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PURIFICATION OF IRIDIUM BY AN AN OXIDATION-DISSOLUTION PROCESS

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ABSTRACT

A method for purifying iridium has been demonstrated and applied to the treatment of about 9 kg of iridium powder and sheet scrap having impurity contents ranging from 0.6 to 3.7%. The process involves high-temperature oxidation of impure iridium to volatile IrO_3, which subsequently condenses as IrO_2. Some impurities remain in the hot zone of the furnace and some pass out of the system as volatile oxides. Impurity oxides that condense with the IrO_2 are leached with various acid solutions. Finally, the purified IrO_2 is reduced to metal with hydrogen.

The iridium was oxidized by contact with oxygen at 1100°C in silica glass tubes. The rate of formation of IrO_2 was faster for sheet scrap and coarse lumps (about 10 g/day per apparatus) than for more finely divided material (about 7 g/day per apparatus), because the latter sintered into a mass of lower surface area. The product iridium was as pure as 99.98%, although some with a residual tungsten content of 300 ppm was only about 99.93% pure. The final product was −40-mesh iridium powder, which was pressed into compacts and sintered in preparation for melting and ultimate fabrication into sheet.

INTRODUCTION

The Multi-Hundred Watt (MHW) radioisotope thermoelectric generator is being developed to supply electrical power for space vehicles. The isotopic heat source of the MHW system uses $^{238}PuO_2$ fuel, which is contained in a spherical cladding. The reference alloy for cladding the fuel is Ir—0.3 wt % W. This alloy has the characteristics needed for this application — namely, high melting point and sufficient strength and oxidation resistance at temperatures in the range 800 to 1400°C. The addition of 0.3 wt % W improves the fabricability and some of the strength properties of iridium. On the other hand, impurities such as Al, Cr, Fe, Si, and some noble metals are believed to be detrimental to fabricability and high-temperature mechanical properties.

Fabrication of fuel spheres and testing of these spheres result in unavoidable contamination of significant quantities of iridium. In addition, commercially available and United States Government stockpile iridium often contain an unacceptable level of certain impurities. For these reasons a method of processing iridium to obtain a minimum purity of about 99.98% was needed. The production rate needed to provide an adequate supply of iridium for the MHW program was estimated to be about 200 troy ouces per month (about 6200 g/month).

Any search for a purification process is confronted with the fact that iridium is the most corrosion-resistant metal known. The metal is completely unattacked by the common mineral acids and aqua regia at ambient and elevated temperatures.[1] It is the most resistant of the platinum metals to the halogens up to 600°C, and is only slightly attacked by fused sodium and potassium hydroxides and by fused sodium bicarbonate.[1] On a commercial scale, iridium is recovered from precious metals concentrates derived from base-metal refining operations.[2] The concentrates are first treated with aqua regia to separate soluble Au, Pt, and Pd from insoluble Rh, Ru, Ir, and Ag. The insoluble residue is smelted with borax, soda ash, lead carbonate, and carbon to form a lead alloy containing the precious metals.

The alloy is treated with nitric acid, which dissolves the silver and lead. The residue is treated with molten sodium bisulphate at 500°C, which dissolves the rhodium and leaves the ruthenium and iridium virtually unattacked. The ruthenium and iridium are heated with sodium peroxide at 500°C. Ruthenium is leached with water from the resulting mixture as soluble sodium ruthenate, and the iridium is left as IrO_2. The IrO_2 is dissolved in hot aqua regia. Treating this solution with nitric acid and ammonium chloride causes the iridium to precipitate as ammonium chloriridate. This compound is ignited and reduced under hydrogen at 1000°C to give metallic powder assaying >99.9% Ir.

A literature search indicated that an oxidation technique might also be used.[3] Several investigators[4,5] have shown that oxidation of iridium with oxygen at elevated temperatures produces volatile IrO_3 by the reaction

$$2Ir\ (s) + 3O_2\ (g) \rightarrow 2IrO_3\ (g)\ .$$

Below 1100°C the volatile oxide dissociates to IrO_2 and oxygen by the reaction

$$2IrO_3\ (g) \rightarrow 2IrO_2\ (s) + O_2\ (g)\ .$$

The basic process then would consist of contacting impure iridium with oxygen at an elevated temperature to form volatile IrO_3, which subsequently condenses as IrO_2 in a cooler part of the system. Some impurities would be expected to remain in the hot zone as relatively nonvolatile oxides and some would pass out of the system as gases. Impurity oxides that condense with the IrO_2 might be removed by selective chemical dissolution. Finally, the IrO_2 would be reduced to metal with hydrogen. The total process involves fewer steps than the commercial process mentioned above and could be conducted on a laboratory scale using simple and readily available equipment. Process variables could be closely controlled, so that a consistently pure product could be obtained.

FEASIBILITY EXPERIMENTS

The oxidation-dissolution process was proven by processing iridium containing up to 3 wt % impurities.[3] The material was oxidized with oxygen in silica glass tubes at 1000 and 1100°C. The IrO_2, which deposited on the cooler parts of the silica glass tubes, was treated with a 1 HF:1 H_2O solution and with aqua regia, then reduced to metal powder with hydrogen at 600°C. Table 1 shows the analyses of three lots of iridium before and after purification. The results show that a product assaying about 99.98% Ir or better can be produced from an alloy (lot 77-41-1), a sheet fabricated from a contaminated electron-beam-melted ingot (lot 77-EB-1), and an arc-melted ingot to which impurities had been intentionally added (lot 77-S-2). The results for lot 77-EB-1 also show that the concentrations of Fe, Mo, Pt, Re, Ru, and W in the purified product were lower at an oxidation temperature of 1000°C than at 1100°C; however, the higher purity was obtained at one-fifth the IrO_2 production rate. Thus, the process involving oxidation and dissolution was found to be capable of producing iridium of adequate purity for the MHW program.

PROCESS DEMONSTRATION

In view of the success of the feasibility experiments, we decided to purify a larger amount of iridium to further evaluate the process. This study was intended to provide information on production rates, product purity, iridium recovery, fabricability of the product, and problems associated with the process. Approximately 9.4 kg of impure iridium was processed in this study, whereas the feasibility experiments had been conducted with only about 200 g.

Equipment

Impure iridium metal was oxidized at 1100°C with the apparatus shown schematically in Fig. 1. The silica glass oxidation tubes were nominally 2 1/8 in. ID × 23 in. long, with a 3/16-in.-ID oxygen inlet tube. A mullite oxidation tube was used in one oxidation experiment conducted at 1300 and 1400°C. The oxygen flowed into the bottom of the oxidation tube through a 1/8-in.-diam hole. Alumina chips covered the hole to a depth of about 1/2 in.; the chips dispersed the oxygen stream and prevented small particles of iridium from falling through the hole when the oxygen was not flowing. The silica glass collection tubes were nominally 1 9/16 in. ID × 23 in. long. These extended into the oxidation tubes through a rubber seal and usually terminated 3 in. below the top of the furnace.

Table 1. Analysis of Iridium Before and After Purification in Oxidation-Dissolution Feasibility Experiments

Element	Impurity Content, ppm by weight						
	Lot 77-41-1		Lot 77-EB-1			Lot 77-S-2	
	Before	After[a]	Before	After[a]	After[b]	Before[c]	After[a]
Al	4	15	4	1	1	300	4
B	0.1	0.2	0.6	0.1	0.2	0.5	0.3
Ca	6	60	0.6	0.6	6	60	6
Co	d	d	d	d	d	195	0.3
Cr	1	8	3	0.2	0.2	200	2
Cu	2	0.5	5	5	5	10	4
Fe	3	10	30	8	2	550	8
Hf	d	d	300	d	d	300	1
Mo	5	5	1500	60	6	500	6
Na	0.3	0.4	0.4	0.3	0.3	1	0.3
Nb	~30,000	15	d	d	d	200	0.1
Ni	1	1.5	0.5	0.1	0.1	260	0.4
P	0.5	0.2	2	0.1	0.4	2	0.2
Pd	2	<0.6	2	0.6	0.6	500	0.6
Pt	1	40	>10,000	30	10	2160	30
Rh	5	5	500	0.4	0.4	870	0.1
Re	d	d	90	5	0.5	2200	15
Ru	5	5	50	7	2	5	0.4
Si	3	9	9	2	2	300	0.8
Ta	3	1	30	d	d	600	25
Ti	5	3	d	0.2	0.2	7	0.2
V	0.8	0.3	3	0.1	0.1	150	9.7
W	10	10	900	25	2.5	2700	3
Zn	d	d	d	d	d	0.3	0.3
Zr	3	<0.3	100	0.3	3	300	0.3
S	4	40	40	3	10	1	10
Th	0.4	0.4	4	d	d	d	d
Ir, %	~97.0	99.976	98.640	99.986	99.995	98.763	99.988

[a] Oxidized at 1100°C.

[b] Oxidized at 1000°C.

[c] Nominal composition.

[d] Not detected. Probably <1 ppm.

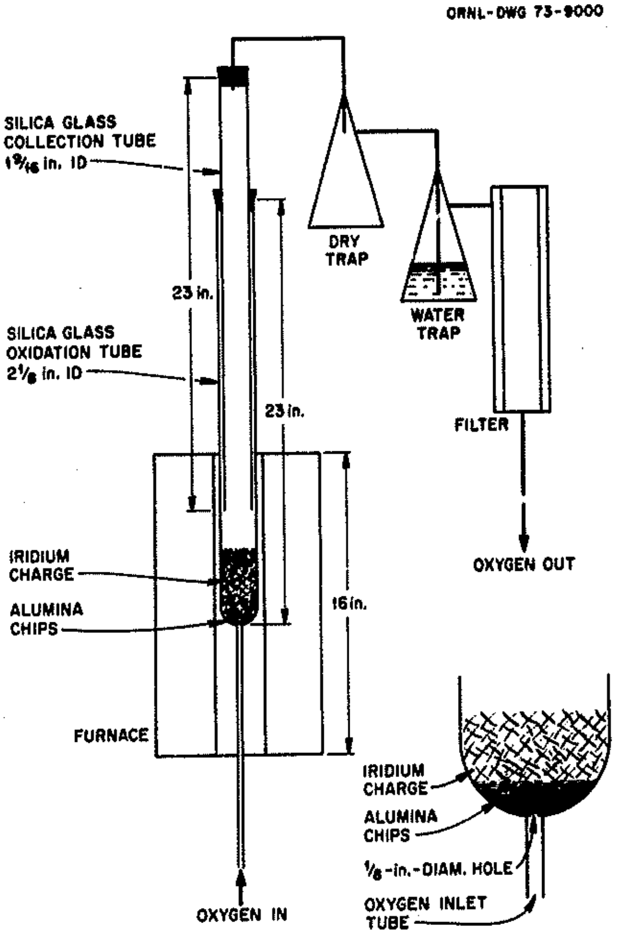


Fig. 1. Schematic of the Oxidation System.

Figure 2 is a photograph of an oxidation assembly. Eleven similar assemblies were operated simultaneously for several months. Figure 3 shows the silica glass oxidation and collection tubes before and after use. The white appearance of the used oxidation tube was caused by devitrification of the silica glass, which always occurred increasingly with time at 1100°C. The black coating on the upper part of the oxidation tube was always quite thin and apparently resulted from random movement of IrO_2 particles. The inner wall of the collection tube became more heavily coated with IrO_2 during an oxidation period. The coating on the lower 2- to 3-in. portion (inside the furnace) was a hard, crystalline deposit, which adhered to the silica glass. Often the deposit filled the cross section of the collection tube at this location. Above the furnace the inner wall of the tube was covered with a fine, loosely adhering powder. Entrained powder deposited in the dry trap, in the water trap, and in the filter. The traps were made of 500-ml Pyrex glass flasks. The principal reason for the dry trap was to prevent accidental

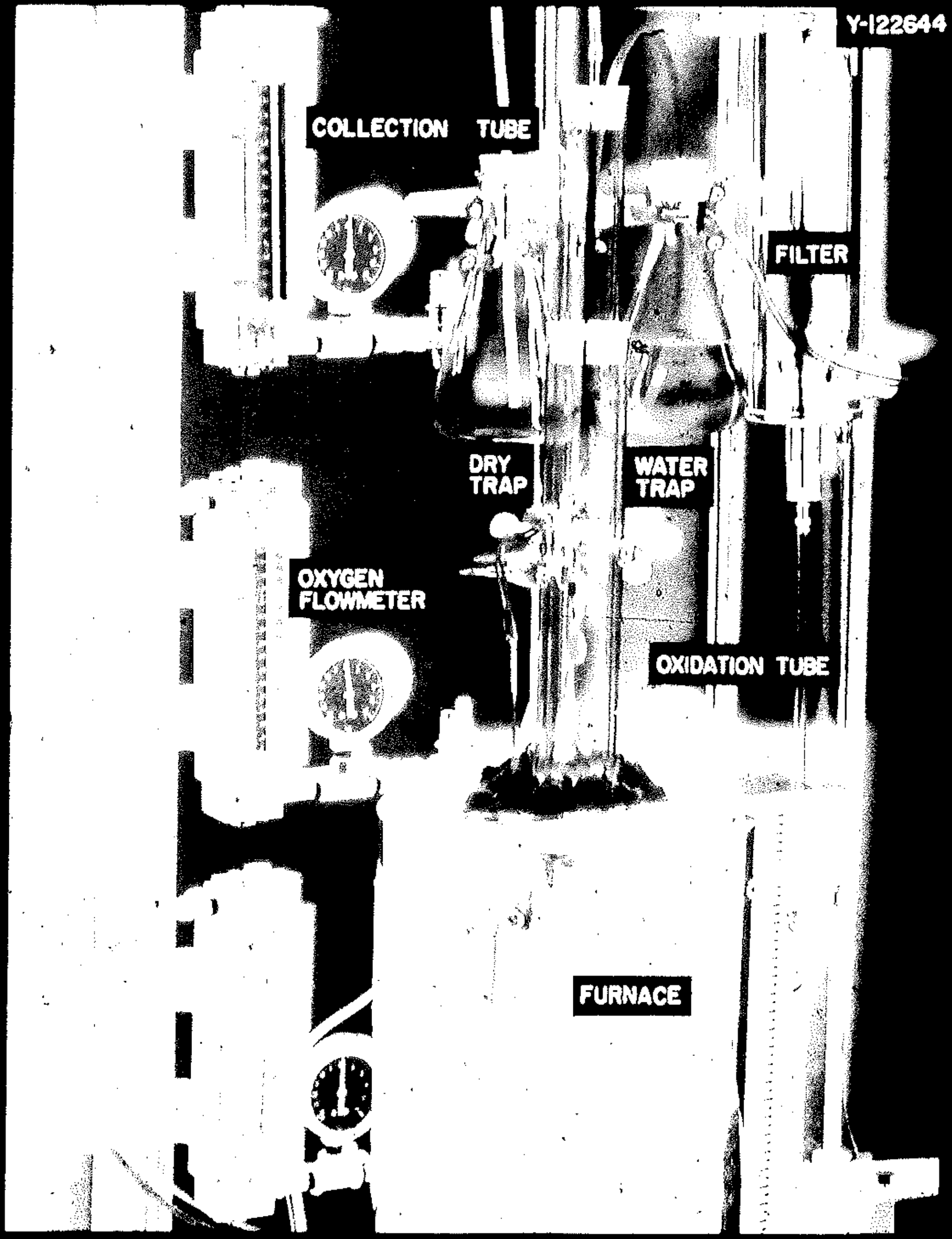


Fig. 2. Oxidation Apparatus.

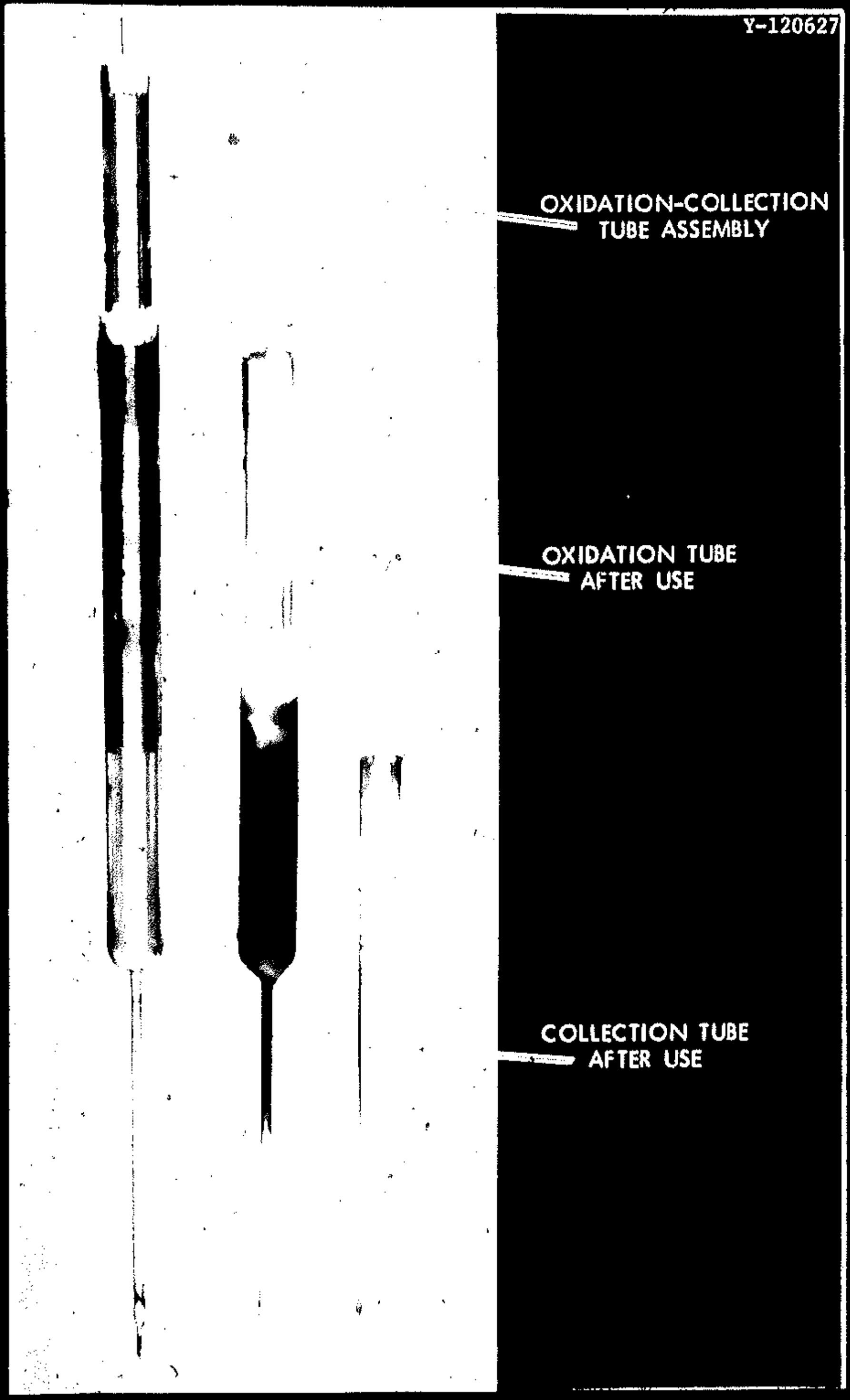


Fig. 3. Silica Glass Oxidation and Collection Tubes.

flow of water into the oxidation tube. Some oxidation tubes were operated without water traps, but all had filters. The filters were nominally 3 in. diam × 12 in. long. The filter medium was blotter paper wrapped on a perforated metal cylinder and very effectively stopped entrained powder.

Procedures

The various steps in the purification process are shown in the flowsheet in Fig. 4. A description of each step follows.

Charge Preparation

Typical iridium charges for the oxidation tubes are shown in Fig. 5. Iridium sheet scrap ranged in thickness from about 0.005 to 0.09 in. This material was cut with hand shears into approximately 3/4 × 3/4 in. pieces. Iridium spheres that had been used in impact tests were about 0.03 in. thick. These were broken into approximately 1/8 × 1/8 in. pieces with a hardened steel mortar and pestle. Iridium powder was pressed at 50 tsi into compacts measuring 1.8 × 1 × ~0.25 in. and sintered for 1 hr at 1000°C in hydrogen. These were broken with a hardened steel mortar and pestle into either −10 +20-mesh granules or approximately 1/4 to 1/2 in. lumps.

Oxidation

A charge of sheet scrap, sphere scrap, or sintered powder granules or lumps was loaded into the oxidation tubes. The furnace was heated to 1100°C with oxygen flowing at the desired rate. Without a steady flow of oxygen, practically no IrO_2 deposited in the collection tubes. Periodically the oxygen flow was stopped, and the collection tubes were taken out of the oxidation tubes for removal of the IrO_2 deposit. The gain in weight of the collection tube during an oxidation period was recorded as the amount of IrO_2 collected even though some of the deposit could not easily be dislodged from the tube. Most of the IrO_2 was easily dislodged from the collection tubes with a stainless steel rod, while adherent deposits were recovered later by dissolving the silica glass with hydrofluoric acid. During a continuous oxidation run for 4 to 8 weeks, the IrO_2 was usually removed from the collection tubes every other day. Longer intervals often resulted in complete filling of the cross section of the collection tubes at the bottom end, and bridging of the deposit to the wall of the oxidation tubes. When this occurred the collection tubes could not be withdrawn from the oxidation tubes without breaking one or both tubes. Oxygen flows were decreased to avoid this problem whenever the collection interval was expected to exceed two days.

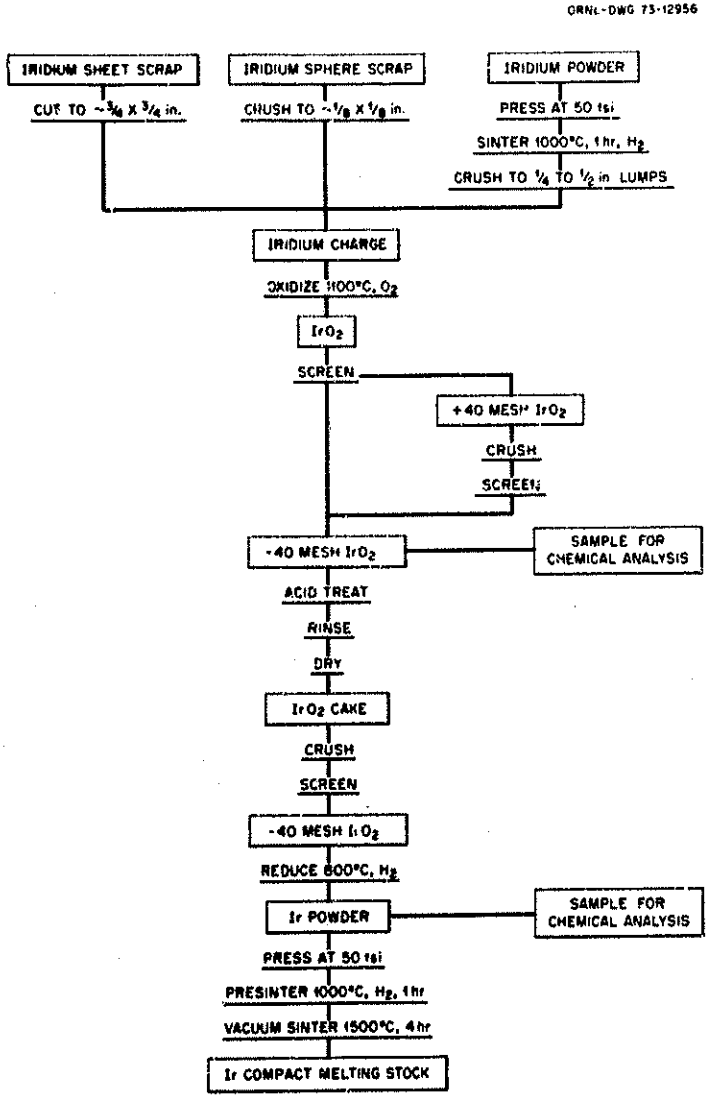


Fig. 4. Flowsheet for Iridium Purified by the Oxidation-Dissolution Process.

Treatment of IrO_2

The IrO_2 removed from the collection tubes, water traps, and filters was screened to separate −40-mesh powder. The remainder was crushed as required to −40-mesh powder with a hardened steel mortar and pestle. Then, 500- to 550-g batches of the powder were leached with acid solutions to

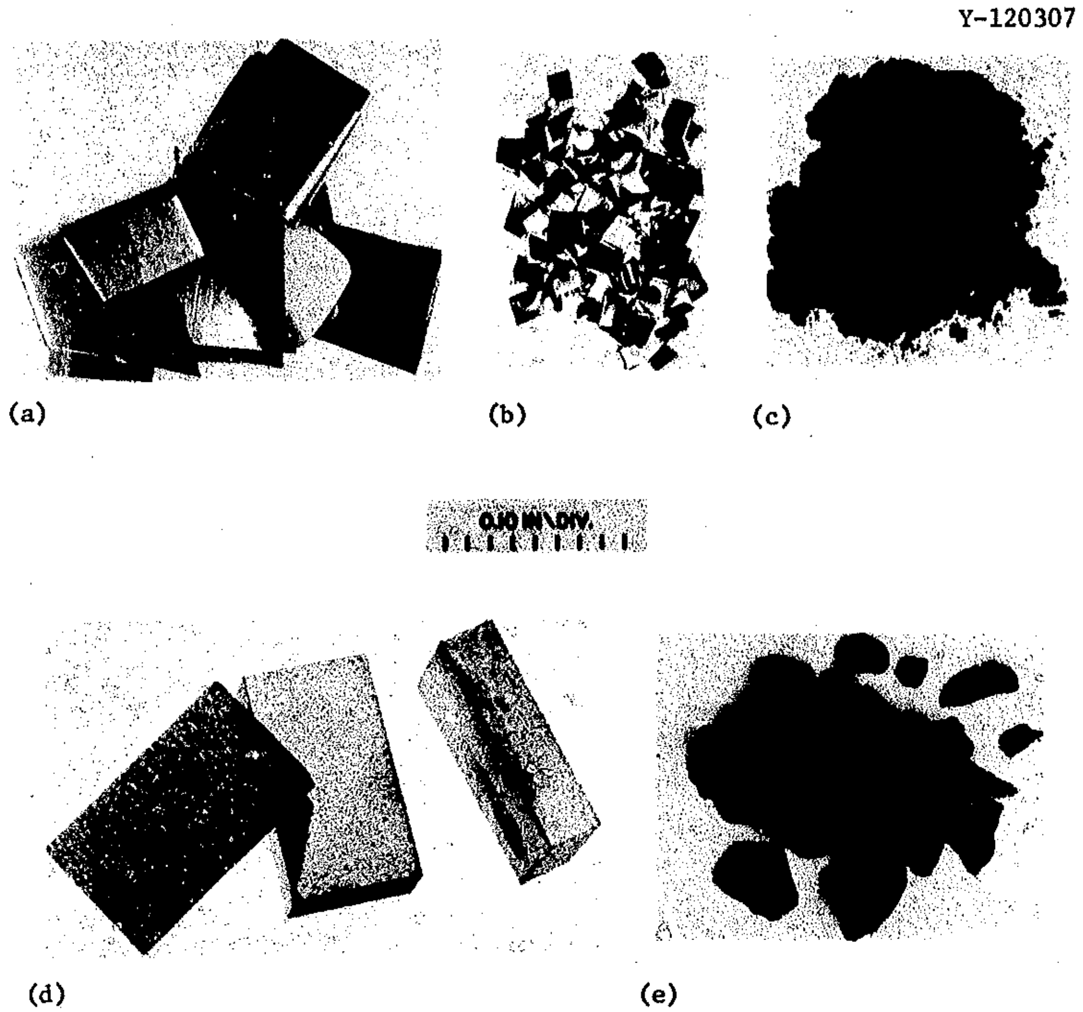


Fig. 5. Iridium Charge for Oxidation. (a) Sheet scrap. (b) Sphere scrap simulated by nickel (the sphere scrap had been consumed by the time of photographing). (c) Powder. (d) Pressed-and-sintered compacts. (e) Broken compact.

dissolve metallic impurities. The acids, conditions, and susceptible impurities are shown in Table 2. For these treatments the powder was placed in 600-ml Pyrex glass beakers, except that plastic beakers were used for hydrofluoric acid. The powder was slurried in the acid by manual stirring with a Teflon rod two or three times during the exposure period. After a minimum exposure of 24 or 48 hr the acid was decanted into a filter, either plastic with filter paper for HF or Pyrex frit for the other acids. The purpose of the filter was to catch very fine powder that floated on the surface of the acid or subsequent rinse water. After the acid was decanted, the powder was slurried in distilled water, which was also decanted into the filter after the powder had settled. At

Table 2. Acid Treatments of IrO_2

Acid	Temperature (°C)	Minimum Time (hr)	Soluble Metal Oxides
1 HF—1 H_2O	25	48	SiO_2, WO_3
concd HCl	90	24	Cu_2O, Fe_2O_3, Mn_3O_4, MnO_2, PbO_2, Pb_2O_3, PtO, ReO_2
3 concd HCl—1 concd HNO_3	40	24	Co_3O_4
concd HNO_3	90	24	B_2O_3, CaO, CoO, CuO, FeO, Fe_3O_4, MgO, MgO_2, MnO, Mn_2O_3, MoO_3, Na_2O_2, NiO, PbO, ReO_3, Re_2O_7, RuO_4, WO_2, ZnO
concd H_2SO_4	90	24	Co_3O_4, CrO_3, MoO_2, TiO, Ti_2O_3, TiO_2

least five such rinses were used before the next acid solution was added. The purpose of these rinses was to wash out soluble salts that might be entrapped in the powder. After the last acid treatment the powder was rinsed about ten times, at which point settling became quite sluggish (the more acid the solution, the faster the powder settled). Then the powder was dried in an oven at about 100°C. The dry powder cake was crushed in the beakers with a Teflon rod, then passed through a 40-mesh screen. Crushing of the dried cake to −40-mesh powder was necessary to avoid larger lumps of partially sintered metal after the hydrogen reduction step discussed below.

Reduction of IrO_2 to Iridium

Samples of −40-mesh powder were reduced to metal with hydrogen at 800°C, then chemically analyzed for impurities. If the analysis indicated that sufficient purity had been attained, the bulk IrO_2 was reduced to metal. About 1200 g of IrO_2 was reduced in two platinum boats in a 2 1/8-in.-ID Inconel 600 tube. About 16 g of water was produced for each 100 g of IrO_2, which generated enough steam to visibly darken the hot zone of the furnace unless large hydrogen flows were used. The hydrogen flow rate was greater than 5600 cm^3/min at the beginning of the reduction and was gradually reduced to 3400 cm^3/min near the end of the reduction. The reduction of 1200 g of IrO_2 required about 4 hr at 800°C. The iridium powder resulting from this treatment was passed through a 40-mesh screen and was then ready for pressing into compacts.

Compact Preparation

Purified iridium powder was formed into melting stock by pressing and sintering. Compacts were prepared by cold pressing 150 g of powder in a 1 × 1.8 in. die at 50 tsi. The pressed compacts were presintered in the same Inconel 600 tube used for IrO_2 reduction. The compacts, resting on platinum sheet, were held at 1000°C for 1 hr in a hydrogen atmosphere. Afterwards, the compacts were vacuum sintered at 1500°C for 4 hr while resting on iridium sheet scrap. The purpose of the presinter at 1000°C was to increase the green strength so that the compacts could be transferred into the vacuum furnace and to drive off the stearic acid lubricant used during pressing. The purpose of the vacuum sintering treatment was to produce a highly dense compact that would not outgas during subsequent electron-beam melting. Some outgassing did occur but was significantly less for vacuum-sintered compacts than for compacts that had been presintered only.

RESULTS AND DISCUSSION

IrO_2 Production Rate

The production of IrO_2 for four different types of iridium charges is shown in Table 3. The average production rate for a given tube was obtained by dividing the total amount of IrO_2 produced by the number of operating days. Since the weight of iridium charge was not the same in each case, the average production rates were normalized on the basis of a 600-g initial charge, the approximate amount used in most experiments. This treatment assumes as a first approximation that the average production rate depends directly upon the initial weight of charge. The normalized values appear in the last column of Table 3. Using these values for comparison the following observations may be made:

1. The lowest production rates were obtained with charges of −10 +20-mesh granules prepared from powder.
2. Approximately the same production rates were obtained with charges of sintered powder lumps and sheet scrap.
3. Production rates varied by a factor of about 2 with similar charges of sheet scrap, the only type of charge for which sufficient data afforded a meaningful comparison.

The lower IrO_2 production rates with −10 +20-mesh charges were unexpected, since the rate of formation of IrO_3 should have increased with increasing surface area of charge. We found, however, that −10 +20-mesh particles partially sintered, which reduced the surface area exposed to the oxygen stream. When sintering occurred, the oxygen was channeled through several holes in the charge. On the other hand, sheet scrap and lumps made from powder compacts did not pack so tightly together, and the oxygen passed through numerous paths in the charge.

The cumulative amount of IrO_2 collected as a function of time is shown by the typical curves in Fig. 6. Curve 1 for a charge of −10 +20-mesh granules shows a decreasing IrO_2 production rate until the sixth day,

Table 3. Production of IrO_2 from Four Different Types of Charges

Tube	Temperature (°C)	Oxygen (cm^3/min)	Initial Iridium Charge (g)	Cumulative Operating Time (days)	Cumulative IrO_2 Produced (g)	Production Rate, g/day	
						Average	Normalized[a] Average
			Sintered Powder Granules, −10 +20 mesh				
3	1100	2000–4000	369	57	201	3.5	5.7
4	1100	1000–3000	250	57	194	3.4	8.2
			Sphere Scrap Granules, −10 +20 mesh				
6A	1100	1000–2000	435	54	244	4.5	6.2
			Sintered Powder Lumps, 1/4 to 1/2 in.				
3B	1100	1000–2000	611	31	388	12.5	12.3
4A	1100	1000–2000	550	31	315	10.2	11.1
			(333)[b]	83	802	9.7	c
			Sheet Scrap, ~3/4 in. squares				
1A	1100	1000–4000	600	33	473	14.3	14.3
1B	1100	1000–2000	438	13	73	5.6	d
2A	1100	1000–4000	600	70	465	6.6	6.6
3A	1100	1000–4000	600	48	580	12.1	12.1
5	1100	1000–2000	620	76	539	7.1	6.9
6	1100	1000–2000	602	42	372	8.9	8.9
7	1100	1000–2000	604	45	459	10.2	10.2
8	1100	1000–2000	600	41	477	11.6	11.6
9	1100	1000–2000	602	39	436	11.2	11.2
9A	1100	1000–2000	787	61	545	8.9	d
10	1100	1000–2000	600	41	527	12.9	12.9
11	1300–1400	1000–2000	622	34	422	12.0	11.6
			(450)[e]	47	531	11.3	c
11A	1100	1000–2000	675	54	504	9.3	8.3

[a] Normalized on the basis of an initial charge of 600 g.

[b] Added on 31st day.

[c] Not computed because charge was added during the run.

[d] Not computed because charge contained much fine material from previous runs.

[e] Added on 34th day.

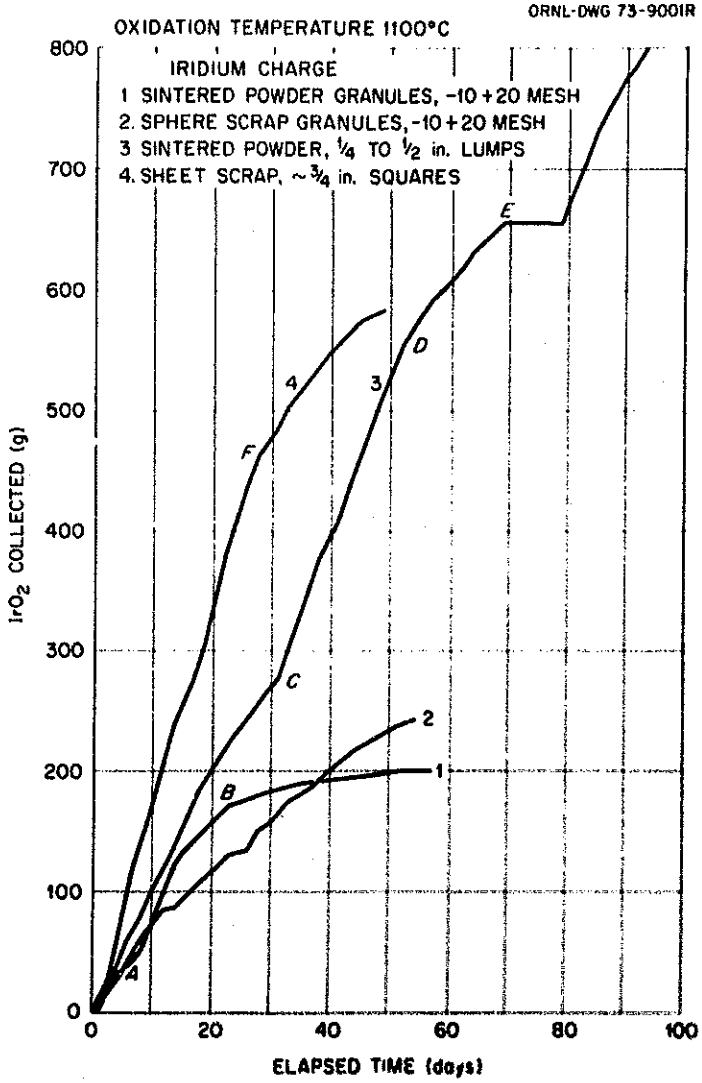


Fig. 6. Production of IrO_2 from Typical Charges of Impure Iridium at 1100°C.

at which time the rate was increased by increasing the oxygen flow rate from 2000 to 4000 cm^3/min (point A). The production rate decreased again on the 14th day and decreased still further on the 23rd day, when the oxygen flow rate was reduced to the original value of 2000 cm^3/min (point B). Thus, the production rate associated with this particular charge depended upon the oxygen flow rate.

The IrO_2 production rate for a sphere scrap charge represented by curve 2 in Fig. 6 shows a gradual decrease over the 54-day oxidation period. During this time the oxygen flow rate was 1000 or 2000 cm^3/min; no relationship of production rate to these flow rates was observed.

A charge of sintered powder lumps produced the results described by curve 3 in Fig. 6. The IrO_2 production rate gradually decreased with a constant oxygen flow rate of 1000 cm^3/min until the 31st day (point C), at which time 333 g of charge was added to the oxidation tube. This addition caused an immediate increase in production rate, which remained steady for an oxygen flow rate of either 1000 or 2000 cm^3/min until the 53rd day (point D) when the rate began to decrease. On the 69th day (point E), the oxygen flow was stopped, but the charge remained at 1100°C for 10 days. When the oxygen flow resumed on the 79th day the production rate was higher than before the 10-day holding period; the reason for the increased rate is not known.

Curve 4 shows the production of IrO_2 from a charge of sheet scrap. This material oxidized faster than any other, producing about 16 g IrO_2/day for the first 30 days. The rate gradually decreased over the 48-day oxidation period with an oxygen flow rate of 1000 or 2000 cm^3/min. When the oxidation was stopped, about 500 g of the original 600-g charge had been collected as 580 g IrO_2.

In general, the production rate in a particular oxidation tube probably decreased with time for the following reasons:

1. Decrease in the amount of charge available for oxidation.
2. Partial sintering of the charge.
3. Oxygen channeling through the charge.
4. Retardation of oxidation by nonvolative oxides, which became increasingly concentrated on the surface of the charge as oxidation progressed.
5. A combination of (2) and (4), where sintering was enhanced by impurity oxides on the surface of particles.

In an effort to determine whether production rates might be increased by increasing the oxidation temperature, tube 11, a mullite tube containing sheet scrap, was operated for 47 days at 1300 and 1400°C. During this period the average production rate was similar to that of tubes operated at 1100°C; however, for about seven days midway through the operating period the production rate was about 30 g/day, or about three times the average rate for the period. Following this high output, the production rate dropped sharply to about 4 g/day. The sudden increase in production rate may have been caused by manually breaking up the partially sintered charge, which was sometimes done in an effort to stimulate production, in conjunction with the higher oxidation temperature. The sharp decline in production rate following the peak was probably caused by a decrease in the amount of charge and by partial sintering.

Production rates might also be increased by increasing the oxygen flow rate, as indicated by curve 1 in Fig. 6. Unfortunately, the condition of the charges changed continuously during oxidation, so that increasing either temperature or oxygen flow rate only temporarily increased the production rate. At any rate, increasing the oxygen flow rate would not be expected to cause a major effect, since only about 0.03% of the oxygen reacts to form IrO_2 during a typical oxidation period.

If each apparatus produced IrO_2 at the rate of 16 g/day shown by curve 4 in Fig. 6 for sheet scrap, 15 apparatus would be required to supply the estimated 6200 g needed each month for fabrication development under the MHW program. Allowing for equipment breakdown and lower-than-average production rates (say 10 g/day) a minimum of 25 apparatus would probably be required. Such an analysis emphasizes the need to increase the production rate per apparatus, thereby minimizing the number of apparatus and the repetitive operations performed with each apparatus.

Product Purity

The effectiveness of the purification process was assessed by comparing the chemical analyses of starting material and finished product, as shown in Table 4. The spark-source mass-spectrographic technique used to obtain these results has an accuracy of approximately 0.5 to 2 times the value reported. Values that differ by only a factor of 2 to 4, therefore, are not considered to be significantly different, while values which differ by a factor of 5 or more are considered to be significantly different.

Powder

The as-received powder had a total impurity content of about 1.5%, as shown in Table 4. Impurities exceeding 400 ppm were Ca, Fe, Ni, Pb, Pt, S, Si, and Tl. As-prepared IrO_2 was substantially lower in each of these elements; however, some other elements that were higher include Mo, Ru, Ti, and W. Iridium powder reduced from the acid-treated IrO_2 had a purity of about 99.97%, with the following major impurities (in parts per million): Pb, 30; Pt, 50; Rh, 30; Ru, 90; S, 30; and W, 30.

Sphere Scrap

The as-received sphere scrap had a purity of only 96 to 97%, with gross amounts of Ca, Fe, Mo, Pt, Rh, and Th (Table 4). Iridium powder reduced from acid-treated IrO_2 had a purity of about 99.98%. Tungsten (70 ppm) was the only impurity having a concentration greater than 20 ppm.

Sheet Scrap

The as-received material weighed about 7000 g and consisted of hundreds of pieces of various thicknesses and shapes. A representative sample for chemical analysis, therefore, could not be identified. Instead of analyzing the starting material, we reduced to metal a sample of IrO_2 resulting from oxidation and analyzed it before any acid treatment. Iridium powder reduced from as-prepared IrO_2 (Table 4) had the following prinicpal impurities: Ca, Cu, Fe, Ni, Pb, Pt, Rh, Si, Ta, and W. Each of these elements decreased in concentration after acid treatment, although the chlorine content increased. The chlorine and sulfur contents were probably residuals from the acid treatments. Iridium reduced from IrO_2 prepared at 1300 and 1400°C was similar in purity to material that had been oxidized at 1100°C except for higher potassium and lead contents.

Table 4. Analysis of Iridium Before and After Purification by Oxidation-Dissolution

Element	Content, ppm (Unless Otherwise Indicated)							
	Powder			Sphere Scrap		Sheet Scrap		
							Ir from IrO_2[b] Prepared at	
	Ir As Received	IrO_2[a]	Reduced Powder[b]	Ir As Received	Reduced Powder[b]	Ir Powder from IrO_2[a]	1100°C	1300, 1400°C
Al	20	5	1	300	0.5	10	2	6
As	0.1	1	<1	0.4	<1	<0.1	0.1	0.1
B	0.2	5	1	9	0.5	6	2	6
Ba	20	<1	<1	0.7	<1	<0.1	<1	<1
Bi	10		<1	100	<1	3	<1	<1
Br	<1	2	<1	2	<1	8	2	2
Ca	600	170	1	2000	3	60	2	0.6
Ce	<1	2	<1	2	<1	2	2	1
Cl	30	15	5	8	10	8	80	30
Co	90	3	0.2	3	0.5	0.3	0.1	0.3
Cr	30	25	2	100	2	30	3	10
Cu	50	4	3	500	3	50	2	2
Fe	1500	25	10	2000	2	200	30	10
Ga	<1	1	<1	0.6	<1	0.2	<1	<1
K	20	15	1	20	3	20	20	200
Mg	1	35	<1	10	<1	1	1	1
Mn	3	1	0.2	10	<0.2	3	0.3	0.3
Mo	10	170	<1	>>1%	5	10	10	3
Na	1	10	0.5	4	0.6	1	4	10
Nb	0.5	<1	<1	50	<1	10	<2	<1
Ni	700	4	3	300	3	100	2	2
Os	40	10	<3	<0.4	<3	<0.4	<1	<1
P	5	1	0.5	20	0.3	2	1	1
Pb	7000	700	30	200	1	60	6	60
Pd	6	<1	<1	20	<1	6	2	<1
Pt	1500	250	50	>1%	20	100	30	3
Rb	<1	5	<1	2	<1	2	2	2
Re	<0.3	<1	<3	2	<3	<0.2	<1	<1
Rh	150	15	30	>>1%	3	150	5	2
Ru	150	500	90	4	10	15	15	5
S	1000	120	30	100	3	30	30	30
Sb	40	<1	<1	0.3	<1	<0.1	<1	<1
Si	900	25	20	25	10	3000	3	3
Sn	6	<1	<1	60	<1	20	<1	<1
Sr	<1	<1	<1	0.5	<1	<1	<1	<1
Ta	<0.3	30	<5	30	<5	300	1	1
Te	0.7	<1	<1	<1	<1	<1	<1	<1
Th	<0.1	<0.1	<0.1	>1%	<0.1	1	<1	<1
Ti	4	125	0.5	1	<0.2	1	5	5
Tl	400	<10	<10	<10	<10	<10	<10	<10
V	30	20	1	1	<0.2	3	0.3	1
W	9	210	30	700	70	2000	300	300
Zn	3	2	<1	300	<1	10	3	1
Zr	0.3	1	<1	300	<1	0.1	0.1	0.1
Ir, %[c]	98.57	99.75	99.97	96.29	99.98	99.38	99.94	99.93

[a] As prepared at 1100°C.

[b] From acid-treated IrO_2.

[c] By difference.

The overall purity of iridium produced from the sheet scrap was about 99.93%, including 300 ppm W. Based upon the results of feasibility experiments, we expected the tungsten content to be lower. The oxides WO_3 and WO_2 may have had sufficiently high vapor pressures to migrate out of the hot zone and subsequently condense with IrO_2; however, WO_3 and WO_2 are soluble in hydrofluoric and nitric acids, respectively. We cannot explain, therefore, why the tungsten content of iridium prepared from sheet scrap, in particular, was much higher than that obtained in feasibility experiments discussed earlier.

Iridium Recovery

A material balance was made to determine the iridium recovery for the purification process starting with the impure charge and ending with the preparation of —40-mesh purified iridium powder. The results of this material balance are summarized in Table 5. The material charged into the oxidation tubes weighed 9425 g, including 90 g (minimum) of impurities. Approximately 96% of the total iridium charged was recovered, either as purified iridium powder (85.4%) or as incompletely purified material (10.7%) remaining in the oxidation tubes when the experiment was terminated. Approximately 4% of the iridium charged was lost during purification.

Table 5. Material Balance for Iridium Purification Process

Material	Weight (g)	Weight (%)
Sheet scrap (99.4% Ir)	6570	
Powder (98.6% Ir)	2396	
Sphere scrap (96.3% Ir)	459	
Total material charged into oxidation tubes	9425	
Less impurities	90	
Total iridium charged into oxidation tubes	9335	100.0
Recovered from oxidation tubes before purification was completed	995	10.7
Total subjected to complete purification process	8340	
Recovered purified iridium	7970	85.4
Lost in purification	370	3.9

Losses occurred at various stages of the process. Part of the material to be purified was in the form of fine (−325 mesh) powder, and the product of oxidation included both a fine powder and material to be crushed to powder. Although the product was crushed to pass a 40-mesh screen, the crushing actually produced much finer material. Fine powder could easily become airborne during various activities and was difficult to recover when involved in accidental spills. The following principal losses occurred in the indicated operations of the oxidation system: (1) iridium lost during crushing of impure powder compacts before charging into oxidation tubes; (2) losses during oxidation when rubber seals failed and allowed IrO_2 to escape from the systems; (3) IrO_2 lodged in the filter medium of the oxidation system; (4) IrO_2 lost during cleanout of the collection tubes; (5) IrO_2 lost during crushing to −40-mesh powder; (6) IrO_2 lodged in Pyrex and paper filters used to filter the acid solutions. Losses during acid treatment of various batches of IrO_2 powder ranged from 0.1 to 1%, indicating that losses due to acid dissolution of IrO_2 were small.

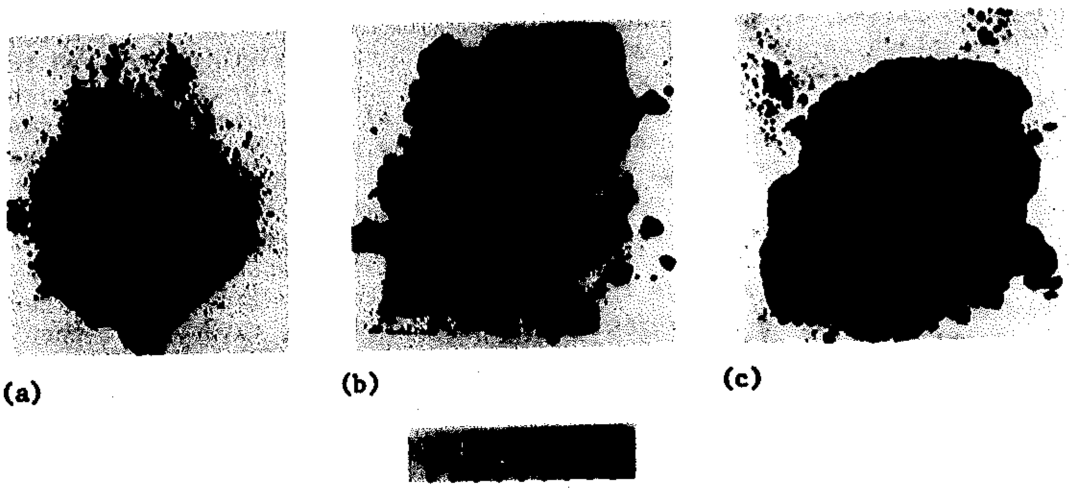
Compacting and Melting

The iridium powder prepared in this study was made into compacts, melted in an electron-beam furnace, and rolled into sheet to demonstrate that the material was fabricable and to provide material for research in the Multi-Hundred Watt program. The −40-mesh powder was blended with either tungsten (0.3 and 1.92 wt %) or rhenium (1.92 wt %), then made into compacts measuring about 1.8 × 1 × 0.3 in. by cold pressing at 50 tsi. The compacts were presintered at 1000°C for 1 hr in hydrogen. This resulted in a density of about 15 g/cm³ ($\rho_{Ir} = 22.5$ g/cm³). After vacuum sintering at 1500°C for 4 hr the density was typically 18.5 g/cm³. The compacts exhibited no unusual behavior during preparation, as compared with compacts prepared from some iridium obtained from commercial sources. Specifically, no difficulty was encountered in pressing the compacts, and normal outgassing and weight loss occurred during vacuum sintering. Figure 7 shows the powder from which a typical pressed-and-sintered compact was prepared.

Comments on the Process

The process as conducted in this study was rather laborious. The impure powder had to be pressed, sintered, and broken into lumps for charging into the oxidation tubes. Finely divided material produced by crushing the sintered compacts had to be recycled. Sheet scrap, which could be sheared into smaller pieces, was more easily prepared as a charge.

The oxidation and collection tubes were made of silica glass. As discussed previously, the IrO_2 sometimes formed a bridge between the collection tube and the surrounding oxidation tube. This occurrence usually resulted in breakage of the oxidation tube. Frequent cleanout



(a) (b) (c)

Fig. 7. Product of the Iridium Purification Process. (a) —40-mesh IrO_2 powder as prepared. (b) +40-mesh IrO_2 deposit as prepared. (c) —40-mesh iridium powder reduced from acid-treated IrO_2. Pressed-and-sintered purified iridium compacts were similar in appearance to the impure compact shown in Fig. 4.

of the collection tubes was necessary to minimize this problem, even though only 10 to 20 g IrO_2/day was being obtained from a single tube.

The hard crystalline IrO_2 deposit, which adhered to the bottom end of the collection tubes, could never be completely removed by mechanical means. This deposit caused cracks in the collection tube, which eventually resulted in a broken tube. Broken pieces with adhering IrO_2 had to be placed in hydrofluoric acid until the two materials separated. Although silica glass tubes were subject to breakage, adhering IrO_2 could be cleanly separated by the acid treatment.

Crystalline deposits of IrO_2 became crystalline masses of iridium when reduced with hydrogen, and were not suitable for blending with other metals; therefore, the crystalline IrO_2 had to be crushed to a smaller size. The material was crushed with a hardened steel mortar and pestle to pass a 40-mesh screen. Many fines were produced by this operation, and much of the crushed material was actually —325 mesh. The fines readily became airborne during the crushing and screening steps, resulting in some loss of material.

Treatment with five acid solutions with five or more washes in distilled water between successive acids followed by eight to ten washes after the last acid was laborious and time-consuming. Possibly we used more acid solutions than were actually required. The use of concentrated solutions of nitric, hydrochloric, and sulfuric acids along with hydrofluoric acid and aqua regia did not yield greater purity than was obtained in feasibility experiments, which used only the latter two solutions.

The most important problem associated with the process is the low IrO_2 production rate per apparatus obtained in this study, which was attributed to partial sintering and oxygen channelling through the charge. A different approach is needed to produce IrO_2. Perhaps a high-temperature flame in an oxygen atmosphere directed at a charge of scrap, lumps, or coarse granules would produce IrO_2 at a higher rate than was obtained in the present study.

SUMMARY AND CONCLUSIONS

A purification process involving oxidation of pure iridium to IrO_2 followed by chemical dissolution of impurities from the IrO_2 was used to treat about 9.4 kg of material. The results of this study allow the following conclusions concerning the process:

The IrO_2 production rate at 1100 and 1400°C decreased with time (Fig. 6). The most probable factors causing the decrease were a decrease in the amount of charge, partial sintering of the charge, and oxygen channelling through the charge.

The IrO_2 production rate at 1100°C was faster for a charge of sheet scrap than for more finely divided material such as coarse granules.

The IrO_2 production rate increased with temperature over the range 1100 to 1400°C, but the factors mentioned above can offset the effect of higher temperature.

The efficiency of oxygen usage was very low (typically about 0.03%); therefore, oxygen flow rate should not significantly affect IrO_2 production rates, although some interdependence was observed in the early stages of some oxidation runs (Fig. 6).

The process can produce iridium with a minimum purity of 99.98% (Table 4).

Tungsten was the only element not always reduced to the levels obtained in smaller scale feasibility experiments (Table 4).

Oxidation of the impure iridium at 1300 to 1400°C resulted in a product having a purity similar to that oxidized at 1100°C (Table 4).

Approximately 96% of the material charged into the oxidation tubes was recovered as purified iridium or as incompletely processed iridium (Table 5). Approximately 4% of the charge was lost during processing.

In pressing, sintering, or melting of the −40-mesh powder product we experienced no difficulties that were attributable to the material itself.

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