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Brian D. Reed, James A. Biaglow, and Steven J. Schneider
Lewis Research Center
Cleveland, Ohio

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Brian D. Reed, James A. Biaglow, and Steven J. Schneider
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Radiation-cooled rockets are used for a range of low-thrust propulsion functions, including apogee insertion, attitude control, and repositioning of satellites, reaction control of launch vehicles, and primary propulsion for planetary spacecraft. The key to high performance and long lifetimes for radiation-cooled rockets is the chamber temperature capability. The material system that is currently used for radiation-cooled rockets, a niobium alloy (C103) with a fused silica coating, has a maximum operating temperature of 1370 °C. Temperature limitations of C103 rockets force the use of fuel film cooling, which degrades rocket performance and, in some cases, imposes a plume contamination issue from unburned fuel. A material system composed of a rhenium (Re) substrate and an iridium (Ir) coating has demonstrated operation at high temperatures (2200 °C) and for long lifetimes (hours). The added thermal margin afforded by iridium-coated rhenium (Ir/Re) allows reduction or elimination of fuel film cooling. This, in turn, leads to higher performance and cleaner spacecraft environments. There are ongoing government- and industry-sponsored efforts to develop flight Ir/Re engines, with the primary focus on 440-N, apogee insertion engines. Complementing these Ir/Re engine development efforts is a program to address specific concerns and fundamental characterization of the Ir/Re material system, including (1) development of Ir/Re rocket fabrication methods, (2) establishment of critical Re mechanical property data, (3) development of reliable joining methods, and (4) characterization of Ir/Re life-limiting mechanisms.

INTRODUCTION

Radiation-cooled rockets are used for a variety of low-thrust propulsion functions, including apogee insertion, attitude control, and repositioning of satellites, reaction control for launch vehicles, and primary propulsion for planetary spacecraft. The majority of radiation-cooled rockets use nitrogen tetroxide (NTO)/monomethylhydrazine (MMH) or NTO/hydrazine (N₂H₄) bipropellant combinations. The key to high performance and long lifetimes for radiation-cooled rockets is the thermal and oxidation limits of the combustion chamber.

The state-of-the-art (SOA) material system for radiation-cooled rockets is a niobium alloy (C103) with a fused silica coating (R512E), which has been in use for over 20 years. Although C103 has a high melting point, it is very susceptible to oxidation, necessitating the protective silica coating. The silica coating, however, has a temperature limitation of 1370 °C. Fuel film cooling is employed in C103 rockets to maintain this thermal limit. The use of extensive amounts of fuel film cooling in low-thrust rocket engines significantly degrades performance and, in some missions, represents a source of plume contamination.

A material system composed of a rhenium (Re) substrate and an iridium (Ir) oxidation-resistant coating offers substantially higher temperature capabilities. Ir-coated Re (Ir/Re) rockets have a maximum operating temperature of 2200 °C, which for NTO/MMH or NTO/N₂H₄ propellants, allows for nearly optimal performance and extended chamber lifetimes. Long-life operation (hours) of Ir/Re rockets, at temperatures from 1925 to 2200 °C, has been demonstrated at 22-, 62-, and 440-N thrust levels (ref. 1), at performance levels significantly above SOA C103 rockets.

Despite demonstrations of Ir/Re rocket performance and life, the technology has not yet been used in flight systems because of fabrication and engineering concerns. There are ongoing NASA- and industry-sponsored efforts to develop flight Ir/Re engines, primarily for applications requiring 440-N thrust levels. Complementing these flight engine development efforts is a program to address concerns that have arisen during development and to provide fundamental characterization of the Ir/Re material system. This report will summarize the ongoing Ir/Re NASA technology program.

Ir/Re DEVELOPMENT HISTORY

In the mid-1980's, an effort was initiated to find a material system capable of sustained operation at 2200 °C in oxidizing rocket combustion environments (ref. 2). Refractory metals, ceramics, composites, and carbon-carbon materials were evaluated as substrate materials. Platinum (Pt) group metals, Engle-Brewer compounds, and ceramics were considered as oxidation-resistant coatings. Monolithic Ir-Re-rhodium (Rh) alloys and ceramic/metal (CERMET) alloys were also considered.

As a result of this material screening, a combination of Re (substrate) and Ir (oxidation-resistant coating) was selected. Re has a high melting point (3175 °C), excellent high temperature strength, and does not have a ductile-to-brittle transition point, which makes it unique among refractory metals. Ir is oxidation resistant and has a temperature capability of 2400 °C and a coefficient of thermal expansion close to that of Re. Fabrication of Ir/Re parts had been demonstrated in an earlier Air Force technology program (ref. 3), in which chemical vapor deposition (CVD) was used to coat a mandrel with Ir and then Re. This CVD process will be described in greater detail later.

Under a NASA technology program with Gencorp Aerojet (ref. 2), 22-N demonstrator rockets were fabricated (by using CVD) and tested on NTO/MMH propellants. One rocket was operated over 15 hr and 2700 cycles, at 2200 °C wall temperature, without failure. A flight-type, 22-N Ir/Re engine demonstrated a specific impulse I_{sp} of 310 sec, at an area ratio of 150:1. This performance is 20 sec above that provided by SOA 22-N, C103 engines. The Ir/Re engine was also subjected to over 100 000 pulses without failure. Figure 1 shows the 22-N Ir/Re rocket firing at a 2200 °C outer wall temperature.

In a follow-on NASA technology program (ref. 4), Aerojet demonstrated an I_{sp} of 305 sec for a 62-N engine (75:1 area ratio) on NTO/MMH. This again represented a 20-sec increase in performance over a 62-N, C103 engine of the same design. In the same technology program (ref. 5), a 440-N engine (286:1 area ratio) was tested for over 6 hr. This flight-type engine achieved 322 sec on NTO/MMH, a 12-sec increase over 440-N class, C103 engines. The production of 62- and 440-N engines also demonstrated the scalability of the process.

Ir/Re technology was proposed for the primary propulsion engine on the Mariner Mark II spacecraft (ref. 6). A mass savings of 600 kg for the Comet Rendezvous and Asteroid Flyby (CRAF) mission was estimated through the use of Ir/Re technology. However, the state of Ir/Re technology was considered immature at the time. As a result, SOA C103 rockets were baselined on Mariner Mark II and ultimately used in the Cassini mission. Ir/Re rockets were proposed as drop-in replacements of the Shuttle Orbiter reaction control system thrusters (ref. 7). In this proposed application increased lifetimes for the chambers, rather than performance, were the drivers.

Currently Ir/Re development efforts center on the production of high-performance, 440-N class rockets for the next generation of apogee insertion engines for geostationary satellites. Ir/Re has the thermal margin to offer nearly the maximum performance possible for NTO/MMH and NTO/N₂H₄ propellants. The same engine class also has application to NASA planetary exploration missions. In the course of these efforts to develop flight Ir/Re engines, concerns have arisen about (1) the reliability and cost of Ir/Re rocket fabrication methods, (2) the integrity of the Re mechanical property data base, (3) the ability to join Re chambers to dissimilar metals, and (4) the nature of Ir/Re life-limiting mechanisms. A NASA program was undertaken to address these concerns (summarized in fig. 2) in order to aid the efforts to bring Ir/Re technology to flight engines.

Ir/Re FABRICATION PROCESSES

Because Re cannot be machined by using conventional metal working techniques, an Ir/Re fabrication process that is cost effective, reproducible, and lends itself easily to production-type operation is critical to the acceptance of this technology for flight systems. Several Ir/Re fabrication options are being explored as discussed in the following sections.

Chemical Vapor Deposition

CVD is currently the only established process for fabricating Ir/Re chambers. CVD is a method of plating which relies on the chemical reaction of a vapor at a surface to form solid structural deposits (ref. 8). Because deposition occurs on an atom-by-atom basis, purity levels above 99 percent are achievable. In CVD processes, gaseous precursors of Ir and then Re are flowed over a heated mandrel that conforms to the contour of the chamber. Upon contact with the mandrel, thermal decomposition of the gaseous precursor occurs, which results in the deposition of the material onto the mandrel. After the Ir and Re layers are deposited in this manner, the mandrel is then chemically

removed, leaving a free standing Ir/Re chamber. Successful production of CVD structures depends on the deposition parameters, including the gaseous precursor of the material to be deposited, the mandrel material and temperature, the gas concentration and flowrate, reaction chamber geometry and pressure, and deposition thickness.

CVD has been used to produce 22- to 440-N class chambers, demonstrating the scalability of the process. The CVD process produces dense, adherent, and high purity Ir coatings. However, there are concerns about the integrity of the CVD Re substrate. The CVD Re substrate is deposited in multiple layers (usually three or four). When heated the individual Re layers tend to separate, allowing slippage (ref. 9). This phenomenon has been shown to lead to some variability of CVD Re mechanical properties, which is highly undesirable for the design and incorporation of flight engines.

Powder Metallurgy Re/Electroformed Deposited Ir

Powder metallurgy (PM) is an alternative fabrication process that shows significant promise. In the PM process, high-purity Re powder is pressed and sintered, producing Re ingots of about 95 percent density. The density of the pressed and sintered Re is then increased to above 99 percent via a hot isostatic pressure (HIP) treatment. After the HIP treatment, the Re ingot is electrical discharge machined into the desired chamber contour. An ongoing technology program (Private communication from M.J. Hamister regarding NASA Contract NAS3-27738-I, July 1996) would modify the PM process to produce near-net shape Re chambers, saving processing time and material. It has been shown that the PM Re process provides repeatable quality and PM samples have tensile strengths comparable to or above those of CVD Re. The PM process is only applicable to the Re substrate fabrication. A separate process is required for application of the Ir coating.

Electroformed deposition (ED) has been used to apply Ir coatings to PM Re substrates (ref. 10). In the ED process, a plating bath acts as an electrolytic cell. The workpiece to be coated serves as the cathode, while the anode is either an aqueous or molten salt solution of the material to be plated. The workpiece is immersed in the bath and current is passed through the anode, transferring ions of the material to the workpiece. To date, molten salt plating baths have been the only successful method of depositing thick Ir coatings. The 22- and 220-N class PM Re substrates have been coated by using ED and tested on various propellant combinations (refs. 11 and 12). It has been found that, to produce an adherent ED Ir coating, it is necessary to perform a post-densification HIP process (ref. 12).

Maturing Ir/Re Fabrication Processes

There are other candidate processes for fabricating the Ir coating or liner, the Re substrate, or the entire Ir/Re chamber. These alternative processes are currently less mature than the CVD and PM Re/ED Ir. Chambers composed of a thin CVD Ir/Re shell, overwrapped with a carbon-carbon fiber weave (which bears the mechanical loads) have also been demonstrated (ref. 13). The key to the acceptance of any these Ir/Re fabrication alternatives is their ability to provide reproducible, production-type quality parts at costs comparable to or lower than CVD and PM Re/ED Ir.

Re MECHANICAL PROPERTY DATA BASE

Accurate data on Re mechanical properties are critical to the design and integration of Ir/Re engines. Tensile and fatigue data are necessary for assessing the engine's ability to survive the stresses induced by the launch vibration environment. Data on annealed samples are particularly important, as they simulate the condition of the engine after hot fire acceptance tests on the ground. Creep data are important in determining the engine's response to multiple, long-duration on-orbit firings.

Currently the data base for Re mechanical properties is scattered. Reported data often do not include the fabrication or material history. This information is crucial to interpreting and applying the data. In particular, there is a lack of data on the manufactured Re forms of interest for rocket applications. To address this data shortfall, a NASA program was initiated to establish a Re mechanical database, with emphasis on CVD and HIP PM Re samples. Tensile, low cycle fatigue, and creep data have been accumulated on Re both at room and elevated temperatures (refs. 14, 15, and 16). Some of the accumulated mechanical data are summarized in tables I to III.

The data collected to date indicate that the properties of Re are strongly dependent on its fabrication method and history. There was some variability in the CVD Re data, probably because of slippage between Re layers at elevated

temperatures. HIP PM Re was characterized by sharp failures with almost no necking of the sample. CVD and HIP PM Re samples completed 100 cycles of fatigue testing and demonstrated sufficient tensile strength for the rocket application (ref. 15). More data, particularly data pertaining to low cycle fatigue, will be required for the proper design of Re engines.

JOINING OF Re TO DISSIMILAR METALS

For the flight engines, the Re chambers need to be joined to injectors and nozzle skirts composed of dissimilar metals. Common injector materials include 304L stainless steel (SS), titanium (Ti), and C103. Since Re is a heavy material and high-temperature capability is not needed downstream of the throat region, Re engines will employ C103 nozzle skirts. Both the injector-to-chamber and the chamber-to-nozzle joints are subjected to thermal cycling from 25 °C to a maximum of 1370 °C, with the number and duration of the thermal cycles dependent on the application.

Because of its reliability and relative ease, electron beam (EB) welding would likely be the preferred method of joining Re chambers to C103 nozzle skirts. However, attempts to EB weld Re directly to C103 have resulted in brittle joints because of the formation of a Re-niobium (Nb) sigma phase (refs. 2 and 9). This brittle intermetallic phase, which forms above 2162 °C, precludes the use of fusion methods in directly joining Re to C103. Brazing and transition joints are alternatives to directly EB welding Re chambers to C103 skirts and will be discussed in the next section.

Brazing

Brazing has been investigated extensively as an alternative to EB welding. Braze materials for joining Re to 304L SS, Hastelloy B2, and unalloyed Nb were evaluated by Aerojet under a NASA program (ref. 2). Palcusil 25, Silcoro 75, Palsil 10, Niore (82 gold (Au)-18 nickel (Ni)), and 50Au-50 copper (Cu) were evaluated for their wetting ability. All of the braze alloys were found to have good to excellent wetting characteristics, with the exception of Silcoro 75 and 50Au-50Cu for Nb. In lap and ring shear testing, Niore joints were found to be the strongest. Re-to-304L SS and Re-to-Hastelloy B2 joints were achieved by using a "parent metal braze" technique. Here only the 304L SS and Hastelloy B2 were melted, wetting the Re and solidifying to form the joint. This technique was used to join a Re chamber to a 304L SS injector in a flight-type, 440-N engine (ref. 5).

TRW investigated methods of joining Re-to-C103 in a NASA program to develop a liquid oxygen/N₂H₄, 440-N class engine (ref. 9). Several braze materials were evaluated for furnace brazing of Re-to-C103, including 65Au-35 palladium (Pd), 50Au-50Pd, and Ti. These three braze joint samples were subjected to thermal aging and thermal cycling tests. The Ti sample showed a small crack at the braze/Re interface, caused by the formation of a brittle phase. The 50Au-50Pd sample showed void areas where there was poor flow of braze and shrinkage which formed cracks. The 65Au-35Pd sample showed only some small voids and no diffusion of the braze material into Re or C103. Diffusion of Nb and Hf (from the C103 alloy) into the braze was found, however. Based on this investigation, the 65Au-35Pd braze alloy was recommended for furnace brazing Re-to-C103.

Although suitable braze materials have been found for joining Re to dissimilar metals, brazing has disadvantages for joining chambers to nozzle skirts. The brazing process often requires a complex design at the interfaces to assure proper wetting of the joining area. Braze layers also have limited strength, temperature, and thermal cycling capabilities. This calls into question the ability of braze layers to survive the rigors of launch vibration and multiple on-orbit firings. An all-welded engine would eliminate these potential problems.

Transition Joints

An alternative to brazing is the use of a transition joint composed of Re and C103. The transition ring can be formed by nonfusion methods. This avoids the formation of a brittle Re-Nb intermetallic, because bond line temperatures never reach 2162 °C. The Re chamber can then be EB welded to the Re side of the joint and the C103 skirt can be EB welded to the C103 side. A transition joint would also be used for the injector-to-chamber joint. Non-fusion joining methods of forming transition pieces include diffusion bonding, explosive bonding, and inertia welding. In diffusion bonding, heat and pressure are applied uniformly to expand one piece into the other. Explosive bonding is a cold welding process that uses controlled explosive detonations to join two pieces. Inertia welding uses the stored energy in a flywheel to impart one piece into a stationary piece.

Flat plate coupons of Re-to-C103 joints, formed by explosive and diffusion bonding were evaluated in a series of shear tests (refs. 16 and 17). Coupons were subjected to thermal cycling, thermal aging, and EB welding of Re and/or C103 tabs. Ultimate shear strength was used as a figure of merit for comparison of as-received coupons. For both explosive- and diffusion-bonded coupons, the joint strength only degraded after being subjected to the combination of C103 EB weld tabs and thermal cycling (100 cycles, from 100 to 1100 °C). This combination apparently resulted in enough interdiffusion between Re and Nb to form an alloy that weakened the joint. This experience indicates that care must be taken when EB welding the chamber and nozzle skirt to the transition joint. An adequate heat sink should be provided during EB welding and the joint design should have a geometry that would keep the bond line temperature below 2162 °C.

TRW evaluated inertia-, diffusion-, and explosive-bonded joint coupons under a NASA technology program (Private communication from M.L. Chazen regarding NASA Contract NAS3-26246). In this testing Re was not directly bonded to C103, since there was concern that diffusion of hafnium (Hf) from C103 into Re would result in a brittle Hf-Re intermetallic phase. Coupons of Re were joined to a Nb-tantalum (Ta) alloy by inertia welding, to pure Ta by diffusion bonding, and to C103 with a Ta interlayer by explosive bonding. A full-size ring configuration was used; it provided a more realistic assessment of the joint integrity than flat plate coupons. Coupons were shear tested after being subjected to shear loading and thermal cycling that simulated the joint's anticipated duty cycle. All of the coupons were found to have more than sufficient margin to withstand the anticipated duty cycle. Based on this full-size ring testing, inertia-, diffusion-, and explosive-bonding are all acceptable methods for forming transition joints.

Ir/Re LIMITING MECHANISMS

Ir/Re Life Model

Life-limiting mechanisms for Ir/Re were investigated in the initial Ir/Re rocket technology programs (ref. 2). The primary mechanism was found to be grain boundary diffusion of Re into the Ir layer. As the Re concentration at the inner wall increases, the oxidation resistance of the Ir coating slowly degrades. At a critical Re concentration level there is a significant increase in the oxidation rate, which results in loss of the Ir coating. By using this failure mechanism, a first-order life model for Ir/Re rockets was established from Ir-Re diffusion and oxidation data. The model is useful in assessing the ability of Ir/Re to survive in different combustion environments.

Thermogravimetric analyses (TGA) were performed at 1540 °C with Ir, Ir-20 percent Re, and Ir-40 percent Re samples at 0.014-kPa oxygen partial pressure and with Ir and Ir-20 percent Re samples in 1.93-kPa oxygen partial pressure (ref. 2). The TGA results and calculated material recession rates are shown in table IV. At 0.014-kPa oxygen pressure, the Ir oxidation rate increased significantly between Ir-20 percent Re (0.361 μm/hr) and Ir-40 percent Re (58.1 μm/hr). Based on these data, the failure criterion for Ir/Re rockets was established empirically as 20 percent Re at the Ir inner surface.

The phase diagram for Ir-Re is shown in figure 3. Here the lower abscissa is weight percentage Re and the upper abscissa is atomic percentage Re. The dashed lines in the phase diagram represent uncertainty associated with the locations of the region boundaries. The Ir-Re phase diagram shows that the Ir-20 percent Re sample was a single-phase solid solution, while the Ir-40 percent Re sample was a two-phase mixture. The two-phase region boundary represents the solubility limit of Re in Ir. The Re-rich phase (which was reported to have a composition of 29 percent Ir and 71 percent Re) accounted for over a third of the Ir-40 percent Re alloy at 1540 °C. The sudden large increase in oxidation rate between the two previous samples was attributed to the Re-rich phase, which was thought to be more susceptible to oxidation (ref. 2). Based on these data, the failure criterion for Ir/Re rockets is probably better set at the Re concentration corresponding to entry into this two-phase region.

Furnace oxidation testing of vacuum arc melted Ir-Re buttons was conducted to test the above hypothesis (ref. 18). Samples were tested at 1500 °C in oxygen partial pressures of 0.69 and 6.90 kPa. Because of porosity in many of the samples, there was a large amount of anomalous oxidation data. The remaining acceptable data (at 0.69-kPa oxygen partial pressure) from the study, that is, data from samples with little or no porosity, is shown in table V. It can be seen that there is an order of magnitude increase in oxidation rate from 19.8 percent (0.369 μm/hr) to 27.6 percent (4.29 μm/hr) Re concentration. The sparsity of acceptable data between 20 percent and 30 percent Re concentrations, however, leaves uncertainty as to whether the oxidation rate increase can be attributed to entry into the two-phase region of the Ir-Re phase diagram (fig. 3).

Diffusion data were collected from CVD Ir-Re samples that had been vacuum annealed at 1400, 1700, and 1900 °C for 8 hr each (ref. 19). Electron microprobe analyses of the samples revealed significant diffusion of Re along Ir grain boundaries, while there was little diffusion of Ir into the Re. Diffusion constants for the samples were

determined from curve fits of the microprobe line scans, with the assumption that there was only diffusion of Re into the Ir layer. As expected, the diffusion constant was found to have an Arrhenius dependence on temperature T and could be fitted to an equation of the following form:

$$D = D_0 \exp(-E/kT)$$

where $D_0 = 3.14 \times 10^8 \text{ cm}^2/\text{sec}$ and $E/k = 1.42 \times 10^4 \text{ K}$. The activation energy for diffusion E was found to be 1.23 eV.

A first-order life prediction model was established for Ir/Re rockets (ref. 20) by using the diffusion rate data in the one-dimensional diffusion equation

$$\partial C/\partial t = D(\partial^2 C/\partial x^2)$$

where C is the Re concentration, t is time, and x is the position normal to the Ir/Re interface. This equation was solved numerically by using the Crank-Nicholson differencing scheme, with the boundary conditions of zero Re flux at the Ir (inner) surface and 100 percent Re concentration at the Ir/Re interface. The inner surface was assumed to be removed at a fixed recession rate based on the TGA data at 1540 °C and 0.014 kPa. The furnace data gathered at 1500 °C and 0.69 kPa could also be used as the basis of the recession rate in the model. The failure criterion was set at 20 percent Re concentration at the inner wall.

This Ir/Re life model is only as valid as the diffusion and oxidation data that it is based on. The diffusion rate data have a predictable dependence on temperature and can probably be extrapolated to higher temperatures with confidence (ref. 20). Oxidation rate data, however, are a strong function of temperature and oxygen partial pressure and cannot be confidently extrapolated. Therefore the life model is only valid within the range of oxygen pressures and temperatures for which Ir-Re oxidation rate data exist. Life model predictions at higher temperatures and oxygen pressures lead to unrealistically long chamber lifetimes. This limits the use of the life model to 1540 °C, until Ir-Re oxidation rate data at higher temperatures can be obtained.

Figure 4 shows the predicted chamber lifetimes for Ir/Re rockets, with Ir coating thicknesses of 50.8 and 101.6 μm (typical of Ir/Re rockets) at 1540 °C. Also plotted in the figure are the chamber lifetimes for C103 rockets, based on rocket engine qualification tests conducted by various rocket manufacturers. An Ir/Re rocket with a 50.8-μm Ir coating was predicted to have an order of magnitude increase in chamber lifetime over that of C103 rockets. Typically Ir/Re rockets would be operated at temperatures higher than 1540 °C for increased performance. If Ir/Re rockets were operated at 1540 °C, performance gains would be sacrificed in lieu of greatly extended chamber lifetimes as in the proposed Shuttle thruster application described earlier (ref. 7). For comparison, a 22-N Ir/Re rocket tested on NTO/MMH propellants (ref. 2) is also shown in figure 4. The rocket had a 50.8-μm Ir thickness and did not experience any erosion or degradation during testing.

Ir Degradation

In the initial Ir/Re technology programs with Aerojet (22-, 62-, and 440-N engines on NTO/MMH), no significant erosion or degradation of the Ir coating was observed. In this early testing, Aerojet used either a cooled section between the chamber and injector or a Pt-Rh liner installed in the head end region of the chamber (refs. 2, 4, and 5). In more recent testing by other rocket companies, Ir/Re chambers have been directly attached to injectors. In this configuration, degradation of the Ir layer in the form of pitting was often experienced in the head end (near-injector) region of the chamber. A reported case of this type of Ir degradation occurred in testing 22-N engines with both NTO/MMH (after 1500 sec of testing) and NTO/N₂H₄ (after 450 sec of testing) (ref. 21).

In the near-injector region of the chamber, it was likely that the flow field was still mixing with oxidizers and combustion radicals present at the wall. In the instances when Ir/Re chambers were run with a cooled-section or liner, the Ir was not exposed to the flow field mixing and combustion processes were complete. The circumstantial evidence, then, would seem to point to exposure of the Ir layer to a mixing, combusting flow field as the cause of the Ir degradation. The cause of the Ir degradation could be due to Ir reactivity with a combustion radical, oxidation of the underlying rhenium through the Ir grain boundaries, or high partial pressures of oxidizers at the wall directly oxidizing the Ir.

The reactivity of Ir and Pt in a fuel-rich air/hydrogen combustion environment has been investigated (ref. 22). Laser-induced fluorescence measurements of Ir and Pt samples found hydroxyl (OH) concentrations significantly above equilibrium. The measurements suggested that atomic oxygen and atomic hydrogen concentrations near the

material surface were also above equilibrium. OH is an intermediate product in NTO/MMH and NTO/N₂H₄ combustion environments. However, no significant difference in the concentration profiles was found between the Ir and Pt samples. The superequilibrium concentrations, then, may not have been the result of the reaction with the material surface, but a characteristic of the combustion environment. Beyond this work, there has been no testing conducted to conclusively determine the causes of the Ir degradation.

Although the direct causes of the Ir degradation are not well understood, the phenomenon can be avoided by only exposing the Ir layer to a well-mixed, well-combusted flow field. This would involve protecting the Ir layer in the relatively low-temperature near-injector region with a low-reactivity liner or coating. The degradation has not occurred in the throat region, where the high-temperature capability of Ir is most needed.

CONCLUSIONS

Ir/Re chamber materials are key to high-performance, long-life, radiation-cooled rocket engines. There has been extensive testing of Ir/Re rockets, on different propellant combinations, at thrust levels up to 440 N. A low-cost, reproducible fabrication process for Ir/Re is critical for its acceptance in flight systems. CVD is the established fabrication process for Ir/Re, although PM Re/ED Ir represents a viable alternative. It has been found that Re mechanical properties are highly dependent on its fabrication process and history. Direct EB welding of Re to C103 nozzle skirts is not possible, because a brittle Re-Nb intermetallic forms at 2162 °C. Alternative Re-to-C103 joining methods include brazing and transition rings formed by nonfusion methods, such as explosive-, diffusion-, and inertia-bonding. The life-limiting mechanism for Ir/Re rockets is the grain boundary diffusion of Re into the Ir layer and the oxidation of the resulting Ir-Re alloy from the inner surface. This mechanism is relatively slow, providing for long Ir/Re chamber lifetimes. Ir degradation experienced in the near-injector region of some Ir/Re rockets was probably the result of exposing Ir to a mixing, combusting flow field. This problem can be avoided by protecting the Ir layer in the (relatively low-temperature) near-injector region with a low-reactivity liner or coating.

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TABLE I.—CHEMICAL VAPOR DEPOSITED RHENIUM TENSILE DATA (REF. 15)

Annealing temperature, °C	Annealing time, hr	Test temperature, °C	0.2 percent yield strength, MPa	Ultimate strength, MPa
None	None	25	310	674
None	None	25	297	663
1482	0.5	25	124	674
1482	0.5	815	359	430
1482	0.5	815	317	440
1482	0.5	1370	200	367
1482	0.5	1370	138	146
1482	0.5	1370	193	344
1650	1.0	25	307	688
1650	1.0	25	285	698
1650	1.0	815	400	465
1650	1.0	815	390	445
1650	1.0	1370	345	456
1650	1.0	1370	267	290

TABLE II.—POWDER METALLURGY (HOT ISOSTATIC PRESSURE)
RHENIUM TENSILE DATA (REFS. 15 AND 16)

Annealing temperature, °C	Annealing time, hr	Test temperature, °C	0.2 percent yield strength, MPa	Ultimate strength, MPa
1650	0.5	25	237	911
1650	0.5	25	232	916
1650	0.5	815	254	562
1650	0.5	815	264	498
1650	0.5	1370	180	216
1650	0.5	1370	191	252
None	None	1370	208	217
None	None	1370	211	220
None	None	1370	171	202
None	None	1370	173	198
None	None	1510	143	151
None	None	1510	138	150
None	None	1650	104	111
None	None	1650	101	107
None	None	1860	105	113
None	None	1925	67.4	73.0
None	None	1925	78.8	79.4
None	None	1925	87.6	98.2
None	None	1925	78.1	92.5
None	None	2090	71.0	80.2

TABLE III.—RHENIUM LOW CYCLE FATIGUE DATA
(REF. 15)

Fabrication method	Test temperature, °C	Stress, MPa	Tension/compression	Cycles completed
CVD	25	152	152	100
CVD	25	152	152	100
CVD	815	276	179	(a)
CVD	815	276	138	100
CVD	815	276	138	11
CVD	815	276	138	12
CVD	1370	138	69	85
CVD	1370	138	69	37
HIP PM	815	138	69	103
HIP PM	815	128	62	^b 20
HIP PM	1370	131	62	100
HIP PM	1370	138	69	100

^aFailed on first cycle.

^bSample was accidentally loaded to 248 MPa in pretest run.

TABLE IV.—THERMOGRAVIMETRIC ANALYSIS OF IRIIDIUM-RHENIUM ALLOYS AT 1540 °C (REF. 2)

Rhenium concentration	Oxygen partial pressure, kPa	Recession rate, μm/hr
0 (pure Ir)	0.014	0.153
20	0.014	0.361
40	0.014	58.1
0 (pure Ir)	1.93	0.865
20	1.93	2.44

TABLE V.—FURNACE OXIDATION TESTING OF IRIIDIUM-RHENIUM ALLOYS AT 1500 °C AND 0.69-kPa OXYGEN PRESSURE (REF. 18)

Rhenium concentration	Recession rate, μm/hr
1.14	0.042
3.08	0.084
3.61	0.059
16.9	0.236
19.8	0.369
27.6	4.29
32.0	7.57
34.8	20.8

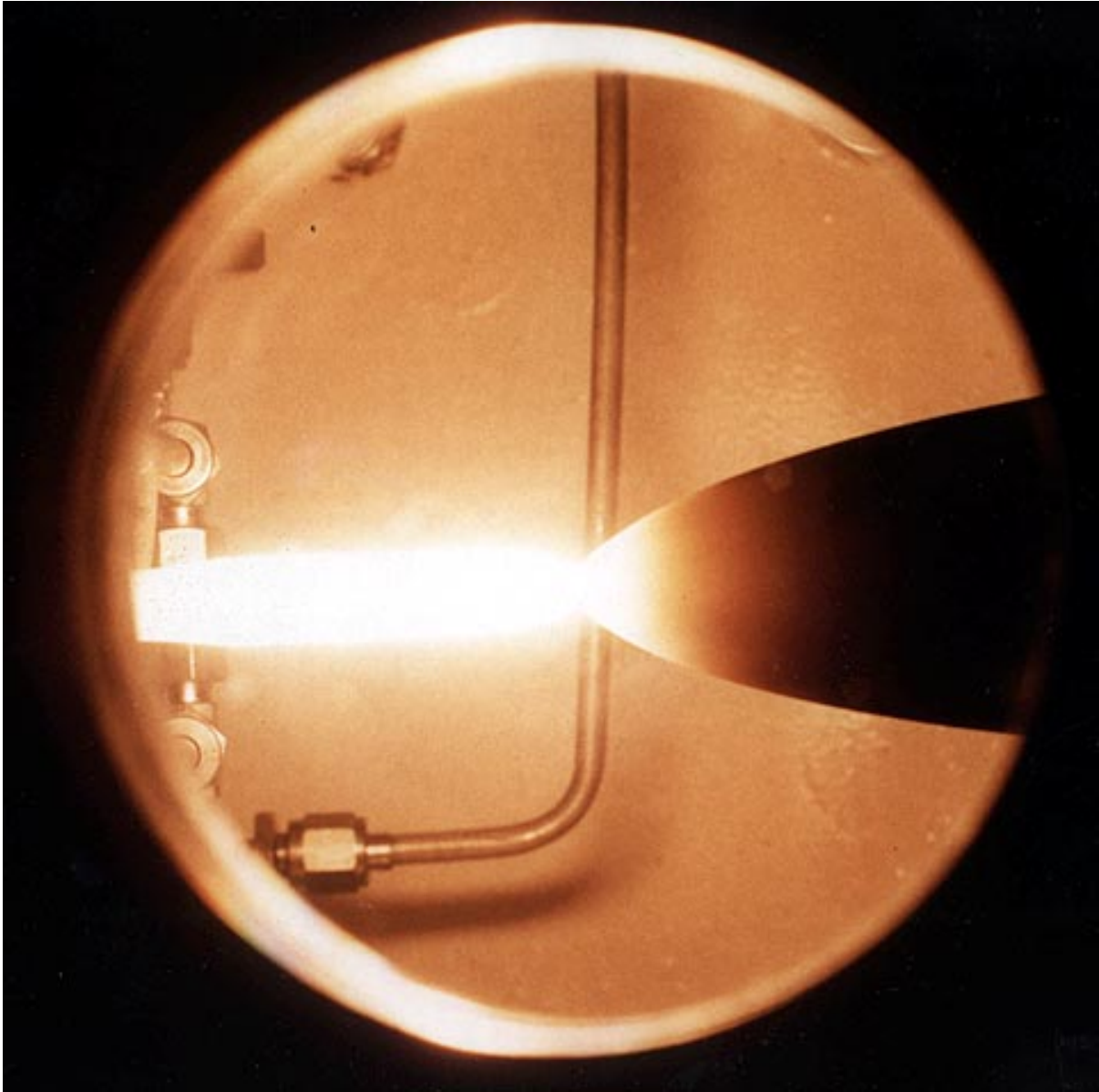
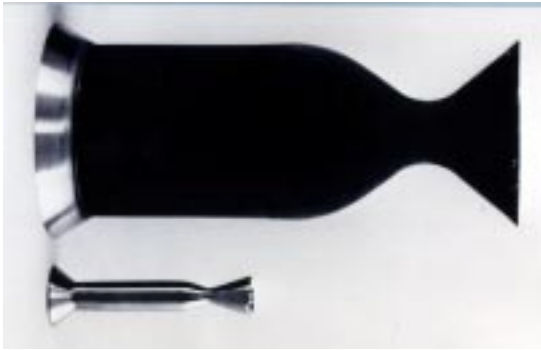


Figure 1.—22-N iridium-coated rhenium rocket firing.

Fabrication Technology



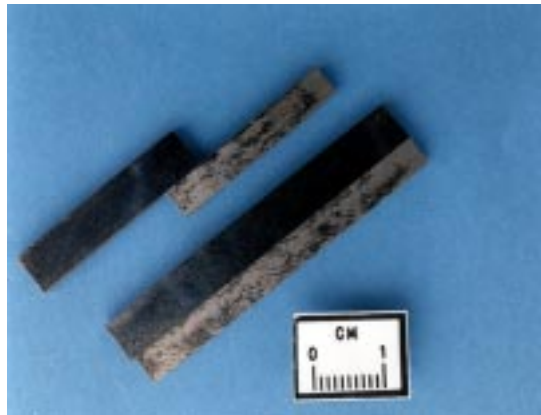
- Low-cost, reproducible fabrication processes

Rhenium Mechanical Properties



- Tensile
- Low cycle fatigue
- Creep

Joining Technology



- Injector to chamber
- Chamber to C103 skirt

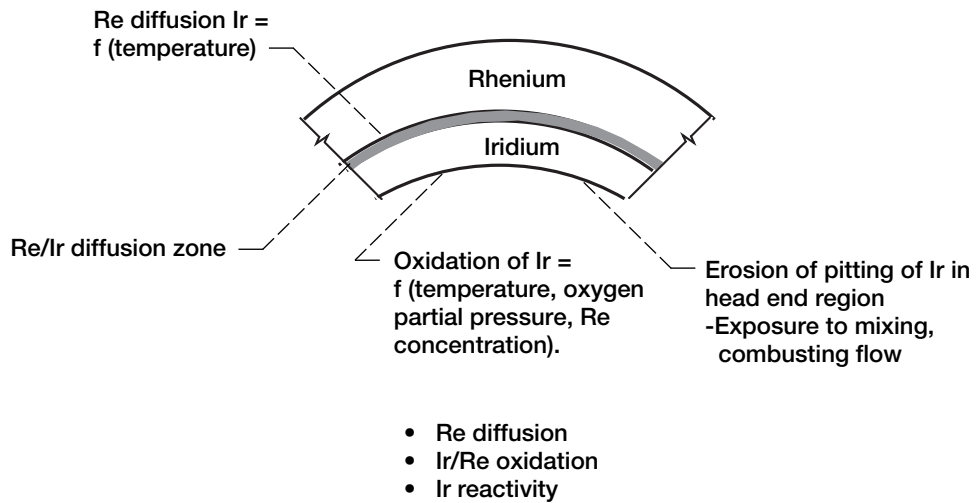


Figure 2.—NASA Research & Technology Program for iridium-coated rhenium chambers.

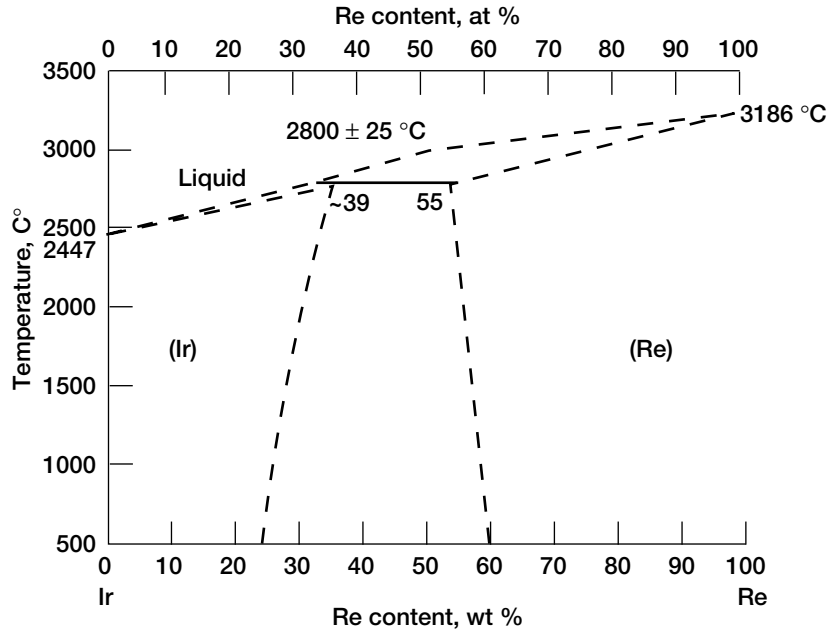


Figure 3.—Iridium-rhenium phase diagram.

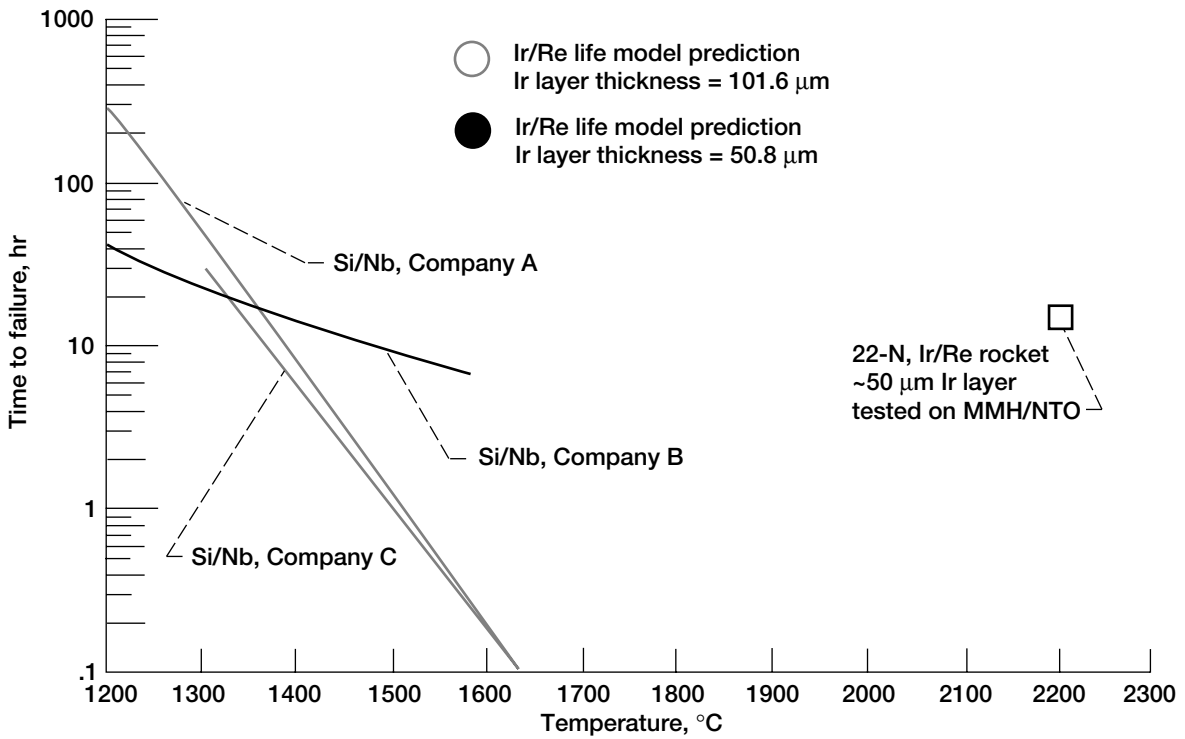


Figure 4.—Time to failure versus temperature for C103 and iridium-coated rhenium rockets.

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13. ABSTRACT (<i>Maximum 200 words</i>) Radiation-cooled rockets are used for a range of low-thrust propulsion functions, including apogee insertion, attitude control, and repositioning of satellites, reaction control of launch vehicles, and primary propulsion for planetary spacecraft. The key to high performance and long lifetimes for radiation-cooled rockets is the chamber temperature capability. The material system that is currently used for radiation-cooled rockets, a niobium alloy (C103) with a fused silica coating, has a maximum operating temperature of 1370 °C. Temperature limitations of C103 rockets force the use of fuel film cooling, which degrades rocket performance and, in some cases, imposes a plume contamination issue from unburned fuel. A material system composed of a rhenium (Re) substrate and an iridium (Ir) coating has demonstrated operation at high temperatures (2200 °C) and for long lifetimes (hours). The added thermal margin afforded by iridium-coated rhenium (Ir/Re) allows reduction or elimination of fuel film cooling. This, in turn, leads to higher performance and cleaner spacecraft environments. There are ongoing government- and industry-sponsored efforts to develop flight Ir/Re engines, with the primary focus on 440-N, apogee insertion engines. Complementing these Ir/Re engine development efforts is a program to address specific concerns and fundamental characterization of the Ir/Re material system, including (1) development of Ir/Re rocket fabrication methods, (2) establishment of critical Re mechanical property data, (3) development of reliable joining methods, and (4) characterization of Ir/Re life-limiting mechanisms.				
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