ADVANCED MATERIALS FOR RADIATION-COOLED ROCKETS

Brian Reed, James Biaglow and Steven Schneider
NASA Lewis Research Center

SUMMARY

The most common material system currently used for low thrust, radiation-cooled rockets is a niobium alloy (C-103) with a fused silica coating (R-512A or R-512E) for oxidation protection. However, significant amounts of fuel film cooling are usually required to keep the material below its maximum operating temperature of 1370 °C, degrading engine performance. Also the R-512 coating is subject to cracking and eventual spalling after repeated thermal cycling. A new class of high-temperature, oxidation-resistant materials are being developed for radiation-cooled rockets, with the thermal margin to reduce or eliminate fuel film cooling, while still exceeding the life of silicide-coated niobium. Rhenium coated with iridium is the most developed of these high-temperature materials. Efforts are on-going to develop 22 N, 62 N, and 440 N engines composed of these materials for apogee insertion, attitude control, and other functions   There is also a complimentary NASA and industry effort to determine the life limiting mechanisms and characterize the thermomechanical properties of these materials. Other material systems are also being studied which may offer more thermal margin and/or oxidation resistance, such as hafnium carbide/tantalum carbide matrix composites and ceramic oxide-coated iridium/rhenium chambers.

IRIDIUM/RHENIUM

A technology program[1] was conducted to find a chamber material system that could operate for long life in a 2200 °C environment. After a literature and vendor survey, iridium-coated rhenium (Ir/Re) was selected. In the same technology program, a 22 N Ir/Re chamber was operated for 15 hours at 2200 °C on monomethylhydrazine (MMH) and nitrogen tetroxide (NTO) propellants with negligible internal erosion. A flighttype 22 N chamber was then fabricated and tested for 1.77 hours on MMH/NTO before a coating failure at the throat. An alteration in the contour design gave a sharp radius of curvature at the throat, which proved to be a stress concentrator. A flighttype 440 N chamber has been successfully tested for 6.3 hours on MMH/NTO. There has been further testing of flighttype 22 N, 62 N, and 440 N Ir/Re engines on MMH/NTO and hydrazine/nitrogen tetroxide (N2H4/NTO) by various rocket companies.[2,3] A 22 N Ir/Re chamber has also been tested for over 14 hours on gaseous hydrogen/gaseous oxygen (GH2/GO2) propellants.

The life limiting mechanisms of Ir/Re chambers were investigated.[4] It was found that rhenium slowly diffuses along grain boundaries into the iridium coating during high temperature operation, so that the concentration of rhenium at the inner surface slowly increases. Oxidation testing at 1500 °C has shown that the iridium oxidation rate increases significantly above a rhenium concentration of 20 percent. Rhenium diffusion into iridium and oxidation of the resulting iridium-rhenium alloy had been identified as the life limiting mechanism for Ir/Re rockets, with 20 percent rhenium concentration at the inner wall surface determined as the failure criterion. Further oxidation testing of iridium/rhenium alloys is being performed to more clearly define the rhenium concentration level where iridium oxidation accelerates.

A potentially more rapid failure mechanism for Ir/Re rockets has been identified in recent testing of Ir/Re

rockets. All of the Ir/Re rocket testing in the initial technology programs were performed with either a cooled section between the chamber and injector or with a platnium/rhodium liner installed in the head end region of the chamber. No problems were experienced with the chambers tested in this manner. However, where Ir/Re chambers were directly welded to injectors, erosion or pitting of the iridium occurred in the head end region of the chamber.[2,5,6] The reasons for this degradation of the iridium coating are not yet certain, but the phenomenon would pose a threat to the long-life, high-temperature advantages offered by this material system. The coating degradation has occurred in the head end, relatively low temperature region of the chamber, where the flowfield was probably still mixing and where oxidizers and combustion radicals may be present at the wall. In the instances when Ir/Re chambers were run with a cooled-section or liner, the iridium was not exposed to the flowfield until it was probably well mixed and nearly completely combusted. It is suspected, based on circumstantial evidence, that the iridium degradation is a result of iridium reactivity with combustion radicals, oxidation of the underlying rhenium through the iridium grain boundaries, or high partial pressures of oxidizers at the wall directly oxidizing the iridium.

Testing of 22 N chambers on GH2/GO2 would seem to support this line of reasoning. One chamber was tested for over 14 hours at mixture ratios from 3 to 8, but with the overwhelming majority of time at mixture ratios between 3 and 4. Testing stopped because of a facility-related failure and posttest material analysis indicated that the chamber could have run for much longer. Another Ir/Re chamber was run at mixture ratio 6, but had a coating failure after 2.6 hours. The iridium had ruptured in the barrel section of the chamber. Both chambers were run with a water-cooled section between the injector and chamber, so they were exposed to well mixed flows. The mixture ratio 6 environment, however, had high partial pressures of oxygen, atomic oxygen, and hydroxyl compared to the low mixture ratio environment. Material analyses of these chambers and of as-fabricated samples of Ir/Re, along with experiences in industry and any required laboratory scale testing, will be used to determine the mechanisms for this iridium degradation phenomenon.

The majority of Ir/Re chambers tested to date have been fabricated using chemical vapor deposition (CVD).[7] The CVD process involves the passing of a gaseous compound of the desired material over a heated mandrel. The material is deposited on the mandrel due to thermal decomposition of the gas at the mandrel surface. Iridium and then rhenium is deposited on the molydenum mandrel, with the mandrel chemically etched out after the CVD processing. Alternate methods of fabricating Ir/Re chambers are being explored including powder metallurgy rhenium, electrodeposition of rhenium and iridium, arc plasma spraying of rhenium, and the use of a rolled, welded iridium liner.

The ability of the Ir/Re engine to survive the launch vibration environment after being hot fired in acceptance tests is critical to the eventual use of the material system. The thermomechanical property database for rhenium, as fabricated by CVD and other methods, is limited, therefore a program is underway to procure rhenium samples fabricated through various means and by various manufacturers and conduct testing to determine the ultimate strength, yield strength, modulus, low cycle fatigue, and creep properties at room and elevated temperatures. It is particularly important to determine the thermomechanical properties of annealed rhenium samples, as this will most closely simulate the behavior of a chamber that has been through acceptance testing. The ability to join the Ir/Re chambers to injectors and nozzle extensions composed of other materials is also a concern.

CERAMIC OXIDE/IRIDIUM/RHENIUM

Ceramic oxide coatings for Ir/Re chambers are being investigated[8] as a way to significantly extend thruster lifetimes and allow operation in more aggressively oxidizing environments, such as stoichiometric (or higher mixture ratio) hydrogen/oxygen. The oxide coatings would serve as a thermal and diffusion barrier for the iridium coating, lowering the temperature at the iridium surface, while also preventing the ingress of oxidizers and egress of iridium oxides. The oxide coatings could also serve as a protector against iridium degradation (assuming that iridium reactivity with combustion radicals or oxidation is the cause). The primary issue with these coatings is their ability to withstand the thermal shock of combustion and repeated thermal cycling.

Seven Ir/Re chambers with yttria-stabilized zirconia and yttria-stabilized hafnia coatings were tested.[9] The chamber structures, coating thicknesses, and fabrication techniques are proprietary to the manufacturer. The purpose of the yttria stabilization is to surpress a phase transformation that occurs at 1650 °C and 1100 °C for hafnia and zirconia, respectively. The nominal test matrix began with short duration (5 and 15 second) tests at mixture ratio 4. This testing was performed to determine the ability of the coating to withstand the thermal shock of combustion, with little or no oxidizers present. Testing was then performed at mixture ratio 6 and 8 (stoichiometric), increasing both the temperature and oxygen partial pressure of the flowfield. At each of these mixture ratios, short (5 and 15 second) and longer duration (300 second) testing were performed. This gave a nominal time of 14 firings and 22 minutes for each chamber.

All seven chambers survived the initial testing intact. In five of the chambers there was cracking, but no spalling of the oxide coating. The other two chambers did not experience cracking or any evidence of coating degradation. Six of the chambers were further tested in a series of ten, 60-second duration runs at mixture ratio 11. Though temperature does not increase at mixture ratios above stoichiometric, the amount of oxygen, atomic oxygen, and hydroxyl increases significantly. The high mixture ratio testing, then, determined the ability of the coating to operate in an aggressively oxidizing environment. Two of the chambers began to show evidence of spalling at the front end in the high mixture ratio testing. Another chamber lost its coating from the throat downstream. The seventh chamber was tested at mixture ratio 16. After 30 firings and 29.2 minutes at mixture ratio 16, burn-through occurred in the converging section of the thruster. The chambers will be sectioned for material analyses. The most promising structures will be fabricated and tested further.

CERAMIC MATRIX COMPOSITES

Ceramic matrix composite (CMC) chambers are also being investigated as a high-temperature material system for radiation-cooled rockets. CMC materials are a lightweight alternative to Ir/Re and also have the advantage of being chemically compatible with the combustion products of hydrazine/chlorine pentaflouride, a propellant combination under consideration for apogee and planetary propulsion applications. There has been extensive development of CMC chambers for divert and similar type propulsion systems. These chambers were always porous to a degree, however in the divert propulsion application, reduction of weight and volume were the primary design drivers and lifetimes were usually under a minute. For the longer life apogee and attitude control propulsion functions, densification of these engines is a major technology issue to be resolved.

Composites composed of silicon carbide fibers and silicon carbide matrix are the most developed chamber

materials for apogee and attitude control applications, with extensive testing of 22 N and 2000 N engines at 1595 °C.[10] A higher temperature CMC option is a composite composed of graphite fibers and a refractory carbide matrix. Hafnium carbide doped with tantalum carbide is a very promising matrix for this material system.[11] Oxidation protection for the graphite fibers are dependent on the in-situ formation of the oxide from the matrix. Hafnia, as mentioned above, undergoes a phase transformation at 1100 °C, which results in a significant volume change and subsequent spalling of the coating after repeated thermal cycling. The presence of tantalum carbide in the matrix leads to a mixed hafnia/tantala layer being form. The technology issue needed to be resolved is the proper percentage of tantalum carbide in the matrix in order to assure the in-situ formation of a stable oxide.

OTHER CANDIDATE MATERIALS

There are other material systems that could be considered (depending on the application) for radiation-cooled rockets. A chamber fabricated from pure iridium would eliminate the rhenium/iridium diffusion mechanism, but there are concerns about its structural integrity as a rocket engine. Tantalum-10% tungsten alloy and woven carbon-carbon fibers could serve as high-temperature substrates, but requires a suitable oxidation-resistant coating for any type of long life applications. Platnium-10% rhodium alloy and grain-stabilized platnium are excellent oxidation-resistant materials that could be considered for very long life (tens of hours), but relatively low temperature (1650 °C) applications. Cermets and intermetallic compounds have also been considered for high temperature rocket operation, but there is a very limited experience base with them.

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