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# Compatibility of Dispersion-Strengthened Platinum With Resistojet Propellants

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## Summary

Resistojets for the space station require long life and multipropellant capability. The choice of available materials to meet these requirements is limited. Dispersion-strengthened platinum was selected to be studied for use as a resistojets material. Past results indicated that dispersion-strengthened platinum should be sufficiently inert in candidate propellant environments and should be capable of operating at moderate temperatures for extended periods of time.

A series of propellant compatibility tests was conducted with platinum strengthened with either yttria or zirconia. The data presented include the results of 1000-hr tests in carbon dioxide ( $\text{CO}_2$ ), hydrogen ( $\text{H}_2$ ), ammonia ( $\text{NH}_3$ ), nitrogen ( $\text{N}_2$ ), steam, hydrazine ( $\text{N}_2\text{H}_4$ ), and methane ( $\text{CH}_4$ ); and 2000-hr tests in  $\text{H}_2$  and  $\text{NH}_3$ .

The platinum samples were tested at 1400 °C in  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2$ , steam, and  $\text{N}_2\text{H}_4$ ; at 500 °C in  $\text{CH}_4$ ; and at 800 °C in  $\text{N}_2\text{H}_4$ . The mass-loss results indicated material life, extrapolated from experimental mass-loss data, in excess of 100 000 hr in all environments except steam and  $\text{N}_2\text{H}_4$ , where material life was  $\geq 45$  000 hr. Generally, on the basis of mass loss, there were no compatibility concerns in any of the environments considered. Optical and scanning electron microscopy were used to determine the effect of propellants on the material surface and to evaluate material stability as a function of resistance to grain growth. The propellant interaction varied from little or no reaction with  $\text{H}_2$  and  $\text{CH}_4$  to evidence of void formation and pitting of samples tested in  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$ . Material stability when measured as a function of grain growth did not appear to be a problem.

## Introduction

Resistojet propulsion systems have the potential for reduced propellant requirements, reduced propellant resupply servicing, and reduced cost, when compared to existing systems. In addition, they have long thruster life, low power consumption, and low spacecraft contamination. These potential benefits make resistojets attractive for space station auxiliary propulsion systems. The resistojets for the space station must be capable of both long life and multipropellant operation. Meeting these requirements is limited by available

materials. Thus, evaluation of potential materials will have 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. Grain growth can result in the formation of voids, physical distortions, and unacceptable reduction in the creep-strength of the material.

Platinum and alloy-strengthened platinum were considered for biowaste resistojets during the Manned Orbital Research Laboratory program of the early 1970's (refs. 1 to 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 (ref. 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 rhodium is not as corrosion resistant as platinum.

Another material developed during this period as a high-temperature, high-strength material for biowaste resistojets was platinum-0.6 percent thoria. The compatibility of this material with carbon dioxide ( $\text{CO}_2$ ) was verified, but no other data were available (ref. 5). Platinum-thoria alloy is no longer manufactured, but the experience gained in producing it was used in developing platinum materials strengthened with either zirconia or yttria for use in high-temperature oxidizing environments where corrosion resistance is necessary.

Preliminary work showed promise for the use of dispersion-strengthened platinum for space station resistojets (ref. 6). This report presents the results of compatibility tests on dispersion-strengthened platinum. The tests were conducted on tube samples representative of the resistojets heater element, which is the hottest resistojets component. A summary of the results of the 1000-hr compatibility tests in  $\text{CO}_2$ , methane ( $\text{CH}_4$ ), hydrogen ( $\text{H}_2$ ), and ammonia ( $\text{NH}_3$ ) is included (ref. 7), together with new data on 1000-hr tests in nitrogen ( $\text{N}_2$ ), steam, and decomposed hydrazine ( $\text{N}_2\text{H}_4$ ), and 2000-hr tests in  $\text{H}_2$  and  $\text{NH}_3$ . The material evaluation included mass-loss measurements, use of optical and scanning electron microscopy (SEM), grain growth evaluation, and 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, and the AES was used to examine the materials for contamination from the various propellants.

## Material Characteristics

The space station resistojet requirements for 10 000-hr life and multipropellant capability are demanding of any material. A material with these capabilities would reduce the thruster maintenance and replacement costs and would enable thruster operation with both oxidizing and reducing propellants that may be on board the space station. Platinum strengthened with yttria or zirconia has the potential to meet these requirements.

Platinum has been recognized for its corrosion resistance in severe environments at high temperatures ( $\geq 1200$  °C) (refs. 8 and 9). However, pure platinum has limited strength and creep resistance at these high temperatures. Dispersion strengthening of platinum was found to significantly increase the high-temperature strength of the material. The process of dispersion strengthening involves strengthening a metal by incorporating a fine, insoluble material uniformly throughout the metal. The dispersoid is nearly insoluble in the metal and very stable at temperatures up to the metal melting point. In addition to increased strength, dispersion-strengthened platinum has greater resistance to grain growth than pure platinum.

Two types of dispersion-strengthened platinum materials are currently available. One is dispersion strengthened with yttria ( $Y_2O_3$ ) and the other with zirconia ( $ZrO_2$ ). Since the oxide content is less than 1 percent by weight in both the materials, the physical and room-temperature mechanical properties of platinum are not significantly changed by addition of these oxides. However, as described earlier in this section, there is improvement in the high-temperature strength, the creep resistance, and the stability of the material as measured by grain growth (refs. 8 and 9).

## Apparatus

Material compatibility tests were conducted in six test cells. The test cells were of two basic configurations, with the major difference being the technique used for maintaining cell pressure. Differences were the result of safety requirements and facility ventilation capabilities. Figure 1 shows a diagram of a test cell arrangement. The tests using  $CO_2$ , steam, and  $N_2$  were run in cells in which flow was controlled by needle valves and exiting gases were drawn to roughing pumps. The  $CO_2$  and  $N_2$  tests were run in the same cell. Each of these cells was fabricated from quartz tubing and was typically 3.81 cm in diameter by 20.3 cm in length. Silicon rubber

O-rings were used to seal the  $CO_2$  test chamber, and Teflon O-rings were used to seal the  $N_2$  and steam test cells.

The  $H_2$ ,  $NH_3$ ,  $N_2H_4$ , and  $CH_4$  tests were run in similar test cells. The chambers were stainless steel with quartz viewing windows. These cells were typically 15.2 cm in diameter by 30.5 cm in length. The  $H_2$  test cell was sealed with copper gaskets, the  $NH_3$  and  $N_2H_4$  cells with nickel-plated copper gaskets, and the  $CH_4$  cell with Teflon gaskets. In the  $H_2$ ,  $NH_3$ , and  $N_2H_4$  tests, needle valves both upstream and downstream of the cells were used for flow control. Roughing pumps were used only to purge the system, and the exiting gases were vented to the atmosphere. For the  $CH_4$  test, flow was controlled by needle valves, and exiting gases were drawn to a roughing pump, as for the  $CO_2$ , steam, and  $N_2$  tests.

All samples were coiled platinum-yttria or platinum-zirconia tubes, except those tested in  $N_2H_4$  at 1400 °C, which were straight lengths of tubes because of a lack of material. The samples were coiled from 0.0203-cm-o.d., 0.025-cm-wall tubing, with about a 43.2-cm length required for each coil. Samples for the 1400 °C  $N_2H_4$  tests were 15.2 cm lengths of the same tubing. The platinum-yttria material required a 30-min anneal at 1000 °C prior to coiling. The platinum-zirconia was ductile enough in the drawn condition to coil without cracking.

The samples were resistively self-heated by a 100-A, 100-V dc power supply. The power was applied to the samples through stainless steel or copper support rods, depending on the gas environment. Sample temperatures were measured by using a two-color optical pyrometer in all tests except those in  $CH_4$ . Since the  $CH_4$  tests were run at temperatures outside the pyrometer range, a calibrated Chromel-Alumel thermocouple was attached to a center coil for temperature measurement. The accuracy of the two-color pyrometer was 1 percent of full scale, and the thermocouple was accurate to about  $\pm 20$  °C, based on calibration.

## Procedure

The samples were cleaned, and their pretest mass was measured by using an analytical balance with an accuracy of  $\pm 1$  mg. Prior to the test, each cell was evacuated and purged with  $N_2$  twice, then evacuated again. The samples were tested in a flowing gas environment at a cell pressure of about  $1.39 \times 10^5$  N/m<sup>2</sup> (20 psia). The cells were brought to operating pressure by closing the gas outlet valve and introducing gas into the chamber. Then, the outlet gas valve was opened and adjusted to maintain the pressure. The gas flow in the decomposed  $N_2H_4$  tests was about 300 standard cubic centimeters per minute (SCCM) to maintain stable operation of the thermal gas generator. The  $N_2H_4$  was decomposed from a liquid to a gas by flowing it through a thermal gas generator. The resulting gas was a mixture of ammonia, hydrogen, nitrogen, and small amounts of water and aniline. The gas flow was about 100 SCCM in all other

tests. All samples were tested at 1400 °C, except those in CH<sub>4</sub> and a sample in N<sub>2</sub>H<sub>4</sub>. The CH<sub>4</sub> tests were run at 500 °C so that solid carbon formation was minimized. Additionally, a test in decomposed N<sub>2</sub>H<sub>4</sub> was operated at 800 °C to determine if the surface reaction was reduced. Each test was run for at least 1000 hr. Two tests in H<sub>2</sub> and NH<sub>3</sub> were extended to determine the effect of longer exposure. Tables I and II summarize test conditions for platinum-yttria and platinum-zirconia, respectively.

Several techniques were used in the evaluation of the compatibility of these materials with the various candidate propellants. Sample mass loss over the period was 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 percent gross mass loss for a sample. This criterion is more stringent than standards accepted by other industries (ref. 10).

The effect of propellant interaction with platinum-yttria and platinum-zirconia was evaluated. Optical and scanning electron microscopes were used to examine the test sample surfaces and cross sections before and after testing. The photographs allowed evaluation of propellant interaction at the material surface and determination of changes in relative grain size.

Auger electron spectroscopy was used to determine the material surface composition only in the 1000-hr tests in CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, and CH<sub>4</sub>. This technique allowed elemental characterization of the surface of the sample. A brief discussion of the results of this evaluation is included in the following section. Further details are available in reference 7.

## Results and Discussion

These experiments were intended to determine the compatibility of dispersion-strengthened platinum with a variety of potential resistojet propellants. The mass-loss and material-analysis results that follow include data on both platinum-yttria and platinum-zirconia.

### Mass-Loss Results

A summary of initial sample masses and mass-loss percentages is presented in table III. The mass-loss values are for 1000 hr of exposure to the indicated environment, except that the values for the last H<sub>2</sub> and NH<sub>3</sub> tests are for 2000 hr of testing.

The platinum-yttria samples had losses in 1000-hr tests ranging from 0.006 percent in CH<sub>4</sub> to 0.206 percent in N<sub>2</sub>H<sub>4</sub>. The mass losses in the 2000-hr tests were 0.110 percent in NH<sub>3</sub> and 0.136 percent in H<sub>2</sub>. The results of the N<sub>2</sub>H<sub>4</sub> tests at 1400 and 800 °C confirmed that operating temperature has a major impact on service life; the mass loss of 0.010 percent for the 800 °C test was more than an order of magnitude lower than that for the 1400 °C N<sub>2</sub>H<sub>4</sub> test. Although these tests

TABLE I.—SUMMARY OF PLATINUM-YTTRIA TEST CONDITIONS

Propellant	Operating temperature, °C	Operating time, hr	Current, <sup>a</sup> A	Voltage, <sup>a</sup> V	
CO <sub>2</sub>	1400	1000	30	6.8	
H <sub>2</sub>	↓	↓	45	7.5	
NH <sub>3</sub>			44	7.5	
N <sub>2</sub>			40	7.0	
Steam			41	9.0	
N <sub>2</sub> H <sub>4</sub>			67	5.5	
CH <sub>4</sub>	500	↓	21	1.8	
N <sub>2</sub> H <sub>4</sub>	800		25	2.8	
H <sub>2</sub>	1400		2000	46	7.0
NH <sub>3</sub>	1400		2000	52	6.2

<sup>a</sup>Test average.

TABLE II.—SUMMARY OF PLATINUM-ZIRCONIA TEST CONDITIONS

Propellant	Operating temperature, °C	Operating time, hr	Current, <sup>a</sup> A	Voltage, <sup>a</sup> V
CO <sub>2</sub>	1400	1000	39	6.3
H <sub>2</sub>	↓	↓	49	7.0
NH <sub>3</sub>			48	7.5
Steam			46	9.0
N <sub>2</sub> H <sub>4</sub>			69	5.5
CH <sub>4</sub>			500	19

<sup>a</sup>Test average.

TABLE III.—DISPERSION-STRENGTHENED PLATINUM MASS-LOSS RESULTS

Propellant <sup>a</sup>	Platinum-yttria		Platinum-zirconia	
	Initial mass, g	Mass loss, percent	Initial mass, g	Mass loss, percent
CO <sub>2</sub>	9.0194	0.033	13.1955	0.012
H <sub>2</sub>	12.6589	.049	13.2124	.023
NH <sub>3</sub>	12.5982	.052	13.0632	.050
N <sub>2</sub>	11.0635	.094	-----	-----
Steam	13.0695	.089	11.5133	.221
N <sub>2</sub> H <sub>4</sub>	4.5987	.206	4.1238	.155
CH <sub>4</sub> at 500 °C	12.6384	.006	11.696	.000
N <sub>2</sub> H <sub>4</sub> at 800 °C	10.7323	.010	-----	-----
H <sub>2</sub> <sup>b</sup>	11.2678	.136	-----	-----
NH <sub>3</sub> <sup>b</sup>	10.9983	.110	-----	-----

<sup>a</sup>All samples tested at 1400 °C, except where noted otherwise.

<sup>b</sup>2000-hr test.

were run at 3.66 N/m<sup>2</sup>, the mass loss was consistent with vacuum evaporation of platinum (ref. 10). This indicates that evaporation may be a loss mechanism, rather than any corrosive attack by the propellants.

The mass-loss results presented were used to extrapolate thruster life (table IV). Previously reported data estimated lifetimes of platinum-yttria samples exposed to CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, and CH<sub>4</sub> at 300 000, 200 000, 200 000, and 1 500 000 hr, respectively (ref. 7). The 1000-hr tests in N<sub>2</sub>, steam, N<sub>2</sub>H<sub>4</sub> at 1400 °C, and N<sub>2</sub>H<sub>4</sub> at 800 °C resulted in thruster life estimates of 106 000, 110 000, 48 000, and 970 000 hr, respectively. The 2000-hr tests in H<sub>2</sub> and NH<sub>3</sub> gave life estimates of 148 000 and 182 000 hr.

All platinum-zirconia samples were tested for 1000 hr in each environment. The mass losses for these samples ranged from no measurable loss in CH<sub>4</sub> to a 0.221-percent loss in the steam environment. The next largest mass loss occurred in the sample tested in N<sub>2</sub>H<sub>4</sub>, which lost 0.155 percent of its original mass. Mass losses in CO<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> were 0.012, 0.023, and 0.050 percent, respectively.

The life estimates of platinum-zirconia previously reported for CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, and CH<sub>4</sub> were 800 000, 200 000, 400 000, and > 1 500 000 hr, respectively. The sample tested in CH<sub>4</sub> showed no measurable mass loss. Both the platinum-zirconia and the platinum-yttria samples tested in CH<sub>4</sub> were tested at a much lower temperature (500 °C) than the other samples to minimize methane decomposition and the resulting carbon deposition.

The life estimates of platinum-zirconia for the steam and N<sub>2</sub>H<sub>4</sub> tests were 45 000 and 64 000 hr, respectively. The platinum-zirconia coiled tube sample tested in steam had the lowest life estimate. Both straight tube samples tested at 1400 °C in N<sub>2</sub>H<sub>4</sub> exhibited low life estimates. The mass loss of these samples may have been lower in a coiled configuration because of the possibility of redeposition of metal on facing sections and on cooler sections of the sample. Regardless of this possibility, the life estimates of 48 000 hr for the platinum-yttria and 64 000 hr for the platinum-zirconia samples

exceeded the anticipated 10 000-hr life requirement for the space station resistojet by at least a factor of four.

The mass-loss and life calculations did not take into account redeposition of the base metal or deposit of contaminants, such as carbon, on the sample surface. On the basis of the information from the AES surface analyses, which are discussed further in the subsection to follow, surface contaminants generally totaled an order of magnitude less than the observed mass losses, and therefore could be considered negligible. After testing, only the test cell used for the steam test had evidence of redeposited metal; all other test cells were clean. These factors indicated that the life estimates based on mass loss were realistic. However, void formation and pitting which occurred in the N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> tests reduced these estimates, as discussed in the following subsection.

### Surface-Analysis Results

After testing, the material was examined for surface contamination, deterioration, and grain growth. Auger electron spectroscopy (AES) and AES with depth profiling were used to examine the possibility of surface contamination. These techniques gave the approximate atomic percent of constituents at the surface and at specified depths below the material surface. The samples tested in CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, and CH<sub>4</sub> were evaluated by this technique. The contaminants that were found on each sample included carbon, H<sub>2</sub>, N<sub>2</sub>, and oxygen (O<sub>2</sub>). The samples tested in H<sub>2</sub> and NH<sub>3</sub> generally had lower levels of surface contaminants than the samples tested in CH<sub>4</sub> and CO<sub>2</sub>. The CO<sub>2</sub> and CH<sub>4</sub> environments produced higher levels of carbon, and the CO<sub>2</sub> also showed evidence of silicon. The source of the carbon was suspected to be hydrocarbon oils from the pumps used to maintain the cell pressure, and the silicon source appeared to be the O-rings used to seal these test cells. The other test cells used roughing pumps only for evacuation and purging, and used either Teflon, copper, or nickel-plated copper gaskets for sealing.

The AES for both platinum-yttria and platinum-zirconia indicated that the samples had surface layers of contamination which extended to depths of about 200 Å. Profiling to greater depth did not reveal any significant reaction. These results indicated that any reactions between the platinum and the propellants tended to occur at the material surface.

The surface deterioration was also evaluated qualitatively by examining the material surface and cross section before and after testing. Cross-sectional views obtained with an optical microscope were also used to evaluate grain growth.

A photomicrograph showing the cross section of the platinum-yttria prior to any treatment is shown in figure 2. The material had a fine grain structure. The platinum-yttria tubing required an anneal before the sample could be coiled to the test configuration. Figure 3 shows the surface and cross section of the platinum-yttria sample after a 30-min anneal, at 1000 °C in vacuum. The surface photograph (fig. 3(a)) shows the initial surface roughness and longitudinal grain pattern resulting from the extruding process. The cross-

TABLE IV.—ESTIMATED THRUSTER LIFE

Propellant <sup>a</sup>	Estimated thruster life	
	Platinum-yttria	Platinum-zirconia
CO <sub>2</sub>	300 × 10 <sup>3</sup>	800 × 10 <sup>3</sup>
H <sub>2</sub>	200	400
NH <sub>3</sub>	200	200
N <sub>2</sub>	106	-----
Steam	110	45
N <sub>2</sub> H <sub>4</sub>	48	64
CH <sub>4</sub> at 500 °C	1500	> 1500
N <sub>2</sub> H <sub>4</sub> at 800 °C	970	-----
N <sub>2</sub> <sup>b</sup>	148	-----
NH <sub>3</sub> <sup>b</sup>	182	-----

<sup>a</sup>All samples tested at 1400 °C, except where noted otherwise.

<sup>b</sup>2000-hr test.

sectional view (fig. 3(b)) provides grain size information for comparison with other samples. Note that some grain growth occurred during the annealing treatment.

Figures 4 and 5 show the platinum-yttria surfaces after 1000 hr at 1400 °C in CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, steam, and N<sub>2</sub>H<sub>4</sub>; at 500 °C in CH<sub>4</sub>; and at 800 °C in N<sub>2</sub>H<sub>4</sub>. Figure 6 shows the platinum-yttria surface after 2000 hr at 1400 °C in H<sub>2</sub> and NH<sub>3</sub>, respectively. The sample exposed to CO<sub>2</sub> showed evidence of a deposit, which was most probably the carbon that was found by the AES experiments. The surface of the N<sub>2</sub>, steam, and both H<sub>2</sub> samples had a similar appearance, with a grain structure running parallel to the extrusion direction. The grain structure on these unetched surfaces is indicative of grain-boundary grooving, which is commonly observed in metals exposed to high temperatures in inert environments. The sample tested at 500 °C in CH<sub>4</sub> appeared unchanged (fig. 5(a)). The samples at 1400 °C exposed to NH<sub>3</sub> and decomposed N<sub>2</sub>H<sub>4</sub> showed a roughened surface with pitting over the entire exposed area (figs. 4(c) and (f)). The pitting observed raised concerns about how much of the material was affected, and what effect this pitting had on the material strength. A sample tested in N<sub>2</sub>H<sub>4</sub>, but run at the lower temperature of 800 °C (fig. 5(b)), showed no evidence of the surface pitting that was so prominent in the 1400 °C test.

Surface and cross-sectional photographs of the extruded platinum-zirconia tube prior to testing are presented in figure 7. The platinum-zirconia samples, which did not require annealing prior to fabricating the coiled samples, had a finer grain structure in the as-drawn condition than the platinum-yttria.

Surface photographs of platinum-zirconia samples tested at 1400 °C in CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, steam, and N<sub>2</sub>H<sub>4</sub>, and at 500 °C in CH<sub>4</sub> are shown in figure 8. In general, these samples exhibited features similar to the platinum-yttria material. The platinum-zirconia sample exposed to CH<sub>4</sub> (fig. 8(f)) appeared similar to the untested sample; however, there was a coating over the material surface that had darkened the color of the sample and that appeared thicker at the center coils. This coating was found by the AES analysis to be carbon.

Cross-sectional photomicrographs of platinum-yttria tested at 1400 °C in CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, steam, and N<sub>2</sub>H<sub>4</sub>; at 500 °C in CH<sub>4</sub>; and at 800 °C in N<sub>2</sub>H<sub>4</sub> appear in figures 9 and 10. The cross sections of samples after 2000 hr in H<sub>2</sub> and NH<sub>3</sub> are shown in figure 11. The platinum-yttria samples tested at 500, 800, and 1400 °C exhibited similar grain size and very little, if any, difference from the annealed sample (fig. 3(b)). Since this grain size was greater than that of the as-drawn platinum-yttria sample, but was approximately the same as that of the sample after the short anneal, this evidence implies that most of the grain growth occurred during the 1000 °C, 30-min anneal. The 2000-hr exposure in H<sub>2</sub> showed no reaction, but there appeared to be slight grain growth. This observed grain growth, which may have been due to sample variability, was not considered significant.

The pitting that appeared in the cross section of the sample

tested in CO<sub>2</sub> was found to be bubbles in the mounting epoxy and so unrelated to the testing. The platinum-yttria samples exposed to CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, steam, and CH<sub>4</sub> showed no evidence of corrosion or deterioration. The cross-sectional views of the two NH<sub>3</sub> samples (figs. 9(c) and 11(b)) and the N<sub>2</sub>H<sub>4</sub> sample run at 1400 °C (fig. 9(f)) show that the pitting evident in the surface photograph 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 hr at 1400 °C in NH<sub>3</sub>, the reaction zone, or the depth of pitting in the material, extended through about one-third the wall thickness. Exposing a similar sample to the same environment for 2000 hr 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, M.V. Whalen, and D.P. Pank at NASA Lewis Research Center, the estimated time for the attack to grow through the entire wall thickness was approximately 5000 hr at 1400 °C; at 1300 and 1000 °C, lifetimes were estimated at about 15 000 and 40 000 hr, respectively. The 1400 °C N<sub>2</sub>H<sub>4</sub> sample showed results similar to the NH<sub>3</sub> sample. Figure 10(b), the cross section of the N<sub>2</sub>H<sub>4</sub> sample operated at 800 °C, showed no evidence of corrosion in either the cross-sectional or surface views. These results indicate that platinum-yttria may be acceptable for operation in NH<sub>3</sub> or N<sub>2</sub>H<sub>4</sub> at lower temperatures. The platinum-yttria samples exposed to CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, steam, and CH<sub>4</sub> showed no evidence of corrosion or deterioration.

Photomicrographs showing cross sections of the platinum-zirconia samples exposed to CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, steam, N<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> are presented in figure 12. The CH<sub>4</sub> sample, which was tested 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. As a comparison, a platinum-zirconia sample was annealed for 30 min at 1000 °C. This test resulted in some slight grain growth similar to that of the annealed platinum-yttria, as shown in figure 13. 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 annealing process rather than during the test, as in the platinum-yttria cases. The platinum-zirconia samples tested in CO<sub>2</sub>, H<sub>2</sub>, steam, and CH<sub>4</sub>, as in the platinum-yttria samples, showed no corrosion or deterioration. The samples exposed to NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> showed a reaction zone extending through about half the cross section. The reaction zone of the platinum-yttria sample exposed to N<sub>2</sub>H<sub>4</sub> was about the same thickness. The samples tested in NH<sub>3</sub> showed a thicker zone for the platinum-zirconia sample. However, further testing by Nathal, Whalen, and Pank indicated that these differences were due to experimental scatter, most likely due to temperature control.

The results of the NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> 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 cross-sectional views. Measurement of the tube diameter before and after testing indicated an increase in outside diameter of as much as 10 percent. 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  $\text{NH}_3$  into  $\text{H}_2$  and  $\text{N}_2$  occurs by a process with an intermediate step in which atomic hydrogen and nitrogen are formed (refs. 11 to 13). The dissociation reaction occurs at the platinum surface, which is acting as a catalyst. Some of the atomic hydrogen and nitrogen can then diffuse into the platinum before combining to form  $\text{H}_2$  and  $\text{N}_2$  gas in the test chamber. These atoms can then coalesce into gas bubbles within the platinum and thus cause the swelling of the tubes. This type of reaction has been observed previously (refs. 12 and 13), where  $\text{NH}_3$  gas was used for internal nitridation of steels. Additionally, no void formation was observed in experiments run by Nathal, Whalen, and Pank in  $\text{H}_2$ ,  $\text{N}_2$ , or  $\text{H}_2/\text{N}_2$  mixtures, because the gas molecules do not dissociate at temperatures near  $1400^\circ\text{C}$  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, as confirmed by the tests at 800, 1000, and  $1300^\circ\text{C}$ . Further testing to determine the influence of these voids on the mechanical properties of platinum is recommended before use of  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  propellants at high temperatures.

## Concluding Remarks

The compatibility of dispersion-strengthened platinum with potential space station resistojets propellants was evaluated. A series of 1000-hr tests of platinum-yttria and platinum-zirconia exposed to gas environments of  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2$ , steam, and  $\text{N}_2\text{H}_4$  at  $1400^\circ\text{C}$ ;  $\text{CH}_4$  at  $500^\circ\text{C}$ ; and  $\text{N}_2\text{H}_4$  at  $800^\circ\text{C}$  was completed. Tests for 2000 hr at  $1400^\circ\text{C}$  in  $\text{H}_2$  and  $\text{NH}_3$  were also performed.

The test sample and operating temperature were representative of a resistojets 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 hr in any of the environments tested; however, the void formation in the  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  samples suggests lower lifetimes. 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 showed some grain growth. Annealing may result in grain growth similar to that of the platinum-yttria samples. The grain growth was not considered a problem; however, the effects, if any, on the performance of a resistojets should be evaluated.

The results indicated that platinum-yttria and platinum-zirconia are compatible with  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , steam, and  $\text{CH}_4$  under the conditions presented here. The reaction found in both materials at  $1400^\circ\text{C}$  when exposed to  $\text{NH}_3$  and decomposed  $\text{N}_2\text{H}_4$  can be reduced by lowering the operating temperature. Both platinum samples should be acceptable for space station resistojets using  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , steam, and  $\text{CH}_4$ . The propellants  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  may also be acceptable if the resistojets operating temperature is lowered.

Lewis Research Center  
National Aeronautics and Space Administration  
Cleveland, Ohio, August 25, 1987

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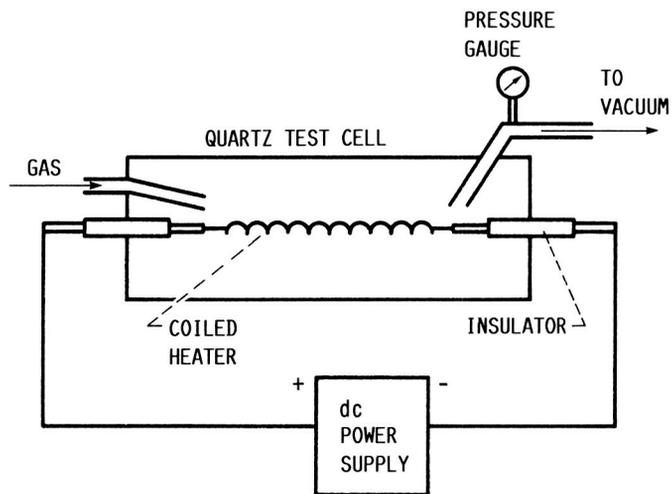


Figure 1.—Material test apparatus.

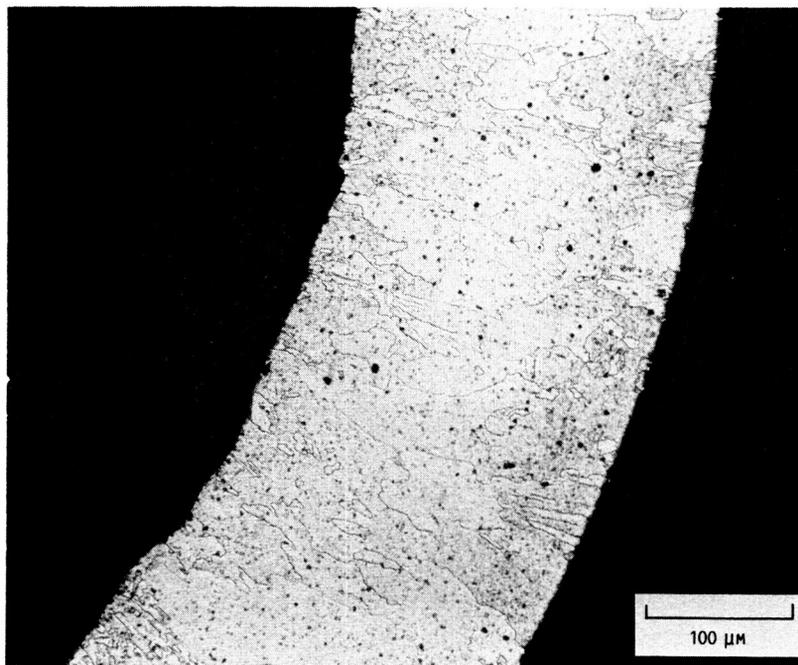
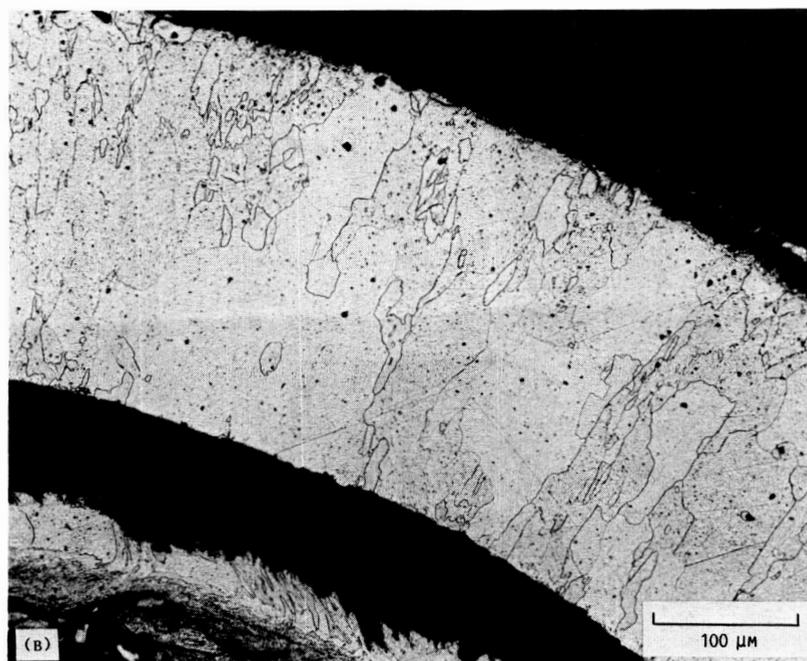
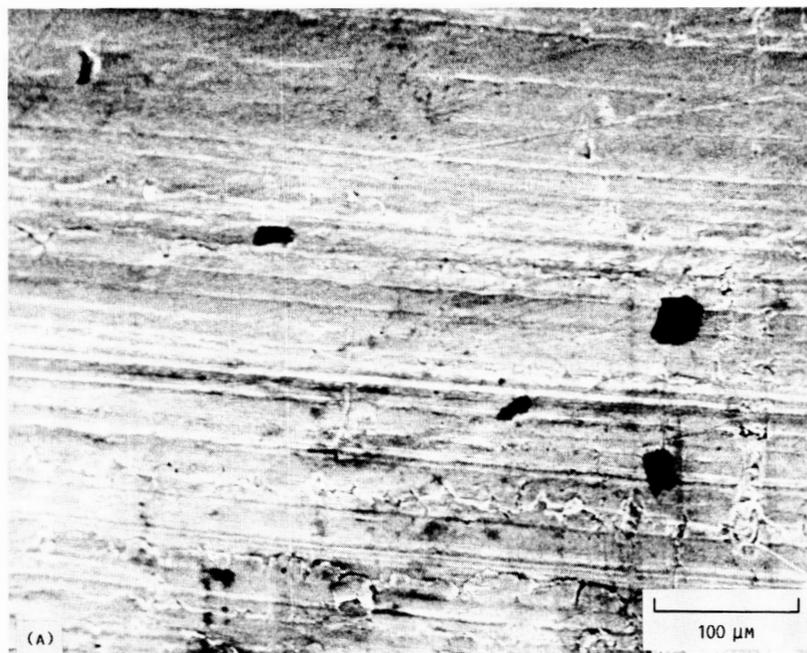


Figure 2.—Cross section of extruded, untreated platinum-yttria.

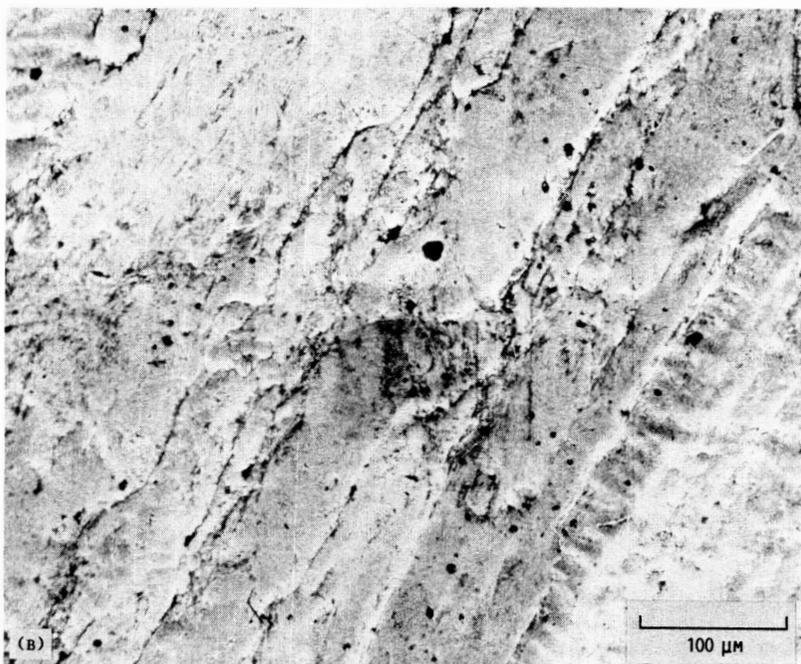
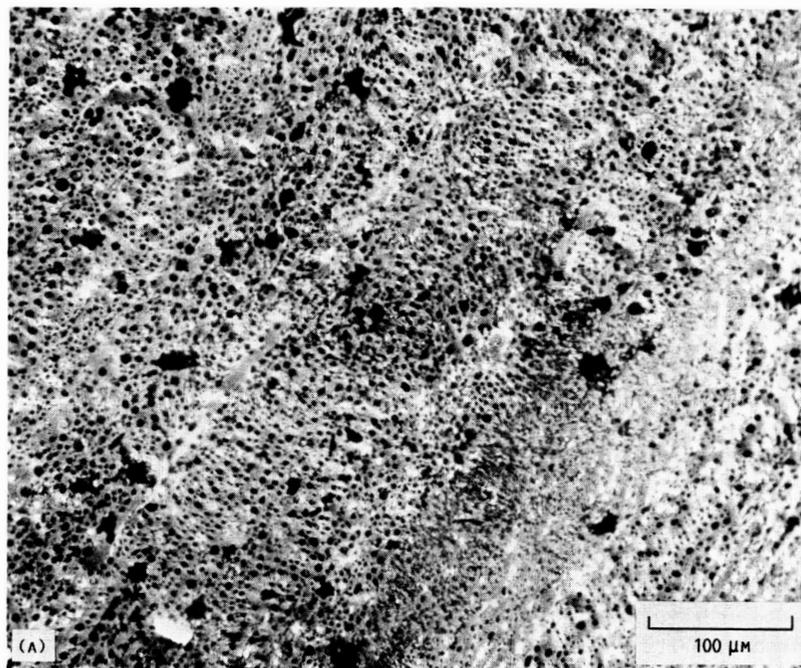


- (a) Surface.
- (b) Cross section.

Figure 3.—Platinum-yttria sample after 30-min vacuum anneal at 1000 °C.

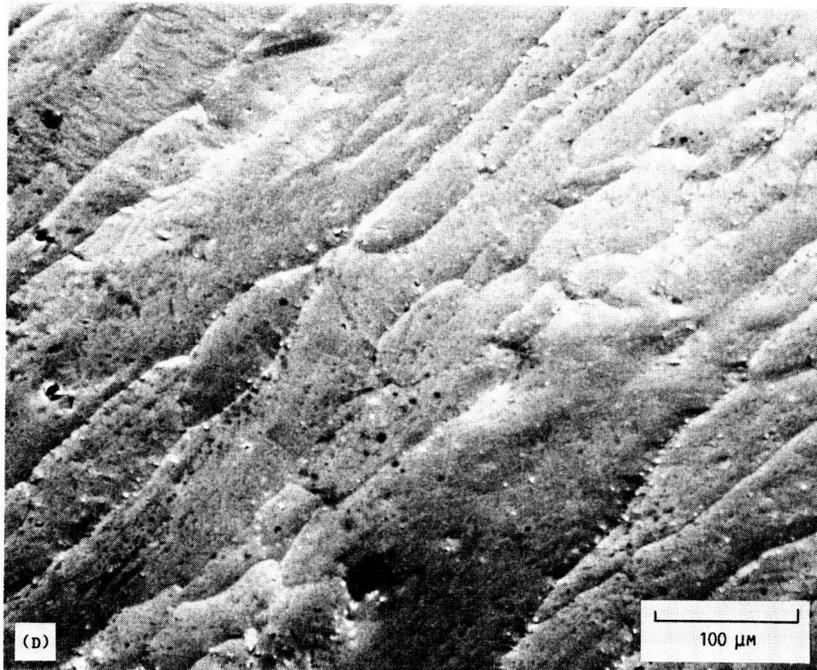
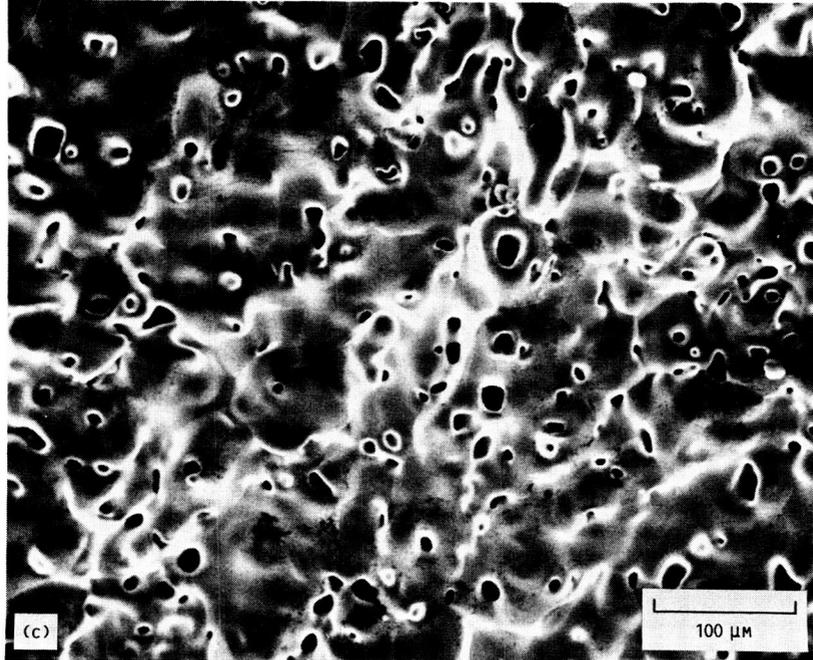
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- (a) CO<sub>2</sub>.
- (b) H<sub>2</sub>.

Figure 4.—Platinum-yttria surface after 1000 hr at 1400 °C.

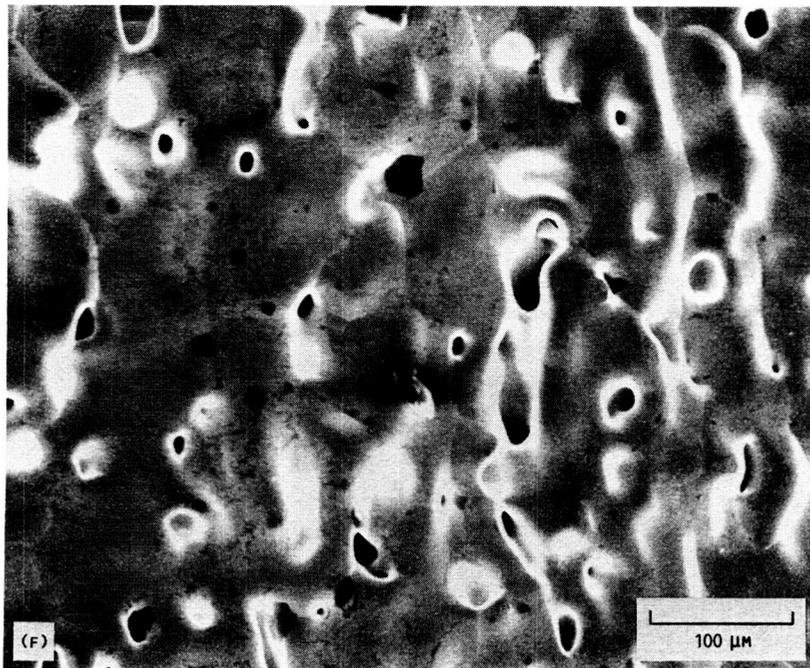
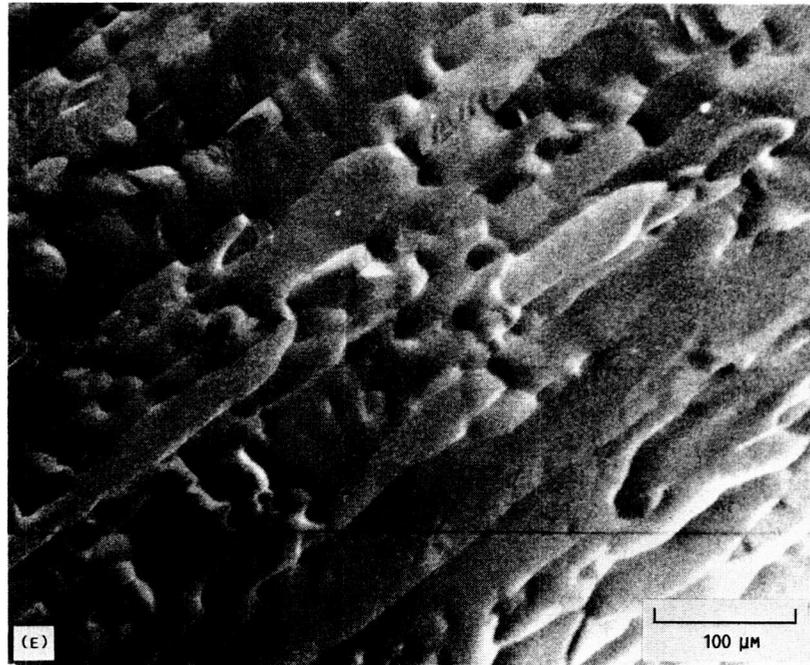


(c)  $\text{NH}_3$ .  
(d)  $\text{N}_2$ .

Figure 4.—Continued.

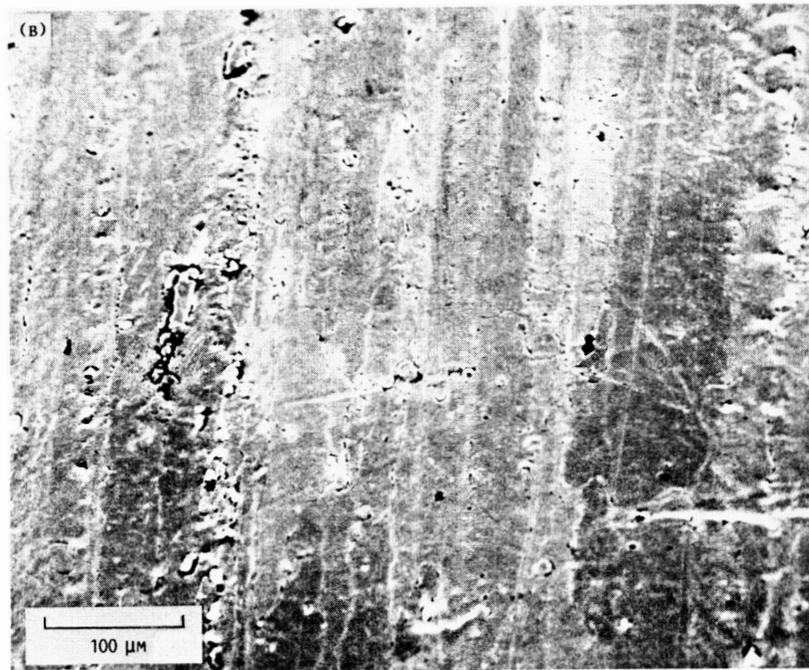
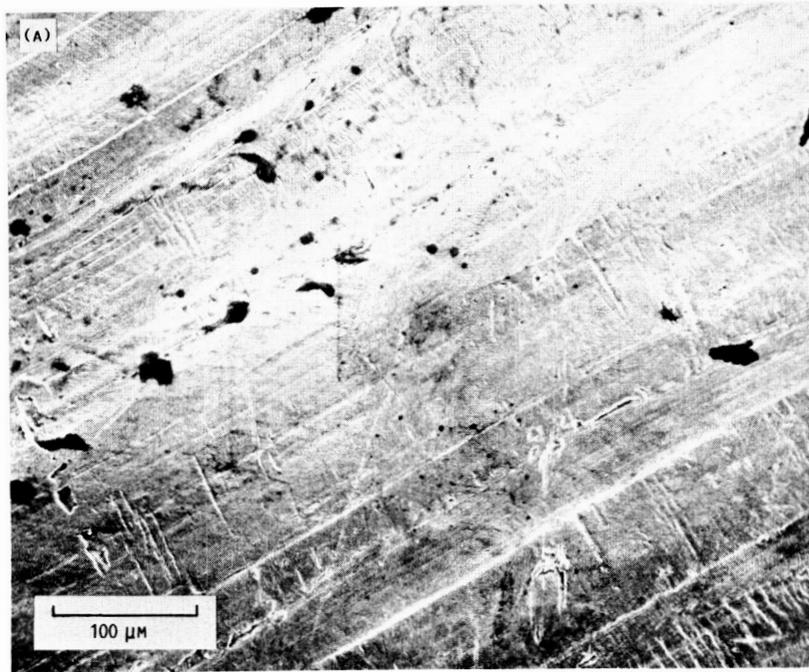
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- (e) Steam.
- (f)  $N_2H_4$ .

Figure 4.—Concluded.

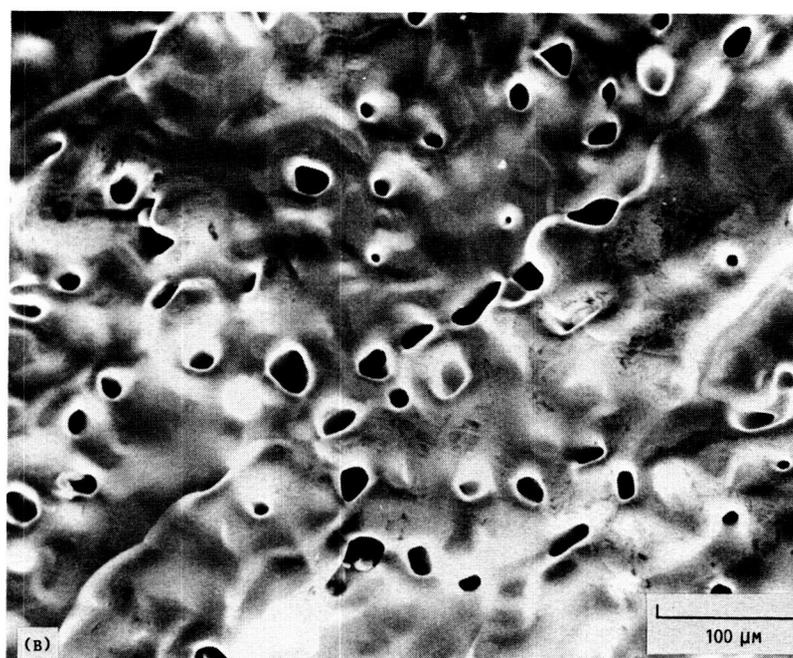
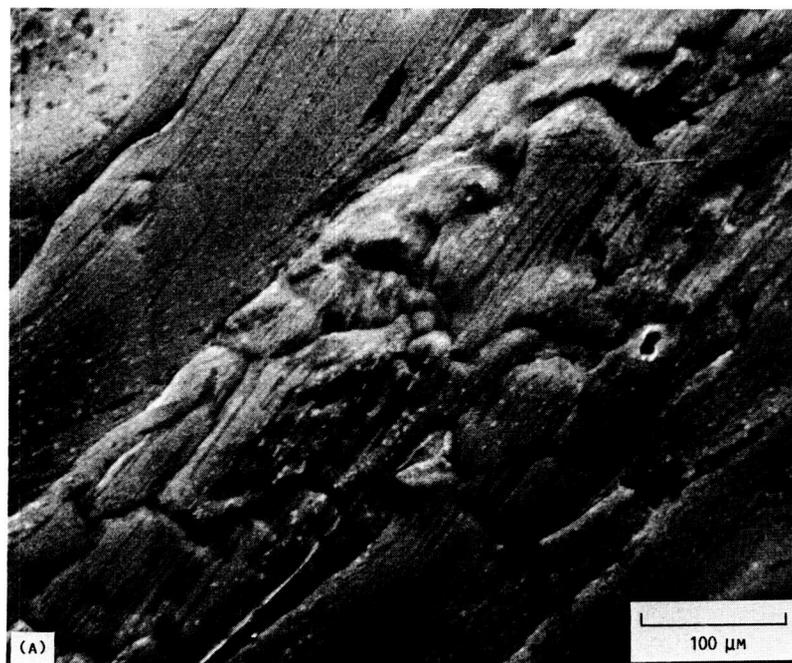


- (a) At 500 °C in CH<sub>4</sub>.  
(b) At 800 °C in N<sub>2</sub>H<sub>4</sub>.

Figure 5.—Platinum-yttria surface after 1000 hr.

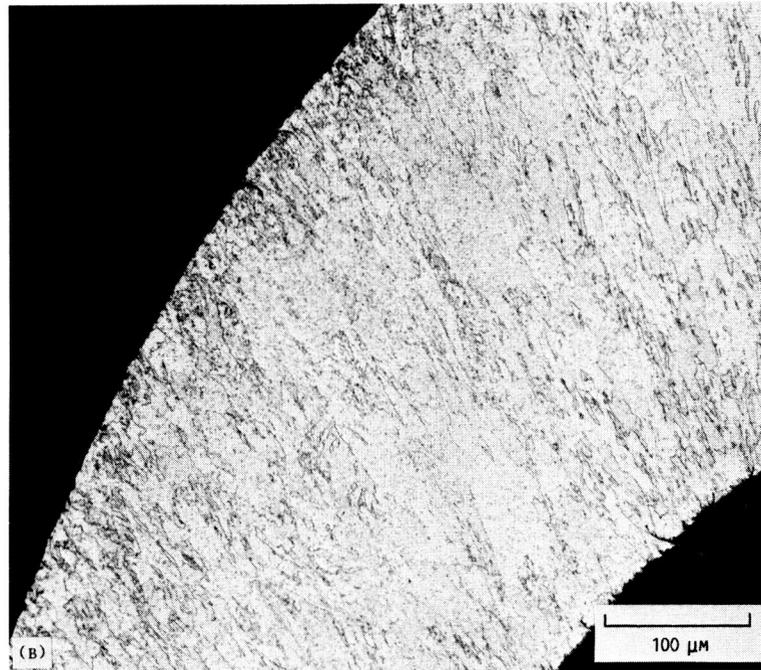
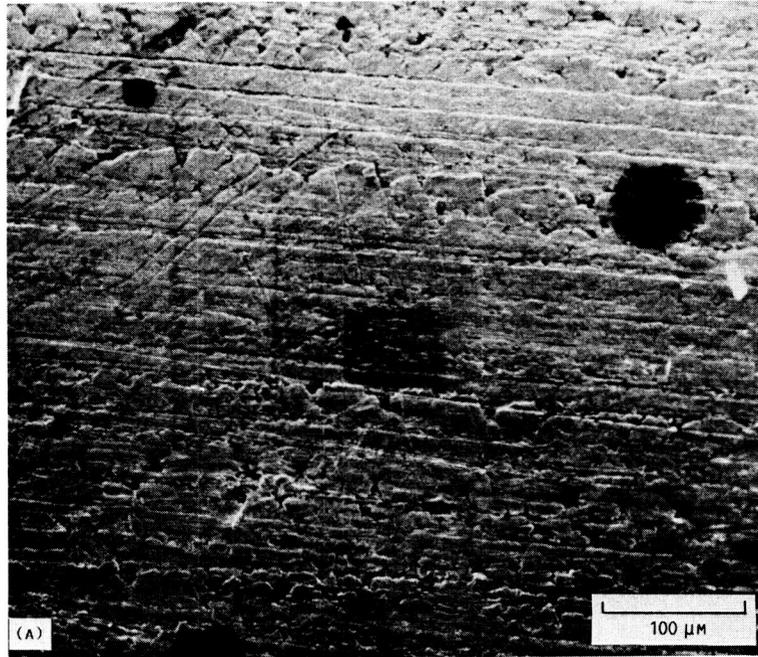
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- (a)  $H_2$ .
- (b)  $NH_3$ .

Figure 6.—Platinum-yttria surface after 2000 hr at 1400 °C.

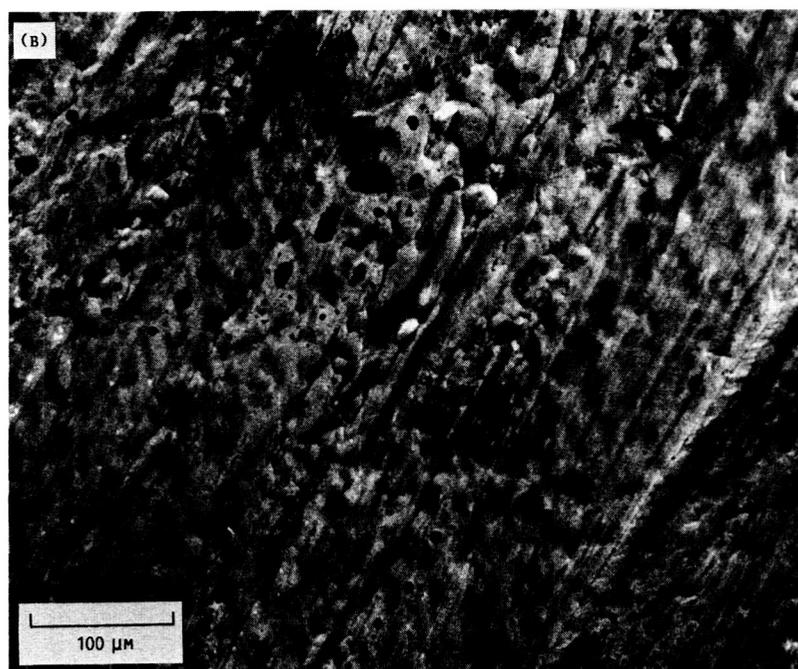
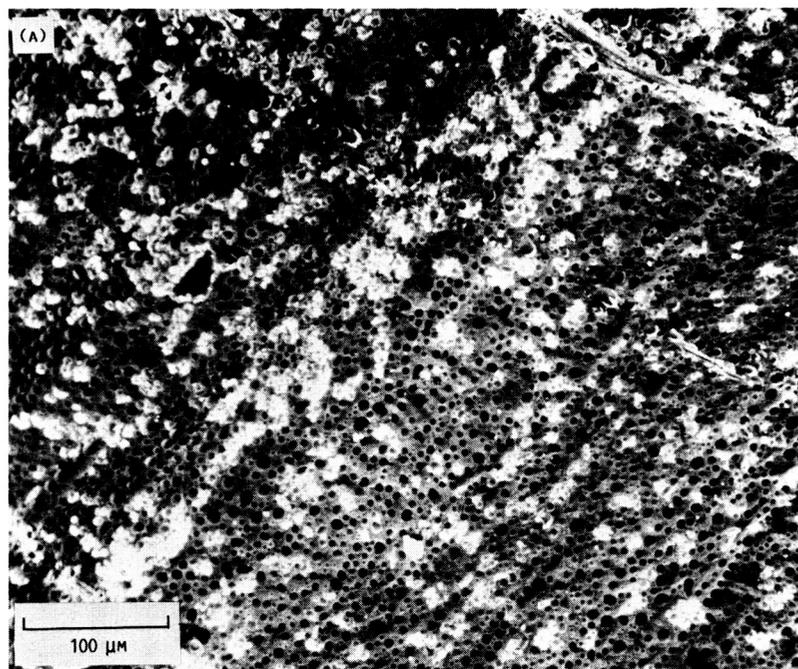


- (a) Surface.
- (b) Cross section.

Figure 7.—Platinum-zirconia sample before testing.

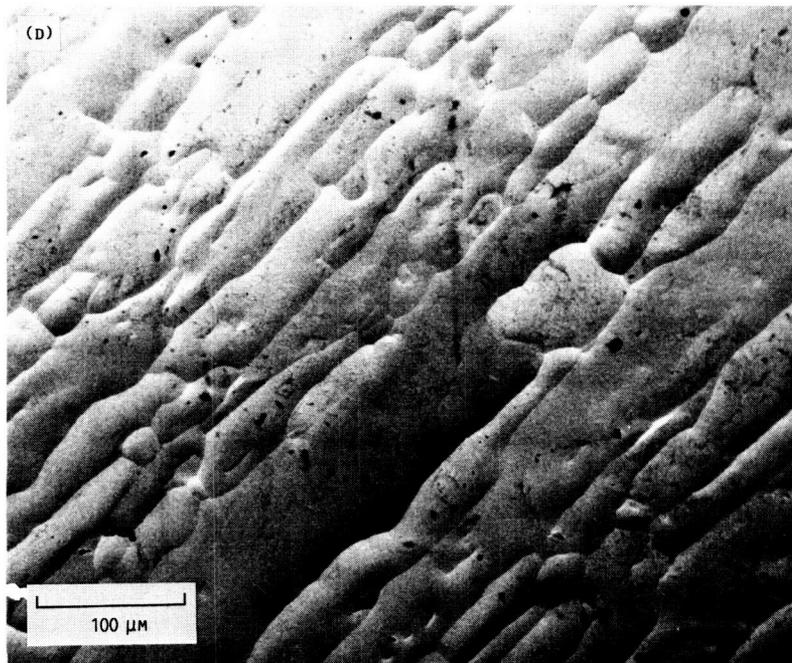
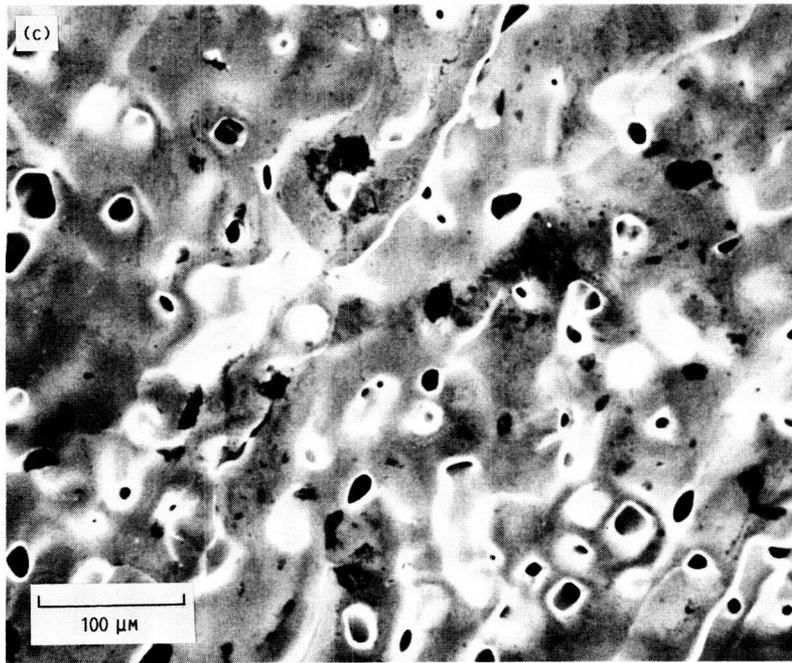
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- (a)  $\text{CO}_2$ .
- (b)  $\text{H}_2$ .

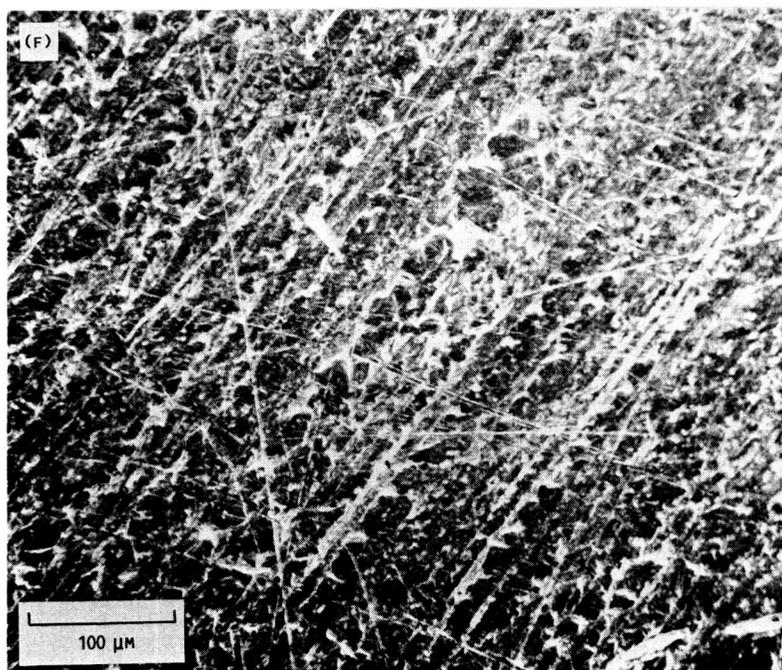
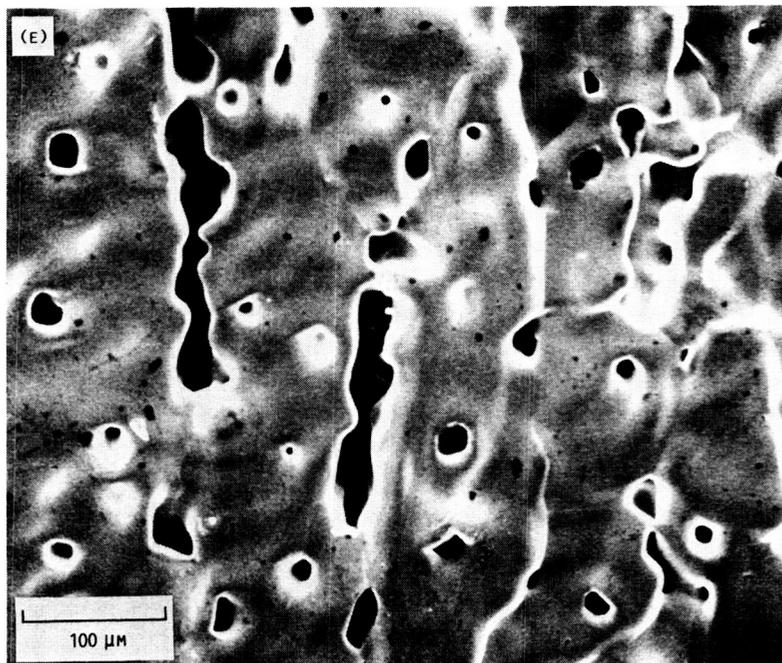
Figure 8.—Platinum-zirconia surface after 1000 hr. All tests at 1400 °C, except  $\text{CH}_4$  at 500 °C.



(c)  $\text{NH}_3$ .  
(d) Steam.

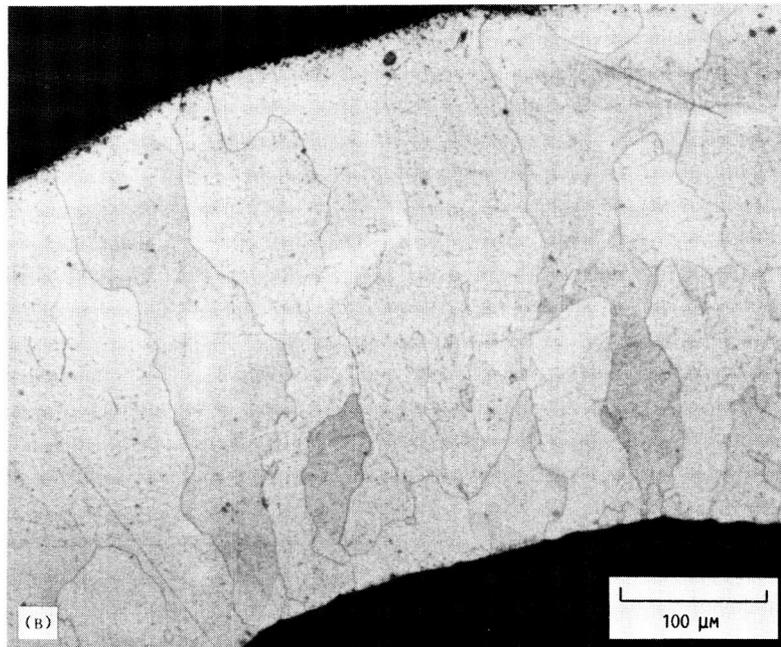
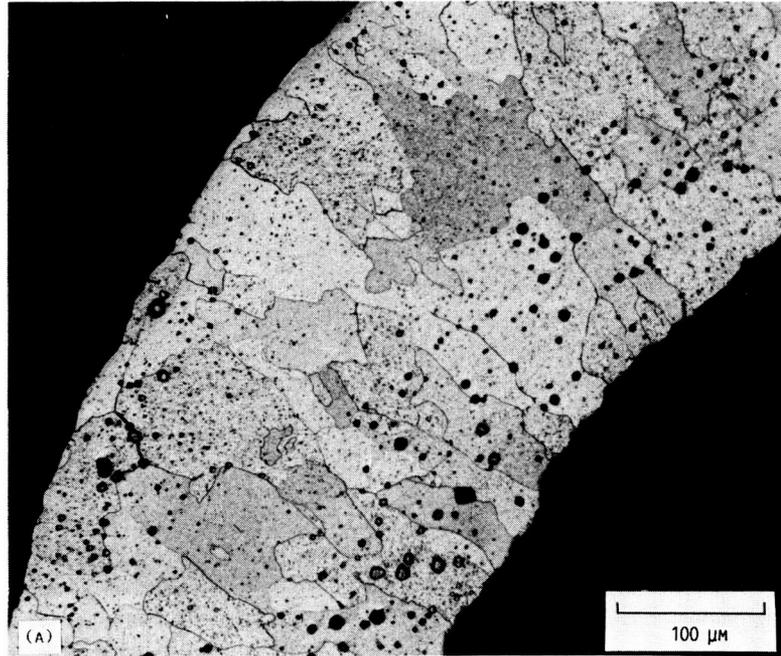
Figure 8.—Continued.

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(e)  $N_2H_4$ .  
(f)  $CH_4$ .

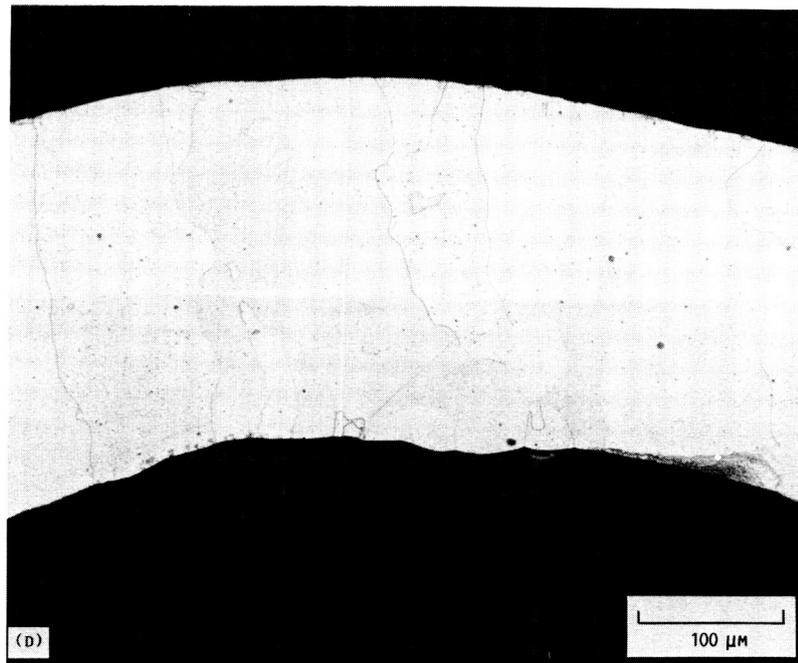
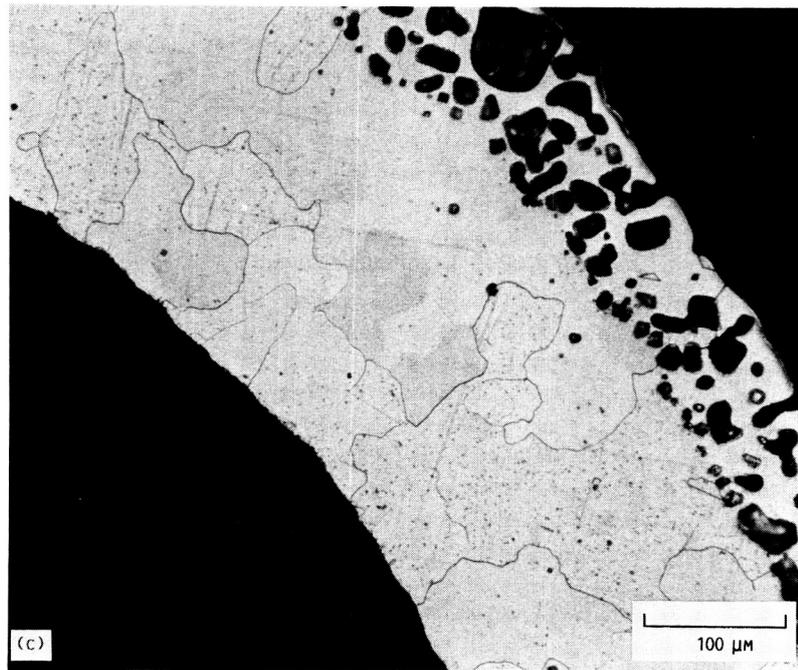
Figure 8.—Concluded.



- (a) CO<sub>2</sub>.
- (b) H<sub>2</sub>.

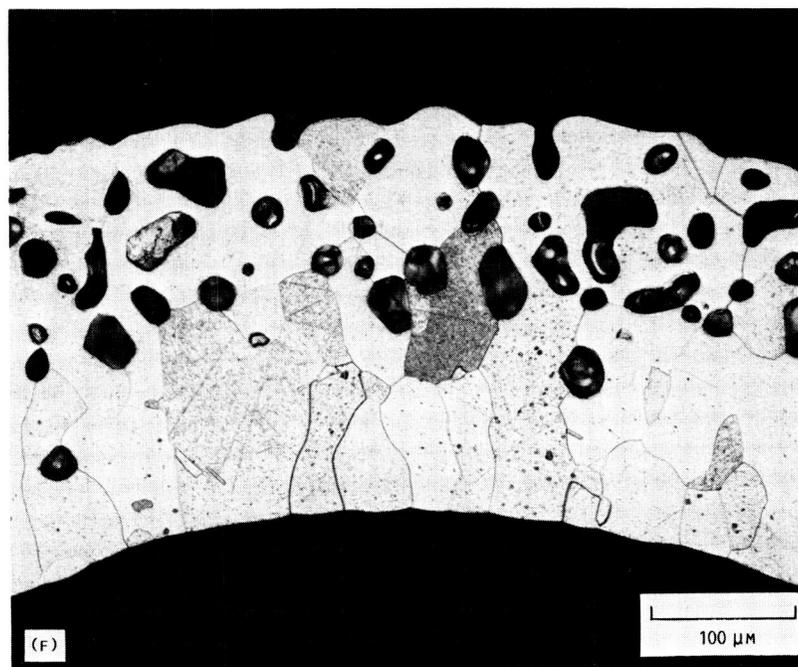
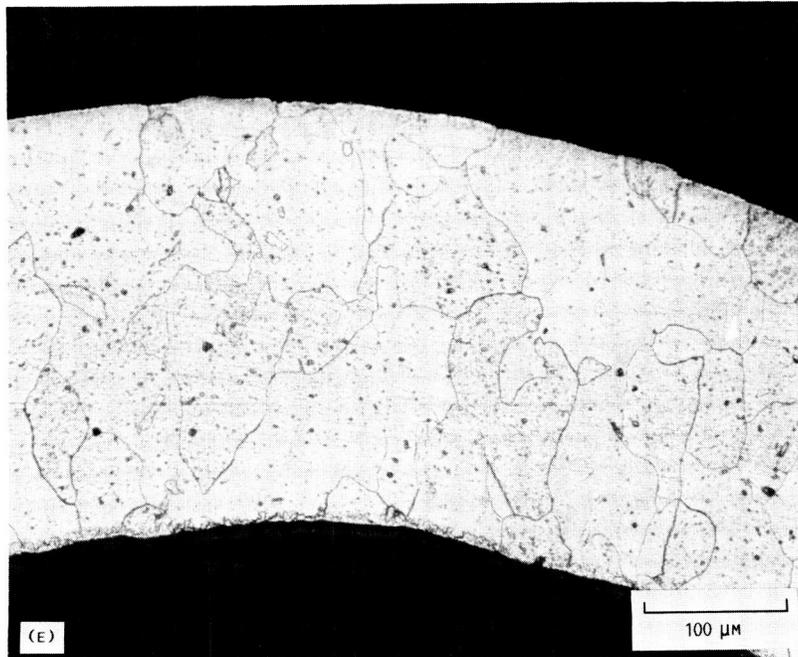
Figure 9.—Platinum-yttria cross section after 1000 hr at 1400 °C.

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(c)  $\text{NH}_3$ .  
(d)  $\text{N}_2$ .

Figure 9.—Continued.

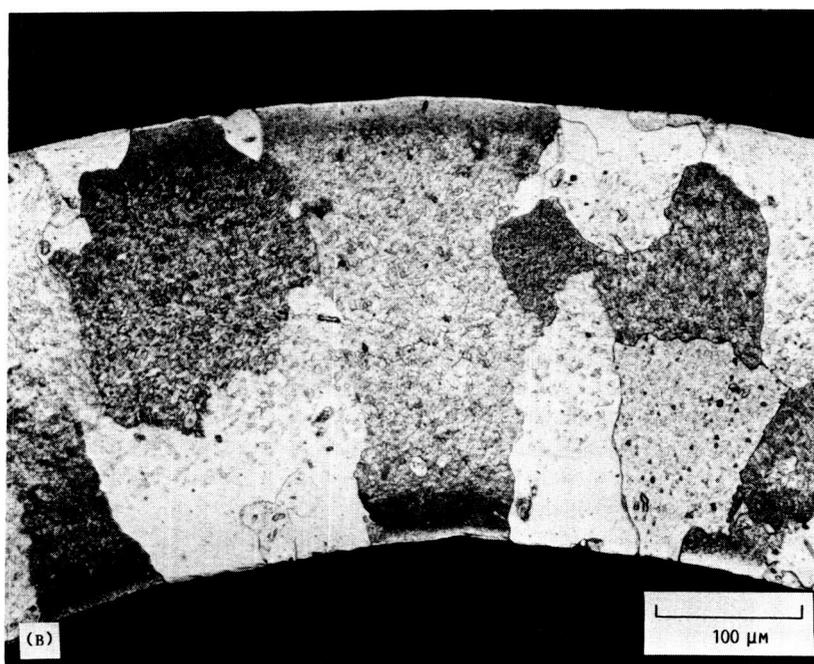
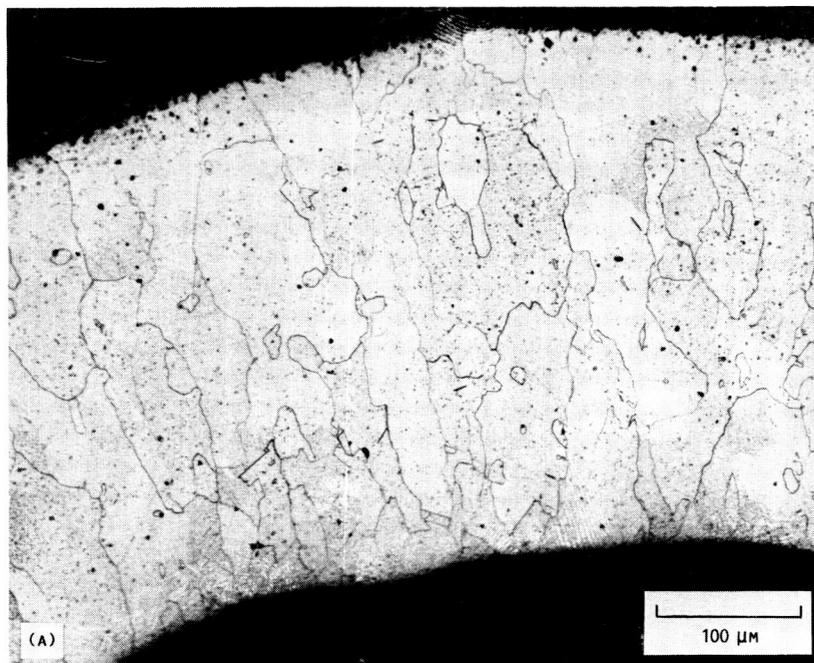


(e) Steam.

(f)  $N_2H_4$ .

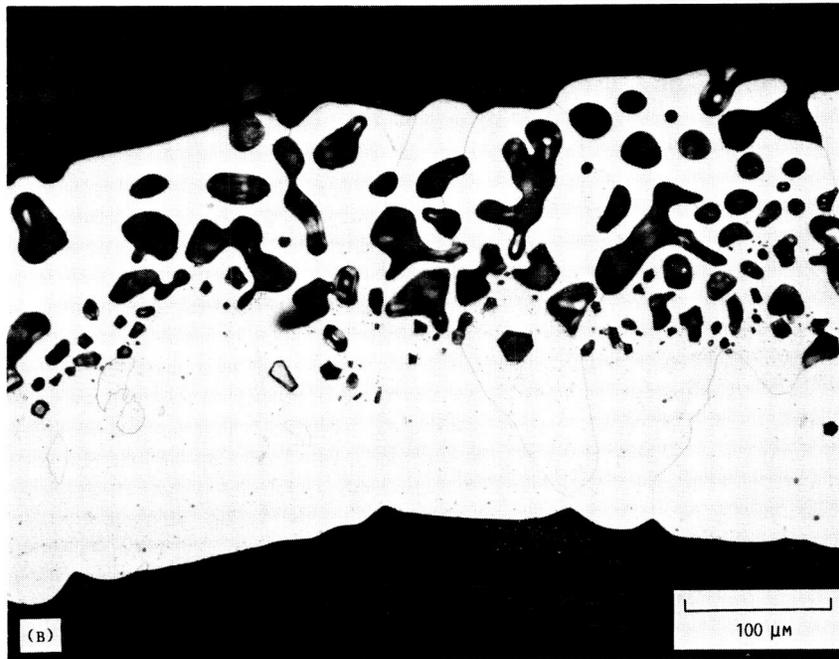
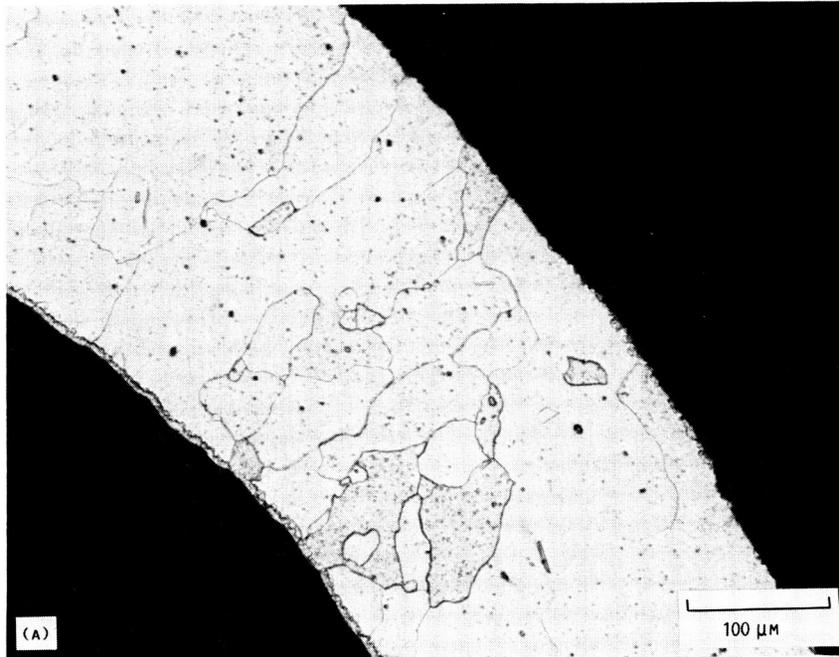
Figure 9.—Concluded.

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- (a) At 500 °C in  $\text{CH}_4$ .  
(b) At 800 °C in  $\text{N}_2\text{H}_4$ .

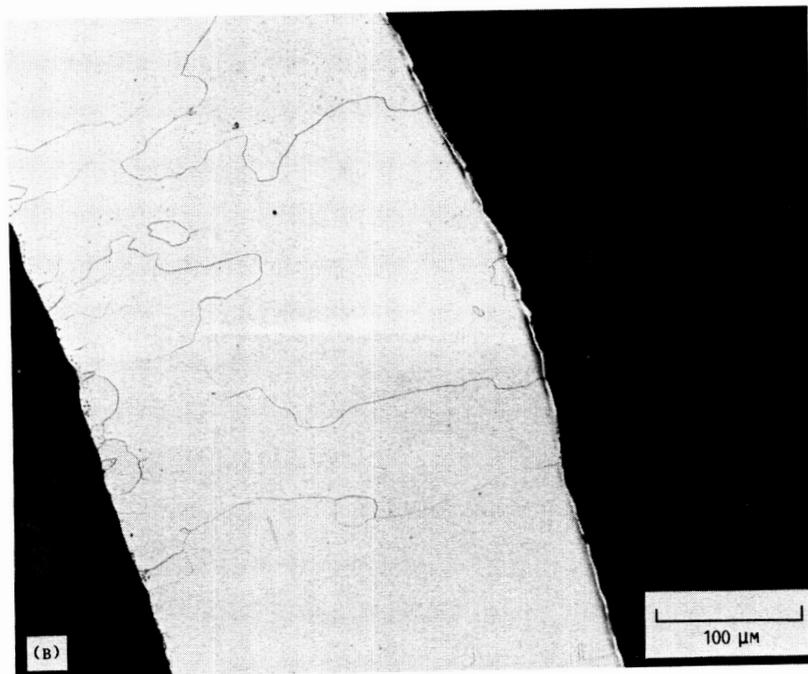
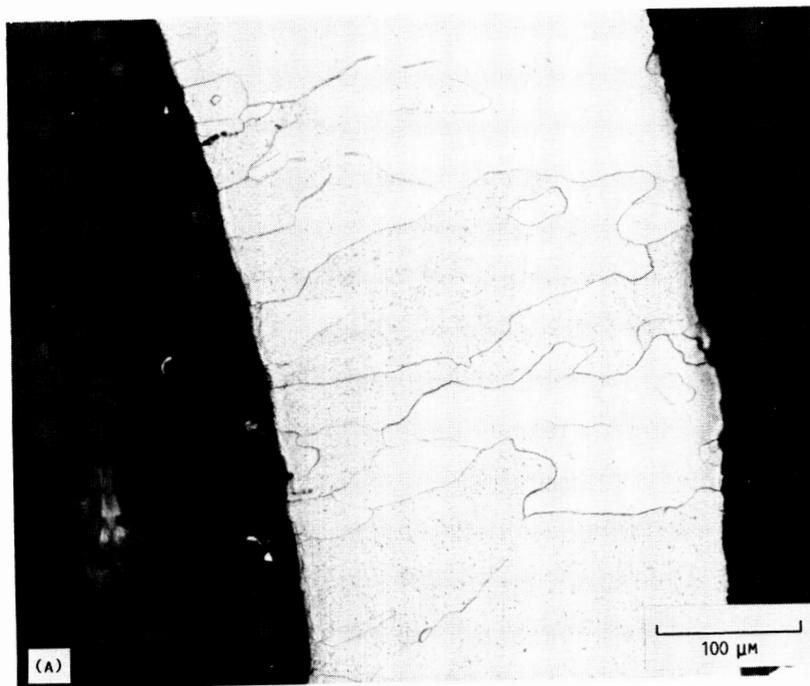
Figure 10.—Platinum-yttria cross section after 1000 hr.



- (a)  $H_2$ .
- (b)  $NH_3$ .

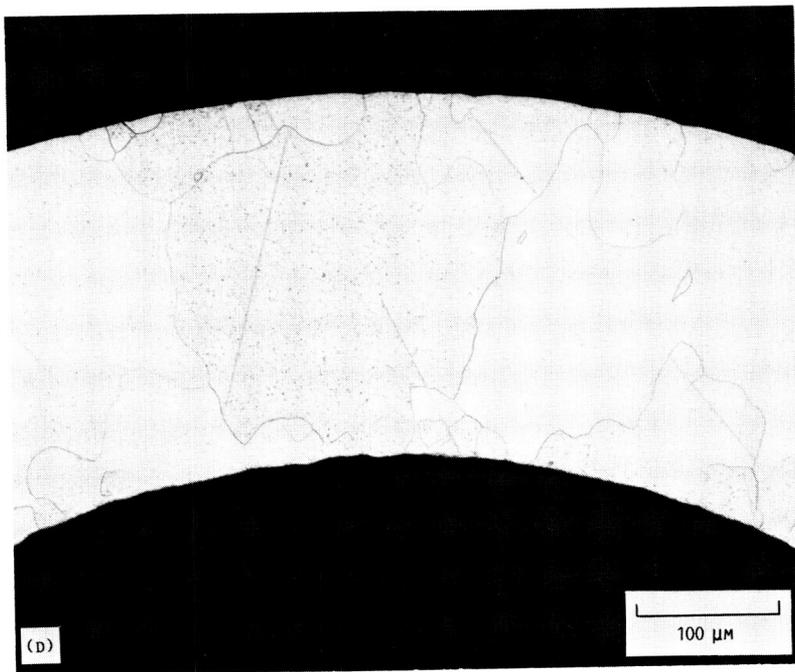
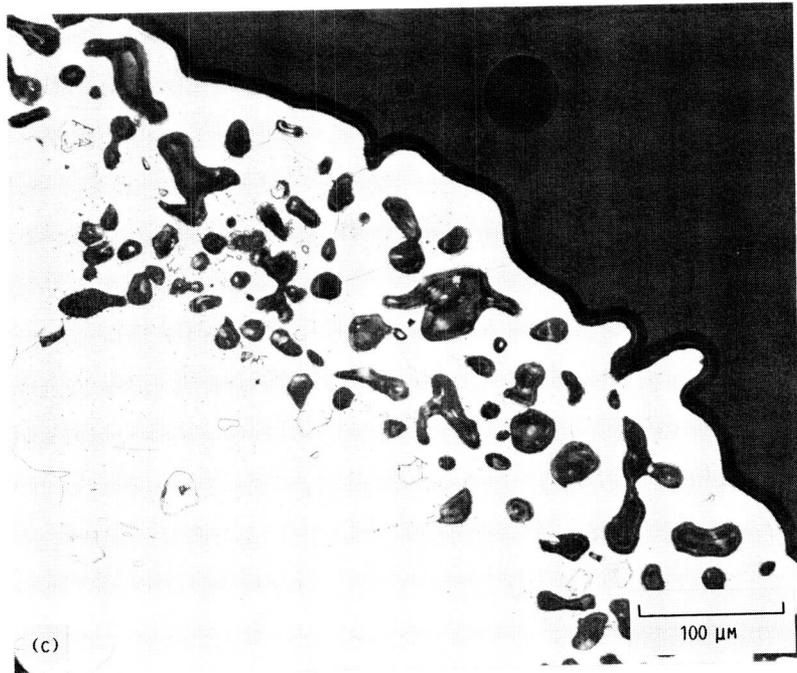
Figure 11.—Platinum-yttria cross section after 2000 hr at 1400 °C.

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(a)  $\text{CO}_2$ .  
(b)  $\text{H}_2$ .

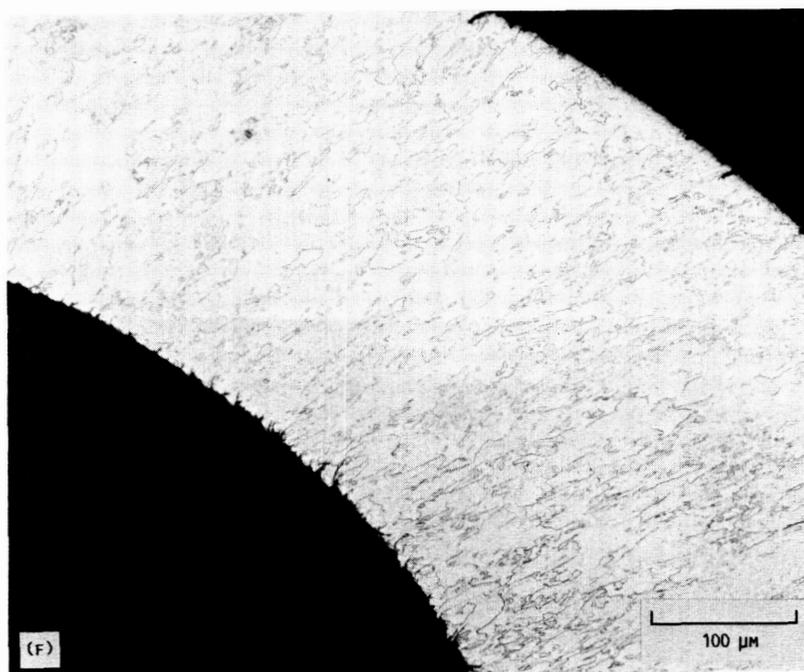
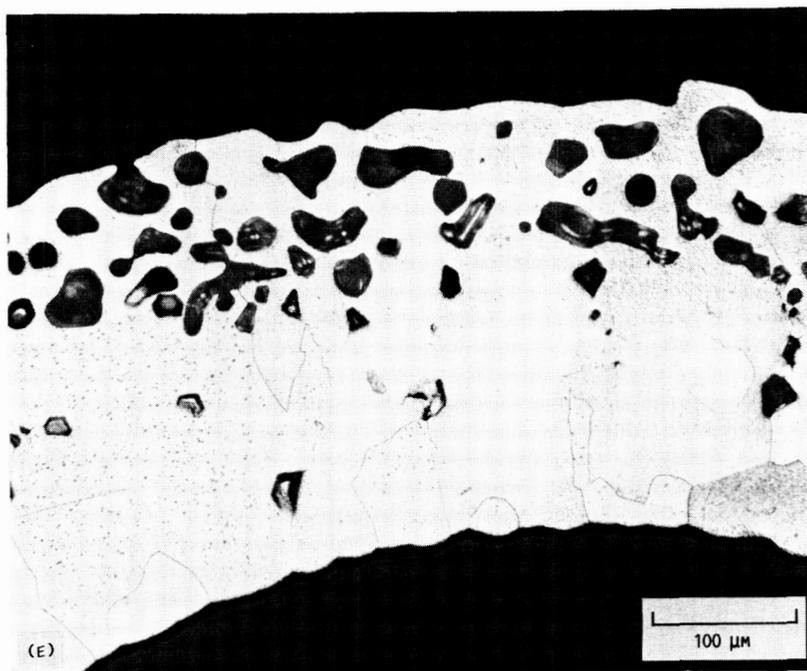
Figure 12.—Platinum-zirconia cross section after 1000 hr. All tests at 1400 °C, except  $\text{CH}_4$  at 500 °C.



(c)  $\text{NH}_3$ .  
(d) Steam.

Figure 12.—Continued.

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(e)  $N_2H_4$ .  
(f)  $CH_4$ .

Figure 12.—Concluded.

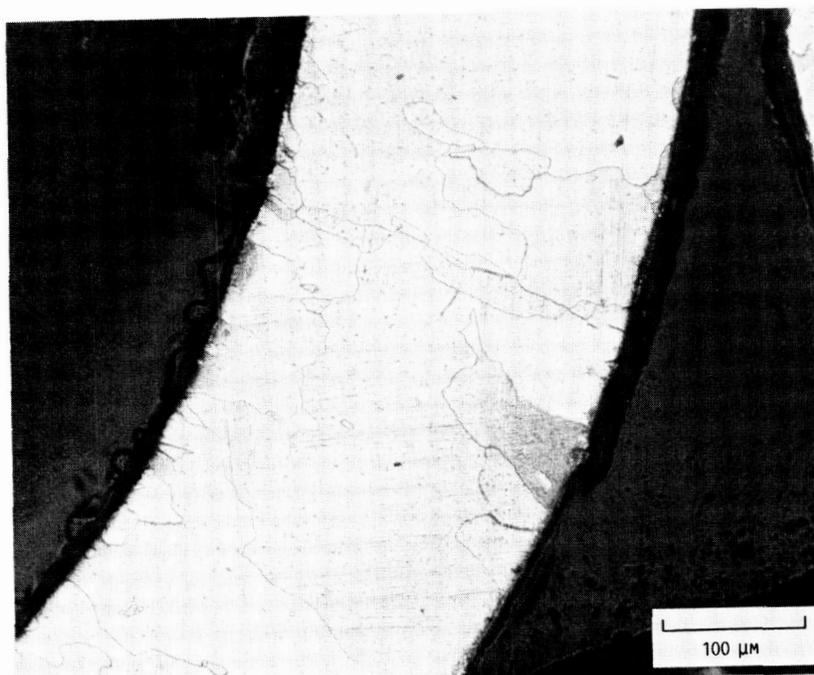


Figure 13.—Platinum-zirconia sample after 30-min vacuum anneal at 1000 °C.

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1. Report No. NASA TP-2765		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Compatibility of Dispersion-Strengthened Platinum With Resistojet Propellants				5. Report Date October 1987	
				6. Performing Organization Code	
7. Author(s) Margaret V. Whalen and Michael V. Nathal				8. Performing Organization Report No. E-3738	
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15. Supplementary Notes					
16. Abstract <p>Resistojets for the space station require long life and multipropellant capability. The choice of available materials to meet these requirements is limited. Dispersion-strengthened platinum was selected to be studied for use as a resistojet material. Past results indicated that dispersion-strengthened platinum should be sufficiently inert in candidate propellant environments and should be capable of operating at moderate temperatures for extended periods of time. A series of propellant compatibility tests was conducted with platinum strengthened with either yttria or zirconia. The data presented include the results of 1000-hr tests in carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), ammonia (NH<sub>3</sub>), nitrogen (N<sub>2</sub>), steam, hydrazine (N<sub>2</sub>H<sub>4</sub>), and methane (CH<sub>4</sub>); and 2000-hr tests in H<sub>2</sub> and NH<sub>3</sub>. The platinum samples were tested at 1400 °C in CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, steam, and N<sub>2</sub>H<sub>4</sub>; at 500 °C in CH<sub>4</sub>; and at 800 °C in N<sub>2</sub>H<sub>4</sub>. The mass-loss results indicated material life, extrapolated from experimental mass-loss data, in excess of 100 000 hr in all environments except steam and N<sub>2</sub>H<sub>4</sub>, where material life was ≥45 000 hr. Generally, on the basis of mass loss, there were no compatibility concerns in any of the environments considered. Optical and scanning electron microscopy were used to determine the effect of propellants on the material surface and to evaluate material stability as a function of resistance to grain growth. The propellant interaction varied from little or no reaction with H<sub>2</sub> and CH<sub>4</sub> to evidence of void formation and pitting of samples tested in NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub>. Material stability when measured as a function of grain growth did not appear to be a problem.</p>					
17. Key Words (Suggested by Author(s)) Dispersion-strengthened platinum Platinum compatibility Resistojet			18. Distribution Statement Unclassified - Unlimited Subject Category 20		
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