Platinum Group Alloy Containers for Radioisotopic Heat Sources

THERMOELECTRIC GENERATORS POWER SPACECRAFT INSTRUMENTS

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The conversion of heat energy, resulting from the decay of plutonium-238 dioxide, to electrical energy for spacecraft requires alloys capable of containing the isotopic fuel at temperatures up to about 2000°C and of withstanding impact velocities of 90 metres per second. The development and properties of a platinum-30 per cent rhodium-8 per cent tungsten and an iridium-0.3 per cent tungsten alloy doped with 40 ppm each of thorium and aluminium, which meet the stringent service requirements, are reviewed.

Voyager I and Voyager II spacecrafts were launched from Cape Kennedy on August 20 and September 5, 1977, and were in a position to explore Jupiter during March 1979. Electrical power for the on-board instruments is supplied by radioisotope thermoelectric generators (R.T.G.s) (1), and these are expected to operate for several years as the spacecraft journey on toward Saturn and Uranus. This power is obtained through the conversion of the heat energy released by the decay of plutonium dioxide ($^{238}PuO_2$) to electric energy with thermoelectric elements such as silicon-germanium. The isotopic fuel is contained within a heat source whose shape and dimensions are designed for maximum power density; but, more importantly, this component must also provide a reliable method of containing the fuel under normal and accident conditions within a 0.64 mm thick alloy capsule. The fabrication and the properties of the fuel-encapsulating alloys developed for this application are reviewed with the objective that the special alloys or processes developed might be used elsewhere.

Fabricable refractory noble metal alloys based on platinum, iridium or rhodium are the only fuel encapsulating materials capable of meeting the requirements of current isotopic heat sources. This restriction becomes evident when one follows a hypothetical mission profile of a R.T.G. aboard a spacecraft from launch followed by an accident. Figure 1 is a sectional view of the 18 cm diameter by 43 cm long heat sources aboard the Voyager spacecraft. The heat source assembly is constructed principally from graphite except for the outer iridium cladding and the iridium alloy capsule containing twenty four golf-ball-size fuel spheres. The capsule temperature for this design is normally 1300°C, but aerodynamic heating of the heat source on re-entry from orbit raises it to peak temperatures of 1600 to 1800°C for a few minutes. Calculations show that the fuel sphere assembly (FSA) consisting of the graphite impact shell, the iridium capsule and the fuel, upon re-entry would impact earth between 1200 and 1400°C at velocities of about 90 m/s. This event is followed by exposure of the alloy to temperatures between 600 and 800°C in air until the FSA is retrieved, possibly as long as one year later. Alternate heat source designs and other accident conditions predict capsule temperatures between 750 and 1900°C and high

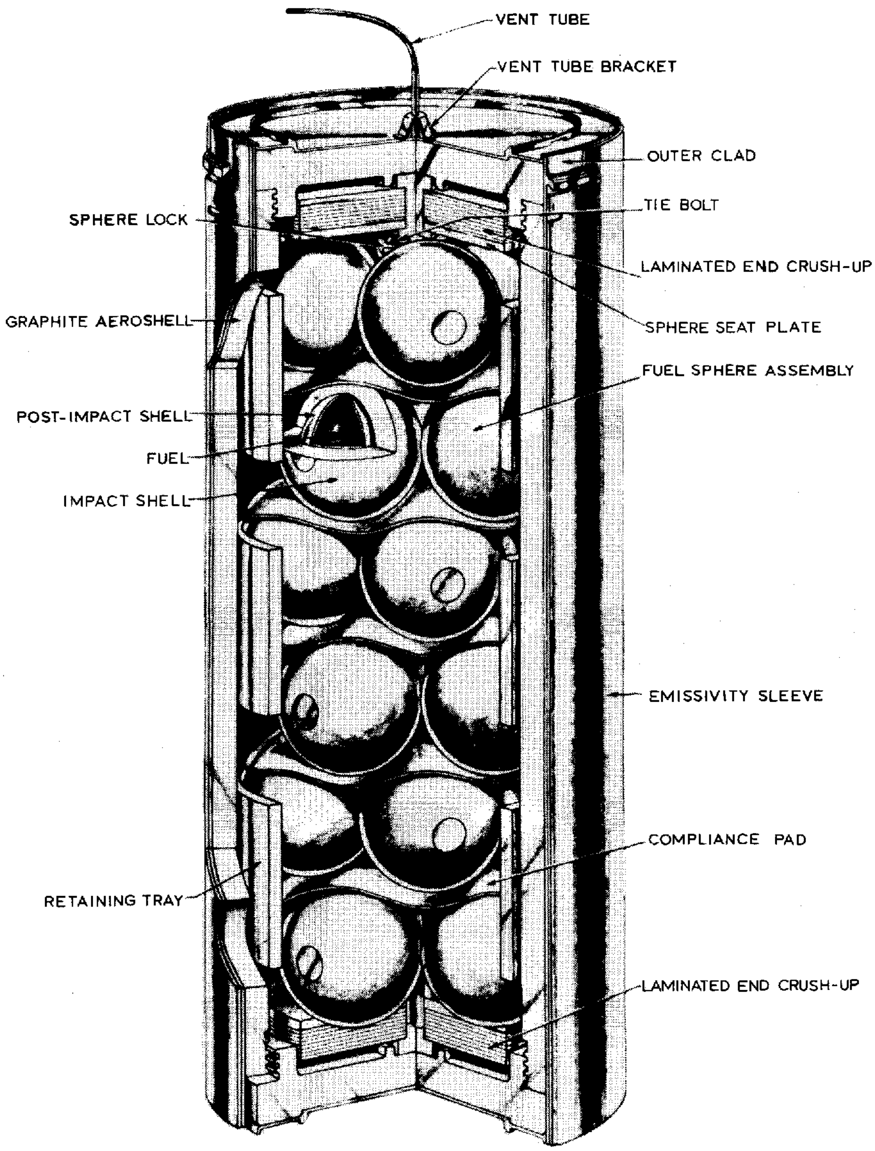

Fig. 1 Multi-Hundred Watt (MHW) heat source design illustrating how the isotopic fuel is contained by the alloy capsule, post-impact shell, in radioisotope thermoelectric generators

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strain rates on impact. These unusual conditions ruled out the conventional superalloys, such as used in the Apollo missions to the moon, on the basis of the service temperature, melting point, and compatibility with graphite and fuel. The multilayered refractory alloy structures such as the platinum-30 per cent rhodium clad tantalum alloys successfully used at lower temperatures in the Pioneer and Viking missions would suffer from oxygen embrittlement by the heat source environment (2) and are incompatible with graphite and

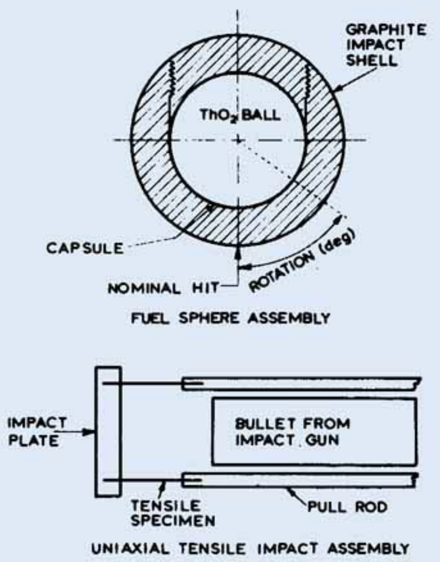


Fig. 2 Schematic arrangement of tests used to characterise impact behaviour of fuel capsule. The graphite impact shell and fuel simulant, ThO_2, sandwich the capsule

fuel at current design temperatures (3).

Early tests verified the reported carbon-iridium and carbon-platinum eutectic melting temperatures of about 2240 and 1734°C, respectively, and showed that the couples were compatible below their eutectic temperatures (4, 5). The compatibility of these metals with $^{238}PuO_2$ (6, 7) and the heat source environment was likewise established (8). On the other hand, the strength of platinum was concluded to be too low to survive impact, and its eutectic temperature with graphite restricted heat source designs to re-entry temperatures to about 1600°C. The deficiencies encountered with the initial evaluation of iridium were more obscure since impact tests of the iridium capsule resulted in as many failures as successes. Because the failures revealed no identifiable trends, it was not clear whether the erratic performance was due to the fuel, graphite, cladding, or interactions between them. Finally, the small vent holes (0.02–0.05 mm) drilled through iridium cladding were often filled with ceramic-like phases containing calcium, tungsten and silicon mixed with vapour-transported iridium. These plugs restricted the venting of helium released by the decay, α-particle emission, of the $^{238}PuO_2$. If the vents plugged completely, the helium pressure buildup would, of course, rupture the capsule.

Alloy Design Considerations

Two new alloys have been developed and qualified for heat source applications. The first is a platinum-base alloy, designated as Pt-3008 (9), which contains 30 weight per cent rhodium and 8 weight per cent tungsten. This alloy affords adequate high temperature strength, has a melting point of 2000°C, and has acceptable fabricability and oxidation resistance. In this alloy system the increase in the melting point and strength with the tungsten level is accompanied by an increase in the oxidation rate and difficulty of fabrication (10). Tests indicate that temperatures should be about 1100°C maximum for normal service and under accident conditions should be held by design to under 1800°C, the carbon-Pt-3008 melting temperature (11).

The second alloy is iridium-0.3 per cent tungsten doped with about 40 ppm each of thorium and aluminium. This alloy, designated as DOP-4 iridium (12), is capable of more severe service conditions than Pt-3008 by virtue of its greater strength and higher melting temperature in contact with graphite, greater than 2200°C. The upper temperature limit for continuous service is about 1400°C. Its development was based on extensive data which showed that neither high purity nor strengthening with up to 4 per cent tungsten (13) or 1 per cent hafnium (14) could prevent brittle intergranular fracture, especially under impact conditions (15). This intrinsic grain boundary weakness, which is concluded to be characteristic of iridium and its alloys, is effectively overcome by the dopants (16).

The technology adopted to produce heat-source-quality cladding includes rather elaborate processes and testing methods not routinely employed. Their use reflects the need for a highly reliable component with reproducible properties and the high sensitivity of the mechanical properties of noble metal alloys to the presence of trace elements. The results of the development work illustrating this interdependence have been extracted from the referenced reports and are presented below. Discrepancies in the existing data uncovered during this work will be mentioned. Development activities not directly related to heat source technology resulted in new data and are included as points of information.

Trace Element Effects Depend on Strain Rates

The schematic arrangement of the tests used to determine the impact behaviour of the fuel capsule is shown in Figure 2. The top drawing is the configuration of the FSA subassembly, which is heated to the impact test temperature, then fired from a gas gun against a granite block to simulate performance under re-entry situations. These tests substitute ThO_2 for PuO_2 but otherwise use materials having the same dimensions as the units installed in a flight system, see Figure 1. The apparatus in the lower drawing tests only the cladding and thus eliminates any influence of the PuO_2, ThO_2, or graphite. The metal projectile at ambient temperature is fired from a gas gun at an end-plate to fracture dual sheet specimens heated to the impact temperature.

Visual evidence of the pronounced effect of trace elements on FSA impact tests is shown by the photograph in Figure 3. The curves on the left, determined by uniaxial impact

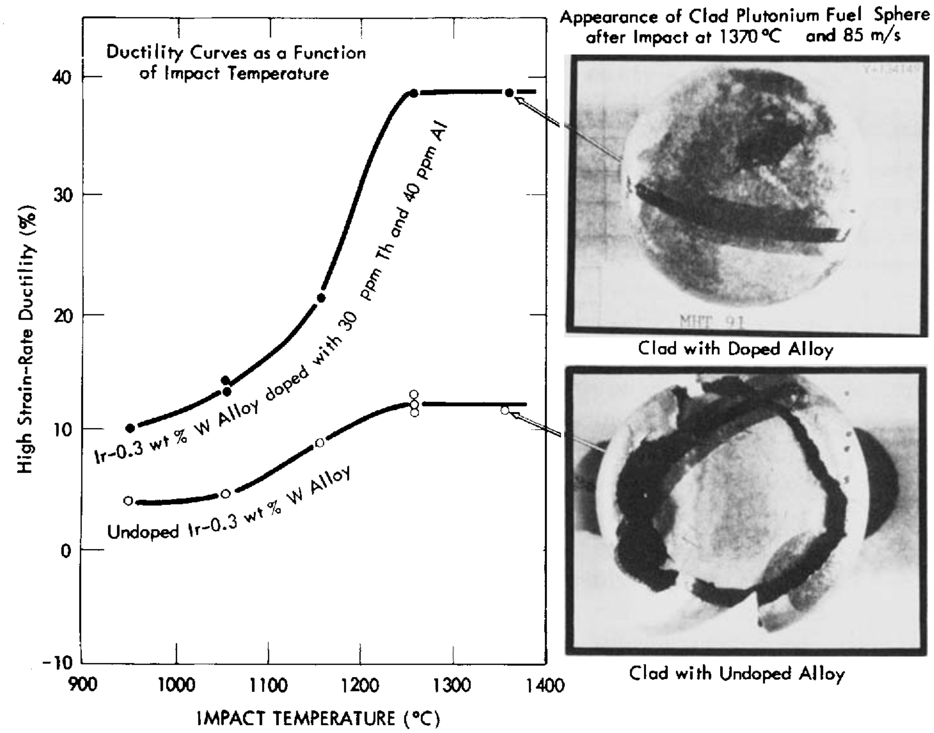
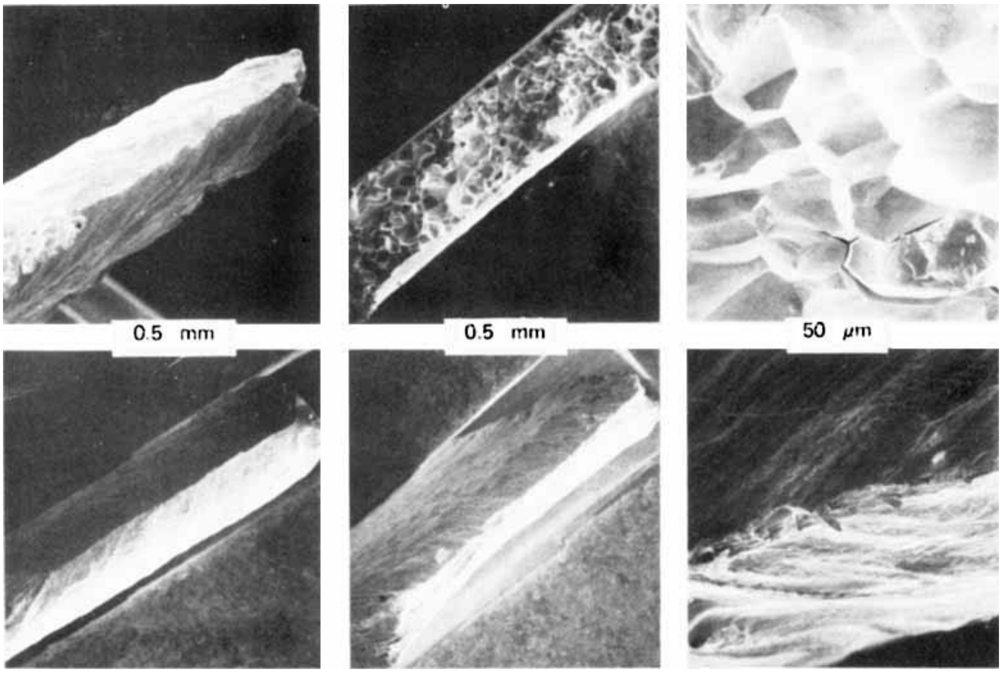


Fig. 3 The ductility curves and the photographs of the fuel spheres after impact show that the high-temperature fracture toughness of iridium fuel cladding is markedly improved by doping with very small amounts of thorium and aluminium



Tensile test at 1093°C and 85 μm/s — Impact test at 1250°C and 85 m/s — Impact test at 1250°C and 85 m/s

Fig. 4 Undoped Ir-0.3% W alloy (top row) is ductile at a test velocity of 85 μm/s but is brittle at 85 m/s. Alloy doped with thorium and aluminium, bottom row, is ductile even at 85 m/s

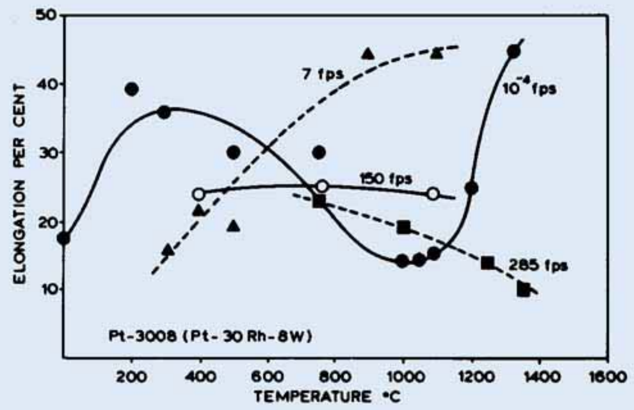
tests, show a four-fold increase in the fracture strain at 1350°C, from 10 to 40 per cent elongation, by doping iridium-0.3 per cent tungsten with only 30 ppm thorium and 40 ppm aluminium, and explain why rupture occurred in the undoped but not the doped alloy. However, at low strain rates, for example less than 0.1 mm/s, nearly all the iridium alloys studied have ductilities of 40 to 60 per cent (13, 16) above 1000°C, and sheet specimens neck to a knife-edge as shown in Figure 4 (left panel). The ductility of the undoped alloys decreases approximately linearly with the strain rate (16), and specimens fail by brittle fracture at test velocities of 85 m/s, whereas the ductility and the fracture mode of the doped alloy remain essentially unchanged (right panels).

The ductility of Pt-3008 at high strain rates in the temperature range of interest, 750 to 1000°C, is greater than at low strain rates, shown in Figure 5, unlike the iridium alloys. The alloy survived impact at 85 m/s in FSA tests between 750 and 1250°C (17). Consequently the effects of impurities rather than dopants were extensively studied to determine which elements were responsible for the pronounced ductility minimum near 1000°C at test velocities below 0.1 mm/s ($\sim 10^{-4}$ fps). Impurities such as boron (18) and phosphorus (19) known to form low-melting phases with noble metals have been implicated. When the alloy is thermally aged for extended times at about 1100°C, the ductility minimum at 1000°C disappears; however, the alloy now becomes brittle at about 1300°C because silicon segregates to the grain boundaries (20).

Role of Dopants in DOP-4 Iridium

Thorium strongly segregates in DOP-4 iridium, its concentration being about 5 to 15 atomic per cent at the grain boundaries compared with only 30 ppm in the bulk. Alloying with at least 5 ppm thorium does not

Fig. 5 The ductility of Pt-3008 between 760 and 1000°C is greater at high than at low strain rates. Test velocities shown are 85, 45, 2.1 and < 10^{-4} m/s



increase the average thorium level at the grain boundaries (21) but does increase the amount of second phase particles, tentatively identified as $ThIr_5$ (16). Aluminium, on the other hand, is distributed in diffuse wavy bands within the grains and is not present in abnormally high levels at the grain boundaries. As might be expected, the dopants tend to produce elongated grains and retard grain growth (22). Figure 6 shows that the impact ductility of doped or undoped iridium-0.3 per cent tungsten depends strongly on the grain size; however, DOP-4 is always more ductile than the undoped alloy for any grain size, implying another beneficial effect of doping.

Environmental Reactions

The alloys are compatible with the heat source environment, which consists of small quantities of gases desorbed from hot structures (13), the dissociation products of compounds such as PuO_2, and volatile impurities in the components. Phosphorus contamination and its segregation to the capsule grain boundaries has occasionally been observed (19, 23); however, the source of this contamination remains to be established. Enhanced grain growth in the iridium capsule occurs in some simulated heat source environments, and the location of these larger grains at the capsule surface suggests that a gas-metal reaction promotes grain growth; however, the potential deleterious effect on impact behaviour can be reduced by increasing the level of thorium from 30 to, for example, 100 to 200 ppm.

Air oxidation of specimens, simulating exposure of the capsule after impact, degrades the tensile properties of Pt-3008 at 800 and 1000°C but not at 600°C, see Figure 7. The progressive loss of ductility at the higher temperatures with time to 3000 h is attributed to the enhanced diffusion of oxygen promoted by tungsten, and the eventual embrittlement beyond 3000 h to the internal oxidation of tungsten to tungsten-rich oxide particles,

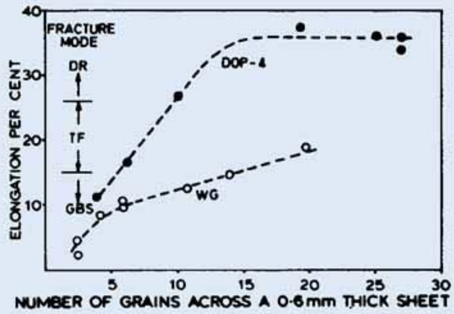


Fig. 6 The impact ductility of DOP-4 iridium at 85 m/s is greater than that of undoped Ir-0.3%W (WG) at 1350°C because of the presence of thorium and aluminium. The ductility of both alloys is sensitive to the grain size. Sheet thickness is 0.6 mm. DR=ductile rupture, TF=transgranular fracture, GBS=grain boundary separation

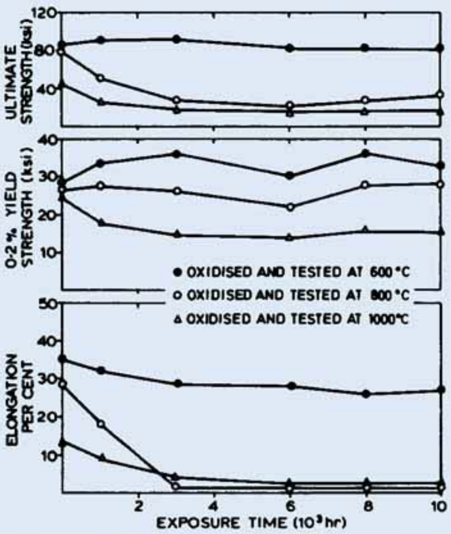


Fig. 7 Air oxidation of Pt-3008 degrades the tensile properties at 800 to 1000°C but not at 600°C. 1 ksi = 6.895 MPa

shown in Figure 8. This result, expected from the studies of Betteridge (24) and Chaston (25), represents the trade-off between increasing the strength and melting temperature of the alloy and lowering its oxidation resistance. In contrast, these characteristics are not observed in iridium alloys. The tensile properties of iridium-0.3 per cent tungsten doped with thorium to 500 ppm are unaffected by oxidation for 1000 h at 670 or 870°C (11); and internal oxidation of iridium-2 per cent tungsten and iridium-4 per cent tungsten was not observed in 1800 h at 770 to 1000°C (13).

The oxidation rates of Pt-3008 in still air, shown in Figure 9, are slightly higher than the accepted values for rhodium and platinum (26). Weight change data, at intervals to 10,000 h, show uniform weight increases in specimens oxidised at 600 and 800°C and weight losses at progressively slower rates at 1000°C. Our reaction rates for unalloyed iridium at 1000°C in air flowing at 0.1 m^3/h (13) are only slightly lower than Phillips' data (26); however, his results are more than two orders of magnitude greater at 870°C and differ by about four orders of magnitude at 770°C. One explanation for the conflicting results is that 24 h tests, such as those used by Phillips, were too short to detect the end of transient oxidation behaviour of iridium, which occurs after about 200 h at 770°C, as shown in Figure 10.

Alloy Processing

Fuel spheres for the heat source are encapsulated in two hemishells, which are joined together by tungsten arc-welding. The hemishells are formed from stress-relieved blanks. Conventional processes are used to fabricate the sheet from which the blanks are cut. Because the alloy properties are sensitive to trace elements and to the microstructure,

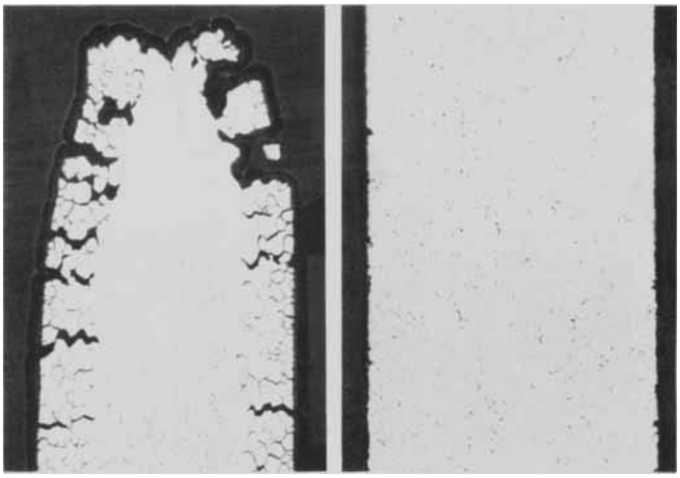


Fig. 8 Cross-section of Pt-3008 oxidised in still air at 800°C. (Left) Surface embrittlement due to oxygen diffusion down grain boundaries after 1000 h exposure. (Right) Tungsten-rich particles after 3000 h exposure embrittle alloy, for the effect of this on some physical properties see Figure 7 ×65

the special steps described below were adopted to ensure property conformance (10,16,17,27).

All vendor-supplied noble metals are pre-purified by arc or electron beam melting. A master alloy of either 50 per cent rhodium or 50 per cent platinum with tungsten is used to prepare Pt-3008, and the dopants in DOP-4 iridium are added as iridium-2 per cent thorium and iridium-2 per cent aluminium.

Arc melting under about 10 kPa (0.1 atm) argon is the preferred method of alloying, as this process eliminates vaporisation losses associated with electron beam melting and the porosity and contamination that occur in induction-melted alloys. Ingots or previously extruded rolling bars are framed in molybdenum and molybdenum cover sheets, heated in air to 1200°C, and cross-rolled to sheet at a finishing temperature of about 900°C. Molybdenum, besides having the same rolling characteristics as the noble metal alloys, is used to facilitate handling and minimise heat losses in the rather small ingots, 19×19×64 mm, and reduces the contamination of the alloy surfaces with imbedded noble metal oxides and foreign particles from the furnace. Any high-temperature process such as annealing or actual service is always preceded by extensive cleaning procedures; these include acid pickling, electrocleaning in 2 *N* or saturated potassium cyanide solution with stainless steel cathodes at 5 to 10 V a.c., and scrubbing. The potassium cyanide solution is required to remove acid-insoluble noble metal oxide films, and imbedded particles which cause weld cracking. Both oxide films and particles, when reduced to metal, are known to restrict helium venting from the capsule.

Recrystallisation of Pt-3008 sheet cold rolled about 50 per cent in thickness begins in 1 h at 950°C and is complete at 1050°C.

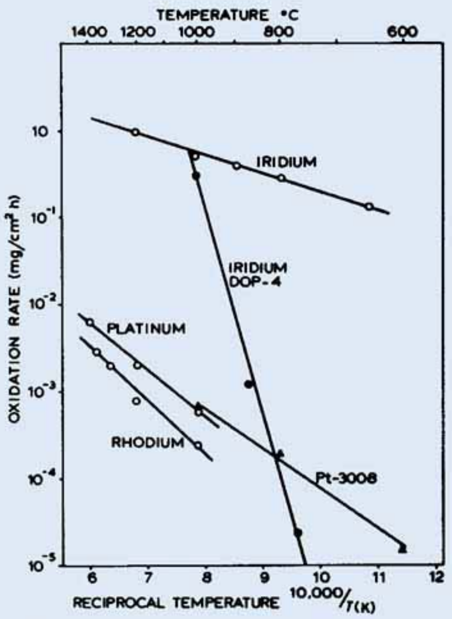


Fig. 9 Oxidation rates of Pt-3008 and DOP-4 iridium are comparable to rates of platinum and rhodium, at anticipated post-impact temperatures of 600 to 870°C

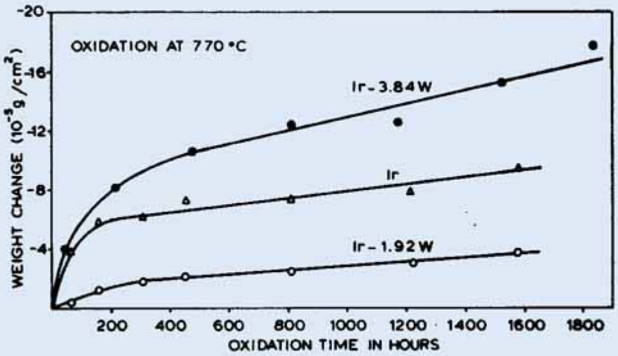


Fig. 10 Iridium and Ir-W alloys exhibit transient oxidation behaviour up to about 200 h of air exposure at 770°C

Hemishells are formed at room temperature on blanks stress-relieved between 850 and 900°C. Also, DOP-4 iridium can be cold rolled approximately 50 per cent in thickness. Anneals for 15 min show that in this condition recrystallisation begins at 1000°C and is complete at 1200°C (22). Hemishells are formed at 900°C from stress-relieved blanks in tooling maintained at about 500°C (28).

In conclusion, the advances in heat source design are a direct result of the desire and/or need to increase the conversion efficiency of heat to electrical energy, long-term reliability, and safety of R.T.G.s. This aim is reflected in the evolution of the fuel capsule from the initial use of conventional superalloys to multilayers of refractory alloys, then finally to the noble refractory alloys. The alloys described above represent the present state of the art and are considered to be the optimum cladding for ^{238}Pu oxide.

Acknowledgements

This review of the major points of work by my colleagues was intentionally brief and does some injustice to the exhaustive work done.

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