Argonne National Laboratory

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by

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ABSTRACT

In a study of the UO_2 - $NdO_{1.5}$ system it was found that urania will take more than 60 mol percent neodymia into solid solution. The melting point of Nd_2O_3 was found to be $2270°C \pm 20°C$. Two compounds of approximately the compositions $MgUO_4$ and MgU_3O_{10} were formed at $1000°C$ and below by reaction between U_3O_8 and MgO with some additional oxygen. At higher temperatures, an extensive solid solution phase which approaches the MgU_2O_7 composition was formed by these two oxides. No reactions were observed in the U_3O_8 - TiO_2 compositions studied.

GENERAL INTRODUCTION

A series of phase equilibrium studies between the uranium oxide, UO_2, and a number of other oxides: namely Al_2O_3, MgO, ZrO_2, and ThO_2, have been reported previously.[1] In addition to these studies the following binary phase equilibrium systems have been investigated and will be discussed in this present paper: UO_2 - Nd_2O_3, U_3O_8 - MgO and U_3O_8 - TiO_2. In some cases these latter studies were not as complete or as reliable as the former studies. This will be discussed in more detail in each binary system.

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Part V: UO_2 - Nd_2O_3

Introduction

A few preliminary tests had indicated that the neodymium oxide, Nd_2O_3, might have a stabilizing influence on UO_2 when heated in air and at least retard its oxidation to U_3O_8. Therefore, it was of interest to investigate the UO_2 - Nd_2O_3 system further.

Two forms of Nd_2O_3 have been reported; the A or hexagonal modification,[2,3] which is the high temperature phase, and the C or cubic,[4] which is the low temperature phase. This transformation is reported to occur between 875°-940°C. Popov and Glockler concluded that tri-valent neodymium was the highest oxidation state possible.

Experimental

Mixtures of UO_2 and Nd_2O_3, ranging in composition from 0 to 100% Nd_2O_3 in 10 mole percent intervals, were prepared as pellets, which were then calcined at 1600°C in a hydrogen-atmosphere electric furnace as described previously.[1] The fired pellets were used to determine the phase relationships at the fired temperatures and to provide solid fragments for the quenching furnace. The quenching technique was similar to that described in the previous papers.[1]

Unfortunately, the Nd_2O_3 was impure, as shown in Table I; however, at a later date, a small amount of an oxide which analyzed 99% Nd_2O_3 was obtained and was used for the melting point determination.

X-ray diffraction patterns were made of the powdered samples using CuK_α radiation and a 114.6 mm. diameter camera.

Discussion of Results

The results obtained after heating the various UO_2 - Nd_2O_3 mixtures are given in Table II and shown in Figure 1. Extensive solid solution of neodymia in urania is indicated, but solid solution of urania in neodymia could not be detected in samples heated at the lower temperatures. However, there was some indication that limited solid solution occurred in high neodymia samples heated above 2000°C.

Many of the samples of 45% to 55% $NdO_{1.5}$, heated at the lower temperatures, showed a few faint extra lines in the X-ray diffraction patterns similar to ones obtained when heating comparable U_3O_8 - Nd_2O_3 compositions. Because of the impure Nd_2O_3 starting material it is not certain whether these extra lines are the result of an impurity phase or whether they actually arise from UO_2 and Nd_2O_3 oxides.

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Although the proposed phase equilibrium diagram shown in Figure 1 is not exact because of the impure Nd_2O_3, the boundary lines shown are probably accurate enough for most practical purposes and may also be used as a guide for more exact work with pure materials.

In order to check the stabilizing effect of Nd_2O_3 on UO_2, small samples of all the compositions heated at 1600°C in hydrogen were reheated in air at 1000°C. The X-ray diffraction patterns of the 0 - 45% $NdO_{1.5}$ showed the presence of the orthorhombic U_3O_8 phase plus a face-centered cubic phase whose lattice constant was somewhat smaller than before reheating. This change in parameter is probably due to an increase in the relative amount of oxygen and/or an oxidation of some of the U^{+4} to U^{+6}. Between 45 - 80% $NdO_{1.5}$ a face-centered cubic phase only was evident, and beyond 80% $NdO_{1.5}$ the hexagonal Nd_2O_3 phase was present before and after heating. In view of the large amount of Nd_2O_3 necessary to maintain a face-centered cubic UO_2 phase, Nd_2O_3 would not be considered as a good stabilizer.

Since most of the samples used for this study were heated and cooled rapidly, very little of the previously reported cubic phase of Nd_2O_3 was found in the X-ray patterns. It was observed that the high Nd_2O_3 samples would disintegrate several weeks after firing; this break-up could have been due to a hexagonal to cubic transformation or to a reoxidation.

Differential thermal analysis did not reveal any change in the Nd_2O_3 between room temperature and 1480°C. The melting point of Nd_2O_3, which was 2270°C ± 20°C, was not sharp with either the original Nd_2O_3 material or the 99% oxide.

The possibility of solid solution formation between UO_2 and Nd_2O_3 should be considered on the basis of ionic size and charge. If it is assumed that the lattice parameter of the C type Nd_2O_3 is 5.51 A., as reported recently by Hund and Peetz[5] in their study of the $UO_{2.67}$ - $NdO_{1.5}$ system, and if it is assumed that the ionic radius of O^{-2} is 1.40 A., as calculated from UO_2 in the previous oxide studies,[1] then the ionic radius of Nd^{+3} is 0.98 A. The computed radius for U^{+4} is 0.97 A. This near identity of ionic size would indicate that the lattice parameter in the UO_2 - Nd_2O_3 system would change very little. The lattice parameters shown in Table III showed only slight variation from the UO_2 parameter as a function of composition. These parameters could not be determined more accurately since the diffraction lines, especially in the back reflection region, became rather diffuse even after adding a relatively small amount of neodymia to urania.

As Nd^{+3} is substituted for U^{+4} in the face-centered cubic lattice, an oxygen deficiency must be created or some of the U^{+4} must be oxidized to U^{+6} in order to maintain a balance of the charges. Since the samples used in this present study were fired in hydrogen or an inert atmosphere

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the oxygen loss is probable. Furthermore, the lattice parameter of the cubic phase of the UO_2 - $NdO_{1.5}$ system was larger than the cubic phase as reported[5] for the $UO_{2.67}$ - $NdO_{1.5}$ system, which would seem to substantiate the creation of an oxygen deficiency since $UO_{2.67}$ already contains a mixture of U^{+4} and U^{+6} ions which produces a smaller cubic phase than the U^{+4} from UO_2.

Conclusion

This study seemed to indicate that the UO_2 - $NdO_{1.5}$ system is a rather unusual solid solution example for ceramic oxides. Of the two cations which are approximately the same size, the Nd^{+3} can be substituted extensively for the U^{+4} even though the two primary oxide structures and the cation valencies are different.

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Part VI: U_3O_8 - MgO

Experimental

Mixtures of U_3O_8 and reagent grade MgO were prepared with compositions varying at 10 mol percent intervals over the entire range of 0 to 100% U_3O_8. After weighing out the components they were mixed in a mechanical mortar for 5 minutes and then pressed into pellets. These pellets were weighed, placed in a platinum boat, heated to 1300°C, and slow cooled. After cooling, they were reweighed and samples were taken for X-ray diffraction studies. Fragments of the initially heated pellets were taken and reheated at 1000°C for 4 weeks and at 1400°C for 2 weeks.

A 50-50 molar mixture was also prepared and suspended from an analytical balance in a platinum wire-wound resistance furnace. This sample was heated under controlled conditions; weight changes were recorded in order to better understand the changes that occur when U_3O_8 and MgO are heated together.

Discussion of Results

The results obtained after heating the various U_3O_8 - MgO compositions in air are given in Table IV and shown in Figure 2. The X-ray diffraction patterns of composition up to 25% MgO heated at 1000°C showed the presence of two phases: U_2O_8 and MgU_3O_{10}. This latter phase is apparently obtained by oxidation according to the following equation:

$$2U_3O_8 + 2MgO + O_2 \rightarrow 2MgU_3O_{10}$$

This magnesium uranate was identified by comparing the X-ray diffraction pattern obtained in this study with the pattern obtained previously from a sample which chemical analysis showed to have this composition. Between 25 and 50 mol percent MgO, MgU_3O_{10} and $MgUO_4$ were found to be present. The $MgUO_4$ phase was identified in the same manner as the MgU_3O_{10} and may be formed by oxidation according to the following equation:

$$2U_3O_8 + 6MgO + O_2 \rightarrow 6MgUO_4$$
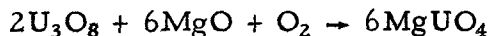
Both of these magnesium uranates yield a complex diffraction pattern and, to date, their crystal structure has not been determined. When composition beyond 50 mol percent MgO were heated to 1000°C the $MgUO_4$ and MgO phases appeared.

Samples of varying composition which were heated to 1200°C or above no longer showed the presence of the $MgUO_4$ and MgU_3O_{10} phases. Instead, a face-centered solid solution cubic phase was obtained. This phase showed a considerable variation in lattice parameter as a function of composition and temperature (Table V) however, the exact extent of this solid solution

area was not determined. It is very likely that there is a considerable variation in the oxygen content from a MgU_2O_7 composition as pointed out by Hoekstra and Katz.[6] A comparison of the lattice parameter of this cubic phase as found in the U_3O_8 - MgO system with the cubic phase found in the UO_2 - MgO binary[1] showed that the lattice constants in the U_3O_8 - MgO system were consistently smaller. This is probably caused by a different valence state of the uranium in the U_3O_8 as compared to UO_2, since there are U^{+4} and U^{+6} ions in U_3O_8 and only U^{+4} ions in UO_2.

The reaction between U_3O_8, MgO and additional oxygen can possibly be best explained by means of a ternary diagram between UO - Oxygen - MgO as shown in Figure 3.

In order to obtain a better understanding of these reactions a few of the compositions were weighed continuously as they were heated according to the method previously described. The weight changes observed may be accounted for in several ways. Losses can be attributed to ignition loss from MgO and possibly from the U_3O_8; to the loss of some uranium by volatilization, probably as UO_3; and to loss of oxygen. Increase in weight can be accounted for by the conversion of UO_2, present as an impurity in the original U_3O_8 component, to U_3O_8 and the formation of the compounds MgU_3O_{10} and $MgUO_4$ which require additional oxygen.

A mixture of 1:1 MgO - $UO_{2.67}$ was heated in a weighing furnace and the weights plotted as shown in Figure 4. The nature of the weight change of this sample which occurred during heating may be explained as follows (See Figure 4):

Stage	Probable Cause
1	Loss of adsorbed and absorbed moisture.
2	Reaction of MgO - U_3O_8 and O_2 to form the low temperature composition MgU_3O_{10}.
3	Loss of oxygen from MgU_3O_{10}.
4	Change of the low temperature composition of MgU_3O_{10} to the high temperature stable compound MgU_2O_7.
5	Loss of oxygen and probably uranium from MgU_2O_7.

By heating compositions which consisted of a mixture of U_3O_8 and $MgUO_4$ with a continually weighing balance, it has been possible to pick up an oxygen change of a few hundredths of a percent and still retain the same

crystalline structure. When the same mixture was heated in 1200°C in helium and quenched, it lost enough oxygen to change the color but not enough loss to detect by weight. Quenching this sample from 1200°C caused the retention of the high temperature cubic phase.

Conclusion

Considerably more work could be done on the U_3O_8 - MgO phase equilibrium system and the reaction of these oxides with oxygen in order to establish the exact temperature and composition range at which the various compounds exist. Apparently in order to carry out such a study it would be necessary to obtain oxygen analyses, differential thermal analyses, and change in weight measurements in addition to the ordinarily required data.

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Part VII: U_3O_8 - TiO_2

Introduction

As part of the program on the basic study of the reactions of uranium oxides with other oxides, it was thought that the reaction between U_3O_8 and TiO_2 might be of interest, especially if the reaction product were similar to aluminum titanate, $Al_2O_3 \cdot TiO_2$, which has low thermal expansion characteristics.

Experimental

Pellets of the composition $U_3O_8 \cdot TiO_2$, or 8.7 weight percent TiO_2, were prepared by pressing. These pellets were then placed in a furnace and samples withdrawn at intervals of 100°C from 600°C to 1500°C. Analyses of the U_3O_8 and TiO_2 are given in Tables VI and VII.

Discussion of Results

Upon heating the pellets consolidation started to occur at 1200°C and maximum shrinkage occurred at 1400°C. At 1500°C the glassy phase seems to have leached out of the pellet leaving U_3O_8; therefore the optimum firing temperature for such a mixture from the ceramic standpoint is approximately 1400°C as shown in Figure 5. The bonding which was obtained apparently came from the TiO_2 and impurities rather than from a TiO_2-U_3O_8 reaction since the X-ray diffraction results did not show any reaction.

ACKNOWLEDGEMENTS

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Table I

NEODYMIUM OXIDE COMPOSITION

	Weight %	Mol %
Nd_2O_3	85.22	77.80
Gd_2O_3	0.92	0.8
MgO	0.08	0.61
Pr_2O_3	2.34	2.18
SiO_2	2.14	11.00
Sm_2O_3	9.29	8.18
Y_2O_3	0.01	
	100.00	100.57

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Table II

HEATING RESULTS FROM UO_2-$NdO_{1.5}$ MIXTURES

Composition (mol %)			Temp. °C	Time	Resulting Phases
UO_2	$NdO_{1.5}$	Analysis			
100		a	1600	24 hrs	F.C.C.
82.2	17.8	b	1600	24 hrs	F.C.C. S.S.
67.4	32.6	b	1600	24 hrs	F.C.C. S.S.
66.6	33.4	a	2392	5 min	F.C.C. S.S.
59.5	40.5	b	2136	1 hr	F.C.C. S.S.
54.2	45.8	b	1600	24 hrs	F.C.C. S.S.
49.7	50.3	b	2148	5 min	F.C.C. S.S.
43.2	56.8	b	1600	24 hrs	F.C.C. S.S. and v.s. unknown
42.8	57.2	a	2453	5 min	F.C.C. S.S. and liquid
34.1	65.9	b	1600	24 hrs	F.C.C. S.S.
26	74	b	1600	24 hrs	F.C.C. S.S.
25	75	a	1981	5 min	F.C.C. S.S.
25	75	a	2135	5 min	F.C.C. S.S.
25	75	a	2241	5 min	F.C.C. S.S. and liquid
18.5	81.5	b	1600	24 hrs	F.C.C. S.S. and S. hex.
17.5	82.5	b	2210	5 min	F.C.C. S.S. and hex and liquid
11.7	88.3	b	1600	24 hrs	F.C.C. S.S. and S. hex.
11.6	88.4	b	1927	5 min	F.C.C. S.S. and hex.
11.9	88.1	b	1978	5 min	F.C.C. S.S. and hex.
11	89	a	2033	5 min	F.C.C. S.S. and hex. and S. liquid.
12	88	b	2241	1 min	Liquid and F.C.C. S.S. and hex.
5.6	94.4	b	1600	24 hrs	Hex. and F.C.C. S.S.
	100	a	1600	24 hrs	Hex. and v.s. unknown and v.s. cubic Nd_2O_3.
	100	a	2266	2½ min	Liquid and solid
	100	a	2278	3 min	Liquid

a - nominal composition   b - chemical analysis

F.C.C. - Face centered cubic   S.S. - Solid solution
v.s. - very slight   S. - Slight
hex. - hexagonal

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Table III

LATTICE PARAMETERS OF UO_2-$NdO_{1.5}$
FACE CENTERED CUBIC SOLID SOLUTION

Sample No.	Composition mol %		a_0 A.	Heat Treatment
	UO_2	$NdO_{1.5}$		
	100		5.4725	Melted in He.
54	84.9	15.1*	5.47	2 hr 1700°C in H_2.
271	84.9	28.6*	5.478	24 hr 1700°C in H_2.
55	71.4	28.6*	Same as 54	2 hr 1700°C in H_2.
56	59.3	40.7*	Same as 55	2 hr 1700°C in H_2.
1076	49.7	50.3**	5.4654	5 min 2148°C in He.
57	48.3	51.7*	5.45	2 hr 1700°C in H_2.
276	29.4	70.6*	5.475	72 hr 1700°C in H_2.
701		100 *	5.52	24 hr 500°C in air.

*As prepared.

**Chemical analysis.

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Table IV

HEATING RESULTS FROM U_3O_8-MgO MIXTURES

Composition (mol %)			Temp. °C	Time	Resulting Phases
$UO_{2.67}$	MgO	Analysis			
96.5	3.5	a	1000	4 wks	U_3O_8 and MgU_3O_{10}
96.5	3.5	a	1400	15 hrs	U_3O_8 and cubic
92.3	7.7	a	1400	16 hrs	U_3O_8 and cubic
90	10	b	1400	15 hrs	U_3O_8 and cubic
81.8	18.2	a	850	2 hrs	MgU_3O_{10} and U_3O_8
81.4	17.6	b	1400	15 hrs	Cubic and U_3O_8
67.1	32.9	b	1400	15 hrs	Cubic
58.6	41.4	b	1400	15 hrs	Cubic and $MgUO_4$
50	50	a	850	2 hrs	$MgUO_4$ and MgO
50	50	a	1200	1 hr	Cubic and MgO
48.5	51.5	b	1400	15 hrs	Cubic and MgO
50	50	a	1400	2 wks	Cubic and MgO
13.1	86.9	b	1400	16 hrs	MgO, $MgUO_4$, and cubic

a = original composition

b = chemical analysis

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Table V

LATTICE PARAMETERS OF THE CUBIC PHASE
IN THE U_3O_8-MgO SYSTEM

Composition mol %	Treatment	a_0
50% $UO_{2.67}$, 50% MgO	1400°C furnace cooled	5.24 A.
50% $UO_{2.67}$, 50% MgO	1200°C and quenched	5.34 A.
66.6% $UO_{2.67}$, 33.4% MgO	1400°C furnace cooled	5.28 A.

Table VI

U_3O_8 SPECTROCHEMICAL
ANALYSIS

Element	Amount, ppm
Ag	5
Al	500
Ca	>1000
Cu	20
Fe	>1000
Mg	100
Mn	70
Na	500
Ni	50
Pb	7
Si	1000
Sn	10

Table VII

TiO_2 SPECTROCHEMICAL
ANALYSIS

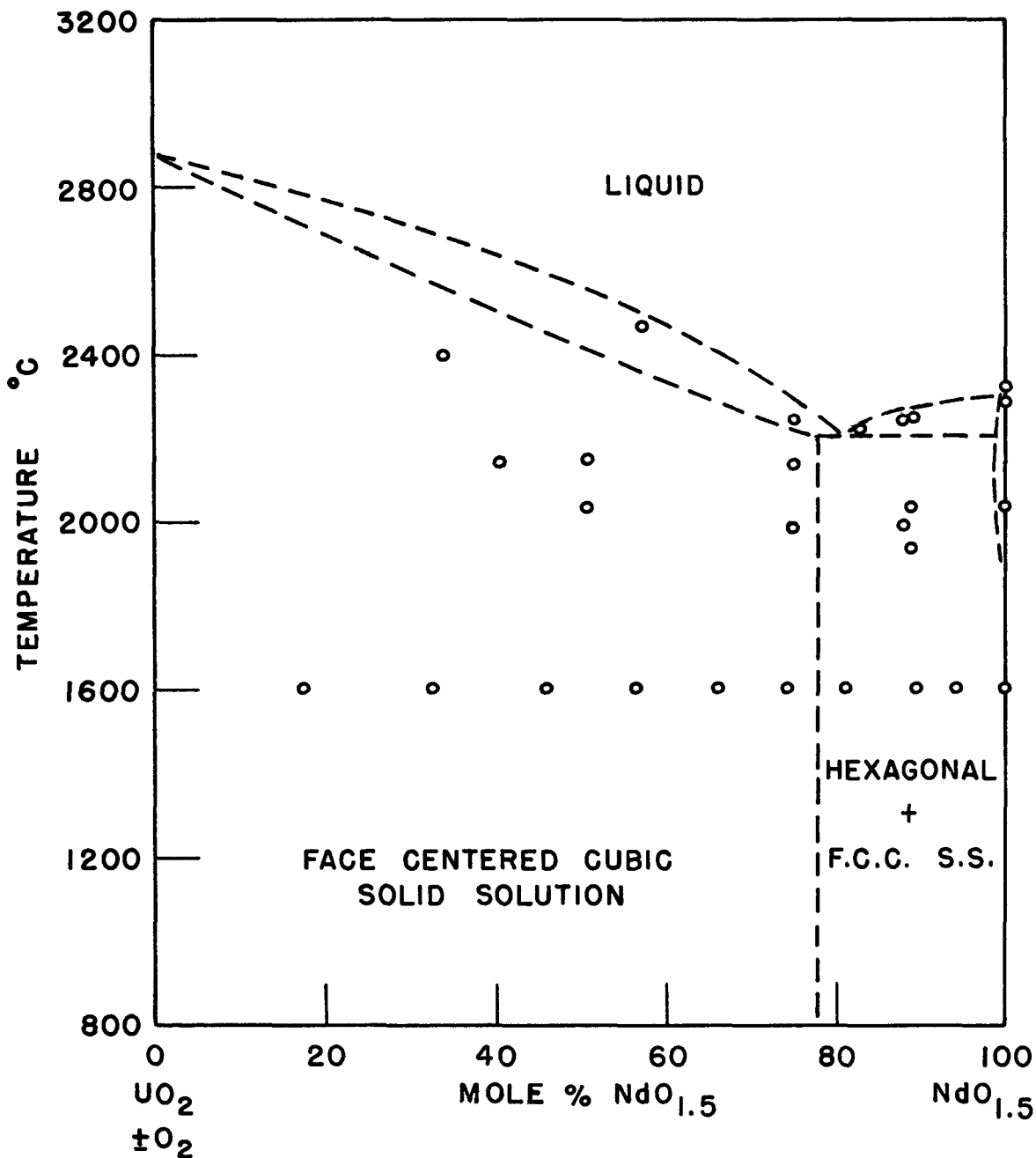| Oxide	Amount, w/o
Al_2O_3	0.03
BaO	0.005
CaO	0.02
Cb_2O_5	0.03
Cr_2O_3	0.0005
CuO	0.0002
Fe_2O_3	0.003
MgO	0.002
MnO_2	0.001
Na_2O	0.005
SiO_2	0.05
ZrO_2	0.02

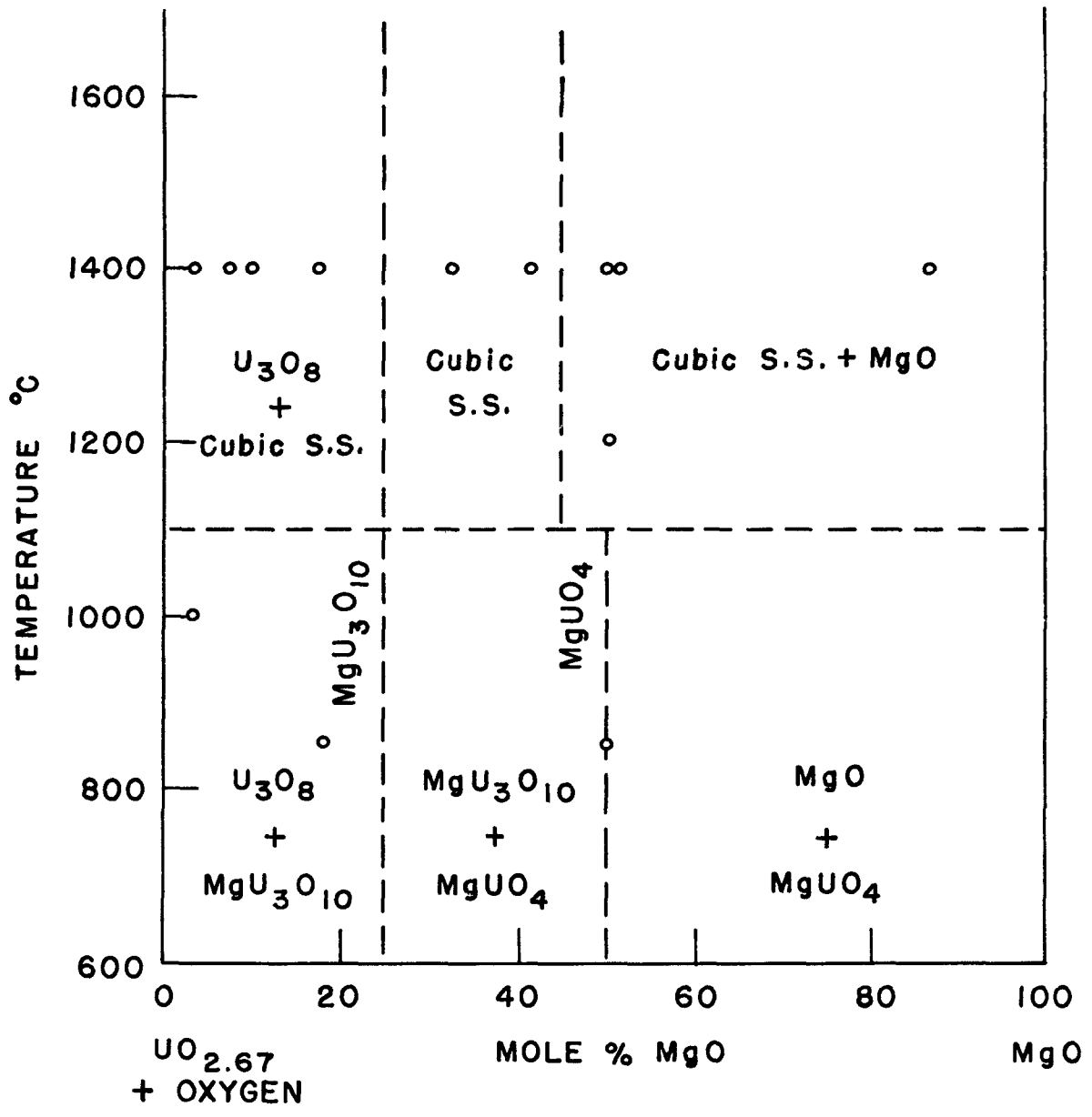FIG. I   PROBABLE UO$_2$ – NdO$_{1.5}$
PHASE EQUILIBRIUM DIAGRAM

FIG. 2   SUGGESTED $(U_3O_8$ + OXYGEN)-
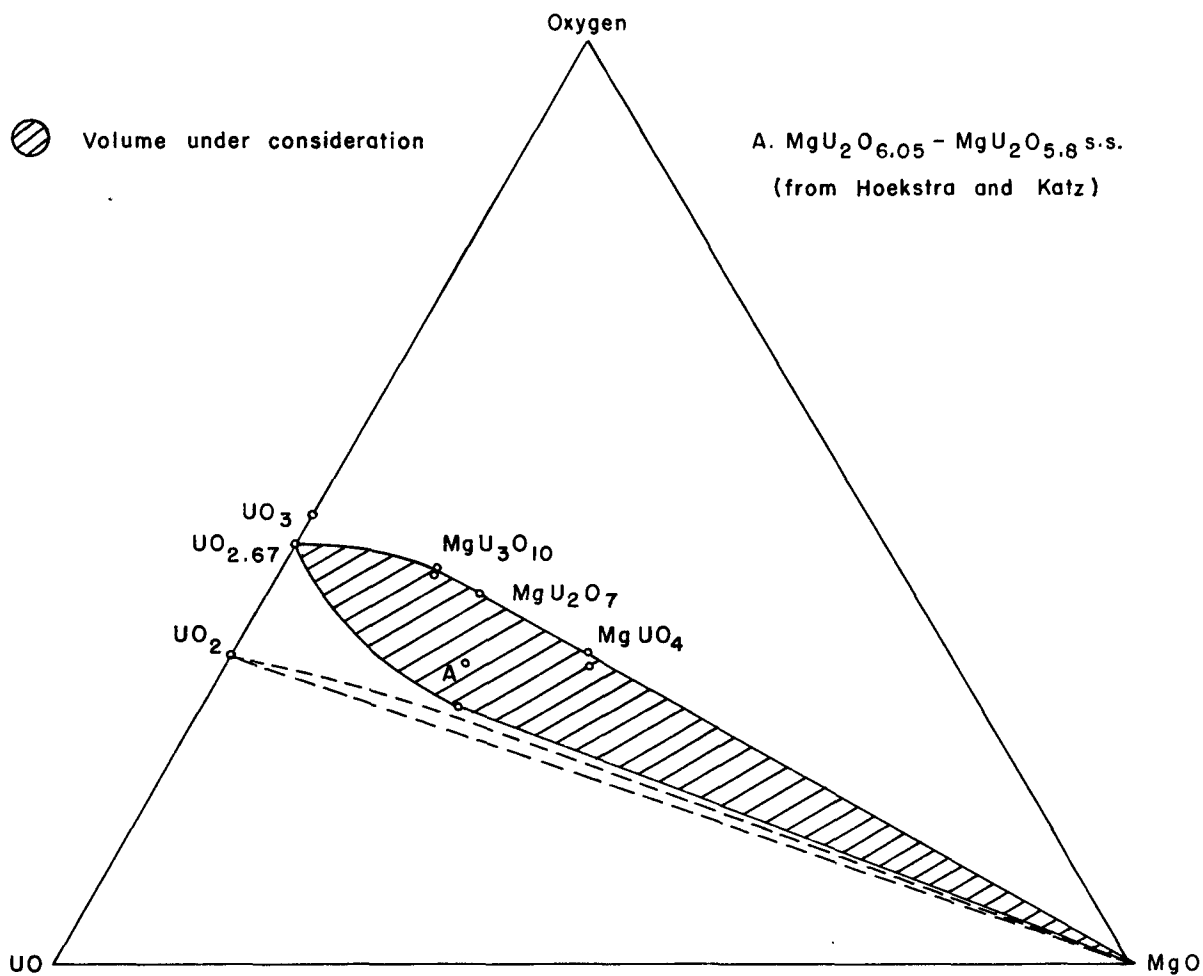MgO PHASE EQUILIBRIUM DIAGRAM
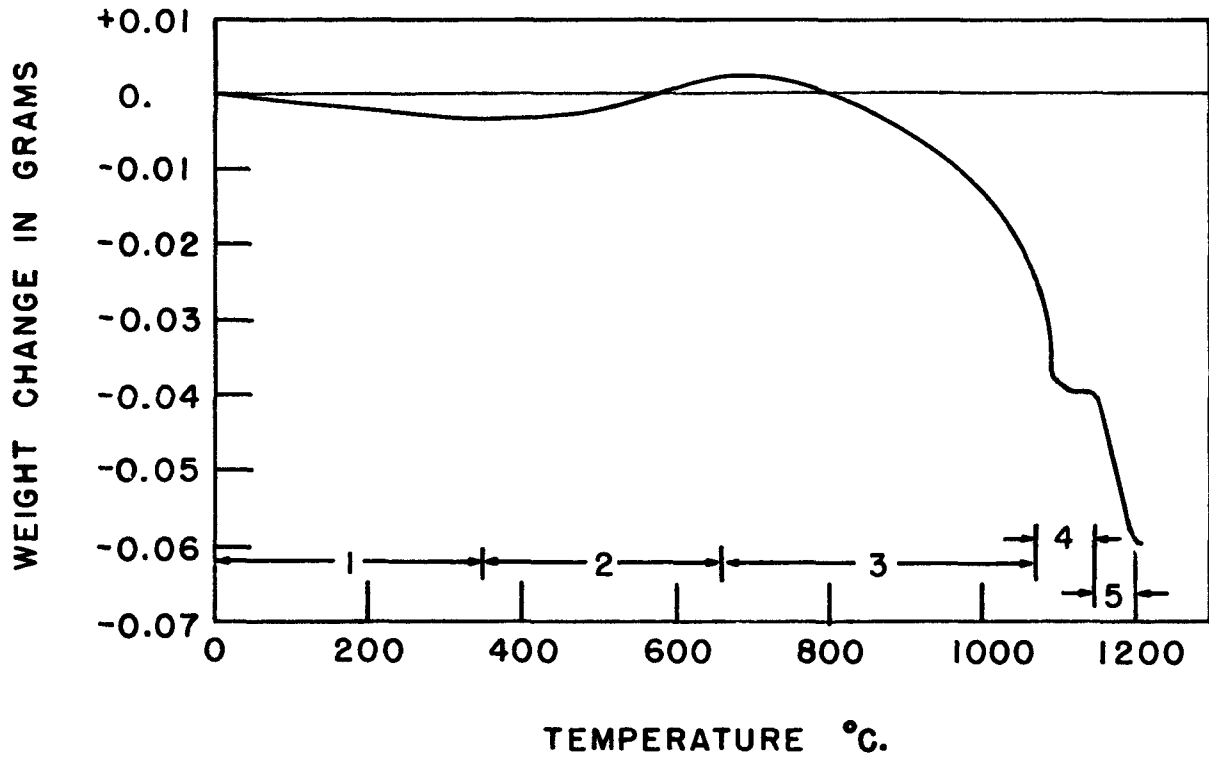
FIG. 3 UO - O - MgO PHASE RELATIONSHIPS

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FIG. 4   WEIGHT CHANGES IN A EQUIMOLAR MIXTURE
OF U_3O_8 - MgO

(10 gram sample of 50% U_3O_8 - 50% MgO heated
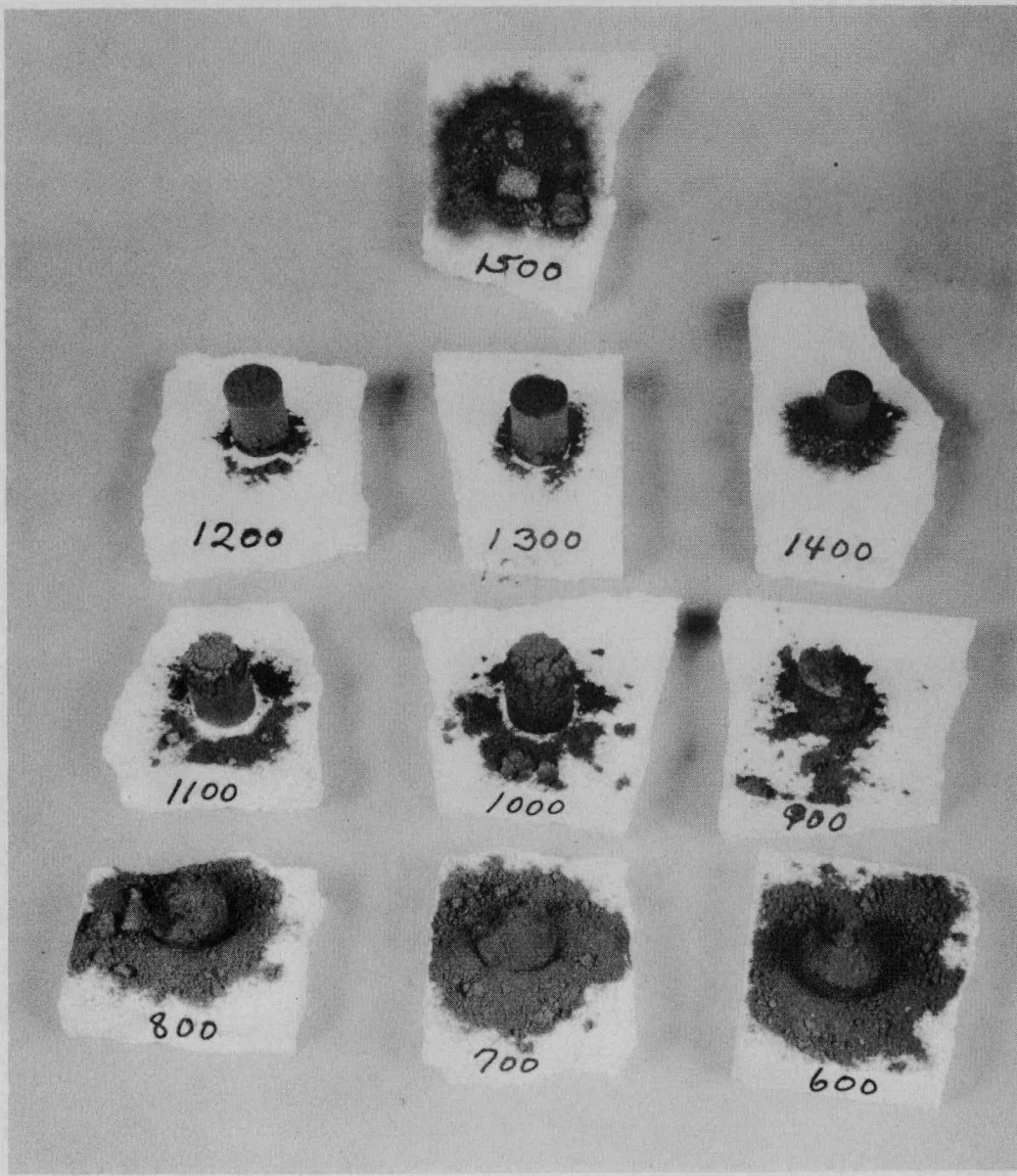slowly in air. Heating curve only.)

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Fig. 5 Pellets of $U_3O_8 \cdot TiO_2$ heated to various temperatures