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Phase Relations in the Ru-Ir-O_2 System in Air

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The equilibrium phase relations were determined in an air environment for the system Ru-Ir-O_2. In air Ru oxidizes at moderate temperatures, to form RuO_2, which in turn dissociates at 1405 °C. Similarly Ir oxidizes to form IrO_2 and dissociates at 1020 °C. The dissociation of RuO_2 and IrO_2 are reversible processes. A ternary equilibrium phase diagram was constructed indicating selected oxygen reaction lines and isotherms. A binary representation of the Ru-Ir-O_2 system in air is given. Up to 1020 °C, RuO_2 reacts with IrO_2 to form a complete solid solution series having the rutile-type structure. At 1345 °C three solid phases, rutile_{ss}, Ru_{ss}, and Ir_{ss}, exist in equilibrium for compositions between approximately 2 and 45 mole percent IrO_2. Above 1405 °C dissociation is complete for all compositions and the phase relations are represented by the Ru-Ir system. At 1500 °C solid solution of Ru and Ir occurs with the addition of up to 45 mole percent Ir and up to 44 mole percent Ru, respectively.

Key words: Dissociation; oxidation; phase relations; Ru-Ir-O_2 system; RuO_2-IrO_2 system; solid solution.

1. Introduction

The present study is part of a program to better understand the behavior of various Pt-group metals heated in an oxidizing environment. Considering the fact that several of these metals are used as secondary standards on the International Practical Temperature Scale (IPTS)[1] [1][2] as well as container materials for high temperature applications, knowledge of the phase relations between these metals, oxygen, and other materials becomes important. This work presents the results of an investigation of the equilibrium relationships between the condensed phases in the system ruthenium (Ru)-iridium (Ir)-oxygen (O_2) in air. Several of the Pt group metals have a strong tendency to oxidize when heated in air at moderate temperatures forming stable condensed phases. At higher temperatures in air, the oxides volatilize and /or dissociate to oxygen and one solid phase, the metal [2].

Even though powdered Ru and Ir oxidize to ruthenium dioxide (RuO_2) and iridium dioxide (IrO_2), when heated in air, complete oxidation is often difficult to obtain. By utilizing RuO_2 and IrO_2 rather than their respective metals as starting materials, an approach to equilibrium could be achieved more readily. The study would still reflect, however, the behavior of the metals in air.

Ruthenium has a hexagonal, magnesium-type structure with $a=2.7058$ Å and $c=4.2819$ Å [3]. The freezing point of Ru has been reported as 2280 °C [4]. Ruthenium dioxide, similar to IrO_2 in having the tetragonal, rutile structure, has unit cell dimensions of $a=4.491$ Å and $c=3.107$ Å [5]. Upon heating, RuO_2 has been reported to dissociate to Ru metal and a vapor phase at 1540 °C in 1 atm oxygen [6].

Iridium has a face-centered cubic, copper-type structure with $a=3.8394$ Å [7]. The freezing point of Ir is given as a secondary reference point on the IPTS. The unit cell dimensions of IrO_2 are reported as $a=4.4983$ Å and $c=3.1544$ Å [8]. Iridium dioxide dissociates to Ir metal and a vapor phase at 1100 °C in 1 atm oxygen [9] and 1020 °C in air [10].

2. Materials

The starting materials used in this study were found by general quantitative spectrochemical analyses[3] to have the following impurities:

Ru: 0.01–0.1% Pd;
0.001–0.01% each Al, Au, Ca, Cr, Fe, and Pt;
< 0.001% each Ag, Cu, K, Mg. Mn, Na, Pb, Si, and Sn;

RuO_2: 0.01–0.1% each Au, Cr, Pd, Pt, Sn, and Zn;
0.001–0.01% each Al, Ca, Co, Cu, Fe, Mg, Pb, Si, V, and Zr;
< 0.001% each Ag, Ir, and Mn;

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[1] This scale (IPTS) applies to all temperatures listed in this paper.

[2] Figures in brackets indicate the literature references at the end of this paper.

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

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

3. Experimental Procedure

Specimens were prepared from 0.4 g batches of various combinations of the end member oxides. Calculated amounts of each oxide, corrected for ignition loss, were weighed to the nearest milligram. Each batch was thoroughly hand mixed, placed in fused silica tubes (sealed at one end) and fired in a muffle furnace for a minimum of 18 hr at 800 and then at 1000 °C. Following the preliminary heat treatment the materials were again thoroughly hand mixed. Portions of each batch were then fired in a platinum alloy wire-wound quench furnace at various temperatures for different periods of time, again using fused silica tubes as the containers. The specimens were air quenched by quickly pulling the silica tube from the furnace. Equilibrium was assumed to have been achieved when the x-ray pattern showed no change after successive heat treatment of the specimen or when the data were consistent with the results from a previous set of experiments.

Sealed platinum tubes were employed as specimen containers for the experiments requiring prolonged heat treatments at temperatures below the dissociation temperatures. Because of volatility, sealed Pt tubes were sometimes utilized in an attempt to maintain composition and to obtain equilibrium more readily. The use of fused silica tubes instead of platinum, at the higher temperatures, was necessary because the metals, frequently found as decomposition products, readily react with platinum. On the other hand, the silica tube did not appear to influence or react with the various oxide samples.

Temperatures in the quench furnace were measured with a 100 percent Pt versus 90 percent Pt–10 percent Rh calibrated thermocouple. All reported temperatures pertaining to quench furnace data are considered accurate to within ±5 °C. The precision of the measurements was estimated to be ±2 °C.

Several experiments were conducted at 1500 °C with mixtures using the metals as the starting materials. Specimens weighing 0.3 g were thoroughly hand mixed, pressed into pellets, and heat treated in an induction vacuum furnace utilizing an iridium crucible as both the susceptor and specimen container. No change in composition was detected due to the iridium crucible. At 1500 °C the normal operating pressure of the system was nominally 7×10^{-5} torr. Temperatures were measured with a calibrated optical pyrometer sighted through a window in the vacuum enclosure into a small hole in the cricible cover. The susceptor-container acted as the blackbody for temperature measurement. This arrangement achieved measurements estimated to be accurate to within ±25 °C or better.

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

4. Results and Discussion

The equilibrium phase diagram for the Ru-Ir-O_2 system in air is given in figure 1. The diagram was constructed from the data listed in table 1. The solid circles illustrate the compositions and temperatures of the experiments conducted. The open circles indicate phase boundaries determined from a plot of the unit cell dimensions. In the ternary plot the dashed lines represent oxygen reaction lines and the heavy lines indicate isotherms. The oxygen reaction lines connect the O_2 apex and the final composition attained upon complete dissociation of the oxide mixture. The dissociation products are either Ru_{ss},[4] Ir_{ss},[5] or Ru_{ss} plus Ir_{ss}. It should be emphasized that these dissociation products are the condensed phases of the system and are always in equilibrium with oxygen. Prior to any dissociation, complete solid solution exists between RuO_2 and IrO_2 (rutile solid solution).[6] The isotherms (heavy lines) represent joins for a given temperature for any series of intersecting oxygen reaction lines. The possible equilibrium assemblages may consist of any combination of rutile$_{ss}$, Ru_{ss}, and Ir_{ss}, depending upon the oxygen reaction line under consideration. The isotherms illustrated were arbitrarily chosen except for those which represent the dissociation temperatures of IrO_2 (1020 °C) and RuO_2 (1405 °C) and that indicating the temperature at which three phases coexist (1345 °C).

Proper interpretation of the diagram can best be accomplished by example. Consider for instance a 50:50 mole percent mixture on the RuO_2-IrO_2 join (25 mole percent Ru: 25 mole percent Ir: 50 mole percent O_2). At all temperatures below approximately 1090 °C, the mixture contains only one solid phase, rutile solid solution (rutile$_{ss}$). As this single phase is heated to higher temperatures, oxygen loss occurs, producing a situation in which two or three solid phases are in equilibrium for a given temperature. These equilibrium assemblages always contain at least one reduced phase, a metal. By following the oxygen reaction lines in figure 1, the specific phases in equilibrium can be established. The oxygen reaction line for the 50:50 mole percent composition is seen from figure 1 to cross a number of isotherms. The intersection of these isotherms with the RuO_2-IrO_2 and Ru-Ir joins indicates the compositions of the phases in equilibrium. At 1100 °C, for example, an original $50RuO_2$:$50IrO_2$ mole percent composition

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[4] Ru_{ss} = ruthenium solid solution having hexagonal structure (Ru_xIr_{1-x}).
[5] Ir_{ss} = iridium solid solution having cubic structure (Ir_xRu_{1-x}).
[6] Rutile$_{ss}$ = solid solution phases having rutile-type structure ($Ru_xIr_{1-x}O_2$).

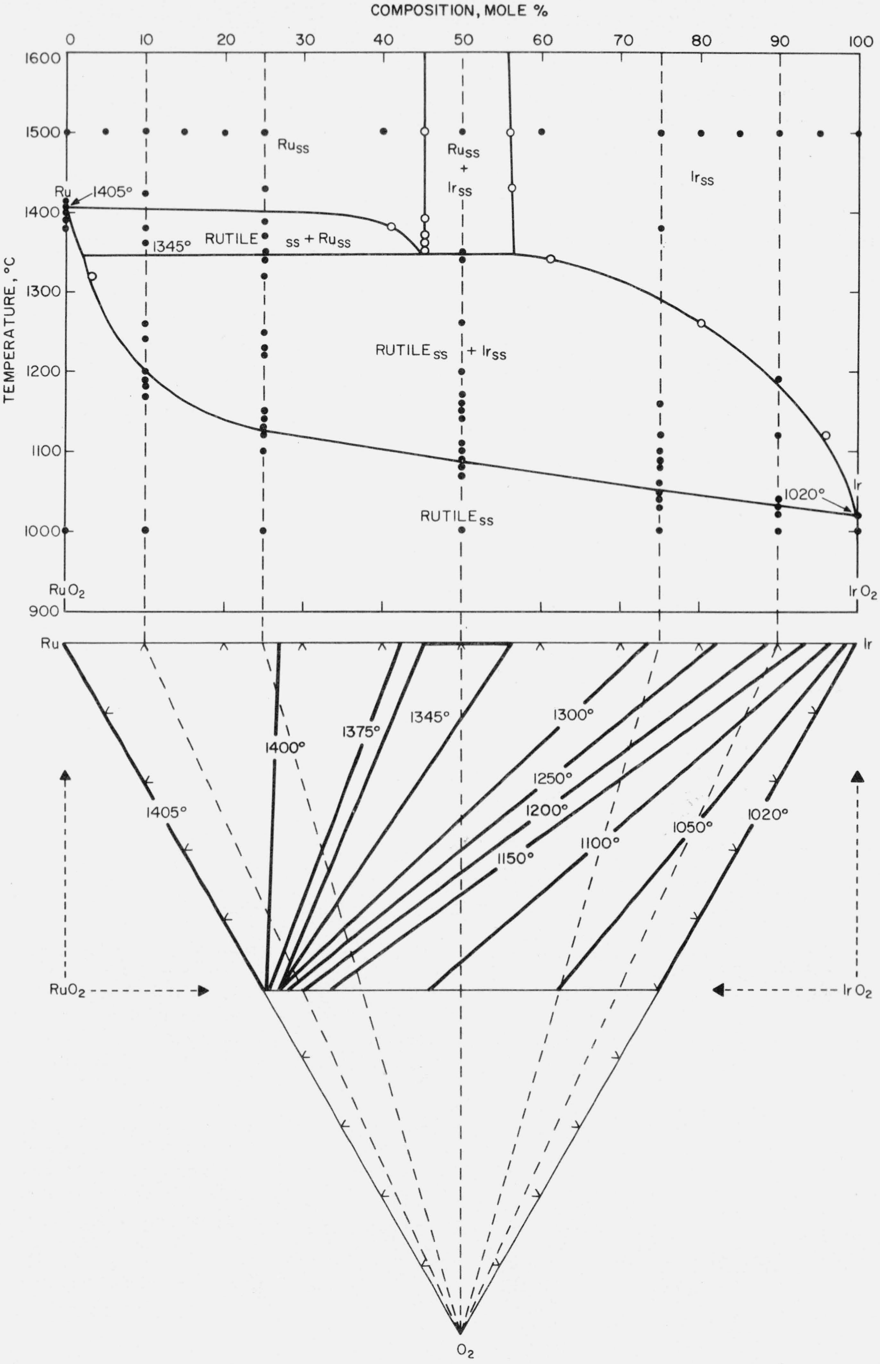

FIGURE 1. *Phase equilibrium diagram for the* Ru-Ir-O$_2$ *system in air.*

Dashed lines represent oxygen reaction lines. Heavy lines indicate isotherms. ● — compositions and temperatures of experiments conducted. ○ — phase boundaries determined from a plot of the unit cell dimensions, ss — solid solution. Rutile$_{ss}$ — phases having rutile-type structure (Ru$_x$Ir$_{1-x}$O$_2$).

TABLE 1. *Experimental data for compositions in the* Ru-Ir-O_2 *system in air*

Composition		Heat treatment [a]		X-ray diffraction analyses [b]	Remarks
RuO_2	IrO_2	Temp.	Time		
mole %	*mole %*	*°C*	*hr*		
100	0	1000	18	RuO_2	
		[c] 1000	20	RuO_2	Quenched in ice water.
		1375	2	RuO_2	
		1385	2	RuO_2	
		1400	2.5	RuO_2	
		1405	2	RuO_2 + Ru	Nonequilibrium.
		1410	2	RuO_2 + Ru	Nonequilibrium.
90	10	1000	18	Rutile$_{ss}$	
		1170	2	Rutile$_{ss}$	
		1180	2	Rutile$_{ss}$	
		1190	2	Rutile$_{ss}$	
		1200	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1240	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1260	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1360	1	Rutile$_{ss}$ + Ru$_{ss}$	
		1380	0.25	Rutile$_{ss}$ + Ru$_{ss}$	
		1425	0.25	Rutile$_{ss}$ + Ru$_{ss}$	Nonequilibrium.
75	25	1000	18	Rutile$_{ss}$	
		[c] 1100	192	Rutile$_{ss}$	Quenched in ice water.
		1120	2	Rutile$_{ss}$	
		1135	2	Rutile$_{ss}$	Ir not detected by x-rays.[d]
		1140	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1150	1	Rutile$_{ss}$ + Ir$_{ss}$	
		1220	1	Rutile$_{ss}$ + Ir$_{ss}$	
		1230	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1250	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1320	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1340	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1350	2	Rutile$_{ss}$ + Ir$_{ss}$	Nonequilibrium; trace of Ir$_{ss}$.
		1370	0.5	Ru$_{ss}$ + rutile$_{ss}$	
		1370	2	Ru$_{ss}$ + Ir$_{ss}$ + rutile$_{ss}$	Nonequilibrium; apparent change in composition due to differential volatilization.
		1390	2	Ir$_{ss}$ + Ru$_{ss}$ + rutile$_{ss}$	Nonequilibrium; apparent change in composition due to differential volatilization.
		1430	0.5	Ru$_{ss}$ + rutile$_{ss}$	Nonequilibrium.
		1430	2	Ir$_{ss}$ + Ru$_{ss}$ + rutile$_{ss}$	Nonequilibrium; apparent change in composition due to differential volatilization; rutile$_{ss}$ probably formed on cooling.
50	50	1000	18	Rutile$_{ss}$	
		[c] 1000	18	Rutile$_{ss}$	Quenched in ice water.
		1070	2.5	Rutile$_{ss}$	
		1080	2	Rutile$_{ss}$	
		1090	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1100	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1110	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1140	3	Rutile$_{ss}$ + Ir$_{ss}$	
		1150	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1160	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1170	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1200	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1260	2	Rutile$_{ss}$ + Ir$_{ss}$	
		1340	2	Ir$_{ss}$ + rutile$_{ss}$	
		1350	1	Ir$_{ss}$ + Ru$_{ss}$ + rutile$_{ss}$	Nonequilibrium.
25	75	1000	18	Rutile$_{ss}$	
		1030	2	Rutile$_{ss}$	
		1040	2	Rutile$_{ss}$	

TABLE 1. *Experimental data for compositions in the* Ru-Ir-O_2 *system in air*—Continued

Composition		Heat treatment [a]		X-ray diffraction analyses [b]	Remarks
RuO_2	IrO_2	Temp.	Time		
mole %	*mole %*	*°C*	*hr*		
		1050	2	Rutile_{ss}	
		1060	2	Rutile_{ss}	Ir not detected by x-rays.[d]
		1080	2	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1090	2	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1100	46	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1120	2	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1160	4	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1380	2	Ir_{ss}	
10	90	1000	18	Rutile_{ss}	
		[c] 1000	20	Rutile_{ss}	Quenched in ice water.
		1020	2	Rutile_{ss}	
		1030	2	Rutile_{ss}	
		1040	2	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1120	2	$\mathrm{Rutile}_{ss}+\mathrm{Ir}_{ss}$	
		1190	3	Ir_{ss}	
Ru	**Ir**				
100	0	1500	4	Ru	
95	5	1500	4	Ru_{ss}	
90	10	1500	4	Ru_{ss}	
85	15	1500	2	Ru_{ss}	
80	20	1500	2	Ru_{ss}	
75	25	1500	2	Ru_{ss}	
		[e] 1500	2	Ru_{ss}	
		[e] 1500	4	Ru_{ss}	
60	40	1500	2	Ru_{ss}	
		[e] 1500	2	Ru_{ss}	
50	50	1500	2	$\mathrm{Ru}_{ss}+\mathrm{Ir}_{ss}$	
		[e] 1500	2	$\mathrm{Ru}_{ss}+\mathrm{Ir}_{ss}$	
		[e] 1500	4	$\mathrm{Ru}_{ss}+\mathrm{Ir}_{ss}$	
40	60	1500	2	Ir_{ss}	
		[e] 1500	2	Ir_{ss}	
		[e] 1500	2	Ir_{ss}	
25	75	1500	2	Ir_{ss}	
		[e] 1500	2	Ir_{ss}	
		[e] 1500	4	Ir_{ss}	
20	80	1500	2	Ir_{ss}	
15	85	1500	2	Ir_{ss}	
10	90	1500	4	Ir_{ss}	
5	95	1500	4	Ir_{ss}	
0	100	1500	4	Ir	

[a] All oxide specimens were heat treated at 800 °C a minimum of 18 hr; unless otherwise indicated, fused silica tubes (sealed at one end) were used for specimen containers and were air quenched. The 1500 °C experiments were conducted in the iridium induction furnace; operating pressure of the system was nominally 7×10^{-5} torr.

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

[c] Sealed platinum tubes were used for specimen containers.

[d] Small amounts of dissociation products (metals) tend to segregate and evade detection by x-ray diffraction. Microscopic examination of the specimens in conjunction with x-ray diffraction data give consistent dissociation temperatures.

[e] Reheat of specimen from previous experiment.

would contain two phases, rutile$_{ss}$ and Ir$_{ss}$. The composition of the rutile$_{ss}$ is estimated to be 58 mole percent RuO_2:42 mole percent IrO_2, while that of Ir$_{ss}$ is about 3 mole percent Ru:97 mole percent Ir. The intersection of the oxygen reaction line and the 1100 °C isotherm represents the total bulk composition (Ru 27, Ir 27, O_2 46 mole percent) at that temperature. At 1345 °C and only this temperature, three solid phases (rutile$_{ss}$, Ru$_{ss}$, Ir$_{ss}$) exist in equilibrium, as illustrated by the triangular isotherm. Above 1345 °C the dissociation is complete for the original $50RuO_2$:$50IrO_2$ mole percent mixture and the phase relations can be established from the true binary Ru-Ir system. Phase relations for other compositions are interpreted in a similar manner by following the appropriate oxygen reaction lines.

The binary-type phase diagram given in the top portion of figure 1 is a projection of certain elements of the three dimensional ternary system Ru-Ir-O_2 on a two-dimensional plane figure. The diagram in effect represents a composite of the true binary system Ru-Ir and the pseudobinary system, RuO_2-IrO_2. By representing the dissociation of RuO_2 and IrO_2 as a type of phase transition in which the vapor phase is ignored, a simple binary representation of the phase relations of the ternary system can be given. This method of illustration has been employed by a number of investigators [11, 12]. The diagram can be interpreted as a binary diagram and the application of the lever law is valid.

Ruthenium dioxide was found to dissociate to Ru metal and presumably oxygen at 1405 °C in air at atmospheric pressure. This value compares favorably with the data (1540 °C in one atm oxygen) given by Bell and Tagami in their study of the Ru-oxygen system [6]. The dissociation of RuO_2 is a reversible process; that is, oxidation of Ru occurs readily at temperatures below 1405 °C. At temperatures of 1300 °C and above RuO_2 becomes very volatile. Bell and Tagami conclude that RuO_3 and RuO_4, stable only in the gaseous state, form on heating Ru in one atm of oxygen [6]. Several experiments were conducted in an effort to produce a stable solid $RuO_{2\pm x}$ in an air environment without success. In one experiment it was observed that prolonged heating of RuO_2 at 1300 °C produced a trace of an unidentified phase. Additional experiments revealed that the RuO_2 volatilized, leaving a phase assumed to be a reaction product of a mixture of RuO_2 and the impurities listed in the spectrochemical analysis. This became evident when a different but purer source of RuO_2 was used. The unidentified phase did not form under the same experimental conditions. Stoichiometric RuO_2 appears to be the only stable condensed phase in an air environment.

It was found in earlier work that IrO_2 dissociates to Ir metal and oxygen at 1020 °C in air [10]. This dissociation is also a reversible process. Other investigators [9, 13] have reported that IrO_2 combines with oxygen to form IrO_3, which is stable only in the gaseous state. Several experiments conducted in this study revealed that IrO_2, similar to RuO_2, is the only stable condensed oxide in an air environment.

This study did not detect any oxygen-deficient rutile solid solution or oxygen-rich metal solid solution. It is possible that nonstoichiometric ternary solid solutions should be indicated in figure 1 (bottom portion) adjacent to the RuO_2-IrO_2 join and likewise the Ru-Ir join. It appears unlikely that this occurs, inasmuch as deviation from stoichiometry was not detected in this study for the uncombined end members.

At temperatures up to 1020 °C in air the RuO_2-IrO_2 system (fig. 1, top portion) acts as a true binary. Above 1020 °C and below 1405 °C, portions of the system become pseudobinary. Above 1405 °C all compositions can be indicated by the true binary Ru-Ir system.

Complete solid solution was found at the lower temperatures between the two rutile end member oxides. Solid solution of Ir in Ru (hexagonal symmetry) occurs with the addition of up to 45 mole percent Ir at 1500 °C. Solid solution of Ru in Ir (cubic symmetry) extends up to 44 mole percent Ru at 1500 °C.

The complete binary representation of the condensed ternary system Ru-Ir-O_2 in air is given in figure 2. The diagram up to 1500 °C was constructed from data obtained in this study and is a reproduction of the binary presented in figure 1. Subsolidus data above 1600 °C were taken from the work of Raub [14]. Solidus and liquidus lines are strictly postulated as a reasonable facsimile of what might actually occur. Except for the melting points of the metallic end members, there are no data available for a more accurate construction.

Unit cell dimensions for the solid solution region between RuO_2 and IrO_2 are plotted in figure 3. The data were obtained from specimens heat treated at 1000 °C. Both *a* and *c* dimensions deviate as expected from the linear line predicted by Vegard's Law. However, for unknown reasons the deviations are not in the same direction. It is also evident that the a dimension for compositions rich in RuO_2 changes very little until about 40 mole percent IrO_2 is added.

Inasmuch as both RuO_2 and IrO_2 have the tetragonal, rutile-type structure and similar reported cationic radii (0.67, 0.68 Å, respectively) [15], it would be expected the unit cell dimensions should be similar. The dimensions for the *a* parameters, however, differ only by 0.005 Å, while the difference for the *c* parameters is 0.05 Å. The larger deviation in the *c* parameters are probably due to crystal field effects resulting from the additional *d*-electron of Ir.

5. Summary

Equilibrium phase relations were determined for the system Ru-Ir-O_2 in air up to 1500 °C. A ternary equilibrium phase diagram was constructed, indicating selected oxygen reaction lines and isotherms. A binary representation of the Ru-Ir-O_2 system in air is given. The diagram represents a composite of the true binary system Ru-Ir and the pseudobinary RuO_2-IrO_2 system. Selected mixtures in the system

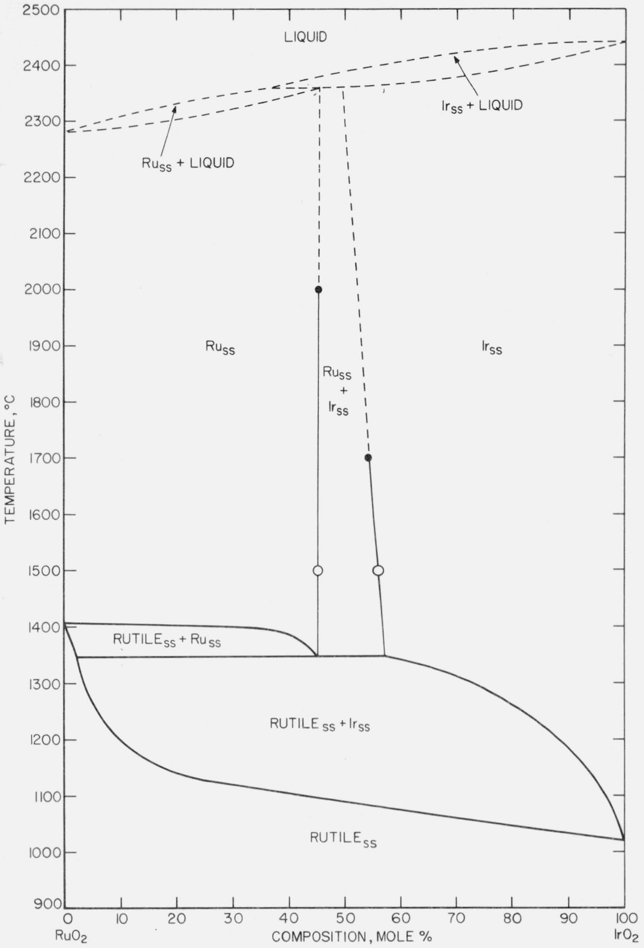

FIGURE 2. *Binary representation of the condensed ternary system Ru-Ir-O$_2$.*

Lower portion is a reproduction of the binary presented in figure 1. Dashed lines represent postulated portion of the diagram. ● — data taken from work of Raub [14]. ○ — data obtained is this study. ss — solid solution.

were studied by x-ray diffraction techniques after various heat treatments. The dissociation temperatures of RuO$_2$ and IrO$_2$ in air were established at 1405 and 1020 °C, respectively. Both the dissociations were found to be reversible. The oxides react to form complete solid solution at temperatures up to 1020 °C. At 1345 °C, three solid phases, rutille$_{ss}$, Ru$_{ss}$, and Ir$_{ss}$, exist in equilibrium for compositions between 2 and 45 mole percent IrO$_2$. Above 1405 °C dissociation is complete for all compositions and the phase relations are represented by the true binary Ru-Ir system. At 1500 °C, solid solution of Ru and Ir occur with the addition of up to 45 mole percent Ir and up to 44 mole percent Ru, respectively.

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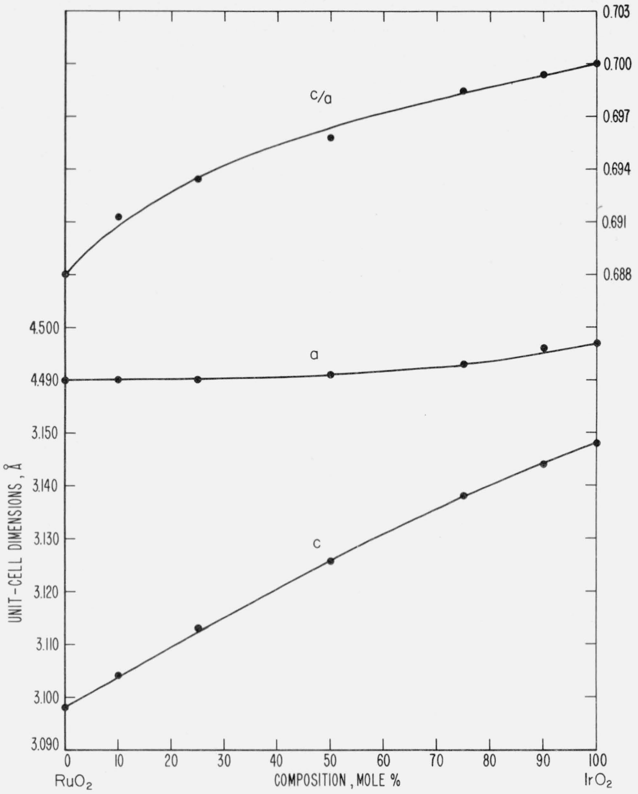

FIGURE 3. *Unit cell dimensions for rutile$_{ss}$ as a function of composition.*

The data were obtained from specimens heat treated at 1000 °C.

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