Space Station Resistojets

THE COMPATIBILITY OF DISPERSION-STRENGTHENED PLATINUM WITH CANDIDATE PROPELLANTS

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Resistojets for space station auxiliary propulsion require both long life and multipropellant capability, and platinum dispersion strengthened with yttria and zirconia has been studied for possible use as a resistojet material. A series of propellant compatibility tests has been conducted, and the results are presented. Generally, on the basis of mass loss, there were no compatibility problems in any of the environments considered. Microscopy showed that the effect of the propellants on the surface of the platinum varied significantly; however material stability, as measured by grain growth, did not appear to be a major problem.

A resistojet is an electrothermal thrust device which produces thrust by expanding a heated gas through a nozzle. The gas is heated as it flows through the resistojet heat exchanger, the temperature being varied by changing the power input to the heater. The resistojet designed for the space station is shown in Figure 1.

To fulfil space station requirements a resistojet must be capable of long life and of operating with a variety of different propellants; however, the choice of materials to meet these requirements is limited. Therefore, the evaluation of potential materials will have a direct application to the development of multipropellant resistojets.

Two major considerations for candidate materials are the life-limiting problem of creep and the compatibility of these materials with potential space station propellants. Creep and grain growth can occur when a material is operated at high temperatures for extended periods of time, and can result in the formation of voids, physical distortions, and an unacceptable reduction in the stress-rupture performance of the material.

Platinum and alloy-strengthened platinum were considered for biowaste resistojets during the Manned Orbital Research Laboratory programme of the early 1970s (1–3). Platinum was assumed to be compatible with candidate propellants, and it was chosen for its excellent corrosion resistance and particularly for its oxidation resistance (4). Pure platinum, although corrosion resistant, was found to lack adequate high-temperature strength. Alloying platinum with rhodium improved the material strength; however, compatibility problems were encountered because the alloy was not as corrosion resistant as pure platinum.

Platinum-0.6 per cent thoria was also developed during this period as a high-temperature, high-strength material for biowaste resistojets. The compatibility of this material with carbon dioxide was verified, but no other data were available (5). This platinum-thoria alloy is no longer manufactured, but the experience gained during its production was used in developing improved dispersion-strengthened platinum materials. Two types of dispersion-strengthened platinum are currently available: one is strengthened with yttria and the other with zirconia. The addition of stabilising oxides, less than 1 per cent by weight in both of the platinum materials, does not significantly change the physical and room-temperature mechanical properties of platinum, but it does improve the high-

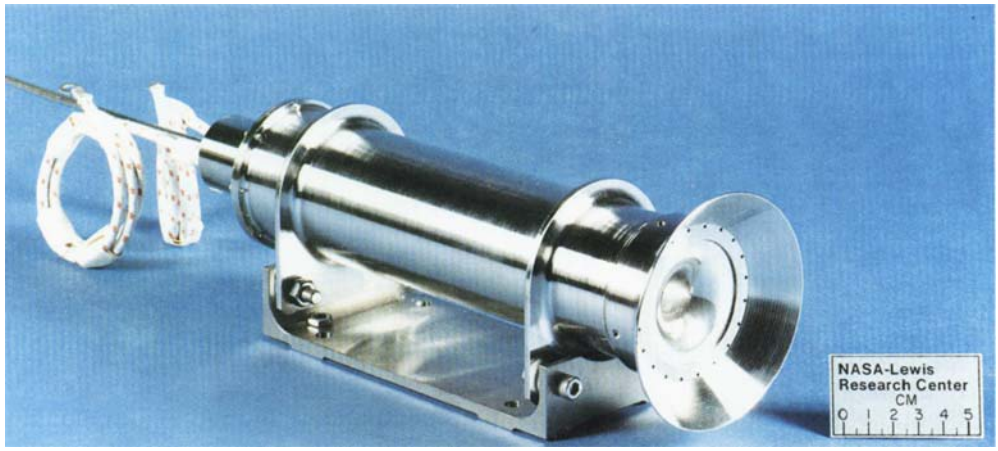

Fig. 1 Electrothermal thrusters are being actively considered as auxiliary propulsion units on the NASA space station. The propulsive thrust is provided by a heated gas which is expanded through a nozzle; the temperature and hence the thrust, being varied by changing the power input to an electric resistance heating coil. Since it would be advantageous to use many of the on-board fluids as propellants in these resistojets—an engineering model of which is shown here—the constructional materials must be compatible with all these fluids under the conditions of use, for at least the design life of the thruster

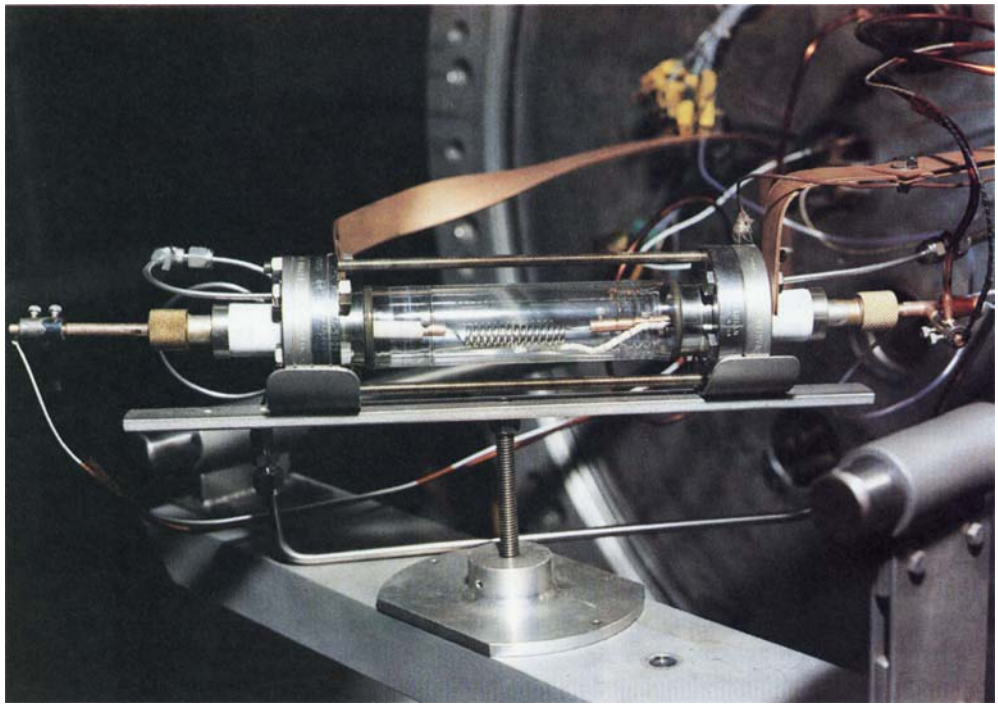

Fig. 2 Constructional materials have been investigated under the operating conditions of a space station resistojet propulsion system, using a stainless steel or a quartz test cell. The compatibility of grain stabilised platinum with carbon dioxide, hydrogen, ammonia, nitrogen, steam, hydrazine and methane has been evaluated by resistively heating a coil of the metal while it is surrounded by gas flowing through the cell, the flow rate being controlled by both upstream and downstream valves. Generally temperatures were measured using an optical pyrometer, but for the test in methane a chromel-alumel thermocouple was employed

Mass-Loss Results for Dispersion-Strengthened Platinum				
Propellant[a]	Platinum-Yttria		Platinum-Zirconia	
	Mass loss, per cent	Estimated thruster life, $\times 10^3$,h	Mass loss, per cent	Estimated thruster life, $\times 10^3$,h
Carbon dioxide	0.033	300	0.012	800
Hydrogen	0.049	200	0.023	400
Ammonia	0.052	200	0.050	200
Nitrogen	0.094	106	–	–
Steam	0.089	110	0.221	45
Hydrazine	0.206	48	0.155	64
Methane at 500°C	0.006	1500	0	>1500
Hydrazine at 800°C	0.010	970	–	–
Hydrogen[b]	0.136	148	–	–
Ammonia[b]	0.110	182	–	–

(a) All samples tested at 1400°C, except where noted otherwise
(b) 2000 hour test

temperature strength, the creep resistance and the material stability, as indicated by limited grain growth (6,7).

Preliminary work showed promise for the use of dispersion-strengthened platinum for space station resistojets (8–10). The present report is a summary of the results of a series of compatibility tests on dispersion-strengthened platinum. The results include 1000 hour compatibility tests in carbon dioxide, methane, hydrogen, ammonia, nitrogen, steam and decomposed hydrazine; and 2000 hour tests in hydrogen and ammonia. The material evaluation included mass-loss measurements, the use of optical and scanning electron microscopy (SEM), grain-growth evaluation, and the use of Auger electron spectroscopy (AES). The mass-loss results were used to estimate thruster life in each propellant, the photomicrographs were used to determine if any material deterioration had occurred and also to examine the materials for evidence of grain growth, while AES was used to examine the materials for contamination by the various propellants.

Experimental Method

Material compatibility tests were conducted in six test cells. The test cells were of two basic configurations, the major difference being the technique used for maintaining cell pressure (9). Differences were the result of safety requirements and facility ventilation capabilities. One of the test cells is shown in Figure 2.

With the exception of the samples tested in hydrazine at 1400°C, all samples were coiled platinum-yttria or platinum-zirconia. The samples were coiled from tube with an external diameter of 0.203 cm and a wall thickness of 0.025 cm, a length of about 43.2 cm being required for each coil. Samples for the 1400°C hydrazine tests were 15.2 cm lengths of this tubing. Prior to coiling, the platinum-yttria material required a 30 minute anneal in vacuum at 1000°C. In the as-drawn condition the platinum-zirconia was ductile enough to coil without cracking.

The samples were resistively self-heated with a DC power supply, and their temperatures were measured using a two-colour optical pyrometer in all tests, except for those in methane. Since the methane tests were run at temperatures outside the pyrometer range, a calibrated chromel-alumel thermocouple attached to a centre coil was used for temperature measurement.

The samples were tested in a flowing gas environment at a cell pressure of about 1.39×10^5 N/m^2. The cells were brought to

the operating pressure by closing the gas outlet valve and introducing gas into the chamber. When the desired pressure was reached, the outlet gas valve was opened and adjusted to maintain the required pressure. The gas flow in the decomposed hydrazine tests was about 300 standard cubic centimetres per minute (SCCM) to maintain stable operation of the thermal gas generator used for the decomposition, the resulting gas being a mixture of ammonia, hydrogen and nitrogen. In all other tests the gas flow was about 100 SCCM. All samples were tested at 1400°C, except for those tested in methane and a sample tested in hydrazine. The methane tests were run at 500°C so that solid carbon formation was minimised. A test in decomposed hydrazine was operated at 800°C to determine if the surface reaction was reduced.

Results and Discussion

Several techniques were used in the evaluation of the compatibility of these materials with the various candidate propellants. Sample mass losses over the period were used as a compatibility indicator. The mass of each sample was measured before and after testing, the mass loss was used to extrapolate thruster life for each propellant environment, which was based on a failure criterion of 10 per cent gross mass loss for a sample.

Photomicrographs of the test sample surfaces and cross-sections before and after testing were used to evaluate propellant interaction at the material surface and to determine changes in relative grain size. Auger electron spectroscopy was used to examine the samples for contamination.

Mass-Loss Results

A summary of the percentage mass losses and the estimated thruster lifetimes for both materials is given in the Table. The mass-loss values are for 1000 hours of exposure to the indicated environment, except that the values for the last platinum-yttria tests in hydrogen and ammonia are for 2000 hours of exposure.

The platinum-yttria samples had mass losses ranging from 0.006 per cent in methane to 0.206 per cent in hydrazine in the 1000 hour tests. The mass losses in the 2000 hour tests were 0.110 per cent in ammonia and 0.136 per cent in hydrogen. Mass losses for the platinum-zirconia samples ranged from no measurable loss in methane to 0.221 per cent in the steam environment. The results of the platinum-yttria tests in hydrazine at 800 and 1400°C confirmed that the operating temperature was significant, because the mass loss of 0.010 per cent that occurred in the 800°C test was more than an order of magnitude lower than the loss at 1400°C. Although these tests were run at gas pressures of 3.66 N/m^2, the weight loss was consistent with vacuum evaporation of platinum (11). This result indicates that evaporation may be the loss mechanism, rather than any corrosive attack by the propellants.

The mass-loss results were linearly extrapolated to give an estimate of thruster life. Based on the 1000 hour tests, the life estimates were lowest in the hydrazine environment for platinum-yttria, and in the steam environment for platinum-zirconia. The 2000 hour tests of platinum-yttria in hydrogen and ammonia produced life estimates of 148,000 and 182,000 hours, respectively. Straight tube samples were used in the 1400°C tests in hydrazine, and these exhibited the lowest life estimates. The mass loss of these samples may have been less if they had been tested in a coiled configuration, because of the possibility of metal being redeposited on facing sections and on cooler parts of the sample. Regardless of this possibility, the life estimates of these and the other samples exceeded the anticipated 10,000 hour life requirement for a space station resistojet by at least a factor of four.

Mass-loss and life calculations did not take into account redeposition of the metal or the deposition of contaminants. On the basis of AES surface analyses, contaminants generally totalled an order of magnitude less than the obtained mass losses, and therefore could be considered negligible. After testing, only the test cell used for the steam test showed evidence of deposited metal; the other test cells were clean.

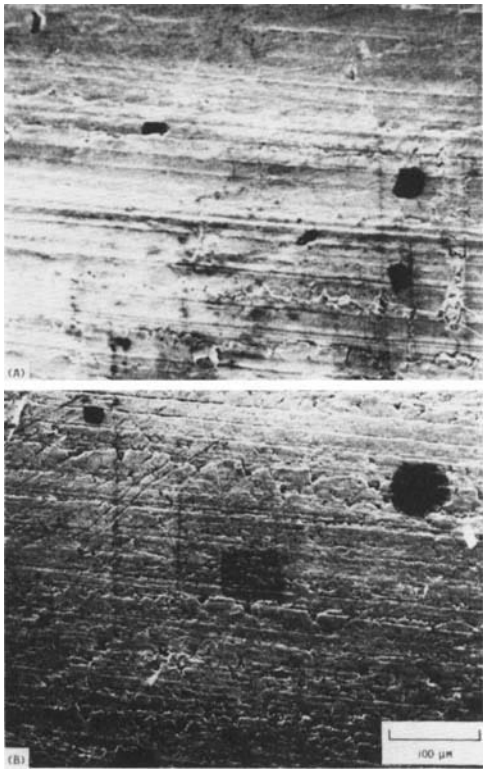

Fig. 3 Prior to testing the platinum-yttria and platinum-zirconia samples exhibited surface roughness and longitudinal striations resulting from the metal working process: (A) platinum-yttria after annealing in vacuum for 30 minutes at 1000°C, (B) platinum-zirconia in the as-drawn condition

These factors indicated that the life estimates based on mass loss were reasonable.

Surface-Analysis Results

Auger electron spectroscopy with depth profiling was used to examine surface contamination in the 1000 hour tests only in carbon dioxide, hydrogen, ammonia and methane (9). This technique allowed elemental characterisation of the surface of the sample. The contaminants found on each sample included carbon, hydrogen, nitrogen and oxygen. For both platinum-yttria and platinum-zirconia AES with depth profiling indicated that the samples had surface layers of contamination which extended to depths of ~200Å. Profiling to greater depths did not reveal any significant reaction. These results indicated that any reactions between platinum and the propellants tended to occur at the surface of the material.

Surface deterioration was also evaluated qualitatively by examining surfaces and cross-sections of the materials before and after testing, and photomicrographs were used to assess propellant interaction at the material surface, and to determine changes in relative grain size.

The platinum-yttria tubing had to be annealed before the sample could be coiled to the test configuration, and some grain growth occurred during the annealing treatment. The platinum-zirconia, which did not require annealing prior to coiling, had a finer initial grain structure than the platinum-yttria. Surface photographs of the annealed platinum-yttria and the as-drawn platinum-zirconia are shown in Figure 3. Prior to testing, the platinum-yttria and platinum-zirconia sample surfaces showed the initial surface roughness and longitudinal pattern resulting from the extruding process. The cross-sectional view provided information on grain size for comparison between samples. Generally, the surfaces of the platinum-yttria and platinum-zirconia had similar appearances after testing in the same environment. The samples exposed to carbon dioxide showed evidence of contamination, which AES analysis found to be a carbon deposit. The sample surfaces from the nitrogen, steam and both hydrogen tests were similiar in appearance, with a grain structure running parallel to the direction of extrusion, as shown by the platinum-yttria in Figure 4. The grain structure on these unetched surfaces was indicative of grain-boundary grooving, which is commonly observed in metals exposed to high temperatures in inert environments. The samples tested at 500°C in methane appeared unchanged. The samples at 1400°C exposed to ammonia and decomposed hydrazine showed a roughened surface with pitting over the entire exposed area, as shown in Figure 5. The pitting observed raised concerns about how much of the material was affected, and what effect this pitting had on the material strength. A

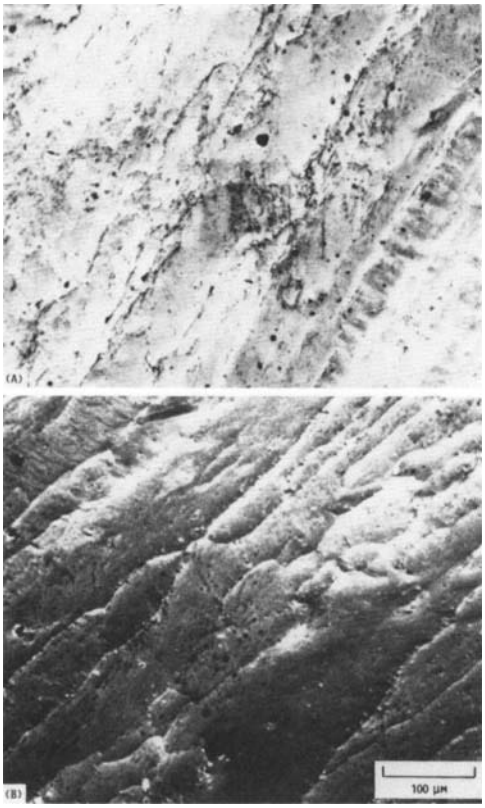

Fig. 4 The appearance of the surfaces of platinum-yttria samples that have been tested in nitrogen, steam and hydrogen were similar, with an elongate grain structure aligned parallel to the direction of working: (A) after 1000 hours at 1400°C in hydrogen, (B) after 1000 hours at 1400°C in nitrogen

platinum-yttria sample tested in hydrazine, but run at only 800°C, showed no evidence of the surface pitting that was so prominent after the 1400°C test.

Cross-sections of the platinum-yttria samples tested at 500, 800 and 1400°C exhibited similar grain size and very little difference from the annealed sample. This is illustrated by the photomicrographs, Figure 6. This grain size was greater than that of the untreated platinum-yttria sample, but approximately the same as the sample after the short anneal. The evidence implies that most of the grain growth occurred during the 30 minute vacuum anneal at 1000°C. The 2000 hour exposure in hydrogen showed no reaction, but there appeared to be some slight grain growth. This was not considered to be significant, and may have been due to sample variability. These results indicate that material stability is not a major concern.

The cross-sections of the platinum-yttria samples tested in ammonia and in hydrazine at 1400°C showed that the pitting, evident on the surface, extended well into the material. In each sample the corrosion was uniform across the tube thickness, with no evidence of accelerated attack at the grain boundaries. After 1000 hours at 1400°C in ammonia, the reaction zone, or the depth of pitting in the material, extended through about one-third of the wall thickness. Exposing a similar sample to the same environment for 2000 hours resulted in a reaction zone extending approximately halfway through the wall thickness. On the basis of a study of this reaction zone by M. V. Nathal,

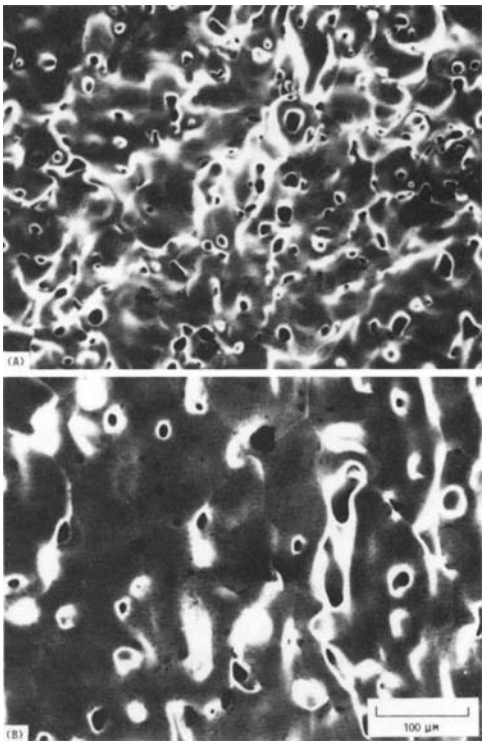

Fig. 5 After 1000 hours at 1400°C, platinum-yttria samples exposed to ammonia and decomposed hydrazine showed surfaces which were roughened and pitted: (A) ammonia atmosphere, (B) hydrazine atmosphere

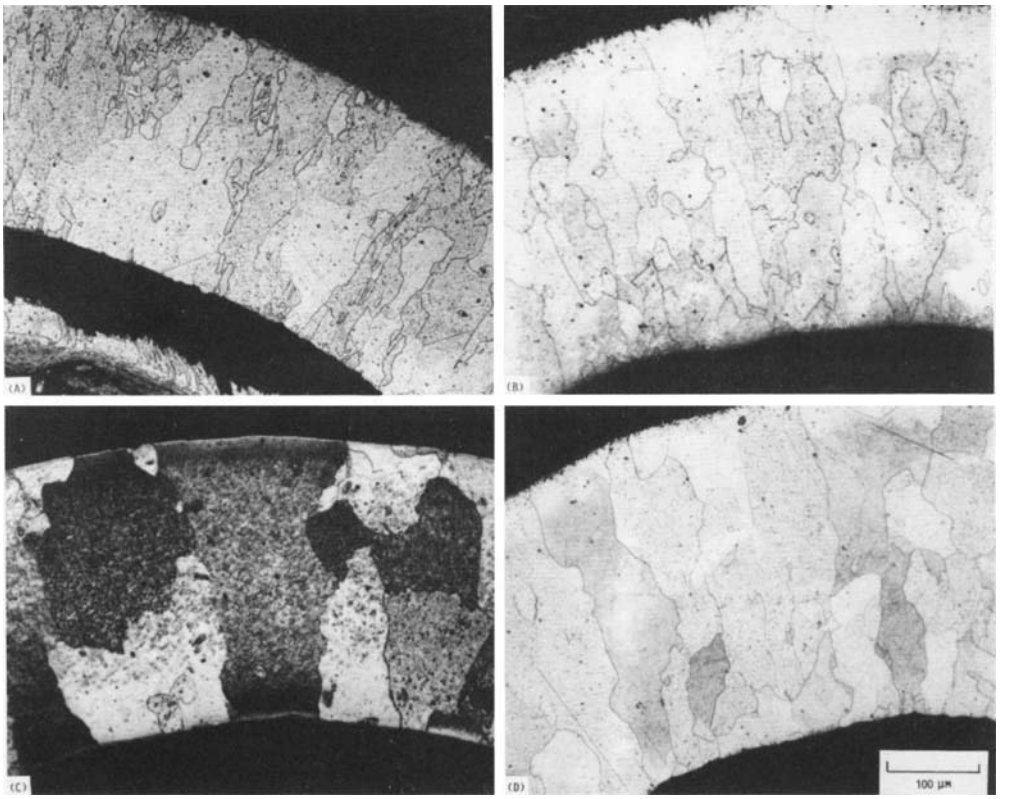

Fig. 6 Cross-sections of platinum-yttria tested at 500, 800 and 1400°C for 1000 hours all showed similar grain sizes to annealed material, suggesting that most of the grain growth occurred during the 30 minute vacuum anneal at 1000°C: (A) after annealing, (B) tested at 500°C in methane, (C) tested at 800°C in hydrazine, (D) tested at 1400°C in hydrogen

M. V. Whalen and D. P. Pank at NASA Lewis Research Center, the estimated time for the attack to penetrate through the entire wall thickness was approximately 5000 hours at 1400°C; at 1300 and 1000°C, sample lifetimes were estimated at about 15,000 and 40,000 hours, respectively. The condition of the 1400°C hydrazine sample was similar to that of the sample run in ammonia. The hydrazine sample run at 800°C showed no evidence of corrosion on either the cross-section or the surface. This result indicates that platinum-yttria may be acceptable for operation in ammonia or hydrazine at the lower temperatures. The platinum-yttria samples exposed to carbon dioxide, hydrogen, nitrogen, steam and methane showed no evidence of corrosion or deterioration.

Platinum-zirconia samples tested in methane at 500°C showed a finer grain size than the samples tested at 1400°C. This can be explained by the fact that the platinum-zirconia samples did not receive an annealing treatment prior to testing. For comparison, a platinum-zirconia sample was annealed for 30 minutes at 1000°C and this resulted in some slight grain growth, similar to that of the annealed platinum-yttria. Thus, in the case of the platinum-zirconia samples, some grain growth occurred during the exposures at 1400°C, but the 500°C exposure was too low for grain growth to occur. If a prior annealing treatment had been performed, all significant grain growth would have occurred during the anneal, rather than during the test, as in the platinum-yttria cases. The platinum-zirconia samples

tested in carbon dioxide, hydrogen, steam and methane, as in the platinum-yttria samples, showed no corrosion or deterioration. The samples exposed to ammonia and hydrazine showed a reaction zone extending through about half the cross-section. The reaction zone of the platinum-yttria sample exposed to hydrazine was about the same thickness. The samples tested in ammonia showed a thicker zone for the platinum-zirconia sample. However, further testings by Nathal, Whalen and Pank indicated that these differences were due to experimental scatter, probably attributable to temperature control.

The results of the ammonia and hydrazine tests for both materials were interesting in that the mass loss measured in these tests was much lower than necessary to form the volume of voids seen in the platinum-yttria cross-section shown in Figure 7. Measurement of the tube diameter before and after testing indicated an increase in outside diameter of as much as 10 per cent. This evidence indicates that the void formation actually caused swelling of the material, rather than being indicative of a loss of material due to corrosion. A suspected mechanism for the void formation involves diffusion of hydrogen and nitrogen atoms into the platinum. The dissociation of ammonia into hydrogen and nitrogen occurs by a process with an intermediate step in which atomic hydrogen and nitrogen are formed (12–14). The dissociation reaction occurs at the platinum surface, which is acting as a catalyst. Some of the atomic hydrogen and nitrogen may then diffuse into the platinum before combining to form molecular hydrogen and nitrogen. These can then coalesce into gas bubbles within the platinum and thus cause the swelling of the tubes. This type of reaction had been observed previously where ammonia gas was used for internal nitridation of steels (13, 14). Additionally, no void formation was observed in experiments run by Nathal, Whalen and Pank in hydrogen, nitrogen, or hydrogen/nitrogen mixtures, because the gas molecules do not dissociate at temperatures near 1400°C and because the molecules cannot diffuse into the platinum to any significant extent. Again, the extent of this void formation can be reduced if operation at lower temperatures is acceptable, and this was confirmed by the tests at 800, 1000 and 1300°C. Further testing to determine the influence of these voids on the mechanical properties of platinum is recommended before the use of ammonia and hydrazine propellants at high temperatures.

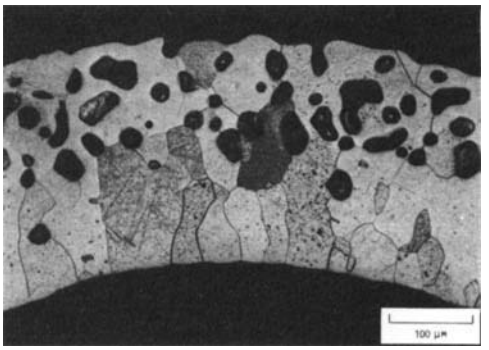

Fig. 7 After 1000 hours at 1400°C in decomposed hydrazine, this cross-section through the wall of a platinum-yttria tube shows a significant amount of porosity, which is not due to the loss of metal by corrosion. However it caused an increase in the outer diameter of the tube

Concluding Remarks

The compatibility of dispersion-strengthened platinum with potential space station resistojet propellants was evaluated. The test sample and operating temperature were representative of a resistojet heating element. The life estimates extrapolated from the mass losses occurring in these tests indicated that platinum-yttria and platinum-zirconia samples would withstand a minimum of 45,000 hours in any of the environments tested. These estimates are greater than four times the expected space station life requirement. The grain growth occurring in the platinum-yttria samples was slight and appears to have occurred during the anneal prior to sample fabrication. The platinum-zirconia samples, except the methane sample, showed some grain growth. Annealing may result in grain growth similar to that of the platinum-yttria samples. The grain growth should not significantly affect the material stability;

however, the effects, if any, on the performance of a resistojet should be evaluated.

The results indicated that platinum-yttria and platinum-zirconia are compatible with carbon dioxide, hydrogen, nitrogen, steam and methane under the conditions presented here. The reaction found in both materials at 1400°C when exposed to ammonia and decomposed hydrazine can be reduced by lowering the operating temperature. Both dispersion-strengthened platinums should be acceptable for space station resistojets using carbon dioxide, hydrogen, nitrogen, steam and methane. The propellants ammonia and hydrazine are also acceptable if the resistojet operating temperature is lowered.

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Fabricating Lithium Niobate Optical Wavelengths

One of the earliest uses of platinum was for the fabrication of crucibles to be used during chemical analysis, and over the years it has found application as a reliable containment material during many specialised processes, often under the most arduous conditions.

A recent communication from workers at the Universität Dortmund, West Germany, describes a new diffusion technique which is regarded as an important step towards the reproducible fabrication of low-loss titanium-diffused $LiNbO_3$ waveguides (A. Neyer and T. Pohlmann, *Electron. Lett.*, 1987, **23**, (22), 1187–1188).

During the fabrication of such waveguides precise control of substrate material stoichiometry, amount of deposited titanium and the diffusion conditions is required. The last are of paramount importance since the in-diffusion of titanium may be accompanied by an outdiffusion of LiO_2 from the $LiNbO_3$ crystal, resulting in an unwanted surface waveguide. This can now be avoided by containing the $LiNbO_3$ in a platinum box loosely closed with a platinum lid, during diffusion at a temperature of 1050°C.

The partial pressure of Li_2O built up in the small enclosed container is thought to prevent strong outdiffusion of Li_2O, but the main advantages of the platinum box are that it does not have to be stabilised by $LiNbO_3$ powder, it is not affected by Li_2O and it provides excellent temperature homogeneity.

Palladium Membrane Reactor

Although a reversible reaction can never be complete under ordinary conditions, if the products can be separated from the reacting mixtures the reaction should finally go to completion, and N. Itoh of the National Chemical Laboratory, Japan, has recently considered the decomposition of cyclohexane to benzene and hydrogen, using a platinum on alumina catalyst (*AIChE J.*, 1987, **33**, (9), 1576–1578). The hydrogen produced diffused out through the palladium wall of the reactor, and under the given conditions the conversion reached 99.7 per cent.