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DEVELOPMENT OF IMPROVED RHENIUM COATINGS FOR FLUORINE ENGINE THRUST CHAMBERS

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ABSTRACT

Coating trials were undertaken to evaluate the application of rhenium to carbon-carbon composite sheet by plasma spraying. The objective was to develop the technique for application of rhenium coatings to hydrazine-fluorine rocket engine thrust chambers. Optimum spray parameters and coating thickness were identified for production of coatings free from continuous defects and with adequate adherence to the substrate. A tungsten underlayer was not beneficial and possibly detracted from coating integrity.

Stress calculations indicated that the proposed operating cycle of the rocket engine would not cause spalling of the rhenium coating. Diffusion rates of hydrogen and other gases through the coating were estimated by reference to data for refractory metals with properties similar to rhenium. Calculations indicated that permeation of gases through the coating would not be significant during the expected life of the thrust chamber.

In addition to plasma spraying, a limited number of exploratory trials were carried out to evaluate the feasibility of applying rhenium coatings by laser melting. Poor wetting of the composite surface by the liquid rhenium precluded production of uniform coatings. Borate/carbonate fluxes did not improve wetting characteristics.

It was recommended that, for sea level firing trials, a thrust chamber be coated with rhenium by plasma spraying, and that this would most appropriately be carried out by a commercial plasma spraying organization.

TABLE OF CONTENTS

LIST OF FIGURES

1. INTRODUCTION

The objective of this program was to identify and develop a rhenium-base plasma coating process for the application of rhenium to lightweight carbon-carbon composite (C-C) thrust chambers to be applied in fluorine-hydrazine (F_2-N_2H_4) propulsion systems.[1-3]

The life requirement of the C-C thrust chamber is a minimum of 4000 sec of accumulated firing time. Hot-firing tests at JPL revealed a localized erosion-corrosion of the C-C thrust chamber which drastically reduced the minimum life of the engine.[2] Subsequent laboratory simulation tests with carbon corrosion coupons revealed that residual water in the Mil-Spec. N_2H_4 catalyzed the decomposition of N_2H_4 to ammonia. The ammonia corroded the C-C surface by reacting with carbon to produce HCN at a minimum reaction temperature of 1093°C.[3]

Minimum engine vacuum performance restricts the amount of cooling by N_2H_4 boundary layer coolant flow to minimize corrosion. Some portion of the C-C chamber must attain a minimum high temperature which is >1093°C. This limits the approach to attaining temperatures <1093°C to eliminate the NH_3/C interaction. Rhenium was selected as an inner liner because of its physical properties and chemical compatibility with the propellant. The liner would act as a diffusion barrier between the NH_3 and carbon while allowing high temperatures for minimum vacuum performance.

In previous JPL trials, two C-C thrust chambers were lined with rhenium by a chemical vapor deposition (CVD) process. Subsequent hot-firing trials gave promising results although some localized exfoliation of the coating took place. This led to the present investigation of other coating techniques. The main effort in this program was directed toward plasma spraying with secondary emphasis on exploratory laser melting.

The tests have provided promising results for plasma-arc deposition. Spraying parameters were established that successfully applied a 10 mil defect-free rhenium coating to C-C coupons. Subsequent homogenization of the as-sprayed coating was performed at 2000°C for 4 hr in flowing argon. Laser melting test trials failed to demonstrate the feasibility of the process as an alternative to plasma spraying.

2. EXPERIMENTAL PROCEDURE

2.1 ESTABLISHMENT OF PLASMA SPRAYING PARAMETERS

In this task, studies were undertaken to determine the optimum spraying parameters to produce a well-bonded rhenium coating on a C-C substrate by plasma deposition. The effects of powder size, standoff distance, coating thickness, heat treatment, and underlayer on coating integrity were investigated.

2.1.1 Materials and Methods

High purity 99.99% rhenium powder (-170 +325 mesh) was procured from JPL. A portion of the received powder was screened into two mesh fractions--i.e., -170 +270 mesh (intermediate), -270 +325 mesh (fine)--for powder size trials. Prior to spraying, all powder fractions were dried at 110°C for 2 hr.

C-C specimens 1 × 2 × ¼ in. were cut from material provided by JPL. Specimens were ultrasonically cleaned in a dilute detergent/distilled water solution at 66°C until clean. A final ultrasonic rinse was necessary to remove any residual cleaning solution followed by drying at 110°C for 15 hr. Precautions were taken to protect specimens from contamination after cleaning.

The plasma spray system consisted of a 40 kW plasmation unit (Plasmadyne, Santa Ana, California) with an SG-1B spray gun (using argon as the plasma gas). Powder feed was provided by a Sylvestor vibrating screen feeder with argon as "carrier gas." An existing jig fixture allowed controlled horizontal standoff distance while assisting manual touch movement at 1 fps as shown in Fig. 1. A thermocouple provided temperature monitoring at the back side of each sample. Temperatures were kept below 500°C to minimize back-side substrate oxidation. All samples were preheated to 200°C prior to spraying.

Heat treatment studies of selected coated samples were conducted in a 1-3/4 in. diameter × 48 in. long graphite-tube resistance furnace provided with water cooling and continuous argon gas flow as shown in Fig. 2. The furnace can achieve temperatures of about 3000°C. During the studies, temperatures of 1650°C and 2000°C were attained in a 6 in. furnace hot zone. This allowed a

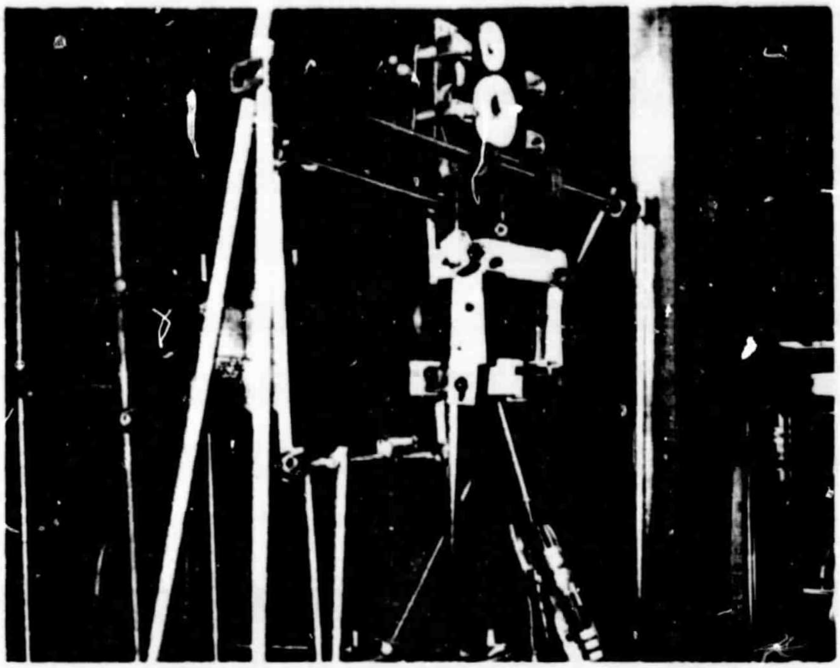

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Figure 1. Plasma-arc spray gun (Plasmadyne) showing assisted manual X-Y traverse jig fixture at fixed standoff distance from clamped substrate.

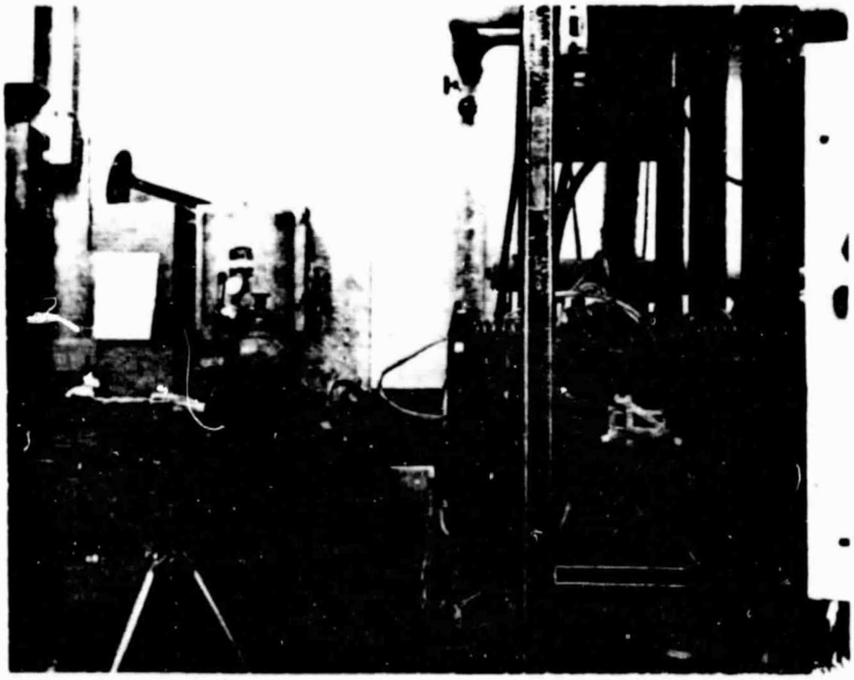

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Figure 2. High-temperature graphite tube furnace showing mounted optical pyrometer and argon gas supply in foreground.

furnace capacity of four coated samples in the hot zone. Furnace out-gassing was conducted at 2000°C for 1 hr with continuous argon purge at 30 cfh. After 4 hr of heat treatment, samples were furnace cooled to room temperature.

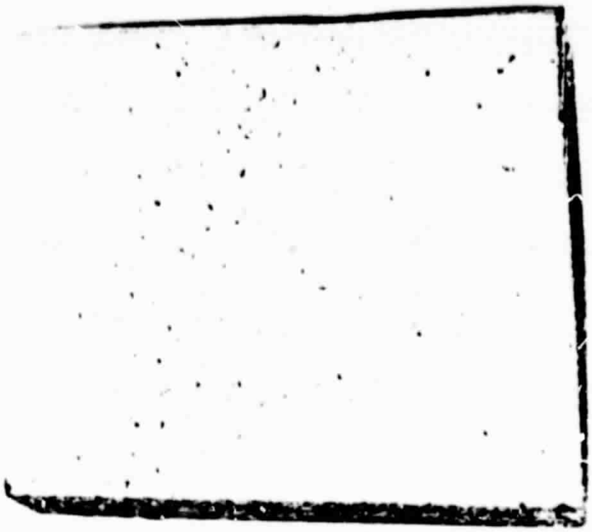
2.1.2 Results

Rhenium has properties (melting point, density) similar to tungsten. Prior to rhenium spraying trials, two tests were conducted with tungsten on graphite using spray gun settings developed from previous experience with tungsten on other materials. Because of the defect-free coatings produced, tungsten spraying parameters were adopted for spraying rhenium. Similar plasma spray gun parameters have been used with iridium on graphite.[4]

In the first four spraying trials, optimum standoff distance was to be established using as-received rhenium powder. Distances of less than 2 in. were not investigated since previous spraying experience had shown excessive overheating of the substrate. Coatings of 10 to 15 mils in thickness were produced at 3 in. standoff. The resulting samples contained many scattered areas of through-porosity, as shown in Fig. 3, with minor coating decohesion at the edges of some samples. In contrast, specimens sprayed at 2 in. exhibited more uniform coverage, better adhesion, and reduced porosity.

Rhenium powder mesh fractions of -170 +325 (as-received), -170 +270 (intermediate), and -270 +325 (fine) were investigated for coating integrity and spraying performance at 2 in. standoff. Plasma gun blockage problems hampered spraying with the fine powder. Coatings of 3 to 5 mils thickness were produced with extensive pinhole through-porosity and nonuniform coverage as indicated in Fig. 4. Spraying with the as-received and intermediate powders showed much better results, although some feeding problems were encountered with the as-received powder. This resulted in noticeably increased porosity. Best overall performance, with the absence of feeding and blockage problems, was achieved using the intermediate powder size. The resulting surface of an optimum coating appears in Fig. 5.

Spraying at 2 in. was further developed to assess the effects of coating thickness. In the light of previous corrosion studies at IITRI by V. L. Hill[5] and allowances for boundary-layer cooling failure, coating thicknesses of 5, 10, and 15 mils were aimed for in the trials. Coatings of 3-5 mils thickness proved to be adherent, but suffered from through-porosity in scattered areas, with otherwise complete coverage. Optimum coating integrity was obtained with

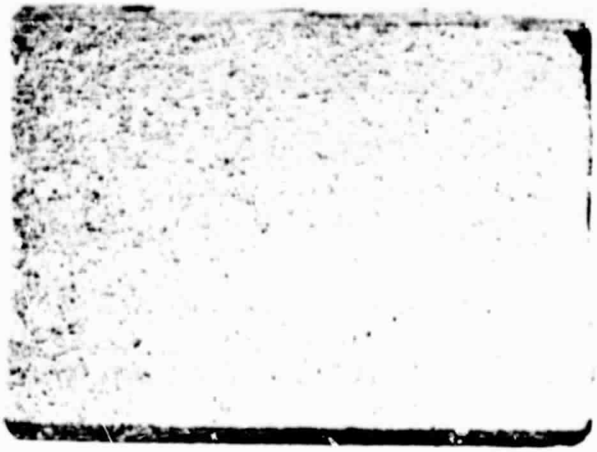


Neg. No. 52903 2.5X

Figure 3. Carbon composite coupon CC-003 sprayed at 3 in. standoff using (-170 +325 mesh) as-received rhenium powder.

Neg. No. 53171 2.3X

Figure 4. Specimen CC-012 plasma-arc sprayed at 2 in. standoff producing a 3-5 mil coating with fine (-270 +325 mesh) rhenium powder. Nonuniform surface coverage and scattered through-porosity are quite evident.



Neg. No. 53172 2.3X

Figure 5. Optimum 7-10 mil plasma-arc sprayed rhenium coating deposited on specimen CC-014 with rhenium powder (-170 +270 mesh) at 2 in. standoff.

Neg. No. 53134 100X

Figure 6. Rhenium powder (-170 +270 mesh) sprayed onto a 10 mil tungsten underlayer on specimen CC-018 at 2 in. standoff. Scattered internal porosity is quite evident in the Re coating.

thicknesses of 7 to 10 mils, giving complete surface coverage, uniform thickness, good adhesion, and the absence of through-porosity.

The effect of underlayer was studied by spraying intermediate size rhenium powder onto a 10 mil tungsten underlayer. The resulting 10 mil rhenium coating was uniform in coverage with no through-porosity. Metallographic examination of the sectioned coating showed mild internal microporosity in the top rhenium layer and intermittent separation at the Re/W interface, as shown in Fig. 6.

Post-spraying heat treatments were conducted at 1630°C and 2000°C for 4 hr in a flowing argon atmosphere. Results at 1650°C showed that recrystallization began after 4 hr. At 2000°C after 4 hr, grain growth in localized areas was apparent.

2.2 LASER COATING TRIALS

The objective of this phase of the program was to investigate the potential of laser surface melting for the application of rhenium to C-C composite. The IITRI CO_2 laser was able to melt the Re without oxidation, but poor wetting between the C-C substrate and liquid Re metal led to the formation of liquid globules. Attempts to improve wetting using varied mixtures of sodium carbonate/sodium borate fluxes and separate additjon of carbon were not successful. All trials indicated poor wetting of the carbon substrate surface by the liquid rhenium.

2.2.1 Materials and Methods

An Avco-Everett Model HPL8 closed cycle transverse flow CO_2 gas laser was utilized in the melting trials. Fully adjustable power levels from 1 to 15 kW can be delivered at 10.6 micron wavelength. Two different beam techniques were used. The integrating system provided the highest uniform energy density over the target area. The oscillating beam technique provided multidirectional planar stirring of the molten metal at lower energy density. Special inert gas shielding was required to prevent oxidation of the coating material and to reduce plasma formation that results in beam scattering.

Substrate specimens 1 × 1½ × ¼ in. were cut from carbon-carbon composite sheet material. Specimens were ultrasonically cleaned in detergent/water solution until clean and given a subsequent ultrasonic rinse in distilled water. Drying was necessary at 110°C for 15 hr to remove residual moisture. All rhenium additions were prepared by mixing them with a dilute solution of cellulose acetate in acetone that acted as a binder. The resultant paste was applied to the carbon surface using a 10 mil thick aluminum sheet mask. The slurry-coated specimens were exposed to the laser beam in a protective argon-helium atmosphere.

2.2.2 Results

(a) First-Phase Laser Trials

In the first three tests, the beam was directed onto a one-inch-square carbon-carbon composite sheet coupon using several power levels to ensure that the rapid thermal cycle did not damage the material. A 4 sec exposure at 10 kW caused only superficial carbon loss.

A total of 12 tests were carried out using tungsten powder and a W-3 wt% C mixture to establish optimum levels of power, exposure time, and cover gas variables. The W-C mixture showed much easier melting and greater fluidity than did the pure metal as shown in Fig. 7a. Imposing a slight oscillation on the beam overcame the tendency for melting to be localized to the center of each beam element. However, the liquid metal displayed little tendency to wet the carbon surface and the coatings produced had poor uniformity and adhesion.

Six tests were carried out using a rhenium powder and a Re-1.5 wt% C mixture. Again, the mixture showed better fluidity than the pure metal, but wetting characteristics were not improved. In an attempt to reduce surface tension, 15 vol% CO_2 was added to the cover gas and the argon content of the argon-helium cover gas mixture was increased from 25 to 40 vol%. CO_2 has been found to improve surface wetting characteristics in trials of laser coating of stainless steels. The argon content of the gas was increased because this gas promotes plasma formation, and it was hoped that this would aid uniform heat distribution. In practice, however, the change in gas composition had little or no effect on the quality of the coating obtained (Figs. 7b, c).

The lower melting temperature of the Re-C mixture compared to that of the W-C mixture allowed the power level to be reduced to 10 kW. This eliminated the slight undercutting of the carbon surface which had occurred when applying the tungsten coatings at a 12 kW power level.

Neg. No. 52976 1X

(a)

Neg. No. 52978 1X

(b)

Neg. No. 52977 1X

(c)

Figure 7. Carbon composite specimens with laser melted deposits of W + 3.0 w/o C and Re + 1.5 w/o C utilizing the oscillating beam technique. (a) Specimen 13, W + 3.0 w/o C laser melted at 12 kW for 16 sec under 75% He/25% Ar gas shield; (b) specimen 15, Re + 1.5 w/o C laser melted at 10 kW for 15 sec under 70% He/30% Ar gas shield; (c) specimen 16, Re + 1.5 w/o C laser melted at 10 kW for 15 sec under 40% He/35% Ar/15% CO_2 gas shield.

(b) Second-Phase Laser Trials

The trials conducted during the first phase indicated poor wetting of the carbon component surfaces by liquid rhenium. Addition of carbon to produce the Re-C eutectic composition gave little improvement. A computer data search failed to identify any fluxes developed or proven specifically for this or similar systems. Special alloys have been developed for brazing refractory metals to graphite, but their melting temperatures are below those required for the present application. An ordinary sodium borate/sodium carbonate flux, used in welding electrodes, was selected for further tests to investigate the possibility of reducing surface tension.

Table 1 shows the five weight combinations of sodium carbonate/sodium borate/rhenium used in the tests. The oscillating laser beam technique was utilized to promote the dispersion of flux through the liquid rhenium. Use of this technique reduced power levels to 5 kW as compared to 10 kW in the first-phase trials.

Ten tests were conducted to investigate the effect of 30 and 50 sec exposures to the 5 kW beam. All results showed no improvement in wetting of the carbon composite surface. It was noted that the increased sodium borate in flux combinations 2, 3, and 5 tended to promote larger globule formation at 50 sec, as shown in Figs. 8a, b, and c.

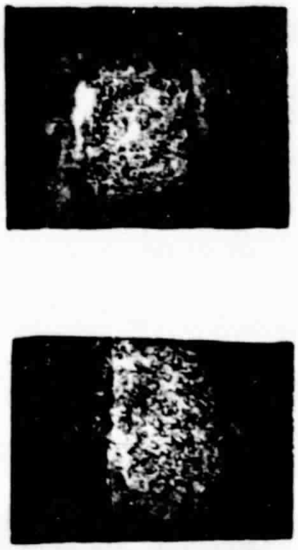
2.3 DIFFUSION OF COMBUSTION SPECIES THROUGH RHENIUM

The interstitial diffusion of hydrogen through wrought metals is known to be much faster than nitrogen or oxygen. As the approximate calculations will show, the concentration of hydrogen at the Re/C interface will be <1 ppm after an engine firing duration of 4000 sec. The diffusion rates of nitrogen and oxygen were not considered to be of major importance because they are very low in comparison to that of hydrogen.

Solubility and diffusion data for nitrogen and hydrogen in rhenium are not readily available. This was confirmed by contacts with experts in the diffusion field, as well as a computer literature search. The solubility and diffusivity of nitrogen and hydrogen in rhenium were approximated by comparison with other refractory metals similar to Re.

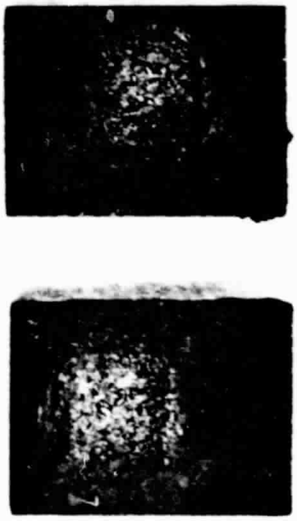
TABLE 1. MIXTURES OF FLUX/RHENIUM POWDER FOR LASER MELTING TRIALS

Combination No.	Mixture Weights
1	$\frac{1\ \text{g}\ Na_2CO_3}{2\ \text{g Re}}$
2	$\frac{0.5\ \text{g}\ Na_2CO_3 + 0.5\ \text{g}\ Na_2B_4O_7}{2\ \text{g Re}}$
3	$\frac{1.0\ \text{g}\ Na_2B_4O_7}{2\ \text{g Re}}$
4	$\frac{0.2\ \text{g}\ Na_2CO_3 + 0.2\ \text{g}\ Na_2B_4O_7}{2\ \text{g Re}}$
5	$\frac{1\ \text{g}\ Na_2CO_3 + 1\ \text{g}\ Na_2B_4O_7}{2\ \text{g Re}}$



Neg. No. 53054 1X

(a)



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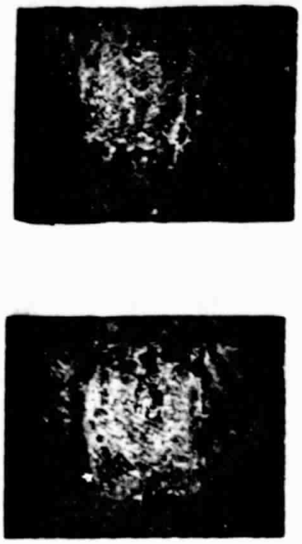
(b)



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(c)

Figure 8. Globular rhenium deposits produced by laser melting of (Re + flux) mixtures 2, 3, and 5. (a) Mixture 3, (b) mixture 2, (c) mixture 5. Laser exposure = 30 sec, power = 5 kW, except for 3B (50 sec).

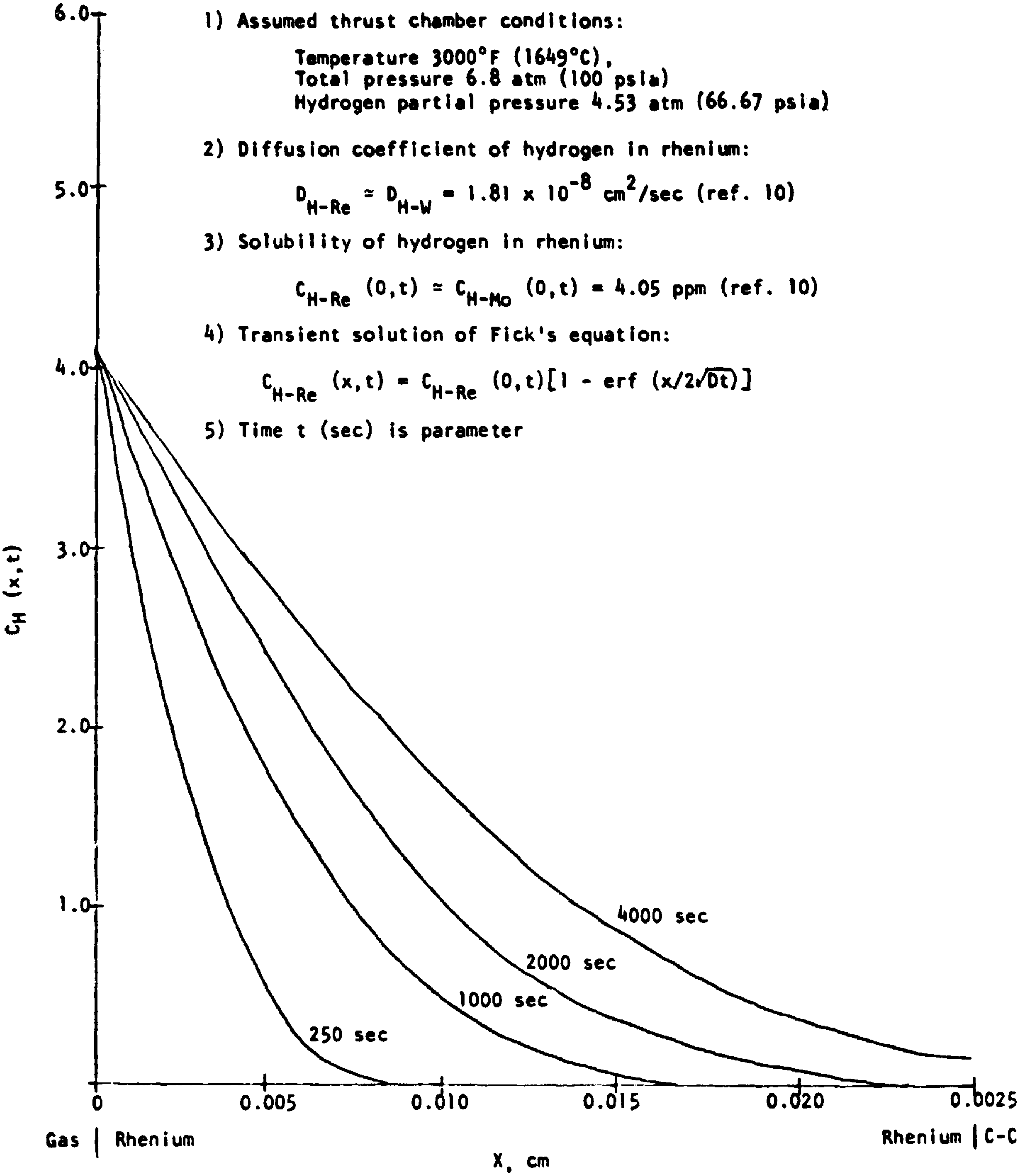
The solubility of interstitial atoms such as hydrogen and nitrogen has been shown to be dependent on the electron/atom ratio[6,7] and the density of state at the Fermi surface of the metal.[7,8] From these two considerations, the solubility of hydrogen in rhenium should be comparable to that in molybdenum.[7-10] Using Sievert's Law and assuming the total decomposition of N_2H_4 at 100 psi (6.8 atm), the solubility of hydrogen in rhenium can be calculated as $\sim$4.0 ppm at 1600°C.

The diffusivity of hydrogen at high temperature is directly related to the vibrational frequency of the rhenium atoms and the distribution of interstitial sites available for hydrogen occupancy. As a first approximation, the vibrational frequency will be considered as controlling the jump rate of the hydrogen atom. From this consideration, the diffusion rate of hydrogen in rhenium should be comparable to that in tungsten (1.81×10^{-8} cm^2/sec).[10]

Diffusion rates are calculated using Fick's second law assuming a semi-infinite plate geometry with diffusion as the rate-limiting step. Results of calculations based on the stated assumptions appear in Fig. 9. The concentration of hydrogen (ppm by weight) is plotted against distance along the coating. Time is used as a parameter where firing times of 250, 1000, 2000, and 4000 sec are considered. The results of the calculations indicate that at no time will the concentration of hydrogen exceed 1 ppm at the Re/C interface. Since the diffusion rates of nitrogen and oxygen are seven to ten times lower than that of hydrogen or H_2O are not expected to form at the Re/C interface . All calculations assume that the permeability of the applied coating is comparable to that of wrought sheet.

2.4 STRESS ANALYSIS

A stress system will be produced by the differential thermal expansion of the rhenium coating and the carbon/carbon substrate during thrust engine start-up and cooling periods. An approximate thermoelastic analysis was conducted to determine the stresses in the rhenium coating due to temperature changes from an initial stress-free state. Stress calculations at location E (Fig. 10), just downstream of the injectors, and location I in the throat section were based on an assumption of two concentric right cylindrical surfaces, uniform temperature distribution, and linear isotropic elastic behavior. The effect of internally applied pressure was also investigated. Details of the calculations appear in Appendix A.



1) Assumed thrust chamber conditions:

Temperature 3000°F (1649°C),
Total pressure 6.8 atm (100 psia)
Hydrogen partial pressure 4.53 atm (66.67 psia)

2) Diffusion coefficient of hydrogen in rhenium:

$$D_{H-Re} \simeq D_{H-W} = 1.81 \times 10^{-8}\ \mathrm{cm^2/sec}\ \text{(ref. 10)}$$

3) Solubility of hydrogen in rhenium:

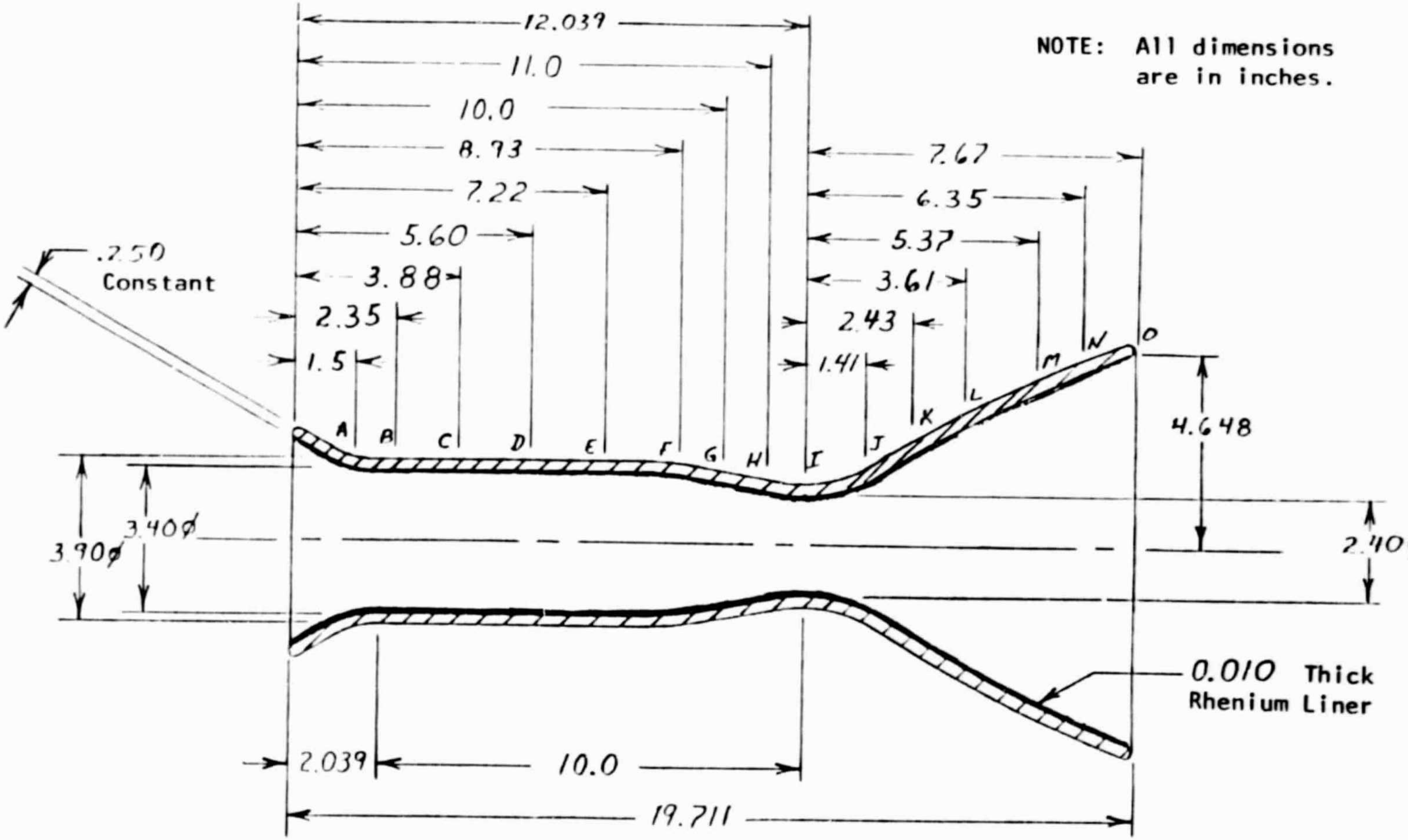
$$C_{H-Re}\,(0,t) \simeq C_{H-Mo}\,(0,t) = 4.05\ \mathrm{ppm}\ \text{(ref. 10)}$$

4) Transient solution of Fick's equation:

$$C_{H-Re}\,(x,t) = C_{H-Re}\,(0,t)[1 - \mathrm{erf}\,(x/2\sqrt{Dt})]$$

5) Time t (sec) is parameter

Figure 9. Approximate calculation of transient concentration of hydrogen in rhenium liner.



NOTE: All dimensions are in inches.

LOCA-TION	TEMP. °F	PRESS. PSI.G.	LOCA-TION	TEMP. °F	PRESS. P.S.I.G
A	590	100	I	2950	56
B	160	100	J	2480	17
C	325	100	K	2090	9
D	345	100	L	1770	5
E	465	100	M	1510	3
F	2700	100	N	1420	2
G	2870	86	O	1320	1.5
H	2900	70			

Figure 10. Cross section of rhenium-lined carbon composite thrust chamber.

The maximum thermal stress at location E operating at 240°C was calculated as -34,380 psi (i.e., compressive). This is less than the yield stress of the material (46,000 psi). A temperature excursion to 363°C may be tolerated before the yield point is exceeded and compressive buckling takes place. The pressure at location E (100 psi) has the beneficial effect of reducing the circumferential stress by 4340 psi.

Operating conditions at the throat (location I) of the thrust chambers are most severe. The circumferential stress reaches values of -193,200 psi which far exceeds the yield stress at the operating temperature of 1650°C. The effect of internal pressure (56 psi) at location I is to reduce the circumferential stress by 1,400 psi, which is quite negligible.

Strain-to-failure data from literature indicate the calculated circumferential strain of -0.004 to be less than the strain-to-failure of 0.015. The result is that cracking of the coating is not expected at location I at the throat even though the stress is high.

3. DISCUSSION OF RESULTS

Plasma-arc spraying test trials have produced uniform and adherent rhenium 7-10 mil coatings free of through-porosity. The preferred spraying parameters determined in the project are given in Appendix B.

Figure 11 shows the microstructure of a sectioned as-sprayed coating applied under optimum conditions with -170 +270 mesh high-purity rhenium powder. The microstructural features show lamellar grains scattered throughout the as-sprayed coating. The homogenization of these areas by recrystallization heat treatment is likely to be beneficial in reducing residual coating stresses from spraying as well as reducing microporosity.

Reference to Figs. 12a and 12b reveals the effect of heat treatment at two different temperatures on the as-sprayed microstructure. Apparent in Fig. 12a is the beginning of recrystallization at 1650°C after 4 hr, with lamellar grains still evident. At 2000°C after 4 hr (Fig. 12b), the initial stages of grain growth have begun in localized areas and very few lamellar grains remain. Heat treatment at the higher temperature (2000°C) for 4 hr will produce a larger grain size and a more homogeneous structure, with reduced microporosity.

Partial mechanical bonding of coatings occurred in some as-sprayed specimens, as shown in Fig. 13. Occurrence of partial bonding in actual thrust chambers might be beneficial. As the thermoelastic stress calculations have shown, the circumferential shear stresses exceed the elastic limit of rhenium at location I in the throat. With limited bonding of the coating, the stresses encountered will be reduced, with some limited buckling possible.

The stress and diffusion rate calculations were based on wrought rhenium properties, which may not be fully representative of actual coating properties; no data for coatings were available. Such calculated results should be used with caution and their limitations noted. A 10% inherent porosity in plasma-sprayed coatings has been reported to improve thermal shock resistance as well as the ability to withstand strain from 0.5 to 1.5% without failure.[11] Although a slight non-continuous porosity will decrease the resistance of coatings to gaseous permeation, this increase should not exceed the tolerance of the coating.

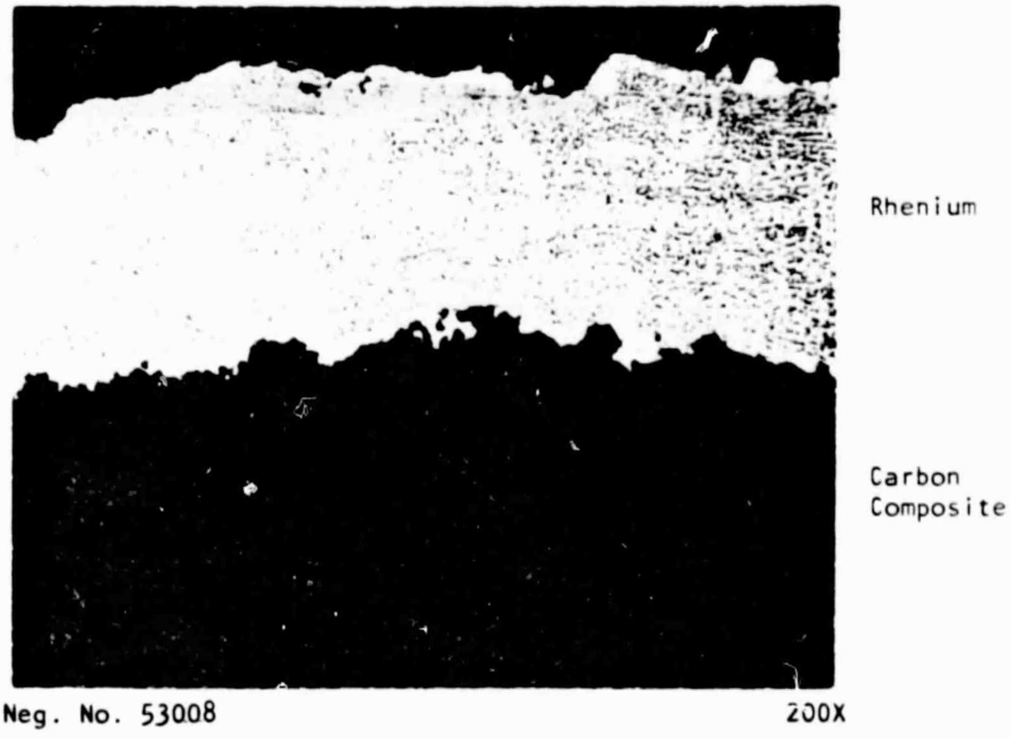
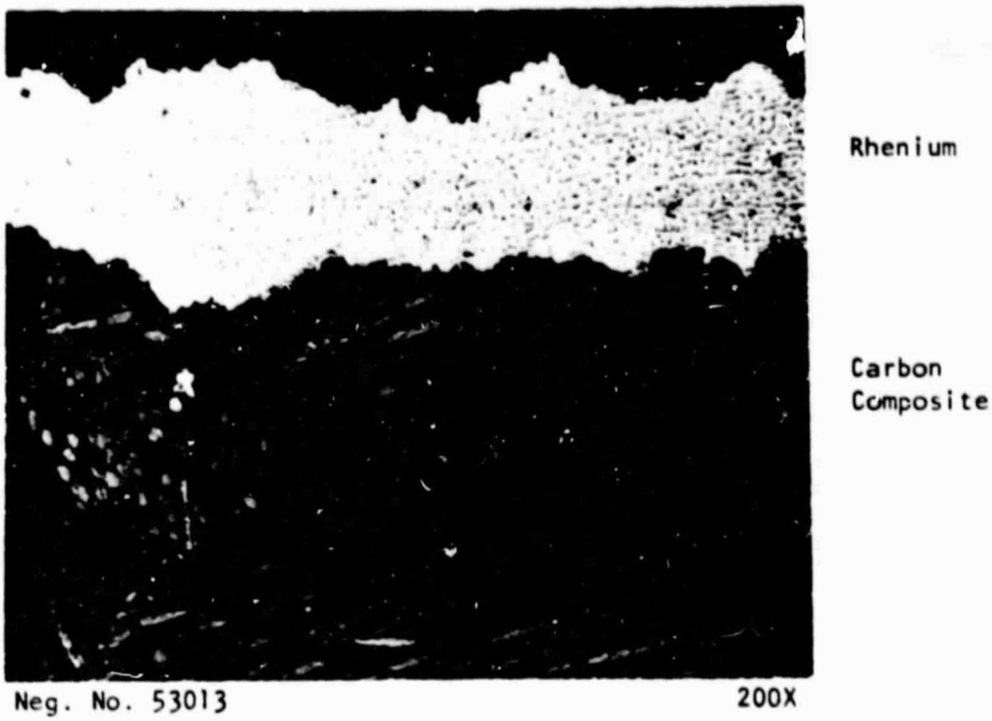
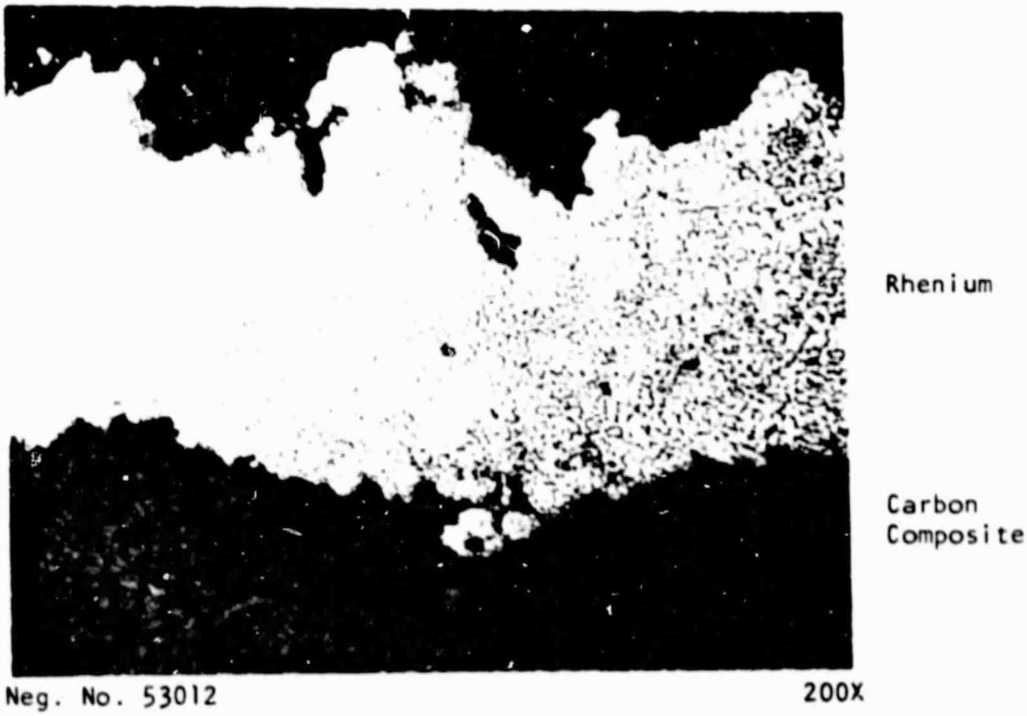


Figure 11. Specimen CC-014 with optimum 7-10 mil plasma-sprayed rhenium coating applied at 2 in. standoff using -170 +270 mesh rhenium powder. Absence of porosity and uniformity of coverage were realized.



(a)



(b)

Figure 12. Plasma-arc sprayed specimens after recrystallization heat treatments. (a) Specimen CC-010, 1650°C for 4 hr in flowing argon; homogenization of as-sprayed structure just beginning. (b) Specimen CC-007, 2000°C for 4 hr in flowing argon; grain growth taking place in scattered areas.

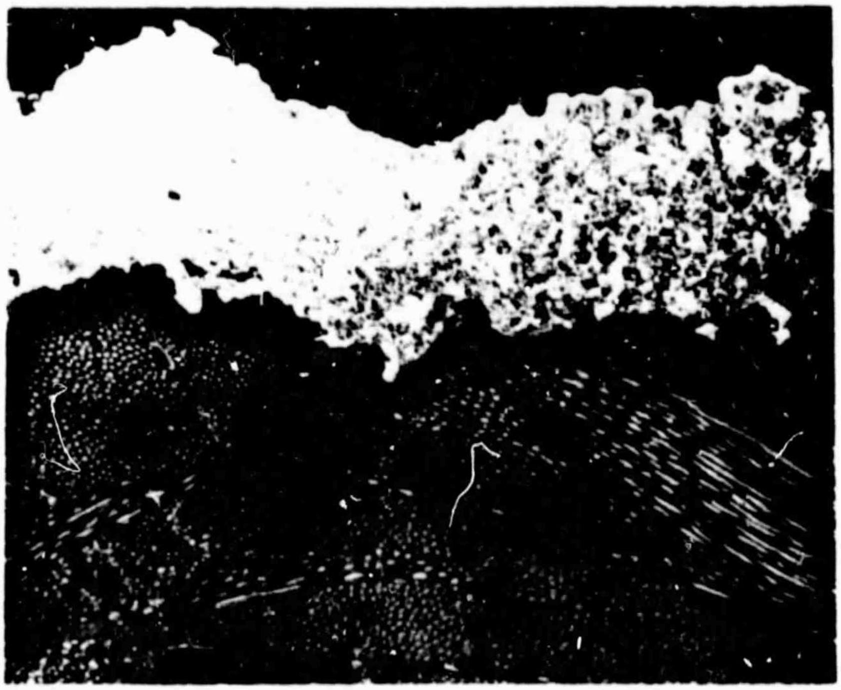


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Figure 13. Specimen CC-009 with separation at the Re/C interface. After spraying with -170 +325 mesh powder, the coating received recrystallization heat treatment at 1650°C for 4 hr.

Consideration was given to W, Mo, and Ta as underlayers for rhenium. All three elements form carbides which aid in producing a metallurgical bond with the carbon substrate. One major drawback with W, Mo, and Ta is their tendency to form hard and brittle intermetallic (σ and χ) phases with rhenium at high temperatures.[12,13] Mo and Ta combined with carbon have additional undesirable properties. The Mo-C system forms a low-melting eutectic at 2200°C compared to 2406°C for Re-C. Localized temperature excursions of 205°C above the throat operating temperature (1650°C) would cause melting at the Mo/C interface. Tantalum, on the other hand, tends to be embrittled when cooled from elevated temperatures to room temperature in hydrogen. The unknown behavior of the intermetallic phases (σ and χ) under cyclic engine conditions adds to the doubt concerning use of Ta and Mo as underlayers. Tungsten has the least questionable properties and can be considered for underlayer application.

The application of plasma-sprayed rhenium coating is relatively simple compared to sputtering techniques. The distribution and properties of coatings obtained by sputtering are very sensitive to geometrical factors, including anode and cathode design and location. Hence, sputtering can produce good coatings on flat surfaces, but is less appropriate for the more complex shape of the internal surface of thrust chambers. Additional difficulties may be caused by the requirement for rigorous surface cleanliness and by the low sputtering yields associated with the harder metals. High vacuum containment is also necessary for this deposition process.

Off-the-shelf plasma-arc systems are available for uniformly spraying large flat areas as well as spraying internal shapes within small volumes with suitable automation. The possible disadvantage with plasma-sprayed coatings is the maximum 90% of theroretical density that can be obtained. However, continuous porosity was not detected in the rhenium coatings sprayed under optimum conditions.

Exploratory laser trials indicated poor wetting of the carbon composite surface by liquid rhenium. Additions of sodium carbonate/sodium borate mixture on carbon had no significant effects on wetting. A major effort would be required to develop a coating process by the laser melting technique.

4. NEW TECHNOLOGY

The experimental and theoretical work performed in the execution of this program utilized existing technologies. These technologies were developed and optimized for a new specific application--that is, the application of rhenium coatings to carbon-carbon composites.

5. SUMMARY AND CONCLUSIONS

1) Work under the project has demonstrated that plasma-spraying can be used to produce uniform coatings of rhenium, free from continuous porosity and through-defects, on carbon-carbon composite substrates.

2) Plasma-spraying trials have established optimum spraying parameters for application of coatings of a satisfactory quality.

3) A brief analysis of sputtering techniques indicated that sputtering is unlikely to be appropriate for applying coatings of a dense metal (rhenium) to curved internal surfaces.

4) Initial trials with laser-melted coatings showed that further work will be required to develop means of improving the wetting characteristics of liquid rhenium on carbon before this method can be used for the present application.

5) Calculations indicated that the rhenium coating will not suffer significant damage due to thermal stresses during firing.

6) Calculations indicated that rhenium coatings in the preferred range of thickness will act as an efficiency barrier to gaseous permeation.

6. RECOMMENDATION

It is recommended that plasma-sprayed coating of rhenium be applied to a thrust chamber for sea-level firing trials by JPL.

IITRI equipment would be unable to produce a satisfactory coating--that is, a coating applied using the parameters developed in this project--because of the small internal diameter of the throat of the thrust chamber. Suitable equipment is owned by Plasmadyne, who have indicated[14] that they would be prepared to undertake the work.

Thus, it is recommended that coating of the thrust chamber be contracted directly by JPL to Plasmadyne.

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APPENDIX A

STRESS CALCULATIONS

1. THERMOELASTIC STRESSES

The calculations assume a system of two concentric right cylinders. Assuming a stress-free initial state for the system, the unrestrained thermal radial expansion of the C-C composite and rhenium cylinders for a uniform temperature change ΔT are:

$$\delta_1 = a_1 \alpha_1 \Delta T \qquad (1)$$

$$\delta_2 = b_2 \alpha_2 \Delta T \qquad (2)$$

where a, b are inner and outer radii of cylinders, respectively

α is the coefficient of thermal expansion

subscripts 1 and 2 denote C-C composite and rhenium materials, respectively.

When the two cylinders are bonded together, a pressure p is exerted at the interface. The radial displacementsthat this pressure would produce on the unrestrained (unbonded) cylinder are:

$$u_1 = \frac{pa_1}{E_1} \left[\frac{a_1 + b_1^2}{b_1^2 - a_1^2} + \nu_1 \right] \qquad (3)$$

$$u_2 = - \frac{pb_2}{E_2} \left[\frac{a_2^2 + b_2^2}{b_2^2 - a_2^2} - \nu_2 \right] \qquad (4)$$

where u is radial displacement (positive outwards)

E is modulus

ν is Poisson's ratio

Equating the difference of the unrestrained thermal expansions (equations 1 and 2) to the difference in radial deflection due to the interface pressure, p:

$$\delta_2 - \delta_1 = u_1 - u_2 \qquad (5)$$

or

$$(b_2\alpha_2 - a_1\alpha_1)\Delta T = \frac{pa_1}{E_1}\left[\frac{a_1^{\,2} + b_1^{\,2}}{b_1^{\,2} - a_1^{\,2}} + \nu_1\right] + \frac{pb_2}{E_2}\left[\frac{a_2^{\,2} + b_2^{\,2}}{b_2^{\,2} - a_2^{\,2}} - \nu_2\right]$$

solving for p and noting that $a_1 = b_2$:

$$p = \frac{(\alpha_2 - \alpha_1)\,\Delta T}{\frac{1}{E_1}\left[\frac{b_2^{\,2} + b_1^{\,2}}{b_1^{\,2} - b_2^{\,2}} + \nu_1\right] + \frac{1}{E_2}\left[\frac{a_2^{\,2} + b_2^{\,2}}{b_2^{\,2} - a_2^{\,2}} - \nu_2\right]} \qquad (6)$$

Then, the maximum circumferential stress in the rhenium cylinder is given by:

$$(\sigma_\theta)_{max} = \frac{-\,2pb_2^{\,2}}{b_2^{\,2} - a_2^{\,2}} \qquad (7)$$

The physical properties of rhenium assumed in the calculations are the following:

Properties of Rhenium

Melting point:	3160° to 3180°C
Thermal expansion:	$\beta[0,0,1] = 12.45 \times 10^{-6}/°C \pm 8\%$
	$\beta[1,0,0] = 4.67 \times 10^{-6}/°C \pm 8\%$
	For calculations β_{mean} (20° to 1000°C) = $6.8 \times 10^{-6}/°C$. This is approximately true for plasma-sprayed coatings where grains should be randomly oriented.
Modulus:	$E = 66.7\ (\pm 2.9) \times 10^{6}$ psi
Strength and ductility:	S = 70,000 psi and $\varepsilon^u = 0.24$*
At room temperature:	S = 164,000 psi, $\varepsilon^u = 0.24$
500°C	S = 114,000 psi, $\varepsilon^u = 0.09$
1000°C	S = 85,000 psi, $\varepsilon^u = 0.01$ to 0.02
1500°C	S = 38,000 psi, $\varepsilon^u = 0.01$ to 0.02

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*ε^u = strain to failure.

The values of various constants used in Equations 6 and 7 for stress calculations at locations E and I in the thrust chamber were:

Location E	Location I
a_1 = 1.700 in.	a_1 = 1.200 in.
b_1 = 1.950 in.	b_1 = 1.450 in.
a_2 = 1.685 in.	a_2 = 1.185 in.
b_2 = 1.700 in.	b_2 = 1.200 in.
α_1 = 1.5 μ ε/°F	α_1 = 1.5 μ ε/°F
α_2 = 3.72 μ ε/°F	α_2 = 3.72 μ ε/°F
ΔT = 400°F	ΔT = 2880°F
E_1 = 6.8×10^6 psi	E_1 = 6.8×10^6 psi
E_2 = 62.4×10^6 psi	E_2 = 43.5×10^6 psi
ν_1 = 0.42	ν_1 = 0.42
ν_2 = 0.49	ν_2 = 0.49

With the assumption of isotropic elastic and thermal properties of both materials, the calculated values of p, $(\sigma_\theta)_{max}$, and the resulting strains $\varepsilon_\theta = \frac{(\sigma_\theta)_{max}}{E_2}$ for the rhenium liner are as follows:

Location E	Location I
p = 302 psi	p = 2,400 psi
$(\sigma_\theta)_{max}$ = -34,380 psi	$(\sigma_\theta)_{max}$ = -193,200 psi
ε_o = -0.0006	ε_o = -0.004

2. INTERNAL PRESSURE EFFECT

The radial displacement of the C-C composite is given by:

$$u_1 = \frac{p_o a_1}{E_1} \left[\frac{a_1^2 + b_1^2}{b_1^2 - a_1^2} + \nu_1 \right]$$

and the displacement of the rhenium liner is:

$$u_2 = \frac{b_2}{E_2 \, (b_2^2 - a_2^2)} \{ 2a_2^2 p_i - [(1 - \nu_2) \, b_2^2 + (1 + \nu_2) \, a_2^2] \, p_o \}$$

where p_i = internal pressure

p_o = pressure at the rhenium/C-C composite interface

Since the concentric cylinders do not separate, continuity requires that $u_1 = u_2$. Noting that $a_1 = b_2$, the resulting expression is:

$$p_o \left\{ \frac{1}{E_1} \left[\frac{b_2^2 + b_1^2}{b_1^2 - b_2^2} + \nu_1 \right] + \frac{(1 - \nu_2) \, b_2^2 + (1 + \nu_2) \, a_2^2}{E_2 \, (b_2^2 - a_2^2)} \right\} = \frac{2a_2^2}{E_2 \, (b_2^2 - a_2^2)} \, p_i \qquad (8)$$

This relates p_o to p_i at the interface.

The maximum circumferential shear stress in the rhenium liner is:

$$(\sigma_\theta)_{max} = \frac{1}{b_2^2 - a_2^2} \{ (a_2^2 + b_2^2) \, p_i - 2b_2^2 \, p_o \} \qquad (9)$$

where p_o is given by Eq. 8 and the other constants are the same as those used for Eq. 6 and Eq. 7.

The resulting stresses are as follows:

Location I	Location E
p_o = 37.91 psi	p_o = 61 psi
p_i = 56 psi	p_i = 100 psi
$(\sigma_\theta)_{max}$ = 1400 psi	$(\sigma_\theta)_{max}$ = 4340 psi
Temperature = 2880°F	Temperature = 400°F

APPENDIX B

RECOMMENDED SPRAYING PARAMETERS

Within the scope of testing conducted at IITRI, the following overall spraying parameters were judged to be the optimal for coating integrity and spraying performance with the 40 kW plasma-spray unit:

a) Rhenium powder size: -170, +270 mesh
b) Standoff distance: 2 in.
c) Coating thickness: 7-10 mils
d) Substrate preheat: ∿200°C
e) Maximum temperature of substrate backside: ∿500°C
f) Post-spray heat treatment: 2000°C for 4 hr
g) Linear travel rate: approximately 1 ft/sec.