>B</u> + A
6	19.8	A + B + C	<u>B</u> + A	<u>B</u> + (A weak)	<u>B</u> + (A weak)
5	24.9	A + B + C	<u>B</u> + (A weak)	<u>B</u> + (A trace)	<u>B</u> + (A trace)
10	27.8	(A,B,C weak)	(B,C weak)	(B,C weak)	(B,C weak)
18	30.0	(A,B,C weak)	(B,C weak)	(B,C weak)	(B,C weak)
11	33.4	(A,B,C weak)	(B,C,D weak)	C weak	C weak
4	35.3	(B,C,D weak)	D + ?	Melted	D + ?
1	39.8	(D,E weak)	(D,E weak)	Melted	<u>D</u> + (E trace)
3	41.5	(D,E weak)	(D,E weak)	Melted	<u>D</u> + (E trace)
17	44.9	(D,E weak)	(D,E weak)	Melted	<u>D</u> + (E trace)
19	47.8	(D,E weak)	<u>D</u> + (E trace)	Melted	<u>D</u> + (E trace)
12	49.9	<u>D</u> intense	<u>D</u> intense	Melted	<u>D</u> intense
20	52.2	<u>D</u> intense	<u>D</u> intense	Melted	<u>D</u> intense
2	55.1	<u>D</u> + (E trace)	<u>D</u> + E	Melted	<u>D</u> + E
21	57.8	D + E	<u>D</u> + E	Melted	<u>D</u> + E
16	60.2	<u>D</u> + E	Melted	Melted	<u>E</u> + <u>D</u>
13	66.4	<u>D</u> + E	Melted	Melted	<u>E</u> + D
14	75.0	E + D	Melted	Melted	E + D
15	85.4	E + (D weak)	Melted	Melted	E + (D weak)

(An underlined letter indicates the compound forming the major share of a mixture)

A = MgO
 B = $3MgO \cdot V_2O_5$
 C = $2MgO \cdot V_2O_5$
 D = $MgO \cdot V_2O_5$
 E = V_2O_5

Table 3
X-Ray Diffraction Data for Compound Compositions in the System $\text{MgO}\cdot\text{V}_2\text{O}_5$
(Copper $\text{K}\alpha$ Radiation)*
(Compounds Containing Vanadium Were Prepared by Sintering 48 Hours at 700°C)

MgO Reagent		$3\text{MgO}\cdot\text{V}_2\text{O}_5$		$2\text{MgO}\cdot\text{V}_2\text{O}_5$		$\text{MgO}\cdot\text{V}_2\text{O}_5$		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
2.434	10	5.71	10	6.27	5	6.23	10	5.78	3
2.106	100	4.72	5	5.71	5	4.37 (R)	3	4.87	2
1.489	50	4.50	35	5.15	5	4.29	55	4.38	100
		3.36	5	4.38	10	3.23	5	4.11	10
		3.29	80	4.27	5	3.14	25	3.50	1
		3.04	20	4.11	10	3.056	100	3.42	1
		3.02	55	3.90	10	2.720	15	2.89	3
		2.86	35	3.70	10	2.303	5	2.77	1
		2.547	100	3.285	15	2.247	2	2.189	20
		2.493	55	3.195	20	2.179	15	2.152	3
		2.460	15	3.168	100	2.154	3	1.920	1
		2.354	5	3.036	10	2.102	3	1.902	1
		2.102 (R)	35	3.025	20	2.083	5	1.865	1
		2.074	35	2.873	5	1.886	5	1.447	1
		1.894	5	2.728	5	1.836	3		
		1.796	5	2.612	10	1.738	3		
		1.745	5	2.540 (R)	20	1.649	3		
		1.714	5	2.494	10	1.596	5		
		1.679	5	2.460	5				
		1.641	5	2.174	5				
		1.617	5	2.106 (R)	5				
		1.584	5	2.079	30				
		1.564	10	1.943	20				
		1.515	10	1.576	25				
		1.489	10	1.529	20				
		1.470	55	1.513	20				

*Maximum $2\theta = 62$ degrees.

[†]Lattice spacing in angstroms.

[‡]Line intensity relative to the strongest line.

R = Residual line from other compounds present.

contained sufficient magnesium oxide to form the compound $3\text{MgO}\cdot\text{V}_2\text{O}_5$, but its x-ray powder pattern more closely matched that of the low-temperature modification of $2\text{MgO}\cdot\text{V}_2\text{O}_5$.

The unidentified compound prepared by Brasunas and Cunningham (13) during the heating of a mixture of reagents in the molar proportion of $6\text{MgO}:4\text{V}_2\text{O}_5:\text{Na}_2\text{SO}_4$ was, from all appearances, predominantly $\beta\text{-SiO}_2$ (β -cristobalite). This probably resulted from a chemical attack on the silica-glass crucible.

In work concerning the sintering of mixtures of MgO with $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ (1) an unidentified series of lines appeared on the x-ray diffraction diagrams. The present research was initiated for the purpose of identifying the compound responsible for the lines, but identification was not possible on the basis of the three magnesium-vanadium oxides described. Data for this unknown compound was detected in specimens containing from 13 to 28 weight-percent MgO, initially, with the balance made up of $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$. Data for this compound is given in Table 4.

Table 4
X-Ray Diffraction Data for Unidentified Compound from Melts Produced
from MgO and $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ (Copper $\text{K}\alpha$ Radiation)*

d(A) [†]	I/I _o [‡]	d(A)	I/I _o	d(A) [†]	I/I _o [‡]	d(A)	I/I _o
6.5	30	2.94	10	3.35	10	2.59	5
4.6	20	2.92	10	3.25	30	2.50	10
4.25	30	2.85	5	3.20	100		
3.73	20	2.74	20	3.11	40		
3.53	20	2.68	5	3.06	80		
				3.02	80		

*Very weak pattern.

[†]Lattice spacing in angstroms.

[‡]Line intensity relative to the strongest line.

