

Apr 3rd, 12:00 AM

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IRIDIUM COATINGS FOR THE PROTECTION OF GRAPHITE RE-ENTRY STRUCTURES

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Abstract

Because of its high strength-to-weight ratio and other desirable features, graphite is desirable for use as structural components that are to be exposed to a high-temperature environment. At elevated temperatures, however, graphite reacts with oxidizing atmospheres, and smooth surfaces having specific engineering properties are degraded into eroded surfaces of lower efficiency.

It has been demonstrated that iridium can be used to protect graphite in air at temperatures to 3600 F for 1 hour or more. Battelle has been conducting a program for the Air Force Materials Laboratory to study the application of iridium and iridium-alloy coatings to graphite, based on a combined plasma-arc deposition and gas-pressure bonding process. A comprehensive program involving the development, fabrication, and testing of these coatings is described.

Introduction

Manned re-entry systems with medium to high lift-to-drag ratios generate incandescent frontal sections upon re-entering the atmosphere. This phenomenon places severe demands on materials that are used in these portions of the vehicle.

This paper deals with the nonablating, constant-geometry, multiple-mission concept of frontal segments designed for operating in the temperature region of from 3000 to 4500 F. Constant geometry is important for manned re-entry systems in order to establish and maintain aerodynamic control. Economics, flexibility, and mission profile necessitate a system able to withstand multiple heating cycles.

Because of its high strength-to-weight ratio and other features, graphite is desirable for use as structural components that are to be exposed to a high-temperature environment. However, at elevated temperatures graphite reacts with oxidizing atmospheres, smooth surfaces having specific engineering properties are degraded into eroded surfaces of lower efficiency.

A variety of materials have been considered as possible oxidation barriers; however, most have been rejected because of compatibility limitations, a thermal-expansion mismatch with the substrate, or the inability to be fabricated into dense, uniform coatings which are well bonded to the substrate. The only really successful coatings explored to date have contained Si and are limited to temperatures below 3000 F.

Iridium has shown great promise for the oxidation protection of graphite in re-entry frontal sections.¹ Complete oxidation protection has been demonstrated in air at various pressures and at temperatures above 3800 F. Iridium was found to be essentially impervious to oxygen diffusion at 3600 F, and did not react with graphite below the eutectic temperature of approximately 4150 F.^{1,2} Iridium also has a very low vapor pressure (2.2×10^{-5} mm of Hg at 3600 F) which indicates that the evaporation rate at reduced pressures will be very small.

The iridium coating itself oxidizes to form volatile oxides; however, the oxidation rate at 3600 F in air has been found to be approximately 5.4×10^{-5} g cm²/sec, corresponding to a recession rate of 0.003 to 0.004 inch per hour.

To function as a protective sheath, the iridium must be formed and maintained without cracks or pinholes. In addition, the coating must be well bonded to the substrate for maximum protection.

Several techniques have been previously utilized in applying iridium coatings to graphite, including slurry dip and fusion, vapor plating, foil cladding, and electroplating. In general the coatings produced by these techniques were well bonded to the graphite and exhibited a fair amount of promise; however, several shortcomings were evident. Briefly, the major drawbacks were continuous porosity, cladding defects, lack of uniformity, columnar grains in the cladding, and contamination of the substrate.

In an attempt to circumvent or avoid these problem areas, Battelle's Columbus Laboratories undertook a program based on a coating technique successfully used for the fabrication of oxidation- and abrasion-resistant coatings for refractory metals; that is, a combined plasma-arc-deposition and gas-pressure-bonding process. The Ceramics and Graphite Branch of the Air Force Materials Laboratory also sponsors a contract on electroplating and vapor plating of iridium on graphite.³

Description of Process

Briefly the combined process involves first the deposition of the iridium coating material on the substrate by a plasma-spraying technique followed by an isostatic pressure compaction at elevated temperatures. Figure 1 is a flow diagram of the entire process.

Initial deposition of the coating by the plasma process enables one to build the coating to thicknesses of from 0.002 to 0.060 inch. The process results in a strongly adherent coating which fills all graphite surface irregularities and can be machined or ground in preparation for a subsequent operation. The use of the plasma process in the initial preparation of the coating also permits compositional changes without interruption of coating continuity in cases where a graded coating concept may be required.

Plasma spraying was conducted using a 60-kw d-c high-velocity plasma torch in conjunction with a high-purity inert-gas spray chamber. The chamber is capable of being evacuated to 10^{-5} torr before back-filling with an inert cover gas. The plasma gun is shown on the floor of an open chamber in Figure 2.

Because plasma-deposited coatings nominally contain a certain amount of entrapped porosity, initial deposition is followed by gas-pressure bonding to achieve full density in the coating and to extrude iridium into the open porosity in the graphite substrate to increase the bond strength.

The iridium-coated graphite structures are encapsulated in close tolerance, vacuum tight metal containers. Sealing of the containers is generally accomplished by heliarc or electron beam welding.

The containers are then leak checked and placed in a high-pressure, high-temperature, cold-wall autoclave where isostatic gas pressure is brought to bear on the container surface while the specimen is at an elevated temperature. A schematic drawing of a typical autoclave is shown in Figure 3.

The autoclave body is sealed on the end with a modified Bridgman seal during pressure application. An internal heater incorporated in the center of the autoclave is insulated from the outer wall by insulation such as bubbled alumina or microquartz. In the larger autoclaves, a smaller, secondary head is incorporated which allows for simple and quick loading. In this equipment, helium or argon gas is used to exert the pressure during bonding. The gas is pressurized by piston-type compressors and can be reclaimed after each cycle.

Following the pressure-bonding process, the external canning material is removed by either mechanical or chemical techniques and the iridium-coated structure surface is buffed to a high luster.

Description of Research

A. Establishment of Fabrication Parameters for Iridium Coatings

Initial studies in this program were designed to establish both the plasma-deposition and gas-pressure-bonding process parameters required to coat graphite with iridium. POCO AXF grade graphite was selected for this phase of the program because of its high density, its isotropic structure, and its coefficient of expansion, which nearly matches that of iridium.

Plasma spray parameters were evaluated by depositing iridium on graphite test coupons at various arc power levels, powder feed rates and gun substrate distances. The plasma-gas flow was maintained at a level necessary to maintain a stable arc with regard to the power input. Following deposition, the coupons were metallographically sectioned and the coating density was measured by a lineal analysis technique. Iridium-to-graphite bonding and ease of coating buildup were judged from metallographic and visual observation.

It was found that coatings having a density of 99+ percent of theoretical could be deposited; however, the coating thickness was limited to approximately 0.002 inch under these spray conditions. Optimum spray conditions, as far as interface bonding and coating buildup are concerned, was observed to occur at a power setting of 400 amperes and a torch-to-work-piece distance of 4 inches. The optimum plasma spray parameters are shown in Table 1.

TABLE 1. PLASMA PARAMETERS FOR DEPOSITING IRIIDIUM

| | |
|------------------------------------|--------------|
| Amperes | 400 |
| Voltage | 28 |
| Arc-Gas Flow | 0.85 SCFM |
| Powder-Gas Flow | 0.25 SCFM |
| Stand-Off Distance | 4 inches |
| Plasma Gas | Argon |
| Enthalpy of Flame (calculated) | 90 kcal/mole |
| Plasma Temperature (calculated) | 10,500 K |

The above spray parameters yielded coatings having a density of 93.3 percent of theoretical. An as-sprayed structure may be seen in Figure 4. It will be noted that the voids are equally dispersed throughout the coating.

Following establishment of the plasma spray parameters, several cylindrical graphite specimens were coated with iridium to determine the optimum gas-pressure-bonding conditions. Because iridium is known to bond to most potential canning materials, it was necessary also to evaluate various barrier-layer compounds that would be inert to both the iridium and the can. Barrier compounds serve the dual purpose of preventing any undesirable reactions as well as aiding can removal following densification.

To determine the best combination of canning metal, temperature, and barrier compound, mild steel, titanium, and molybdenum containers were loaded with the iridium-coated test samples with various barrier layers between the coating and the can. ZrC, ZrO₂, BN, Al₂O₃, HfO₂, and SiC were evaluated. The specimens were sealed by electron-beam welding and subjected to bonding runs conducted for 2 hours under a pressure of 10,000 psi at temperatures of from 1950 to 2150 F.

Upon subsequent metallographic examination of the bonded specimens, it was noted that coating densification had occurred as low as 1950 F, thus enabling the use of mild-steel containers. Boron nitride appeared to be the most favorable barrier layer material, with alumina a close second. The mild-steel container could be easily removed from both

materials by chemical means. A photomicrograph of the graphite-iridium-boron nitride-mild steel interfaces after bonding at 1950 F and 10,000 psi for 2 hours is shown in Figure 5. Note that there are no pores apparent in the coating and that the mild steel is not bonded to the iridium.

Iridium coatings 0.010 in. in thickness were then applied to several graphite rods using the previously described coating parameters. Boron nitride was employed as a barrier-layer material. Following can removal, the rods were centerless buffed to a high surface finish for use in coating-characterization studies. Three of the coated rods are shown in Figure 6.

B. Coating Characterization

In order to evaluate the coatings, the rods were subjected to a number of destructive and non-destructive tests to evaluate impurity levels, grain structure, uniformity, presence of defects, and bond integrity.

To ascertain whether or not the fabrication process results in any increase in the impurity level of the iridium, a sample of the coating was removed from the rod and evaluated by spectrographic techniques. The results of this analysis are shown in Table 2 along with the analysis of the as-received iridium powder.

TABLE 2. IMPURITY CONTENT OF IRIIDIUM COATING AND OF AS-RECEIVED POWDER

| Impurity | Impurity Content, ppm | |
|----------|-----------------------|--------------------|
| | Coating | As-Received Powder |
| B | 100 | ND |
| Ca | <10 | <10 |
| Cr | ND | ND |
| Cu | T | T |
| Fe | 50 | ND |
| Mg | 10 | ND |
| Mn | <30 | ND |
| Ni | T | ND |
| Pd | 20 | 20 |
| Pt | T | ND |

TABLE 2. (CONTINUED)

| Impurity | Impurity Content, ppm | |
|----------|-----------------------|--------------------|
| | Coating | As-Received Powder |
| Rh | T | T |
| Si | <20 | 10 |

T = Trace

ND = Not Detected

The slight increase in the impurity level following coating, notably in the case of boron and iron, probably from incomplete surface clean-up following can removal.

Bonding between the coating and the substrate was also evaluated by a thermal cycling test. One end of a 4-inch-long rod was placed in a water-cooled copper chill block and the other end was inductively heated to 2100 C in approximately 3 minutes. The cool end of the specimen achieved a maximum temperature of approximately 300 C during this time. After 5 minutes at temperature the rod was cooled to black heat and thermal cycle repeated. Following the second cycle, the rod was removed and examined. It was found that the coating bond was still sound and had not parted from the substrate. The specimen is shown in Figure 7. The different coloration along the length of the rod is a result of the different temperature zones.

The grain structure was examined metallographically. The coating was electroetched in a solution of 10 gm KCN and 100 cc H₂O at 6 volts a-c. The etched structure is shown in Figure 8. As this was an extremely strong etch, the grain boundaries were severely attacked, resulting in excessive grain fall-out. This accounts for the porosity shown in the etched structure as no pores could be observed in the as-polished condition.

Bond integrity was also ascertained by ultrasonic techniques, which revealed that the bond was continuous along the length of the rod; that is, there were no void areas or interruptions between the iridium and the graphite.

Several specimens were also examined for coating defects by the Zyglo dye-penetrant test. The test employed was ASTM designation E-165-65. In this type of test the specimens are treated with "post-emulsified" dye which penetrates all pores or microcracks. Subsequent examination under ultraviolet light reveals the defect.

The results of this examination revealed that there is an end effect over the last 0.25 inch of the rod. This area is believed to be a result of the ends not being subjected to the full isostatic pressure during the gas-pressure-bonding treatment because of the rigid metal end plugs in the pressure-bonding cans. This effect can be avoided through the use of porous-metal end spacers in the cans. The center 4.5 inches of the 5-inch-long specimens were shown to be completely devoid of any pinholes or microcracks.

Coating uniformity was ascertained through the use of the Magnetic Reaction Analyzer device, which generates eddy currents in the coating at various depths depending on the frequency. The reaction field produced by the eddy currents are measured by a Hall-device probe. The eddy currents produced are a function of the material properties, thickness, and geometry. By careful calibrations, the coating thickness can be accurately measured. It was found that the circumferential thickness variation was 0.00033 mil. The variation in the thickness over a 4-inch length was found to be 0.00045 inch.

Tests are being conducted on intentionally defected specimens using a differential Hall-device probe to ascertain the presence of pinholes or microcracks beyond the sensitivity of the Zyglo dye-penetrate tests.

Conclusions

The plasma-arc-deposition and gas-pressure-bonding technique is an acceptable method for producing defect-free, uniform, well-bonded coatings of iridium on graphite.

The work reported in this paper represents only a portion of the entire program. Additional studies are being conducted on iridium-alloy coatings to improve the emissivity of the system and to achieve better high-temperature oxidation protection. The feasibility of the coating technique is also being ascertained for use with other graphite grades which have widely varying expansion and structural characteristics. Oxidation test specimens are also being prepared for measurements at an Air Force-designated facility. The final phase of the program will be to adapt the process to a variety of complicated shapes including leading-edge components, nose cones, and nozzle inserts. As a sidelight to the program, the emittance of iridium and iridium-doped coatings is being measured in both air and vacuum at temperatures up to 2000 C.

References

- (1) "High Temperature Protective Coatings for Graphite", Union Carbide Corporation, MLTDR 64-173, Parts I thru IV.
- (2) "Iridium Base Alloys and Their Behavior in the Presence of Carbon", AFML-TR-66-290.
- (3) AFML Contract No. AF 33(615)-3617, General Technologies Corporation.

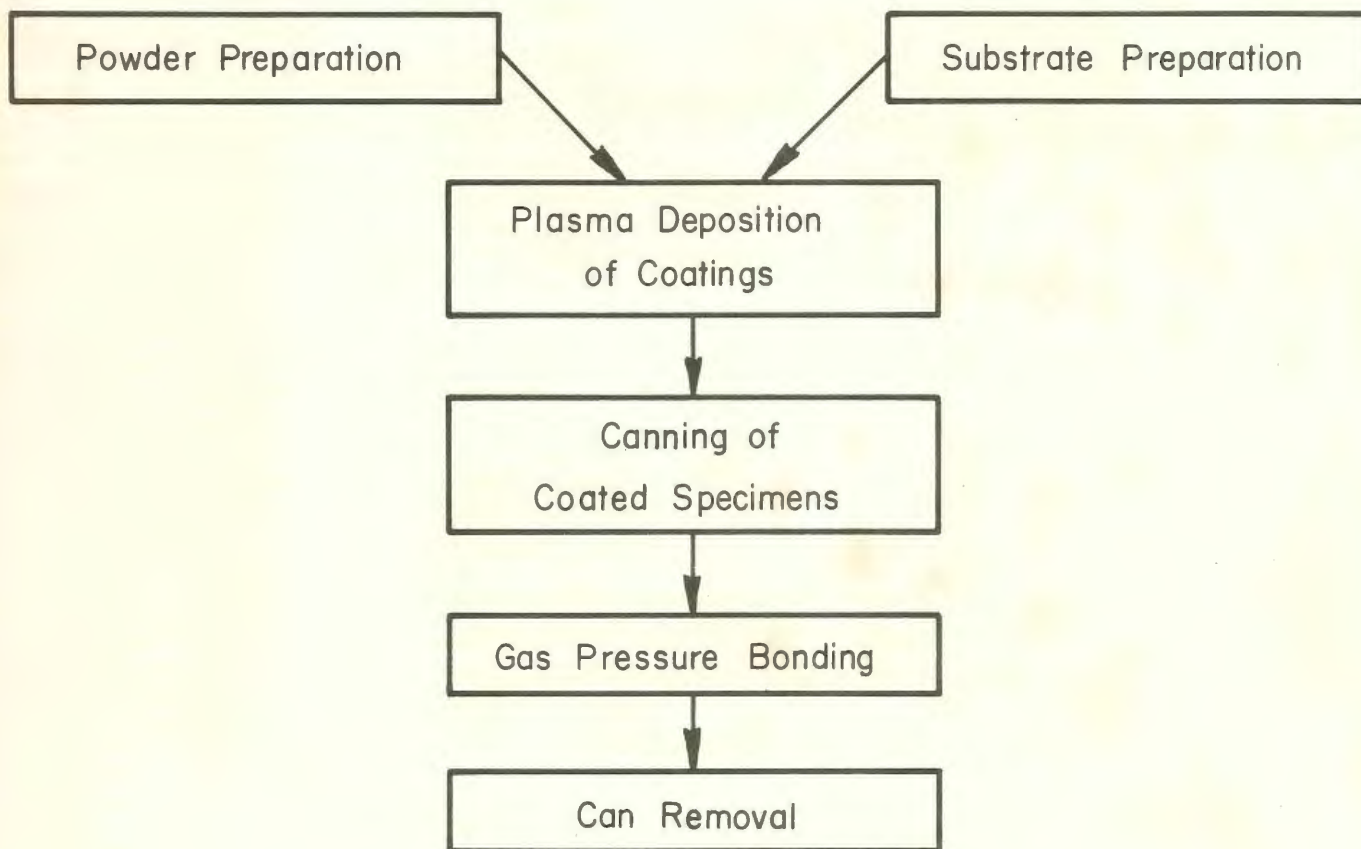


FIGURE 1. FLOW DIAGRAM OF PLASMA-GAS PRESSURE BONDING COATING PROCESS

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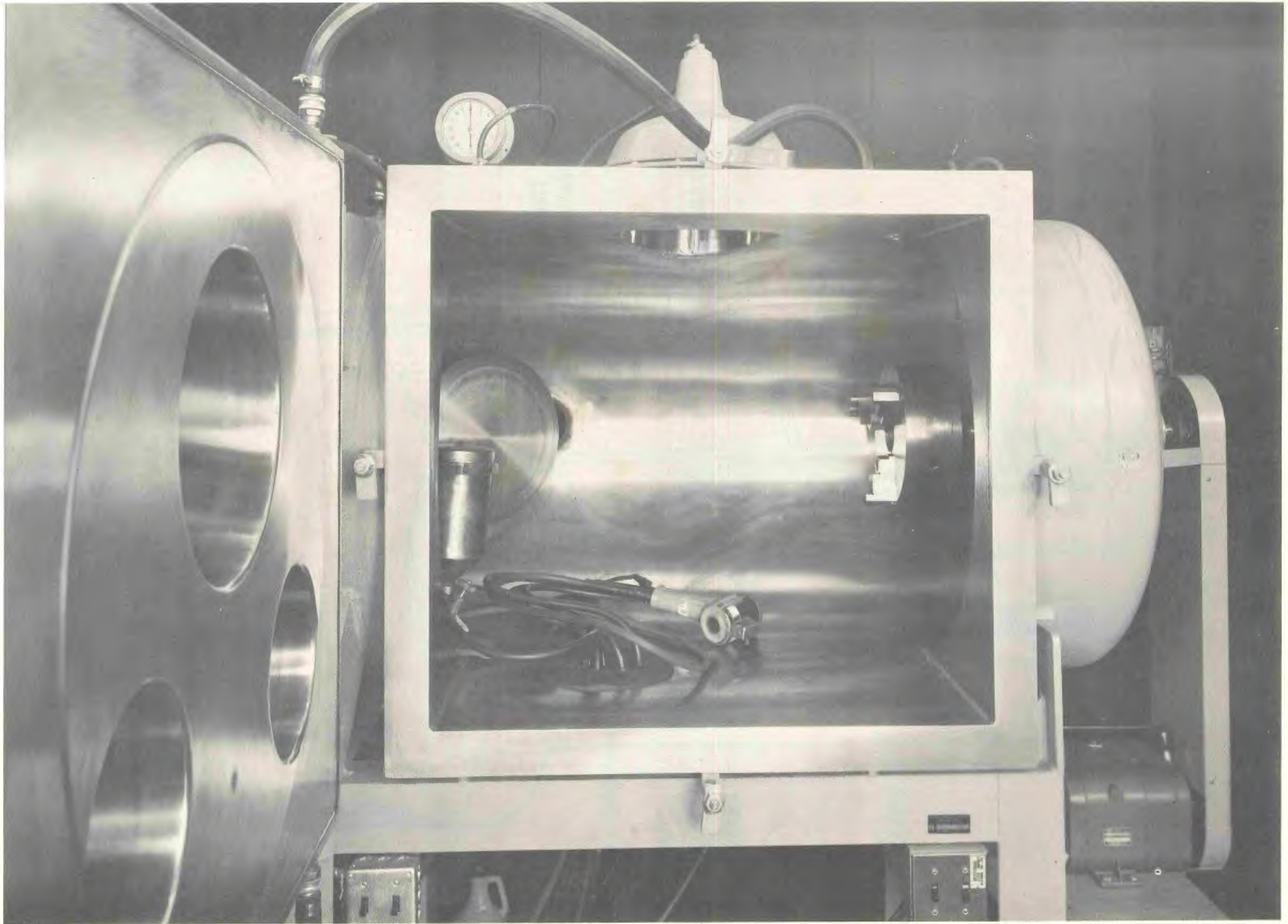


FIGURE 2. PLASMA TORCH AND SPRAY CHAMBER

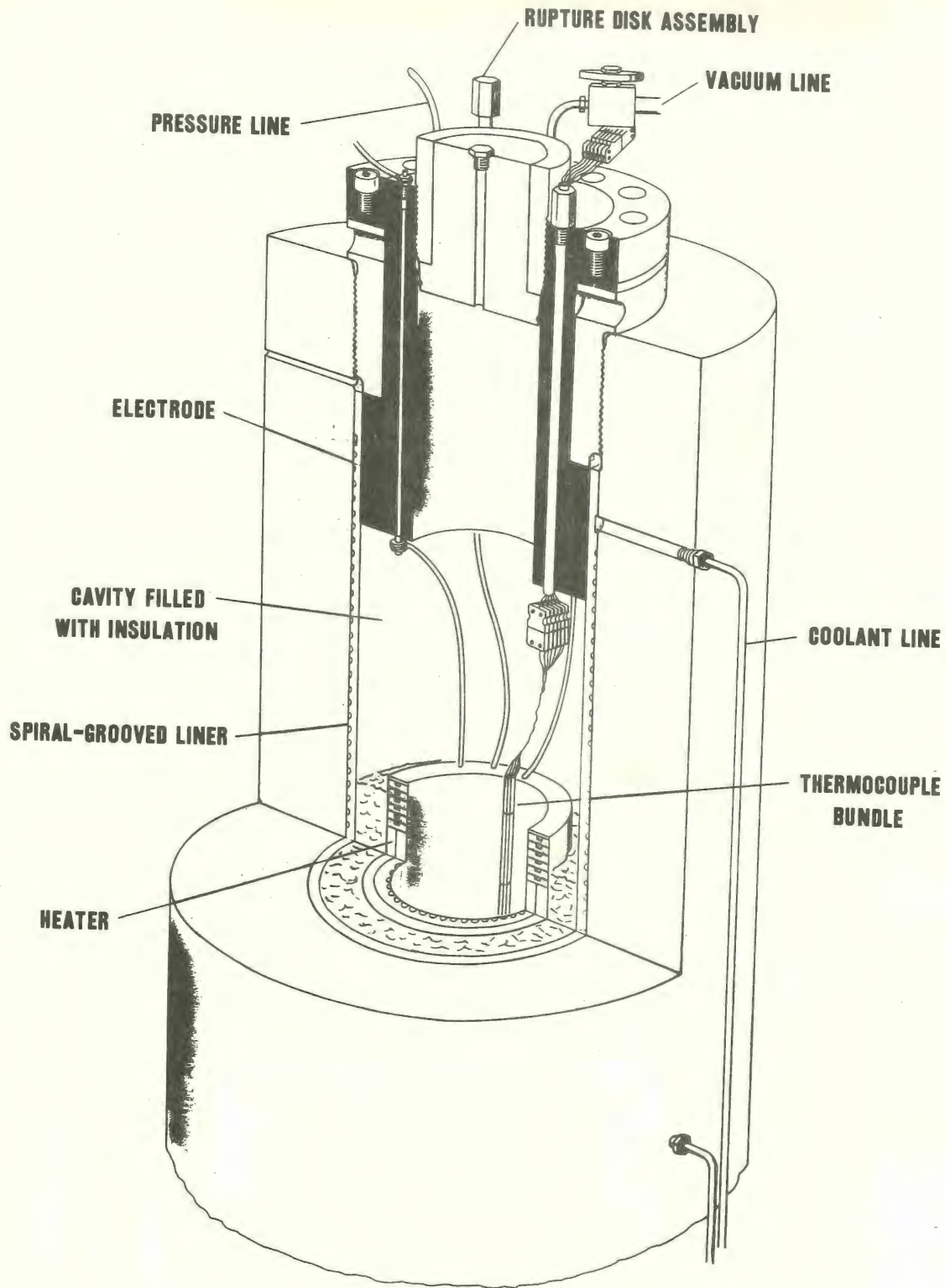


FIGURE 3. SCHEMATIC CROSS-SECTIONAL DRAWING
 OF A GAS-PRESSURE-BONDING AUTOCLAVE

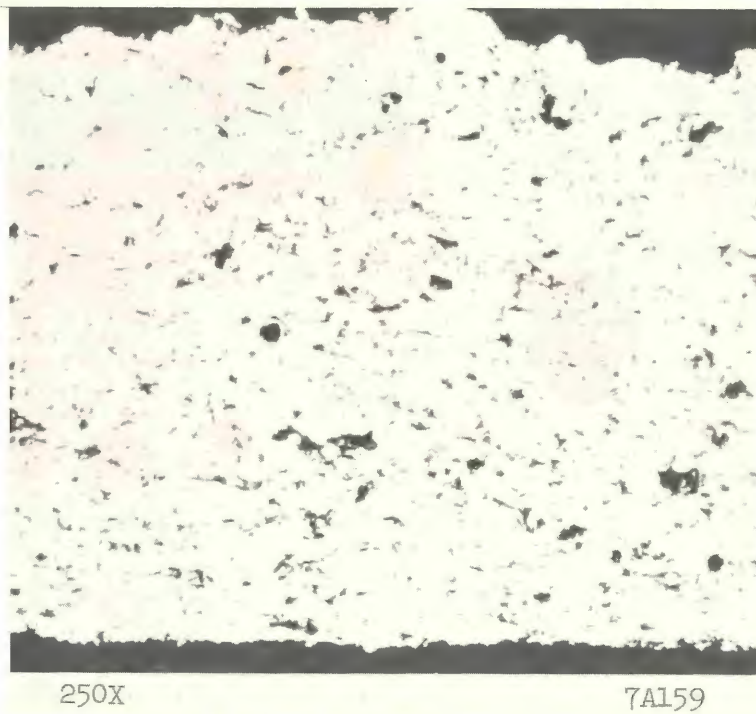
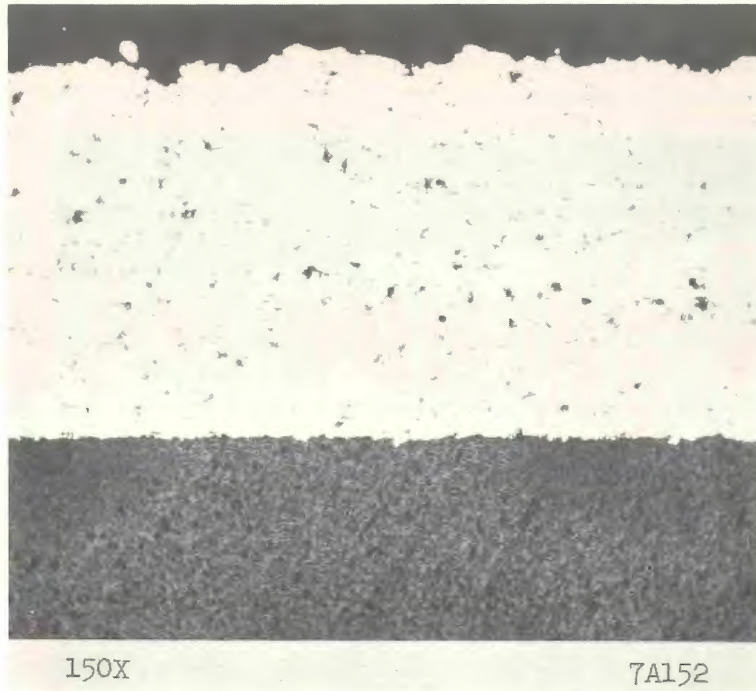


FIGURE 4. IRIIDIUM COATING PLASMA DEPOSITED ON GRAPHITE

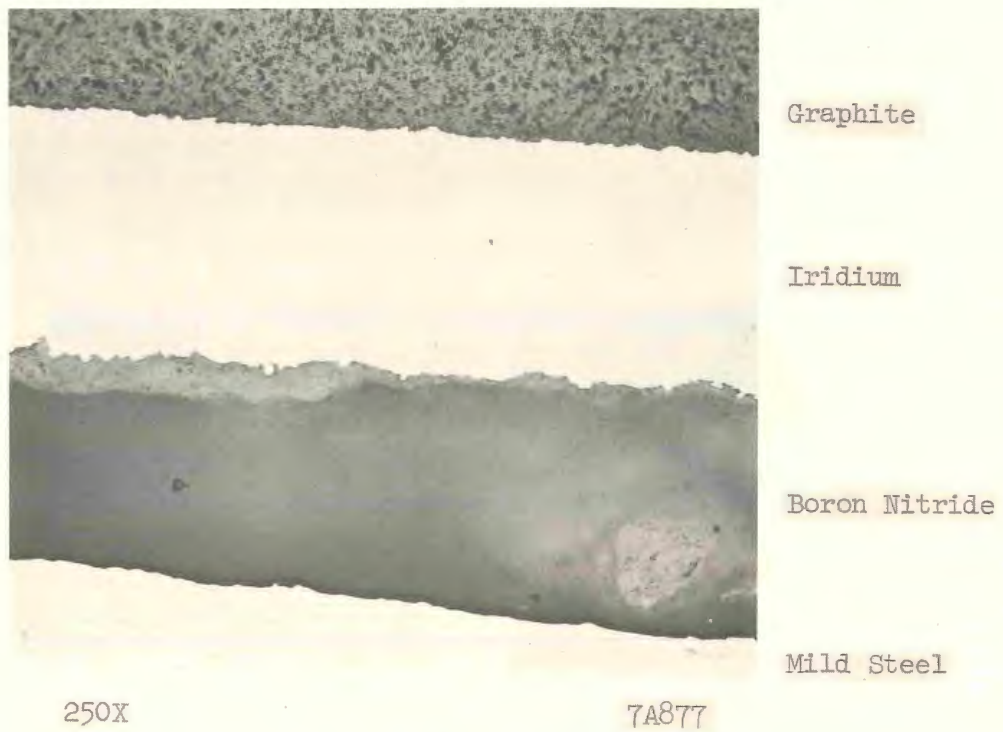


FIGURE 5. THE GRAPHITE-IRIDIUM-BORON NITRIDE-MILD STEEL INTERFACES AFTER BONDING AT 1950 F AND 10,000 PSI FOR 2 HOURS