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AUTHOR(S): Lynn B. Lundberg

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

# REFRACTORY METALS IN THE SPACE AGE

by

Lynn B. Lundberg

## ABSTRACT

Growth in the utilization of refractory metals (Zr, Hf, V, Nb, Ta, Cr, Mo, W, Re, Ru, Os, Rh, Ir) has seen a steady but measured increase in recent years because of their special properties. Their high melting points and concomitant high temperature strengths allow for such things as higher thermodynamic efficiencies in heat engine designs, but other properties such as practical superconductivity at reasonable temperatures and resistance to highly corrosive chemicals are probably being utilized more in today's applications. Current applications range from the use of niobium-base alloys in superconducting magnets to the use of zirconium containment vessels for corrosive chemicals. Recently developed applications of refractory metals are surveyed in relation to their unique properties, and some plans for their utilization in future space applications are discussed. New innovations in alloy composition and fabrication that have opened doors to new applications of the refractory metals are also discussed.

## INTRODUCTION

Refractory metals are characterized by those transition elements that make up the lower right-hand corner of the periodic table. They can be found in Groups IVA to VIII. The classification 'refractory metal' is somewhat arbitrary, but it is usually applied to the elements Zr, Hf, V, Nb, Ta, Cr, Mo, W, Re, Ru, Os, Rh, and Ir. As indicated in Table I, they all have melting points in excess of 2100 K, and the highest melting metal is tungsten, 3685 K. Technetium is also classed as a refractory metal, but because it is not naturally occurring and because even its most stable isotopes are radioactive, it has found little or no application. Consequently, technetium will not be included in this discussion.

Refractory metals and alloys are usually perceived as being used in applications that demand survivability at the highest temperatures—for example, the use of tungsten wire as a filament in incandescent lamps. However, as we will see, the primary uses of several refractory metals do not involve high temperatures.

Along with the advent of the Manhattan Project and the resulting nuclear age came great strides in the development of our understanding and utilization of refractory metals. For example, because of its low absorption cross-section for thermal neutrons, zirconium and its alloys were developed for use in nuclear reactors for electrical power generation. However, the conclusion of the project that put men on the moon, the Apollo Program, marked a significant downturn in the progress of the development of refractory metals and alloys. It is fair to say that the major developments in refractory metal technology occurred in a thirty year period ending about 1972. In the meantime there has been a slow but steady development of new applications for refractory metals and alloys even though the rate of development of new alloys has been drastically reduced.

This paper provides a discussion of some current and near-term applications of the refractory metals and their alloys. The paper is not intended to review the uses of these materials but rather to illustrate some unique applications that derive from their unusual properties.

## GROUP IVA REFRACTORY METALS

### Zirconium

Pure zirconium melts at 2125 K and has a close-packed hexagonal crystal structure up to 1135 K where it transforms to body-centered cubic. Most of the applications for zirconium are restricted in operating temperature so as to prevent this transformation from occurring. Zirconium is a very reactive metal that burns with a brilliant white light when reacted with oxygen. Because of this property, zirconium foil has been used for many years as the illumination source in photo-flash bulbs. In spite of its high level of reactivity, zirconium has excellent corrosion resistance due to the development of very stable, adherent surface layers that strongly inhibit further reaction.

As previously mentioned, zirconium has special properties that are very useful in the core of a nuclear reactor. Its low absorption cross-section for thermal neutrons and excellent resistance to corrosion by water make zirconium and its alloys uniquely suited for use in water-cooled nuclear-power reactors. Many reactors operating in this country today utilize zirconium alloys for the fuel cladding. The most commonly used alloys for nuclear applications are those that contain up to 2 wt% tin or 3 wt%

niobium. The use of zirconium in this application has been on a steady decline in recent years, following more or less the current decline of the nuclear power industry.

The use of zirconium in the chemical industry is not new—it has been used, for example, in urea fertilizer manufacturing for nearly 30 years[1]—but because of changes in economics and a re-examination of overall cost considerations, there has been recent growth in the application of zirconium in the chemical industry where corrosion resistance is the primary concern.

Zirconium's resistance to corrosion by concentrated nitric, sulfuric, and hydrochloric acids is particulary outstanding.[2] It is also resistant to most organic acids and nearly all alkaline solutions. The resistance to corrosion by hot nitric acid of the unalloyed zirconium produced by Teledyne Wah Chang Albany (TWCA), Zircadyne 702, is compared graphically in Fig. 1 with several commonly used corrosion resistant metals and commercial alloys.

At present, zirconium is used mostly as a construction material in the chemical processing industry. The components which are commonly fabricated from zirconium include heat exchangers, stripper or drying columns, reactor vessels, piping, pumps, and valves. The heat transfer capabilities of zirconium compares with most stainless steels (See Table I). Structure size has not been a serious fabrication problem as a column has been fabricated from zirconium that is over 33 m long and over 2 m in diameter.

**TABLE I. Selected Properties of Refractory Metals**

| Element | Melting Point (K) | Room Temperature Thermal Conductivity (W/m · K) | Room Temperature Young's Modulus (GPa) |
|---|---|---|---|
| Zr | 2125 | 21.1 | 99 |
| Hf | 2495 | 23 | 137 |
| V | 2178 | 31 | 130 |
| Nb | 2741 | 53 | 103 |
| Ta | 3269 | 54.4 | 186 |
| Cr | 2148 | 67 | 248 |
| Mo | 2883 | 142 | 320 |
| W | 3683 | 160 | 407 |
| Re | 3453 | 71.2 | 460 |
| Ru | 2583 | 117 | 469 |
| Os | 3300 | 87.6 | 558 |
| Rh | 2236 | 150 | 380 |
| Ir | 2720 | 147 | 517 |

## Hafnium

Even though hafnium metal has a high melting temperature (2495 K) and exhibits chemical behavior much like zirconium, it is not generally used for structural applications by itself or as the base metal in an alloy. The primary source of this metal is as a by-product from the production of nuclear-grade zirconium. Its primary usage is as an alloying element in other metals such as niobium, tungsten, or nickel. Hafnium foil has been used as the illumination material in special high-intensity photo-flash bulbs. It has been found to be a very effective minor addition to coatings that are applied to gas-turbine hot sections to improve the oxidation resistance of these components.

## GROUP VA REFRACTORY METALS

### Vanadium

The primary use of vanadium is as an alloying agent in steel. The favorable neutronic properties of vanadium have long been appreciated, and recently V-15Cr-5Ti has become one of the prime candidates for application in nuclear fusion devices as a first-wall material that contains the fusion reaction products and the coolant or tritium breeding material. This application requires this alloy to operate up to only 875 K.[3]

### Niobium

Niobium, sometimes called Columbium, which has a melting temperature of 2741 K has been proposed for high-temperature nuclear applications but has never been operated in anything but developmental systems. There is new interest in applying alloys such as Nb-1Zr in nuclear reactors intended for supplying electrical power to spacecraft.[4] The proposed uses include fuel cladding, reactor coolant containment, and high-temperature structures. The resistance of niobium-base alloys to attack by alkali metals at high temperatures is well known and is needed along with high-temperature strength in these power-system applications.

Niobium and its alloys are being considered for use in the first-wall containment structures of magnetic confinement fusion energy devices. The potential alloys for use in this application were recently identified by Pionke and Davis.[5] The expected use of niobium-base alloys in this area is not firmly established because they will be used only if an economic advantage can be gained over competing materials of construction.

A relatively new and exciting application of niobium-base alloys is in superconducting electromagnets. These magnets, which are capable of producing very high magnetic fields in highly confined spaces, are planned for use in magnetic-confinement nuclear-fusion devices, but a currently developing and equally exciting application is in the area of high-resolution, magnetic-resonance systems used for diagnostic imaging in humans. This is a remarkable technique in that high-resolution, tomographic images can be obtained nonsurgically in most parts of the human body.

Nb-Ti (45-55 wt% Ti) alloys and $Nb_3Sn$ have practical superconductivity for magnet applications at temperatures slightly below 20 K. These materials are 'type II' superconductors, which means they can operate to very high magnetic fields, often of the order of tens of teslas, before their superconductivity is quenched. Also, type II superconductors can operate at current densities up to 10 $GA/m^2$. (A review of the characteristics and theory of type II superconductors can be found in Ref. 6.).

For magnet applications, these materials are typically produced in wire form in which the superconductor has been drawn into fine filaments that are surrounded by high-conductivity copper. The cross-section of a typical Nb-Ti superconducting magnet wire is presented in Fig. 2. This design results in magnet wire that provides optimal steady-state performance along with resistance to damage due to momentary, localized loss of superconductivity.

The production of the multifilamentary wires used to wind the superconducting magnets is an extremely sophisticated exercise in metal working. In the case of Nb-Ti, it involves placing superconductor rods into holes drilled into a copper bar which is extruded and then drawn into wire. This process produces a wire that is made up of many continuous superconductor filaments that are completely surrounded by and metallurgically bonded to copper.

The process is slightly more complicated in the production of $Nb_3Sn$ multifilament superconducting magnet wire because of the brittleness of this intermetallic compound. For this material, it is necessary to start with pure niobium rods that are reacted with tin that is included in the starting composite structure after the wire has been drawn to final size.

Another relatively new application for niobium is in the construction of sodium vapor lamps such as those commonly used for street lighting. In this application, advantage is taken of two fortunate quirks of nature, which are 1) that the thermal expansion behaviors of niobium and alumina ($Al_2O_3$) are nearly identical and 2) that both of these materials are resistant to attack by sodium vapor at high temperatures. A typical lamp configuration is seen in Fig. 3. The niobium electrodes are hermetically sealed into the ends of either a translucent alumina (Lucalox) or a transparent alumina (single crystal saphire) tube. A small quantity of sodium is introduced into this sealed assembly and heated electrically to vaporize it and produce the characteristic orange-yellow light by thermal excitation of sodium vapor.

A true 'space age' application of niobium-base alloys is illustrated by the use of C-103 (Nb-10Hf-1Ti) in small rocket engines. Niobium-base alloys are being utilized extensively in small rocket engines used primarily for spacecraft attitude control. A bi-propellant rocket thruster currently produced by the Marquardt Company can be seen in Fig. 4. The combustion chamber and nozzle of this thruster are made from C-103 that is coated with a fused silicide coating for corrosion prevention. The combustion chamber is electron-beam welded to a bare C-103 injector. The use of C-103 in these rocket engines allows them to be operated, uncooled, at temperatures in excess of 1300 K.

## Tantalum

Tantalum and its alloys are used primarily in the electronic industry for capacitors and in the chemical industry.[7] As previously noted in Fig. 1, tantalum has excellent resistance to corrosion by acids and bases. Because of its excellent corrosion resistance and good fabricability, tantalum is being applied more and more in the chemical industry. Typical applications include bayonet heaters, vapor condensers, multitube heat exchangers, thermowells, reaction vessels, and loose-lined or clad equipment. Most of these applications take advantage of the high thermal conductivity of tantalum which is about three times that of zirconium or Austenitic stainless steels.

Hydrogen embrittlement has been a problem in the use of tantalum in the chemical industry, but new alloys such as Ta-2 wt% Mo have been found to be much less susceptible to hydrogen embrittlement in severe corrosion environments.[8]

Tantalum-base alloys are being considered for space nuclear-power applications.[4] Alloys such as T-111 (Ta-8W-2Hf) are being considered for application in the reactor system because of their high temperature strength and resistance to attack by lithium.

## GROUP VIA REFRACTORY METALS

Even though this group of refractory metals has many practical applications, the pure metals all suffer from brittle behavior near room temperature and below. This behavior has a devastating impact on the fabricability of these metals. In spite of their low-temperature brittleness, all the metals of this Group have good high-temperature strength, which makes them useful in many applications.

### Chromium

Chromium is used for such things as an alloying agent in steel, nickel- and cobalt-base superalloys, and bright finish electroplating. It is a primary ingredient in stainless steels. The pure metal and most high-chromium alloys are brittle at room temperature so that no significant applications have developed for them.

### Molybdenum

A recent symposium covered many of the current and near-term applications of molybdenum and its alloys.(9) These applications included such things as isothermal forging dies, gas turbine rotors, glass-melting electrodes, and semiconductor heat sinks.

An isothermal forging process called Gatorizing, developed and patented by Pratt and Whitney, utilizes the molybdenum alloys TZM (Mo-0.5Ti-0.08Zr) or MHfC (molybdenum strengthened with HfC) for the dies that are used to form superalloys such as IN100 into complex shapes in one squeeze at high temperatures.(10) The diagram in Fig. 5 indicates the general characteristics of the process. TZM and MHfC are used because they have high strength and hardness in the temperature range 1145 to 1475 K, have high thermal conductivity, and are machinable using conventional methods.

A recent study demonstrated that a silicide-coated, uncooled TZM turbine wheel could be used in a short-life gas turbine engine.(11) A small turbojet demonstrator engine was operated successfully with this type of turbine wheel for 7 h with a maximum turbine inlet temperature of 1616 K.

Molybdenum is being used at an increasing rate for electrodes in the melting of glass with electric power.(12) In this process, illustrated in Fig. 6 an electrical current is passed through molten glass which is maintained in a molten condition by the resultant ohmic heating. Molybdenum is quite resistant to attack by the molten glass, but it must be protected from air oxidation above 800 K.

Molybdenum is being used for semiconductor heat sinks because it has a thermal-expansion coefficient close to silicon and because it has a high thermal conductivity.(13) (See Table I for a comparison of thermal conductivity of the pure refractory metals.) It is one of the best materials for dissipating the heat generated in silicon semiconductor devices during operation.

The high thermal conductivity of molybdenum is also one of the properties that make this metal useful for mirrors in high-powered lasers. Other properties of molybdenum that prove useful for this application include its high stiffness and its ability to be polished to a highly reflecting finish.

Because of its high reflectivity and high melting point, molybdenum is being used extensively for heat shields in high-temperature inert atmosphere/vacuum furnaces. Most of the high-temperature parts of the majority of the hot isostatic pressing (HIP) furnaces going into service today use molybednum for heat shields and resistance heating elements. HIP processing of metal parts is a new and rapidly growing industry today.

Other interesting applications for molybdenum and its alloys include those found in mini-thruster rocket motors used for satellite station keeping. An augmented catalytic hydrazine decomposition mini-thruster design recently developed by the Rocket Research Company[14] is shown schematically in Fig. 7. Because of its good resistance to attack by hydrazine decomposition products, Mo-41Re is used for many of the parts that come in contact with the hot gases such as the heat exchanger inner- and outer-body and the thruster nozzle. Pure molybdenum is being used for the radiation heat shields in this design.

Molybdenum has many useful properties, but the pure metal and many of its alloys are brittle near room temperature. This is a strong deterrent to the use of this metal because the room temperature brittleness causes considerable difficulty in fabrication and handling. Brittleness in molybdenum is drastically reduced by the addition of large amounts of rhenium, but due to the high cost and density of rhenium, high-rhenium Mo-Re alloys have seen only limited use. An application of Mo-41Re has already been mentioned. However, by taking advantage of a phenomenon called solid solution softening in this alloy system, brittleness can be greatly reduced by adding only 11 to 13 wt.% rhenium to molybdenum.[15] These particular alloys are being considered for application in space nuclear-power systems.[4]

## Tungsten

Because it is the highest-melting metal known to man, tungsten is in a unique category. However, in the recrystallized condition, it suffers from brittleness at temperatures well in excess of room ambient. As previously mentioned, one of the most common uses of pure tungsten is as an incandescent filament. Before the development of the transistor it was also used extensively as a hot cathode material in vacuum tubes. Pure tungsten sheet or foil is frequently used for radiant-heat shields in high-temperature vacuum furnaces with the capacity to operate in the vicinity of 2800 K.

A recent improvement in the application of tungsten for incandescent filaments has come as a result of applying solution softening to tungsten. Tungsten is solution softened by the addition of about 5 wt.% rhenium, which yields filaments with drastically reduced failure rates in cyclic applications such as flashing marque lights. A similar alloy is used for the augmentation heater element in the augmented catalytic thruster previously described (see Fig. 7).

There is considerable interest in the use of pure tungsten prepared by a chemical vapor deposition process for an emitter surface in a nuclear-heated thermionic electrical power generator to be used in space.[4] The emitter structure would also be used to contain the nuclear fuel, $UO_2$, and it would be expected to operate for very long times at emitter temperatures in the neighborhood of 1700 K.

Because of good ion emission properties, tungsten with 2-5 wt.% $ThO_2$ is commonly used for electrodes in gas tungsten arc-welding devices. This material is also used in some high-temperature applications where good creep strength is required.

## GROUP VIIA REFRACTORY METAL

### Rhenium

As seen in Table I, rhenium metal is the second highest-melting refractory metal. Its use has been very limited, partly because of its scarcity. Most of the rhenium produced in the US comes as a by-product of copper ores. A recent application of rhenium has been as a catalyst in the production of unleaded gasoline. As a result of this application, the cost of rhenium was temporarily driven to very high levels when unleaded gasoline was forced on the scene by mandate of the US Government. The demand has since diminished so that rhenium metal powder is currently selling for around $300 per pound. This is nearly a 10-fold reduction in price from its previous high.

Pure rhenium metal has also seen application as a hot catalyst in hydrazine monopropellant mini-thrust rocket engines similar to that seen in Fig. 7. A similar design considered several years ago used the radioactive decay heat of $^{238}$Pu instead of an electrically heated wire as the heat source.[16] Pure rhenium metal is also being considered for use as the heat exchanger and nozzle of the augmented catalytic thruster shown in Fig. 7.[14]

## GROUP VIII REFRACTORY METALS

### Ruthenium

Ruthenium is used as a hardener for platinum and palladium alloys which are used for such things as long-wearing, high-performance electrical contacts. High-ruthenium alloys are used for pen points because of their high hardness. A significant space age application for ruthenium is in thick-film paste systems used for printed circuit elements.[7]

### Osmium

Osmium has the distinction of having the highest elastic modulus of all of the refractory metals. As with ruthenium, this refractory metal is used in applications requiring high hardness. Applications of osmium include fountain-pen nibs, phonograph needles, and electrical contacts.[7]

### Rhodium

Rhodium metal is not generally used in either the pure form or in high-rhodium alloys, but it finds considerable application in platinum-base alloys. These alloys are used in hostile, elevated-temperature environments for crucibles, furnace windings, glass-working equipment, thermocouples, and especially catalysts. Small amounts of pure rhodium are used for such applications as reflective coatings on mirrors, plating of sliding electrical contact surfaces, and a nontarnishing finish plate on jewelry articles made of white gold or silver.[7]

Rhodium plate is used to improve the heat-shield performance of the external shell found around the augmented catalytic thruster illustrated in Fig. 7.

### Iridium

A major use for iridium is as a crucible material for producing large, pure, defect-free single crystals for the electronic industry. Iridium is also used as an alloying element to harden platinum and is used in spark plugs for jet engine igniters.[7]

This refractory metal also has a space age application. Ir-1W is used as a container material for $^{238}PuO_2$ in radioisotopic thermoelectric generators (RTGs) used to power deep-space probes such as Galileo and Ulysses.[17] The alloy is used in this application both for its chemical compatibility with $PuO_2$ and its oxidation resistance at very high temperatures. A cutaway view of a 250-W heat-source module currently used in some of these devices is seen in Fig. 8. The iridium containment shell is buried deep inside secondary containment structures that are required to prevent dispersal of the $^{238}PuO_2$ into the earth environment during atmoshperic reentry of the spacecraft or other unplanned events.

## CONCLUSION

This sampler of the applications of refractory metals should serve to illustrate their extreme utility and should indicate the fact that they represent much more than a group of laboratory curiosities. As we learn more about this class of metals, their utilization is certain to grow into areas unimagined at this point in time.

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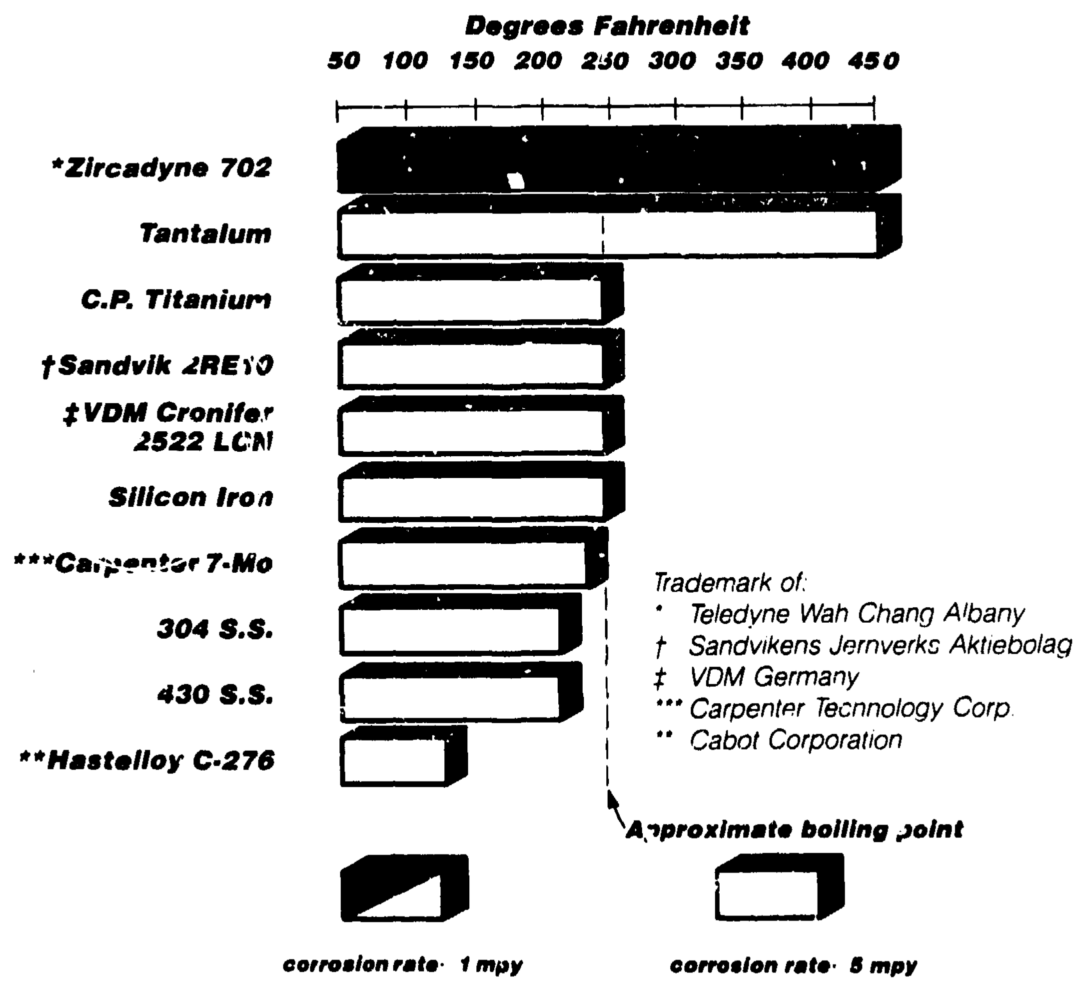


**Fig. 1.** Comparison of the corrosion resistance of Zircadyne 702 (ASTM 60702) with various metals in 60-65% nitric acid. (From Teledyne Wah Chang Albany.)

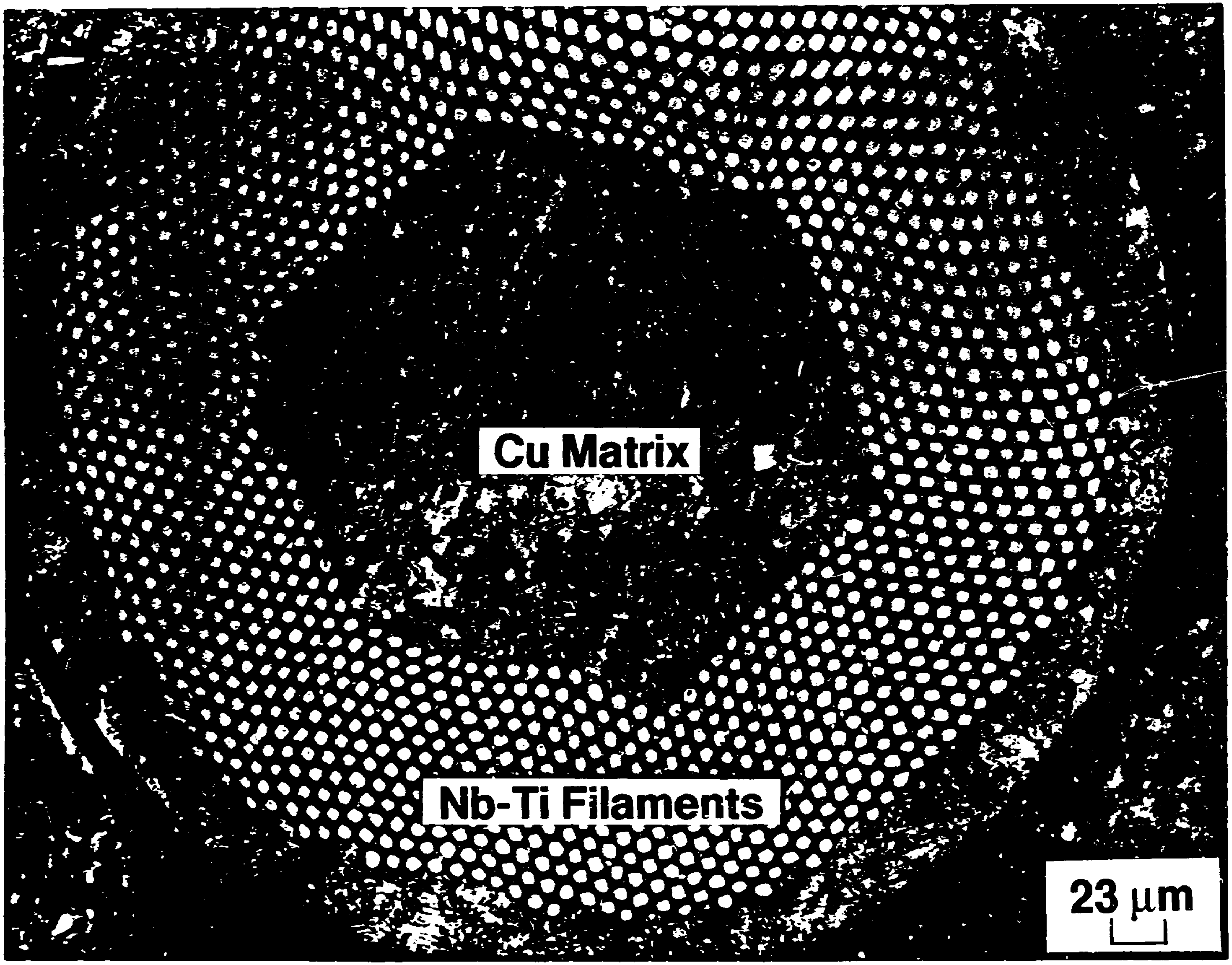


Fig. 2. Superconducting magnet wire cross-section.

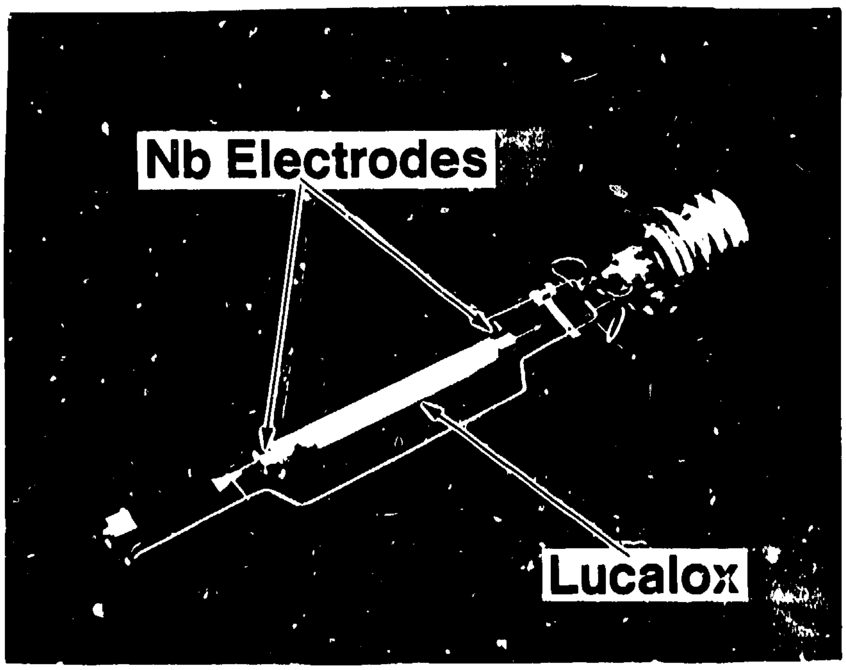


Fig. 3. Sodium vapor lamp with the envelope removed.

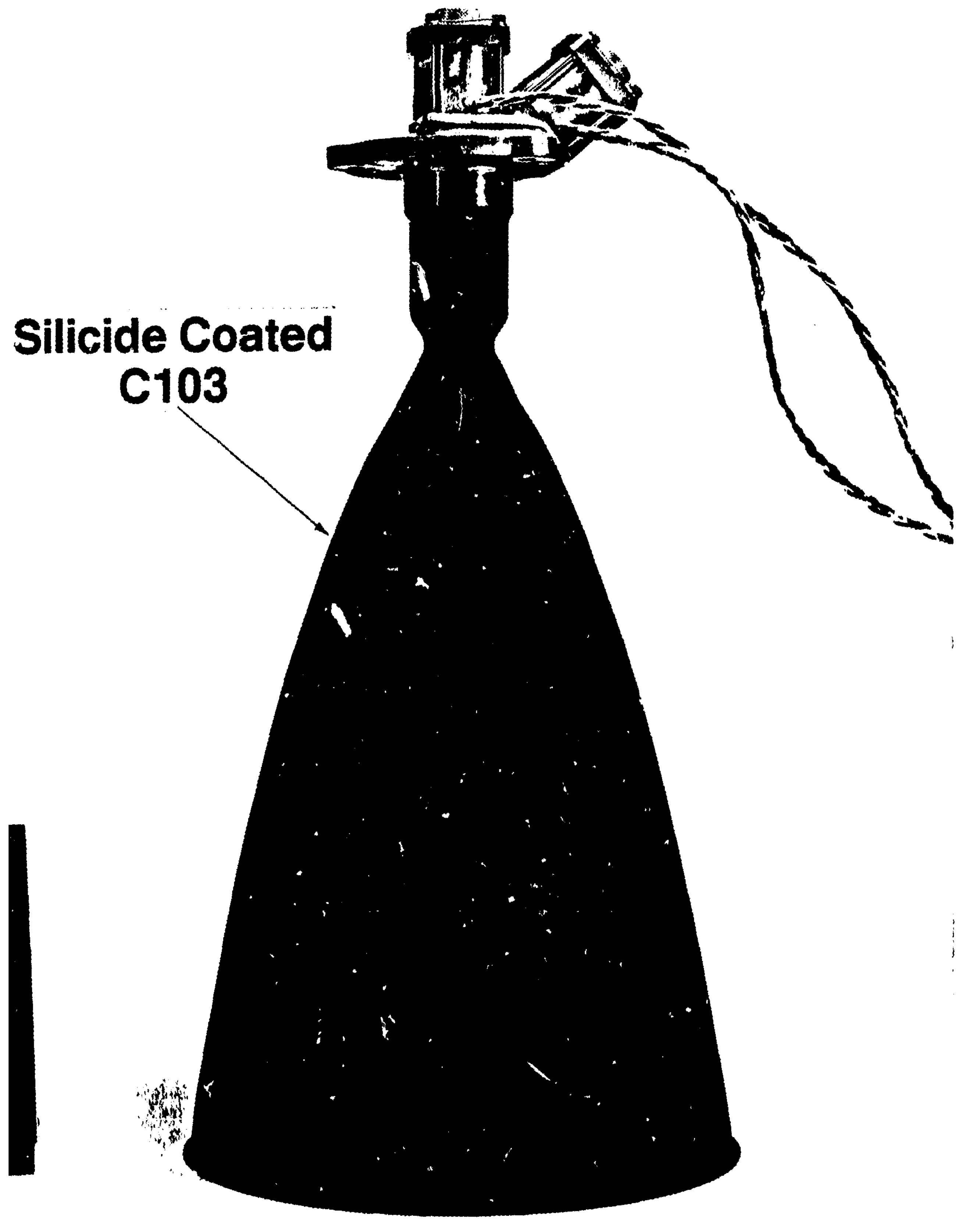


Fig. 4. The 100 Lbf bi-propell· nt rocket thruster, Model R4D-11, produced by the Marquardt Company.

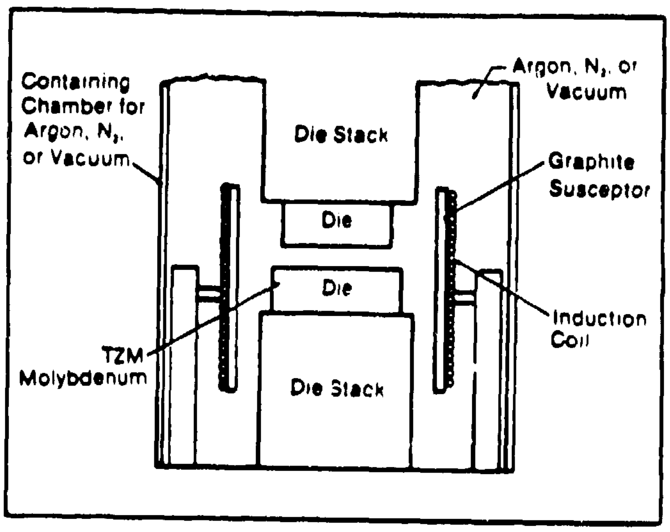


Fig. 5. Schematic diagram of a Gatorizing forgi ng press.[10]

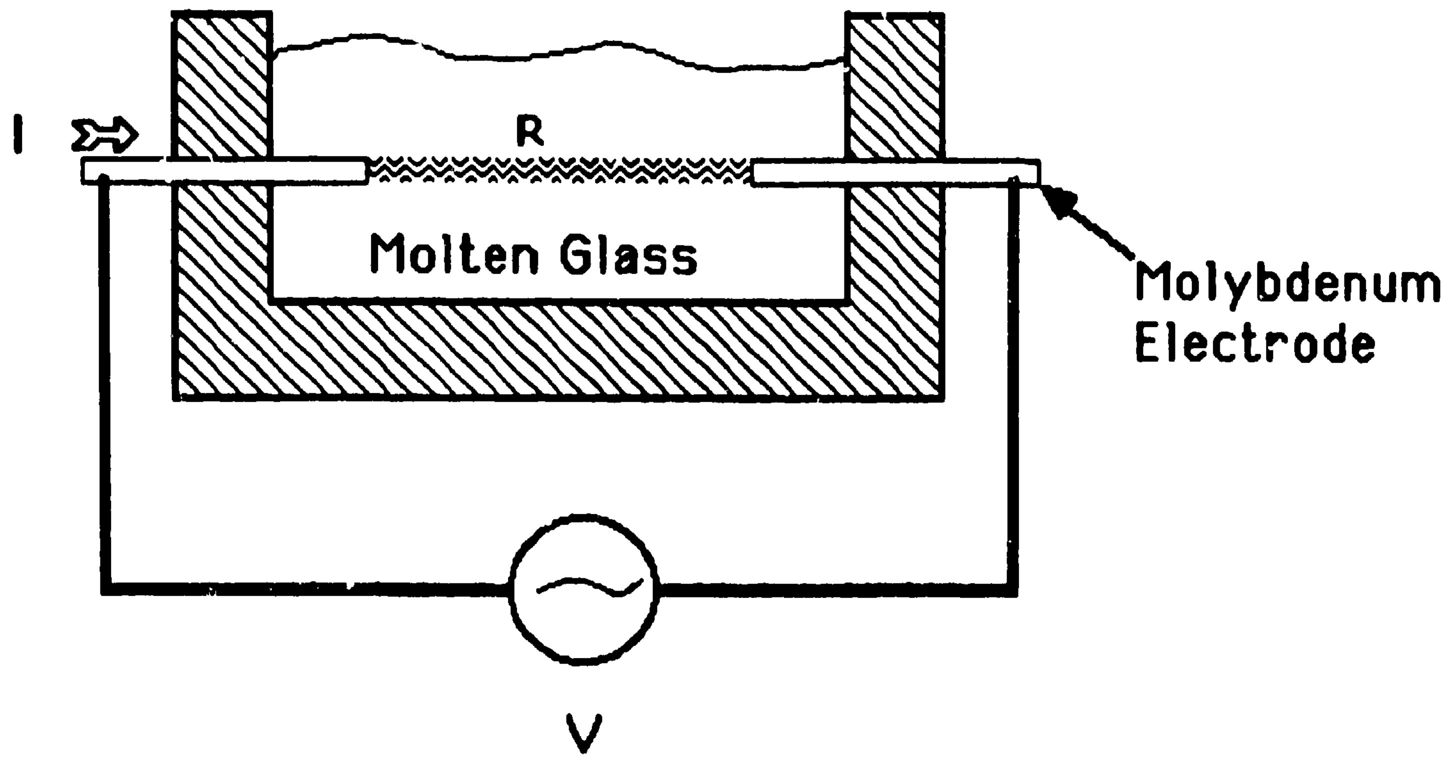


Fig. 6. Schematic of an electric glass-melting furnace.[12]

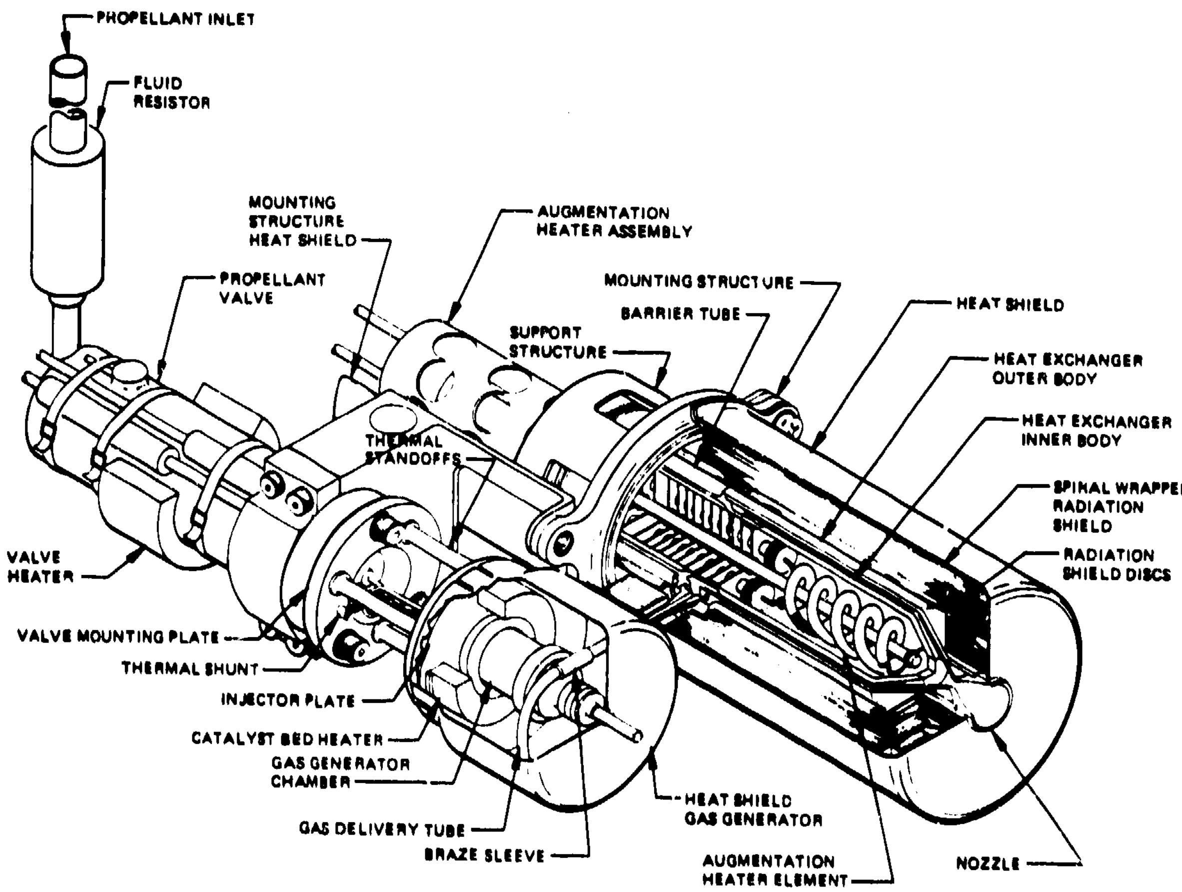


Fig. 7. Augmented catalytic thruster design layout.[14]

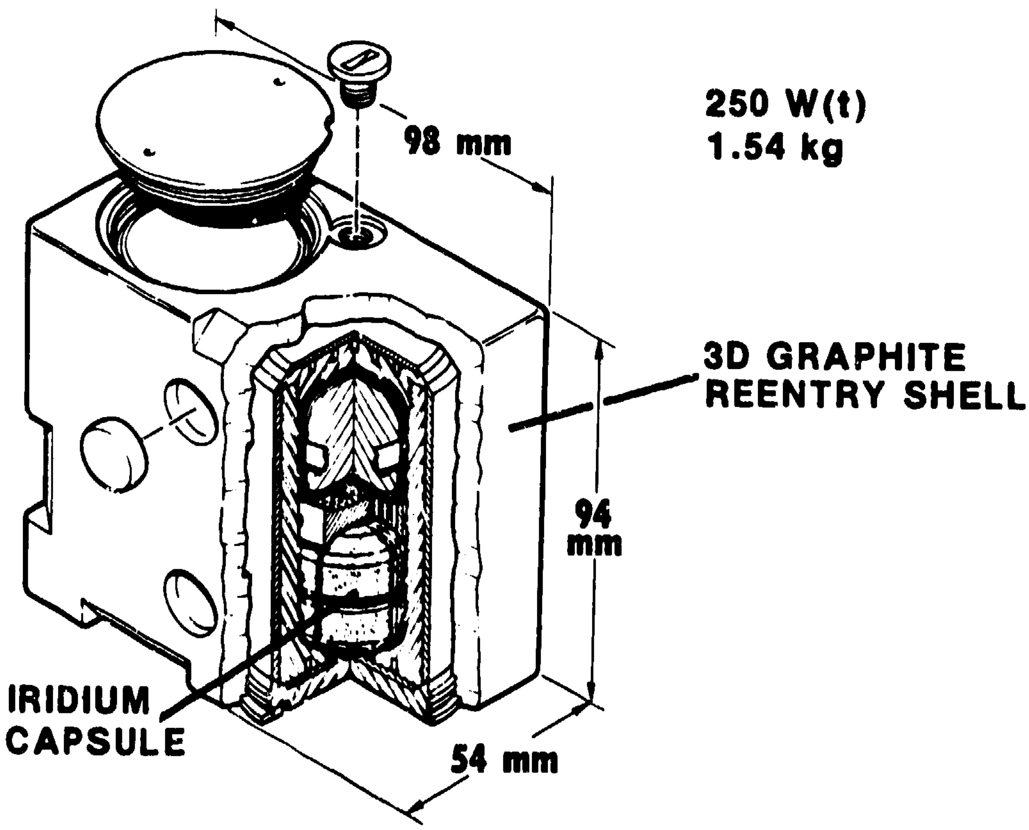


Fig. 8. Radioisotopic General-Purpose Heat Source used in RTGs for space power.