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Phase Relations Between Iridium and the Sesquioxides in Air

S. J. Schneider, J. L. Waring, and R. E. Tressler[1]

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A study has been made by x-ray diffraction analysis of the reactions that occur in an air environment between Ir and IrO_2 and each of the following: Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, In_2O_3, Sc_2O_3, and Al_2O_3. In air Ir oxidizes at low temperatures to form IrO_2 which in turn dissociates at 1020 °C. The pseudo binary Nd_2O_3-IrO_2 was studied in detail inasmuch as it typified many of the Ln_2O_3-IrO_2 systems. Two compounds, $Nd_2O_3 \cdot 2IrO_2$ and $3Nd_2O_3 \cdot 2IrO_2$ occur in the system. The former, a cubic pyrochlore type phase, dissociates upon heating at 1190 °C. The 3:2 compound dissociates to the solid phases, Nd_2O_3 and Ir, at 1300 °C. Prior to dissociation, the 3:2 compound undergoes an apparent polymorphic transition at 1195 °C which may be related to an oxygen loss. Up to at least 2000 °C no further reaction occurred between Ir and Nd_2O_3. All B- and C-type rare earth oxides formed cubic pyochlore type compounds with IrO_2. Each of these compounds subsequently dissociated upon heating. No apparent reaction occurred between IrO_2 and either In_2O_3, Sc_2O_3, or Al_2O_3.

1. Introduction

As part of the program at the National Bureau of Standards to obtain accurate melting points of the metal oxides [1][2], a study has been initiated to determine what effect, if any, various refractory metal containers have upon possible standard oxides. The type of reaction between appropriate container materials such as iridium (Ir) or tungsten (W) and an oxide can be best characterized through a thorough study of their equilibrium phase relations. As the first in a series of phase equilibria investigations, the present paper reports results obtained in a study of portions of the Nd-Ir-Oxygen and related systems in an air environment.

Preliminary information indicated that powdered Ir has a tendency to oxidize to IrO_2 when heated in air at moderate temperatures. Since complete oxidation is difficult to achieve, IrO_2 rather than Ir metal was selected as one end member of the system. By utilizing IrO_2, an approach to equilibrium could be achieved more readily. The study would still reflect, however, the behavior in air of Ir metal in combination with Nd_2O_3 and other oxides.

Iridium has a face-centered cubic, copper type structure with $a=3.8394$ Å [2]. The freezing point of Ir is 2443 °C, a value which is given as a secondary reference point on the International Practical Temperature Scale (IPTS)[3] [3]. Iridium dioxide (IrO_2) is similar to TiO_2 in having the tetragonal, rutile structure with $a=4.4983$ Å and $c=3.1544$ Å [4]. Upon heating, IrO_2 has been reported to dissociate to the metal and a vapor phase at 1100 °C in one atmosphere oxygen [5].

Neodymium sesquioxide (Nd_2O_3) has been reported to occur in three polymorphic forms; the A, B, and C rare earth oxide structure types [6, 7]. The hexagonal A type ($a=3.831$ Å, $c=5.999$ Å) [8], is generally regarded as the stable modification of Nd_2O_3 although there has been some controversy regarding the existence and stability of the B and C types [6, 7]. The melting point of Nd_2O_3 is not well established. The one value reported in the literature lists the melting point as 2272 °C for material having a purity of 99 percent [9].

Since little data are available on either Ir of IrO_2 in combination with oxides, the present study was broadened somewhat to include, in addition to Nd_2O_3, the following materials: Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, In_2O_3, Sc_2O_3, and Al_2O_3.

[1] Mr. Tressler is currently a graduate student at Pennsylvania State University.
[2] Figures in brackets indicate the literature references at the end of this paper.
[3] This scale (IPTS) applies to all temperatures listed in this paper.

2. Materials

All starting materials employed in this study had a purity of 99.7 percent or greater. With the exception of Ir, IrO_2, and Al_2O_3, the oxides were used in previous investigations and their spectrochemical analyses are reported elsewhere [10, 11, 12]. The Ir, IrO_2, and Al_2O_3 samples were found by general qualitative spectrochemical analysis [4] to have the following impurities:

Ir 0.01–0.1% each Pd, Pt and Si;
0.001–0.01% each of Ag, Cu, and Fe;
0.0001–0.001% each Al and Mg;
and < 0.0001%, Ca.

IrO_2 0.01–0.1%, Pt;
0.001–0.01% each Al, Cu, Fe, Pd, and Si;
0.0001–0.001% Mg; and < 0.0001% Ca.

Al_2O_3 0.01–0.1% each Ga, Pb and Si;
0.001–0.01% each Cu, Fe, and Mg;
0.0001–0.001% each Ag, Ca, and Cr.

3. Experimental Procedure

Specimens for the oxide-IrO_2 studies were prepared from 0.5 g batches of various combinations of the end members. Calculated amounts of each oxide, corrected for ignition loss, were weighed to the nearest milligram. Each batch was thoroughly hand mixed, placed in Pt tubes and fired at 800 or 1000 °C a minimum of 19 hr in a muffle furnace.

Following the preliminary heat treatment, a portion of each calcined batch was placed in a small Vycor tube (sealed at one end) and fired in a Pt alloy quench furnace at various temperatures for different periods of time until equilibrium was attained. The Vycor tube containing the specimen was air quenched by quickly pulling the tube from the furnace. Equilibrium was assumed to have been achieved when the x-ray pattern showed no change after successive heat treatments of a specimen or when the data were consistent with the results from a previous set of experiments.

The use of Vycor tubes instead of Pt for experiments above 1000 °C was necessitated by the fact that Ir, frequently found as a decomposition product, readily reacts with Pt. On the other hand, the Vycor tube did not appear to influence or react with the various oxide samples.

Temperatures in the quench furnace, controlled to within ±3 °C, were measured with a 100 percent Pt versus 90 percent Pt–10 percent Rh thermocouple. All reported temperatures pertaining to quench furnace data are considered accurate to within ±5 °C.

Several experiments were conducted with mixtures having 1:2 mole ratios of oxide to Ir metal. Specimens of this type were prepared from two gram batches. After each batch was mechanically mixed it was heat treated at three different temperatures; specifically, 1000 °C for 12 hr, 1400 °C for 1 hr and ≈ 2000 °C for 1/2 hr. A small iridium pellet was used as a setter material. A program controlled tube furnace was employed for the 1000 and 1400 °C treatments. An induction furnace [11] utilizing an iridium crucible as both the susceptor and specimen container was used for the 2000 °C treatment. Temperatures were measured with a calibrated optical pyrometer sighted through a small hole in the crucible cover. The optical pyrometer temperature measurements are estimated to be accurate to within ±25 °C or better.

All specimens were examined by x-ray diffraction techniques at room temperature using a high angle recording Geiger counter diffractometer and Ni-filtered Cu radiation.

4. Results and Discussion

4.1. Nd_2O_3–IrO_2 and Nd_2O_3–Ir Systems in Air

The equilibrium phase diagram for the combined Nd_2O_3–IrO_2 and Nd_2O_3–Ir systems in air is given in figure 1. The diagram was constructed from the data listed in table 1. The solid circles indicate the compositions and temperatures of the experiments conducted. It should be emphasized that figure 1 does not represent a true binary system, but a composite of the true binary, Nd_2O_3–Ir, and the pseudo binary, Nd_2O_3–IrO_2, in the Nd–Ir–Oxygen ternary system. At the lower temperatures the oxygen content of the specimens closely conform to the compositions represented by the pseudo binary Nd_2O_3–IrO_2 system. As the temperature is increased, the compositions of the solid phases change by an apparent oxygen loss to those indicated by the Nd_2O_3–Ir join. By considering this dissociation as a type of phase transition in which the vapor phase is ignored, a simple binary representation of the phase relations in a portion of the ternary system can be given. This method of illustration has been employed by a number of investigators, notably A. Muan in his work on iron oxides [13, 14].

At 1020 ± 5 °C in an air environment at atmospheric pressure, IrO_2 was found to dissociate to one solid phase, Ir metal. This value favorably compares with the 1015 °C dissociation temperature at 160 mm Hg oxygen pressure calculated from the data given by Cordfunke and Meyer in their study of the Ir–Oxygen system [5]. The dissociation of IrO_2 is apparently a reversible process. For practical purposes the dissociation can be represented as a type of polymorphic transformation.

[4] The spectrochemical analyses were performed by the Spectrochemical Analysis Section of the National Bureau of Standards.

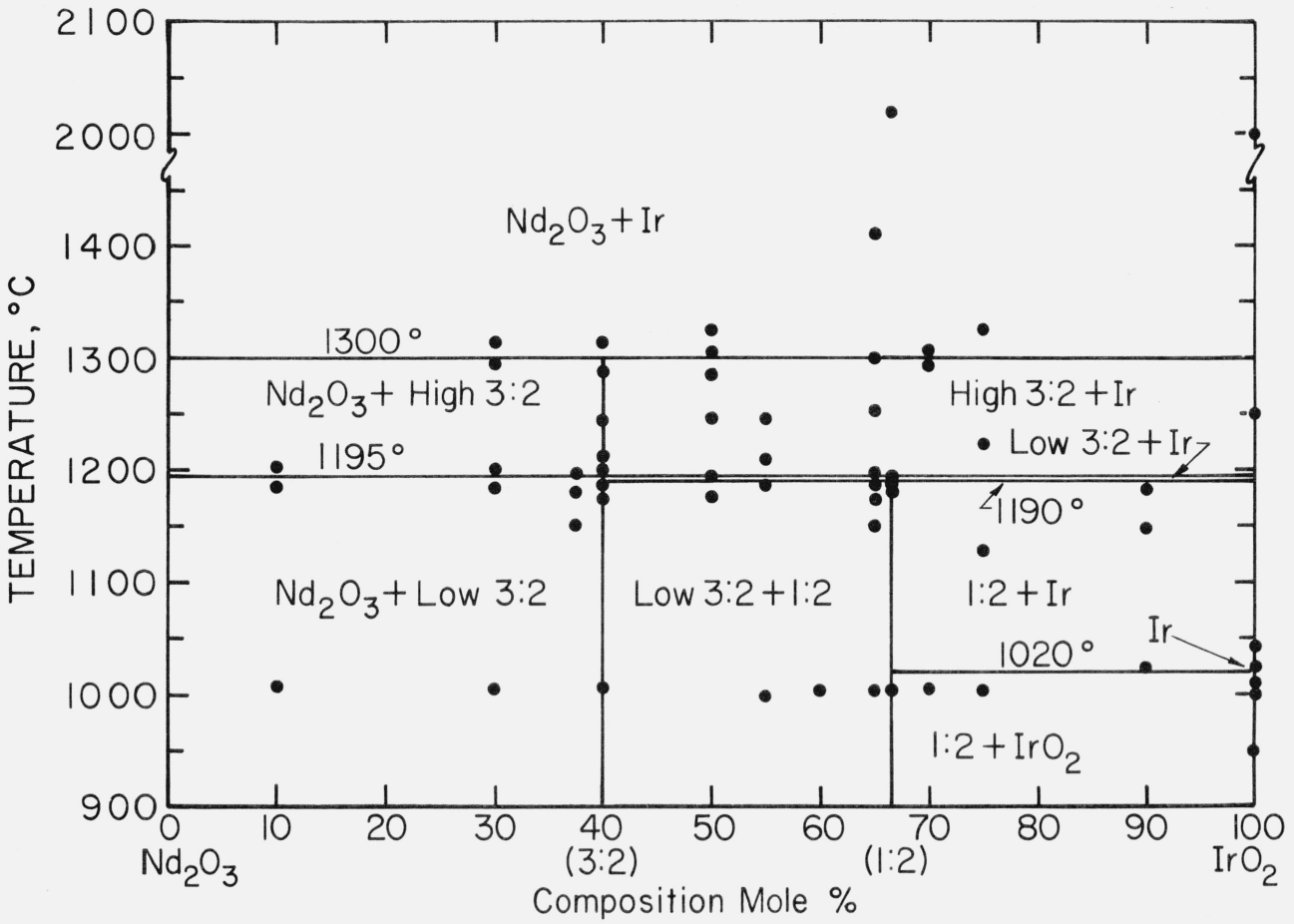

FIGURE 1. *Composite phase equilibrium diagrams for the* Nd_2O_3–IrO_2 *and* Nd_2O_3–Ir *systems in air.*

●–compositions and temperatures of experiments conducted in an air environment.

Low 3:2–$3Nd_2O_3 \cdot 2IrO_2$.

High 3:2–$3Nd_2O_3 \cdot 2IrO_x$; x is probably less than 2.

1:2–$Nd_2O_3 \cdot 2IrO_2$ (pyrochlore type compound).

Ir–iridium metal.

TABLE 1. *Experimental data for compositions in the* M_2O_3–IrO_2 *and* M_2O_3–Ir *systems in air*

System	Composition	Heat treatment		X-ray diffraction analyses[b]	Remarks
		temp.[a]	Time		
	Mole %	*°C*	*hr*		
Nd_2O_3–IrO_2	90:10	1009	19	Nd_2O_3 + low $3Nd_2O_3 \cdot 2IrO_2$	
		[c]1185	19	Nd_2O_3 + low $3Nd_2O_3 \cdot 2IrO_2$	
		1202	20	Nd_2O_3 + high $3Nd_2O_3 \cdot 2IrO_2$	Possibly small amount of low 3:2 present.
	70:30	1009	19	Low $3Nd_2O_3 \cdot 2IrO_2$ + Nd_2O_3	
		[c]1185	60	Low $3Nd_2O_3 \cdot 2IrO_2$ + Nd_2O_3	
		[c]1201	19	Low $3Nd_2O_3 \cdot 2IrO_2$ + high $3Nd_2O_3 \cdot 2IrO_2$ + Nd_2O_3	Nonequilibrium.
		[c]1296	20	High $3Nd_2O_3 \cdot 2IrO_2$ + Nd_2O_3	Possibly small amount of low 3:2 present.
		[c]1315	19	Nd_2O_3 + high $3Nd_2O_3 \cdot 2IrO_2$ + Low $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium: low 3:2 probably formed on cooling; Ir not detected by x rays[d]; high 3:2 present only in minor amounts.

TABLE 1. *Experimental data for compositions in the* M_2O_3–IrO_2 *and* M_2O_3–Ir *systems in air*—Continued

System	Composition	Heat treatment		X-ray diffraction analyses[b]	Remarks
		temp.[a]	Time		
Nd_2O_3–IrO_2 (cont.)	62.5:37.5	1151	70	Low $3Nd_2O_3 \cdot 2IrO_2 + Nd_2O_3$	
		1180	21	Low $3Nd_2O_3 \cdot 2IrO_2 + Nd_2O_3$	
		[c]1198	22	Low $3Nd_2O_3 \cdot 2IrO_2$ + high $3Nd_2O_3 \cdot 2IrO_2 + Nd_2O_3$	Nonequilibrium.
	60:40 (3:2)	1009	19	Low $3Nd_2O_3 \cdot 2IrO_2$	
		1175	20	Low $3Nd_2O_3 \cdot 2IrO_2$	
		[c]1188	20	Low $3Nd_2O_3 \cdot 2IrO_2$	
		[c]1200	60	Low $3Nd_2O_3 \cdot 2IrO_2$ + high $3Nd_2O_3 \cdot 2IrO_2 + Nd_2O_3$	Nonequilibrium.[e]
		1211	20	High $3Nd_2O_3 \cdot 2IrO_2$	Possibly some low 3:2 present.
		[c]1243	20	High $3Nd_2O_3 \cdot 2IrO_2$	Possibly some low 3:2 present.
		1290	1.75	High $3Nd_2O_3 \cdot 2IrO_2$	Possibly some low 3:2 present.
		1313	1.75	$Nd_2O_3 + Ir$	
	50:50	1178	20	Low $3Nd_2O_3 \cdot 2IrO_2 + Nd_2O_3 \cdot 2IrO_2$	
		[c]1195	22	Low $3Nd_2O_3 \cdot 2IrO_2$ + high $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium; Ir not detected by x rays.[d]
		1247	16	High $3Nd_2O_3 \cdot 2IrO_2 + Ir$	
		1289	3	High $3Nd_2O_3 \cdot 2IrO_2 + Ir$	
		[c]1305	1.75	High $3Nd_2O_3 \cdot 2IrO_2 + Nd_2O_3 + Ir$	Nonequilibrium.
		1325	5	Nd_2O_3	Ir not detected by x rays.[d]
	45:55	1000	19	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	
		1188	20	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	
		[c]1210	68	High $3Nd_2O_3 \cdot 2IrO_2$	Ir not detected by x rays.[d]
		1249	20	High $3Nd_2O_3 \cdot 2IrO_2$	Ir not detected by x rays.[d]
	40:60	1005	20	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	
	35:65	1005	20	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	
		1151	19	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	
		[c]1173	22	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	
		1187	17.5	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	Possibly small amount of high 3:2 present.
		[c]1198	17.5	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$ + high $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium; Ir not detected by x rays.[d]
		1253	16	High $3Nd_2O_3 \cdot 2IrO_2 + Ir$	
		1300	3	High $3Nd_2O_3 \cdot 2IrO_2 + Ir$	
		1411	1	$Ir + Nd_2O_3$	Reheat of 1173 °C specimen.
	33.3:66.7 (1:2)	1005	19	$Nd_2O_3 \cdot 2IrO_2$	
		1180	90	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium; small amount of IrO_2 probably lost by volatilization.
		[c]1189	42	$Nd_2O_3 \cdot 2IrO_2$ + low $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium; small amounts of IrO_2 probably lost by volatilization.
		[c]1191	20	$Nd_2O_3 \cdot 2IrO_2 + Ir$ + low $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium.
	30:70	1007	18	$Nd_2O_3 \cdot 2IrO_2 + IrO_2$	
		1295	19	High $3Nd_2O_3 \cdot 2IrO_2 + Ir$	
		[c]1308	19	$Nd_2O_3 + Ir$ + high $3Nd_2O_3 \cdot 2IrO_2$	Nonequilibrium.
	25:75	1005	19	$Nd_2O_3 \cdot 2IrO_2 + IrO_2$	
		1030	92	$Nd_2O_3 \cdot 2IrO_2 + Ir$	
		1226	16	Low $3Nd_2O_3 \cdot 2IrO_2$ [f]+ high $3Nd_2O_3 \cdot 2IrO_2 + Ir$	Nonequilibrium.
		1325	4.5	$Ir + Nd_2O_3$	
	10:90	1027	5	$Nd_2O_3 \cdot 2IrO_2 + Ir + IrO_2$	Nonequilibrium.
		1150	16	$Nd_2O_3 \cdot 2IrO_2 + Ir + IrO_2$	Nonequilibrium.
		1181	67	$Nd_2O_3 \cdot 2IrO_2 + Ir$	
	0–100	0	0	Amorphous to x rays	"As received" material.
		950	16	IrO_2	
		1010	64	IrO_2	
		1011	16	IrO_2	
		[c]1017	16	IrO_2	
		1018	18	IrO_2	
		1022	16	$IrO_2 + Ir$	Nonequilibrium.
		1026	3	$IrO_2 + Ir$	Nonequilibrium.
		1047	12	Ir	
		2000	0.5	Ir	
Sm_2O_3–IrO_2	33.3:66.7 (1:2)	1000	100	$Sm_2O_3 \cdot 2IrO_2$	
		[f]1205	19	$Sm_2O_3 \cdot 2IrO_2$	
		[f]1216	19	$Sm_2O_3 \cdot 2IrO_2$ + unknown phase	Nonequilibrium; Ir not detected by x rays[d]; unknown phase similar to low $3Nd_2O_3 \cdot 2IrO_2$.
		[f]1229	19	$Sm_2O_3 \cdot 2IrO_2 + Ir$ + unknown phase	Nonequilibrium; unknown phase similar to low $3Nd_2O_3 \cdot 2IrO_2$.

TABLE 1. *Experimental data for compositions in the* M_2O_3–IrO_2 *and* M_2O_3–Ir *systems in air*—Continued

System	Composition	Heat treatment		X-ray diffraction analyses[b]	Remarks
		temp.[a]	Time		
Eu_2O_3–IrO_2	33.3:66.7	1000	100	$Eu_2O_3 \cdot 2IrO_2$	
	(1:2)	[f]1207	64	$Eu_2O_3 \cdot 2IrO_2$	
		[f]1215	64	$Eu_2O_3 \cdot 2IrO_2$	
		[f]1225	16	$Eu_2O_3 \cdot 2IrO_2$ + unknown phase	Nonequilibrium; Ir not detected by x ray.[d]
		[f]1231	16	$Eu_2O_3 \cdot 2IrO_2$ + unknown phase	Nonequilibrium; Ir not detected by x ray.[d]
		[f]1346	19	Eu_2O_3 + Ir	
Gd_2O_3–IrO_2	33.3:66.7	1000	100	$Gd_2O_3 \cdot 2IrO_2$ + Gd_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1218	19	$Gd_2O_3 \cdot 2IrO_2$ + Gd_2O_3	Nonequilibrium.[e]
		[f]1235	19	$Gd_2O_3 \cdot 2IrO_2$ + Gd_2O_3	Nonequilibrium.[e]
		[f]1242	19	$Gd_2O_3 \cdot 2IrO_2$ + Gd_2O_3 + Ir	Nonequilibrium.[e]
Dy_2O_3–IrO_2	33.3:66.7	[f]1000	100	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1170	92	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3	Nonequilibrium.[e]
		[f]1200	19	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3	Nonequilibrium.[e]
		[f]1242	19	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3	Nonequilibrium.[e]
		[e]1260	20	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3 + unknown phase	Nonequilibrium.[e]
		[e]1301	4	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3 + unknown phase	Nonequilibrium.[e]
		[f]1351	19	Dy_2O_3 + Ir	
Ho_2O_3–IrO_2	33.3:66.7	1000	100	$Ho_2O_3 \cdot 2IrO_2$ + Ho_2O_3 + IrO_2	Nonequilibrium.
	(1:2)	[f]1218	19	$Ho_2O_3 \cdot 2IrO_2$ + Ho_2O_3	Nonequilibrium.[e]
		[f]1235	19	$Ho_2O_3 \cdot 2IrO_2$ + Ho_2O_3 + Ir	Nonequilibrium.[e]
Y_2O_3–IrO_2	33.3:66.7	1000	100	$Y_2O_3 \cdot 2IrO_2$ + Y_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1210	19	$Y_2O_3 \cdot 2IrO_2$ + Y_2O_3	Nonequilibrium.[e]
		[e]1216	4	$Y_2O_3 \cdot 2IrO_2$ + Y_2O_3	Nonequilibrium.[e]
		1225	19	$Y_2O_3 \cdot 2IrO_2$ + Y_2O_3 + unknown phase	Nonequilibrium.[e]
		1351	19	Y_2O_3 + Ir	
Er_2O_3–IrO_2	33.3:66.7	1000	100	$Er_2O_3 \cdot 2IrO_2$ + Er_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1215	64	$Er_2O_3 \cdot 2IrO_2$ + Er_2O_3	Nonequilibrium.[e]
		[e]1225	64	$Er_2O_3 \cdot 2IrO_2$ + Er_2O_3	Nonequilibrium[e]: 1:2 phase reduced in amount from that of previous heat treatment. Ir not detected by x rays.[d]
		1346	19	Er_2O_3 + Ir	
Tm_2O_3–IrO_2	33.3:66.7	1000	100	$Tm_2O_3 \cdot 2IrO_2$ + Tm_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1199	19	$Tm_2O_3 \cdot 2IrO_2$ + Tm_2O_3	Nonequilibrium.[e]
		[e]1226	19	Tm_2O_3 + $Tm_2O_3 \cdot 2IrO_2$	Nonequilibrium[e]; 1:2 phase reduced in amount from that of previous heat treatment; Ir not detected by x rays.[d]
		1351	19	Tm_2O_3 + Ir	
Yb_2O_3–IrO_2	33.3:66.7	1000	100	$Yb_2O_3 \cdot 2IrO_2$ + Yb_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1161	19	$Yb_2O_3 \cdot 2IrO_2$ + Yb_2O_3	Nonequilibrium.[e]
		[f]1173	19	$Yb_2O_3 \cdot 2IrO_2$ + Yb_2O_3	Nonequilibrium.[e]
		[f]1199	19	Yb_2O_3 + Ir + $Yb_2O_3 \cdot 2IrO_2$	Nonequilibrium.
		[f]1226	19	Yb_2O_3 + Ir	
Lu_2O_3–IrO_2	33.3:66.7	1000	100	$Lu_2O_3 \cdot 2IrO_2$ + Lu_2O_3	Nonequilibrium.[e]
	(1:2)	[f]1161	19	$Lu_2O_3 \cdot 2IrO_2$ + Lu_2O_3	Nonequilibrium.[e]
		[f]1170	19	$Lu_2O_3 \cdot 2IrO_2$ + Lu_2O_3	Nonequilibrium[e]: 1:2 phase reduced in amount from that of previous heat treatment; Ir not detected by x rays.[d]
		[e]1200	19	Lu_2O_3 + Ir + $Lu_2O_3 \cdot 2IrO_2$	Nonequilibrium.
		[f]1309	19	Lu_2O_3 + Ir	
In_2O_3–IrO_2	33.3:66.7	1000	100	In_2O_3 + IrO_2	
	(1:2)	1256	19	In_2O_3 + Ir	
Sc_2O_3–IrO_2	33.3:66.7	1000	100	Sc_2O_3 + IrO_2	
	(1:2)	1256	19	Sc_2O_3	Ir not detected by x rays.[d]
Al_2O_3–IrO_2	33.3:66.7	1000	100	Al_2O_3 + IrO_2	
	(1:2)	1256	19	Al_2O_3 + Ir	
Nd_2O_3–Ir	33.3:66.7	1000	12	$Nd_2O_3 \cdot 2IrO_2$ + Ir + IrO_2	Nonequilibrium.
	(1:2)	[e]1400	1	Ir + Nd_2O_3 + $Nd(OH)_3$	Nd_2O_3 commonly hydrates at room temperature.
		[e]2020	.75	Ir + Nd_2O_3 + $Nd(OH)_3$	Nd_2O_3 commonly hydrates at room temperature.

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TABLE 1. *Experimental data for compositions in the* M_2O_3–IrO_2 *and* M_2O_3–Ir *systems in air*—Continued

System	Composition	Heat treatment		X-ray diffraction analyses[b]	Remarks
		temp.[a]	Time		
Nd_2O_3–Ir (cont.)	0:100	0	0	Ir	"As received."
		1000	6	IrO_2 + Ir	Nonequilibrium.
		[c]1000	20	IrO_2 + Ir	Nonequilibrium; greater amount of IrO_2 present from that of previous heat treatment.
		[c]1000	116	IrO_2 + Ir	Nonequilibrium.
		[c]1040	18	Ir + IrO_2	Nonequilibrium; smaller amount of IrO_2 present from that of previous heat treatment.
		[c]1250	5	Ir + IrO_2	Nonequilibrium; only small amount of IrO_2 present. IrO_2 probably formed on cooling.
Sm_2O_3–Ir	33.3:66.7 (1:2)	1000	12	$Sm_2O_3 \cdot 2IrO_2$ + IrO_2 + Ir + unknown phase	Nonequilibrium; unknown phase similar to low $3Nd_2O_3 \cdot 2IrO_2$.
		[c]1400	1	Sm_2O_3 + Ir	
		[c]2030	0.50	Sm_2O_3 + Ir	
Eu_2O_3–Ir	33.3:66.7 (1:2)	1000	12	$Eu_2O_3 \cdot 2IrO_2$	
		[c]1400	1	Eu_2O_3 + Ir	
		[c]2020	0.50	Eu_2O_3 + Ir	
Gd_2O_3–Ir	33.3:66.7 (1:2)	1000	12	$Gd_2O_3 \cdot 2IrO_2$ + Gd_2O_3 + IrO_2 + Ir	Nonequilibrium.
		[c]1400	1	Gd_2O_3 + Ir	
		[c]2015	0.50	Gd_2O_3 + Ir	
Dy_2O_3–Ir	33.3:66.7 (1:2)	1000	12	$Dy_2O_3 \cdot 2IrO_2$ + Dy_2O_3 + IrO_2 + Ir	Nonequilibrium.
		[c]1400	1	Dy_2O_3 + Ir	
		[c]2015	0.50	Dy_2O_3 + Ir	
Y_2O_3–Ir	33.3:66.7 (1:2)	1000	12	$Y_2O_3 \cdot 2IrO_2$ + Y_2O_3 + IrO_2 + Ir	Nonequilibrium.
		[c]1400	1	Y_2O_3 + Ir	
		2010	0.50	Y_2O_3 + Ir	
Lu_2O_3–Ir	33.3:66.7 (1:2)	1000	12	$Lu_2O_3 \cdot 2IrO_2$ + Lu_2O_3 + IrO_2 + Ir	Nonequilibrium.
		[c]1400	1	Lu_2O_3 + Ir	
		[c]2080	0.50	Lu_2O_3 + Ir	
Al_2O_3–Ir	33.3:66.7 (1:2)	1000	12	Al_2O_3 + Ir + IrO_2	Nonequilibrium.
		[c]1400	1	Al_2O_3 + Ir	
		2010	0.5	Al_2O_3 + Ir + IrO_2	Nonequilibrium; IrO_2 probably formed on cooling.
		2055	0.5	Al_2O_3 + Ir	Specimen partially melted.

[a] All specimens in the Nd_2O_3–IrO_2 system heat treated at 800 °C a minimum of 24 hrs prior to the listed heat treatment.

[b] The phases identified are given in order of the relative amount present at room temperature.

[c] Reheat of the previous specimen.

[d] Iridium dioxide (IrO_2) in combination with other oxides, upon dissociation, forms small Ir metal grains which are generally detectable by microscopic examination. X-ray patterns of these specimens often fail to show reflections representing Ir unless there is anomalous intensity due to orientation of the grains.

[e] Small amount of IrO_2 probably lost by volatilization.

[f] Reheat of 1000 °C specimen.

As IrO_2 is heated to temperatures near its dissociation temperature, it becomes somewhat volatile. Cordfunke and Meyer [5] conclude that IrO_2 combines with oxygen to form IrO_3 which is stable only in the gaseous state. Efforts to produce solid IrO_3 in the present work proved unsuccessful. The condensed vapors from heated samples of either IrO_2 or Ir always were identified as IrO_2. The problem of the volatility of IrO_2 in the present study was minimized greatly by reacting the end members at low temperatures. The volatilization of IrO_2 was sufficiently inhibited by reaction to consider the listed compositions (cation to metal ratio) of table 1 as being near correct.

Two intermediate binary compounds occur in the Nd_2O_3–IrO_2 system. One phase, a 1:2 compound, is stable up to 1190 °C where it dissociates to two solid phases and a vapor phase, presumably oxygen. The composition of the 1:2 compound corresponds to that of an $A_2B_2O_7$ pyrochlore type phase. Table 2 gives the x-ray pattern of $Nd_2O_3 \cdot 2IrO_2$ indexed on the basis of the typical face-centered cubic symmetry ($a = 10.383$Å) of the pyrochlore structure.

TABLE 2. *X-ray diffraction powder data for* $Nd_2O_3 \cdot 2IrO_2$ (CuK$_\alpha$ *radiation*) [a]

hkl [b]	*d* [c]	I/I_0 [d]
111	6.00	6
311	3.140	4
222	3.003	100
400	2.673	43
511/333	2.0035	3
440	1.8370	46
622	1.5661	40
444	1.4994	11
800	1.2986	6
622	1.1913	11
840	1.1613	10
844	1.0601	9
10,22/666	0.9995	9
880	.9174	3
11,33/973	.8813	3
10,62	.8772	9
12,00/884	.8652	9
12,40	.8205	3

[a] X-ray pattern obtained from specimen heat treated at 1005 °C for 19 hrs in air.
[b] The Miller indices are those representing a fcc unit cell with $a = 10.383$ Å.
[c] Interplanar spacing.
[d] Relative Intensity.

The other binary phase was found to occur in the system at the 3:2 composition. This compound, $3Nd_2O_3 \cdot 2IrO_2$, similar in behavior to the 1:2 phase, also dissociates to two solid phases (and vapor) at 1300 °C. At 1195 °C, the 3:2 compound appears to undergo a polymorphic transformation. The unindexed x-ray powder patterns of both the high and low forms are given in table 3. Because the transformation temperature of the 3:2 compound and the dissociation temperature of the 1:2 phase are approximately the same, it appears likely that an oxygen loss may have produced the apparent polymorphic phase change. Therefore, the phase designated high 3:2 in figure 1, may be, in reality, an oxygen deficient phase, $3Nd_2O_3 \cdot 2IrO_x$, where x is less than 2.

At temperatures above 1300 °C the system under consideration no longer can be represented by the pseudo system, Nd_2O_3–IrO_2. Through dissociation, the system had changed to the Nd_2O_3–Ir binary. Up to temperatures of 2000 °C, Nd_2O_3 and Ir do not react in the solid state. Presumably no solid state reaction would occur below melting. No definite conclusions can be made concerning the melting characteristics of the system until further experimental work has been performed.

It should be noted that figure 1 pertains only to the phase relations of the system in an air environment at atmospheric pressure. Any change in oxygen pressure would greatly change the diagram. To emphasize this, limited experiments were carried out utilizing sealed Pt tubes as containers. In every instance the pressure in the tube was sufficient to raise the temperatures of dissociation of mixtures of the compounds with IrO_2 20 to 150 °C. For unexplained reasons pure IrO_2 could not be heated to temperatures in excess of 1000 °C without tube failure due to the high internal pressure.

TABLE 3. *X-ray diffraction powder data for the "high" and "low" forms of* $3Nd_2O_3 \cdot 2IrO_2$ (CuK$_\alpha$ *radiation*) [a]

"Low" $3Nd_2O_3 \cdot 2IrO_2$ [b]		"High" $3Nd_2O_3 \cdot 2IrO_2$ [c]	
d [d]	I/I_0 [e]	*d* [d]	I/I_0 [e]
3.34	11	4.65	7
3.20	100	4.06	32
3.00	11	4.02	11
2.85	16	3.70	4
2.73	18	3.28	8
2.64	34	3.12	7
2.379	5	3.09	28
2.199	5	2.85	100
2.110	6	2.84	56
2.076	5	2.72	4
2.050	4	2.57	4
2.013	5	2.494	7
1.940	5	2.443	13
1.897	36	2.424	13
1.875	11	2.418	8
1.840	4	2.110	7
1.808	3	2.091	18
1.763	5	2.030	13
1.725	6	2.005	28
1.633	13		
1.601	18		
1.596	16		
1.545	10		

[a] The x-ray patterns of these specimens show only broad and generally weak peaks. Therefore, only the more intense, readily measurable reflections are reported.
[b] X-ray pattern obtained from specimen heat treated at 1009 °C for 19 hrs in air.
[c] X-ray pattern obtained from specimen heat treated at 1243 °C for 20 hrs in air. The high form may be oxygen deficient with the formula corresponding to the type $3Nd_2O_3 \cdot 2IrO_x$ where x is less than two.
[d] Interplanar Spacing.
[e] Relative Intensity.

4.2. Other M_2O_3–IrO_2 Systems in Air

Montmony and Bertaut [15] have previously reported the existence of pyrochlore type compounds in mixtures of rare earth sesquioxides and IrO_2. In order to confirm the earlier work and to investigate these compounds more fully, M_2O_3:$2IrO_2$ mole ratio mixtures were prepared from IrO_2 and either Sm_2O_3, Eu_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Y_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, In_2O_3, Sc_2O_3, and Al_2O_3.

Tables 1 and 4 summarize the results obtained for this set of experiments. All 1:2 mixtures containing the rare earth oxides and Y_2O_3 formed face-centered cubic pyrochlore type compounds. Unfortunately, some of the compositions contained, in addition to the pyrochlore type phase, small amounts of the pure rare earth oxide. In all probability an unknown quantity of IrO_2 was lost by volatilization before complete combination occurred. The possibility still remains, however, that the true composition of the pyrochlore phase does not correspond to the idealized $Ln_2Ir_2O_7$ formula. Evidence for "off composition" pyrochlore compounds have been reported elsewhere [16].

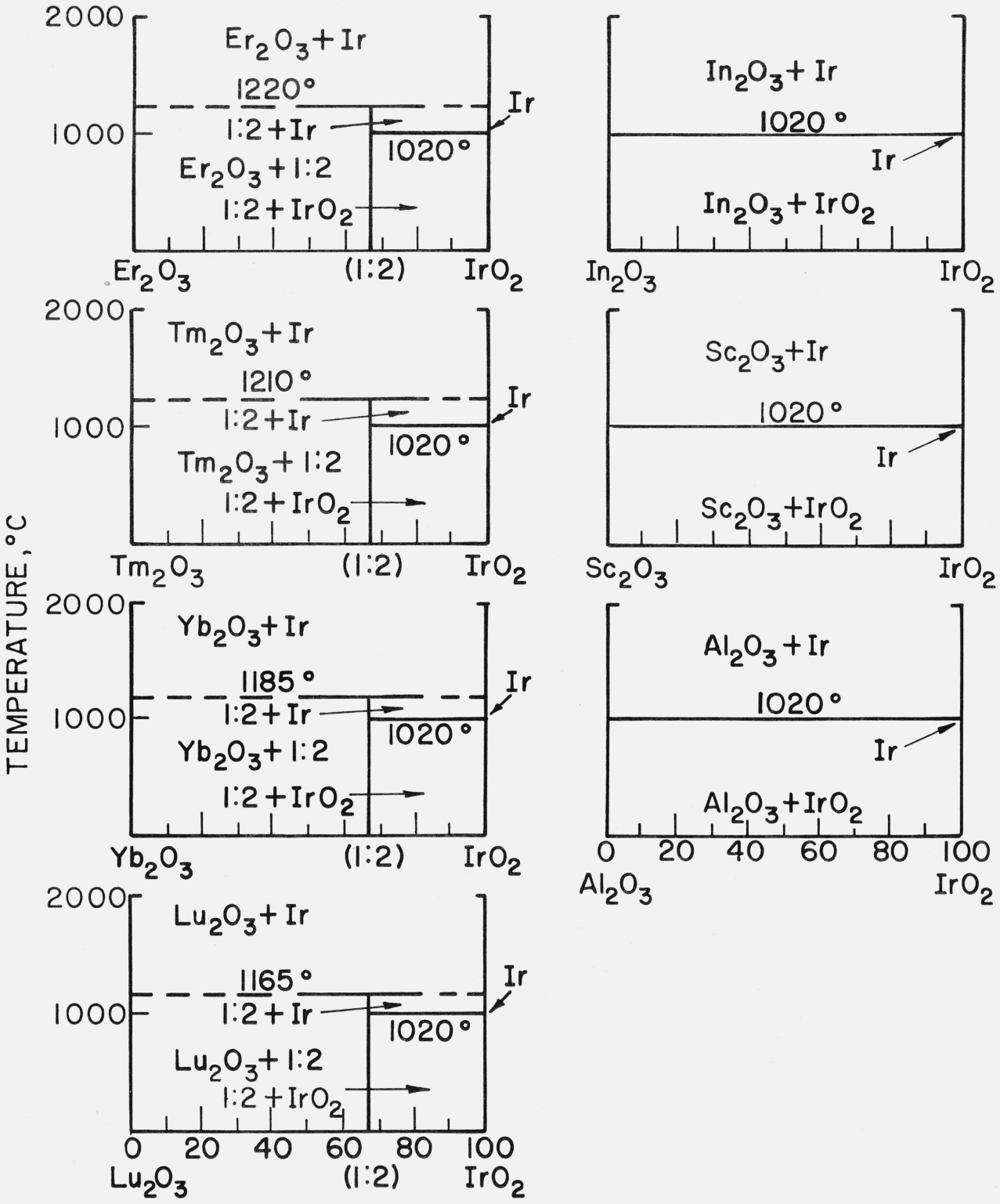

FIGURE 2. *Predicted composite phase equilibrium diagrams for various* M_2O_3–IrO_2 *and* M_2O_3–Ir *systems in air.*

For clarity experimental points are not included. See table 1 for exact compositions and temperatures studied. All experiments conducted involved only the M_2O_3:$2IrO_2$ compositions in an air environment. Ir–Iridium metal, 1:2–$M_2O_3 \cdot 2IrO_2$.

As expected, the unit cell dimensions of the cubic pyrochlore compounds decrease in a linear manner as the size of the rare earth cation decreases. In a manner similar to $Nd_2Ir_2O_7$, all the compounds dissociated at temperatures above 1020 °C, the decomposition temperature of IrO_2. The dissociation temperatures (table 4) when plotted as a function of the radius of the rare earth cation do not change linearly as do the unit cell dimensions. As the size of the cation is decreased, the dissociation temperature at first increases, approaching a maximum for $Dy_2Ir_2O_7$ and then decreases to a minimum for $Lu_2Ir_2O_7$.

Under the conditions of the experiments In_2O_3, Sc_2O_3, and Al_2O_3 did not react even partially with IrO_2. X-ray patterns of these mixtures after heat treatment at 1000 °C show only reflections representing IrO_2 and the admixture oxide. Additional heat treatment at 1256 °C failed to cause combination and only succeeded in dissociating the IrO_2. The resultant mixture contained the refractory oxide and Ir metal.

It is evident that the Nd_2O_3–IrO_2 system is representative in a general way of the other M_2O_3–IrO_2 systems. Using it as a guide, figure 2 gives a number of the subsolidus phase diagrams for various systems as predicted from the data tabulated in table 1.

The In_2O_3–IrO_2, Sc_2O_3–IrO_2, and Al_2O_3–IrO_2 systems are rather simple and straightforward inasmuch as there is no detectable reaction between end members in the solid state. These diagrams indicate only the dissociation of IrO_2, the point at which the system reverts to the true M_2O_3–Ir system.

The diagrams for the Er_2O_3–IrO_2, Tm_2O_3–IrO_2, Yb_2O_3–IrO_2, and Lu_2O_3–IrO_2 systems in air are slightly more complicated, each indicating the occurrence of a 1:2 compound. Studies of 1:2 compounds show that they dissociate to the solid phases M_2O_3 and Ir. If other phases occurred in the systems, they necessarily would have to dissociate at lower temperatures than the 1:2 compound. If other compounds existed which were stable at temperatures greater than the 1:2 dissociation temperatures, they would appear as a decomposition product of the pyrochlore type phase. As stated previously, this was not the case. On the basis of the more complete Nd_2O_3–IrO_2 study, the existence of phases other than the 1:2 is not considered likely for these systems.

Additional experimentation is needed before the Sm_2O_3–IrO_2, Eu_2O_3–IrO_2, Gd_2O_3–IrO_2, Dy_2O_3–IrO_2, Ho_2O_3–IrO_2, and Y_2O_3–IrO_2 systems can be drawn. Each of the 1:2 compounds occurring in these systems dissociates to a mixture of solid phases, generally consisting of Ir and an unidentified phase.

4.3. M_2O_3–Ir Reactions

In order to establish whether or not the results found for the M_2O_3–IrO_2 studies were indicative of Ir in combination with various oxides, a limited number of experiments were performed involving oxide-Ir mixtures. Table 1 gives the data obtained for 1:2 mole ratio (oxide:metal) mixtures heat treated in an air environment. It is apparent that Ir oxidizes at least partially to IrO_2, which, in turn reacts with the admixture oxide to form the same pyrochlore type compounds listed in table 4. At higher temperatures the pyrochlore type compounds dissociated as expected and further reaction between end members did not take place.

TABLE 4. $Ln_2O_3 \cdot 2IrO_2$ *pyrochlore-type compounds*

Compound	Radius of Ln^{+3} [a]	Dissociation temperature [b]	X-ray data	
			Symmetry	Unit cell dimension
	Å	°C		Å
$Nd_2O_3 \cdot 2IrO_2$	1.04	1190	cubic	10.383
$Sm_2O_3 \cdot 2IrO_2$	1.00	1210	cubic	10.313
$Eu_2O_3 \cdot 2IrO_2$	0.98	1220	cubic	10.293
$Gd_2O_3 \cdot 2IrO_2$	.97	1240	cubic	10.265
$Dy_2O_3 \cdot 2IrO_2$	.92	1250	cubic	10.207
$Ho_2O_3 \cdot 2IrO_2$	.91	1225	cubic	10.180
$Y_2O_3 \cdot 2IrO_2$	≈.91	1220	cubic	10.177
$Er_2O_3 \cdot 2IrO_2$	.89	1220	cubic	10.163
$Tm_2O_3 \cdot 2IrO_2$	.87	1210	cubic	10.134
$Yb_2O_3 \cdot 2IrO_2$	.86	1185	cubic	10.115
$Lu_2O_3 \cdot 2IrO_2$	.85	1165	cubic	10.096

[a] All radii of the rare earth cations taken from Arhens [17] with the exception of Y^{+3} which was estimated by Roth and Schneider [4].

[b] Dissociation temperatures are applicable only to those specimens heated in air.

Unfortunately, Ir either alone or in combination with an oxide, never completely oxidized to IrO_2. As indicated by microscopic examination, IrO_2, as it forms, appears to coat the Ir grains and thus tends to inhibit additional oxidation. At temperatures just below the IrO_2 dissociation temperature, IrO_2 is somewhat volatile. As the metal forms IrO_2, the oxide is lost by vaporization and a steady state is reached where the metal:oxide (Ir:IrO_2) ratio of the remaining material appears to remain approximately constant. In essence, true equilibrium at low temperatures could not be obtained in the M_2O_3:2Ir mixtures because of the inherent difficulty in achieving complete oxidation of Ir. Except for the presence of Ir at low temperatures, the data for the M_2O_3:2Ir compositions completely substantiated the M_2O_3–IrO_2 studies. Also, these data, in effect, establish the reversibility of the various transformations (dissociation) discussed earlier.

In all the aforementioned experiments, every effort was made through thorough mixing and prolonged heat treatment to react Ir with the various oxides. Even with these precautions, Ir while in the metallic state appears to be unreactive with the oxides studied and thus seems quite acceptable as a container material for high temperature application in an air environment.

The fact that Ir oxidizes at low temperatures does not appreciably detract from its use as a container since all phases containing IrO_2 subsequently dissociate.

4.4. Summary

Selected mixtures in systems involving Ir or IrO_2 and various sesquioxides were studied by x-ray diffraction techniques after heat treatment in an air environment. Iridium, in air, oxidizes almost completely to IrO_2 at low temperatures. The dissociation temperature of IrO_2 in air at atmospheric pressure was established at 1020 ±5 °C. Iridium in combination with the sesquioxides also forms IrO_2 which in turn reacts with a number of the oxides to form binary compounds. The pseudo binary system Nd_2O_3–IrO_2 exemplified the typical type of reaction and was studied in detail. Two phases, a compound believed to be $3Nd_2O_3 \cdot 2IrO_2$ having unknown symmetry and a cubic pyrochlore type compound $Nd_2O_3 \cdot 2IrO_2$, with $a = 10.383$ Å, occur in the system. The 3:2 and 1:2 compounds dissociate at 1300 and 1190 °C respectively. Above 1300 °C the system corresponds to the Nd_2O_3–Ir join in the Nd–Ir–O ternary system. No further reaction appears to take place between Nd_2O_3 and Ir up to 2000 °C.

Pyrochlore type compounds also were found to occur at the 1:2 mixture of either Sm_2O_3, Eu_2O_3, Gd_2O_3, Ho_2O_3, Y_2O_3, Dy_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, or Lu_2O_3 with IrO_2. Each of these compounds also dissociated upon heating at temperatures above the dissociation temperature of IrO_2. Mixtures of either In_2O_3, Sc_2O_3, or Al_2O_3 with IrO_2 did not react at temperatures up to 2000 °C. The phase diagrams for a number of the M_2O_3–IrO_2 systems have been predicted.

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