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# Iridium-Coated Rhenium Thrusters by CVD

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THRUSTERS BY CVD (NASA) 12 P CSDL 21H

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### SUMMARY

Operation of spacecraft thrusters at increased temperature reduces propellant requirements. Inasmuch as propellant comprises the bulk of a satellite's mass, even a small percentage reduction makes possible a significant enhancement of the mission, in terms of increased payload. Because of its excellent high temperature strength, rhenium is often the structural material of choice. It can be fabricated into free-standing shapes by chemical vapor deposition (CVD) onto an expendable mandrel. What rhenium lacks is oxidation resistance, but this can be provided by a coating of iridium, also by CVD. This paper describes the process used by Ultramet to fabricate 22-N (5-lbf) and, more recently, 445-N (100-lbf) Ir/Re thrusters; characterizes the CVD-deposited materials; and summarizes the materials effects of firing these thrusters. Optimal propellant mixture ratios can be employed because the materials withstand an oxidizing environment up to the melting temperature of iridium, 2400 °C (4350 °F).

### INTRODUCTION

Rhenium and iridium, two of the three heaviest metals, hardly would seem suitable as the stuff spacecraft engines are made of. Yet in fact, these obscure metals have made possible a significant improvement in the performance of satellite orbit insertion and reaction control thrust chambers. The properties of rhenium and iridium which made this both possible and practical include the following:

- The very high melting temperatures of these metals: 3180 °C (5760 °F) for rhenium and 2440 °C (4420 °C) for iridium.
- The high temperature strength and thermal shock resistance of rhenium, which surpass those of all other elements and almost all alloy systems.
- The high temperature chemical inertness of iridium, a platinum group metal.

- The ability to fabricate both of these metals to net shape by chemical vapor deposition (CVD).

## BACKGROUND

The majority of a satellite's mass consists of the propellant needed for orbit insertion and attitude control. Improvements in engine efficiency increase the allowable payload in direct proportion to propellant savings.

Specific impulse is the usual measure of rocket engine propulsion efficiency. This is basically the momentum of the combustion products leaving the exhaust nozzle divided by the mass of the reactants (the propellant). As in all thermal engines, reaction temperature is the determinant of efficiency. Yet the limitation on the efficiency of rocket engines until now is not the maximum temperature available from the combustion process, but rather the ability of the materials comprising the engine to withstand the interrelated thermal, mechanical, and chemical effects of combustion.

Oxidation-resistant coatings and cooling are employed to overcome this material limitation. A typical liquid bipropellant engine is a disilicide-coated niobium alloy chamber employing nitrogen tetroxide ( $N_2O_4$ , or NTO) and monomethyl hydrazine (MMH). In order to keep the wall temperature below the nominal upper use temperature of 1320 °C (2400 °F), 30 to 40 percent of the fuel is injected as a film along the surface of the combustion chamber (ref. 1). In addition to providing cooling, the fuel film also forms a barrier to the oxidizer, which is injected centrally. Even so, in order to keep oxidation to an acceptable limit, oxidizer/fuel mixture ratios (MRs) must be kept at levels substantially below those which yield optimal specific impulse.

Film cooling extracts a significant penalty in performance. New chamber materials able to withstand higher temperatures and reduce or eliminate fuel film cooling can provide important economic gains for a space mission.

Rhenium was recognized by the Jet Propulsion Laboratory as an excellent candidate in this respect. In collaboration with Ultramet, JPL produced several rhenium and rhenium-coated thrust chambers, and test-fired them with a variety of propellants to obtain performance data (refs. 2, 3, and 4). Using fluorine/hydrazine, steady state throat temperatures of nearly 2000 °C (3630 °F) were sustained for ten minutes or so without any apparent corrosion or erosion of the rhenium. Aerojet TechSystems also has investigated rhenium thrusters fabricated by Ultramet. For the NTO/MMH propellant system with fuel film cooling, Aerojet reported that uncoated rhenium can operate at steady state up to about 2065 °C (3750 °F) and a mixture ratio of 1.5 without appreciable material loss. Measurable regression is observed, however, in the optimal performance range of  $MR = 1.65$  to 2.0, yielding limited chamber life. Uncoated rhenium is unsuitable for more than a few hundred pulsing (on/off) cycles because uncontrolled startup and shutdown transients result in material oxidation. Clearly, rhenium needs to be protected from oxidation if the optimal combustion conditions for NTO/MMH are to be attained.

Fortunately, a coating material which meets these requirements exists in the form of the platinum group metal iridium. Iridium bonds to, but does not form a eutectic with, rhenium (ref. 5); its thermal expansion is very close to that of rhenium; and it is reasonably resistant to oxidation up to its melting

point. None of the platinum group metals is completely inert to oxidation; at high temperature, all but osmium form a volatile oxide resulting in linear recession of the surface. Recession rates are shown in figure 1 (ref. 6).

Ever since the early 1960s, a number of attempts were made to produce coatings of iridium on various refractory substrates, without much success. Iridium has been electrodeposited from fused salt (sodium and potassium cyanate) baths. The resultant coatings, however, were porous and brittle, and proved ineffective in preventing oxidation of the base metal (refs. 7 and 8). Plasma spraying of platinum and iridium likewise resulted in porous deposits. Gas-pressure bonding can eliminate porosity and enhance adhesion, but it is cumbersome and not applicable to complex shapes (ref. 9). CVD was attempted by several investigators, but adhesion, adequate thickness, and impermeability were not achieved (refs. 10, 11, 12, and 13). Iridium can be sputtered, but the deposition rate is slow and the process is not adaptable to intricate shapes (ref. 14).

## FABRICATION

Fabricating a refractory metal into the thin-shell configuration of a thrust chamber is a real challenge. The refractory metals are typically very brittle, impossible to draw and very difficult to machine. They also tend to be expensive, so that hogging a shape out of a billet is not cost-effective.

Chemical vapor deposition (CVD) is a process that has been used with great success in such cases. CVD is best known in the semiconductor industry as a method of fabricating integrated circuits from thin layers of exotic materials with precisely controlled composition and purity. Another use of CVD has been developing rapidly: the building up of thick structural layers of (usually) refractory metals and ceramics.

CVD has been studied scientifically for more than a century, but only recently has this technique left the laboratory and become a production tool. CVD is a method of plating which relies on the chemical reaction of a vapor at a surface to form solid structural deposits. Since this occurs on an atom-by-atom basis, impurity levels are typically less than 0.1 percent and densities are those of the bulk material. The CVD process utilizes a gaseous compound of the element to be deposited, which is flowed over a heated substrate, resulting in thermal decomposition or reduction of the gaseous compound and subsequent deposition of the material onto the substrate. The first layer forms at nucleation sites; after the substrate is fully covered, growth continues on the crystal faces of the deposit.

Successful CVD -- dense, adherent coatings -- depends on experimentally determining the optimal deposition parameters. These parameters include the gaseous compound of the material to be deposited, substrate temperature, gas concentration, flow, pressure and geometry within the reaction chamber, coating thickness, and substrate material. For the coating to have high integrity and adhesion to the substrate, the substrate either must have a similar coefficient of expansion to that of the deposited material, or form a strong chemical or metallurgical bond with it. The thinner the coating, the less similar the coefficients of expansion need be. Where coating and substrate form no intermetallic bond and have widely differing coefficients of expansion, a good bond can often be achieved by using a thin interlayer of a third material.

The essential requirements of a CVD facility are that the substrate be maintained at the correct temperature and the plating gases be supplied in the correct ratio and at the correct pressure. The substrate is typically heated resistively, inductively, or in a hot wall furnace. The composition of the plating gases is determined by the type of reaction to be used. The same materials may be deposited using different compounds and different reactions at different temperatures, with each producing good coatings but different crystal structures. Compounds and alloys can be deposited by simultaneous codeposition of the appropriate elements. Some of the plating gases are volatile liquids or solids which are commercially available. In other cases, the compounds are made in situ as required.

The schematic of a typical CVD apparatus is shown in figure 2. In this case, rhenium is being deposited onto a mandrel. Chlorine gas is fed into a chamber containing rhenium metal. The rhenium is heated initially to 500 °C (930 °F) and reacts with the chlorine to form rhenium pentachloride ( $\text{ReCl}_5$ ). The rhenium need only be heated initially, since the reaction is exothermic and sufficient heat is produced to sustain it. The  $\text{ReCl}_5$  then passes over the mandrel, which has been heated to 1200 °C (2200 °F) by the induction coil. At the hot mandrel surface, the  $\text{ReCl}_5$  decomposes, with rhenium metal depositing on the mandrel and chlorine gas passing out the exhaust. The rhenium in this form can be used as a coating or, by making it sufficiently thick and removing the mandrel, a free-standing structure can be obtained.

The procedure developed at Ultramet for depositing iridium uses iridium pentanedionate as the precursor compound. This organometallic compound is also known as iridium acetylacetonate (IR ac-ac in short), with the structural formula  $\text{Ir}(\text{CH}_3\text{COCHCOCH}_3)_3$ . It is obtained commercially as a solid, in either powder or crystal form. The schematic of a typical CVD apparatus for depositing iridium is shown in figure 3. Ir ac-ac is heated resistively in the horizontal arm of the glass chamber. The carrier/reaction gases sweep the sublimed IR ac-ac vapor past the part to be coated, which is heated by a 450 kHz magnetic field; iridium plates out on the part, while the reaction products are exhausted. The precise details of this process are proprietary.

The process used for fabricating iridium-coated rhenium thrusters is interesting because of its novelty. The first step is to fabricate a mandrel whose surface conforms to the inside surface of the thrust chamber. This mandrel is made of a material which is metallurgically compatible with the thruster materials: it must be dimensionally stable at process temperatures, not form a eutectic, have a similar thermal expansion, and be easy to remove afterward. Molybdenum and graphite are often used for the mandrel.

The second step is to deposit the iridium coating on the mandrel, typically 25 to 50 microns (1-2 mils). Depositing the iridium at this stage makes it much easier to inspect for defects, as compared to inspecting a deposit on the inside surface of the thruster later on. Furthermore, bonding of the iridium to the rhenium occurs at the higher temperature of the rhenium CVD process.

The third step involves depositing rhenium to a thickness of 1 mm (40 mils) or more. The deposition process is modified at the final stage to leave the rhenium with a highly dendritic (needlelike) grained surface which has a high emissivity. This aids in radiative cooling of the chamber during

operation. The ends are machined to proper length and the mandrel is chemically or electrochemically dissolved out, leaving a free-standing thrust chamber.

Two types of Ir/Re thrusters have been fabricated thus far. The first is a low-thrust, 22-N (5-lbf) chamber for orbit insertion, station keeping, or attitude control. Figure 4 shows an iridium-coated mandrel and a completed thruster. The "black" rhenium surface is quite evident. These 22-N thrusters burn either NTO/MMH (for Aerojet) or gaseous O<sub>2</sub>/H<sub>2</sub> (for NASA).

The second class of thruster is a 445-N (100-lbf) high-performance NTO/MMH thrust chamber designed for spacecraft trajectory corrections and orbit changes. This is a candidate for the JPL Mariner Mark II spacecraft propulsion system. Figure 5 shows the mandrel and a completed thruster.

### METALLOGRAPHIC ANALYSIS

The iridium/rhenium deposits are evaluated in three ways:

- The ends of the chambers, which are machined off, are sectioned, serving as analysis surrogates for the adjacent material.
- A coated mandrel may be sacrificed for metallographic analysis.
- Thrusters which have completed life cycle hot-fire tests are sectioned.

The first method is useful in assessing the quality of the bond between the iridium and rhenium, and in inspecting for porosity and voids in the deposits. The second method is used to evaluate the thickness distribution of the deposits, as well as for the foregoing. The third method reveals any adverse effects which occur as a consequence of firing, including any loss of iridium as a result of oxidation.

The micrographs in figures 6 and 7 are typical of the 22-N chamber inlet end section (first method). Both the rhenium/iridium and iridium/molybdenum interfaces are visible in the polished and etched section shown in figure 6. Only the rhenium/iridium interface is visible in the polished, unetched section shown, at greater magnification, in figure 7. The quality of the iridium/rhenium bond appears to be excellent. There is no sign of porosity in the iridium or the rhenium. A problem has been encountered in the fabrication of the much larger 445-N (100-lbf) thrusters, in that spalling of the iridium coating has occurred in the nozzle region. Examination of adjacent unspalled material shows evidence of impaired bonding and voids within the deposits. This problem is being addressed via a NASA Lewis-sponsored technology program.

### HOT-FIRE TESTING

Several 22-N (5-lbf) Ir/Re thrust chambers were fabricated by Ultramet for the Air Force Rocket Propulsion Laboratory (now the Astronautics Laboratory) (ref. 15) and for NASA Lewis Research Center (ref. 16). Prior to this development, oxidizer/fuel mixture ratios had been kept suboptimal to avoid burnthrough of the rhenium. The imperviousness of iridium made it possible to raise the NTO/MMH mixture ratio to at least 1.65, the level constrained by the

tankage system. Under this more oxidizing condition, the chamber temperature reaches over 2200 °C (4000 °F) (ref. 17). Nonetheless, one Ir/Re nozzle has survived over 4000 cycles and 15 hours of continuous operation with no measurable change in throat dimensions. None of the 22-N chambers has experienced a failure originating at the surface facing the combustion. The two failures which have occurred resulted from chemical attack from the outside due to the leakage of oxygen into the altitude simulation cell; this, of course, could not occur in a true space environment.

Two 445-N (100-lbf) Ir/Re thrust chambers were hot-fired by Aerojet earlier this year (1988). One has accumulated over four hours of firing at temperatures up to 2000 °C (3630 °F). Some blisters have appeared, but they apparently do not extend to the rhenium interface because there has been no weight loss or other sign of rhenium attack. The other unit has been hot-fired for 3000 seconds to date. Both units remain serviceable and await additional testing. Some problems with spalling of the iridium coating in the nozzle region during deposition were experienced with these larger nozzles. Because the region involved is depleted of oxygen during firing, the thrusters were completed despite the missing iridium, with no adverse effect on operation. Thrust chambers now are being fabricated for the more severe conditions imposed by the gaseous O<sub>2</sub>/H<sub>2</sub> propellant used by NASA.

#### CONCLUDING REMARKS

- Rhenium can be fabricated into a thin-shelled chamber which can withstand the stresses encountered in a rocket engine operating at over 2200 °C (4000 °F).
- Iridium protects rhenium from NTO/MMH combustion gases at 2100 to 2200 °C (3800-4000 °F) for at least 15 hours.
- Chemical vapor deposition (CVD) is a practical fabrication process for both iridium and rhenium in rocket engine applications.

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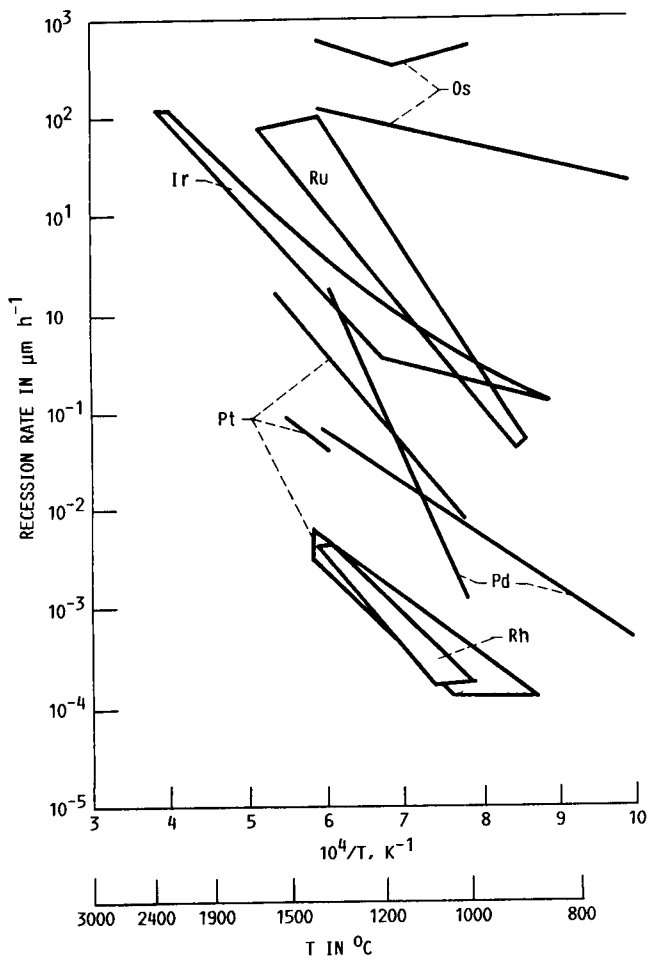


FIGURE 1. - METAL LOSSES OF THE PLATINUM GROUP METALS DURING HIGH-TEMPERATURE OXIDATION IN AIR.

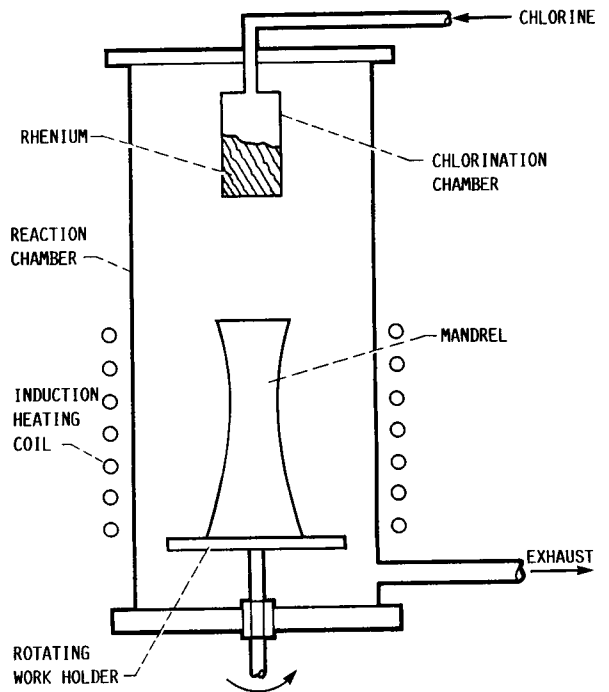


FIGURE 2. - TYPICAL CVD APPARATUS.

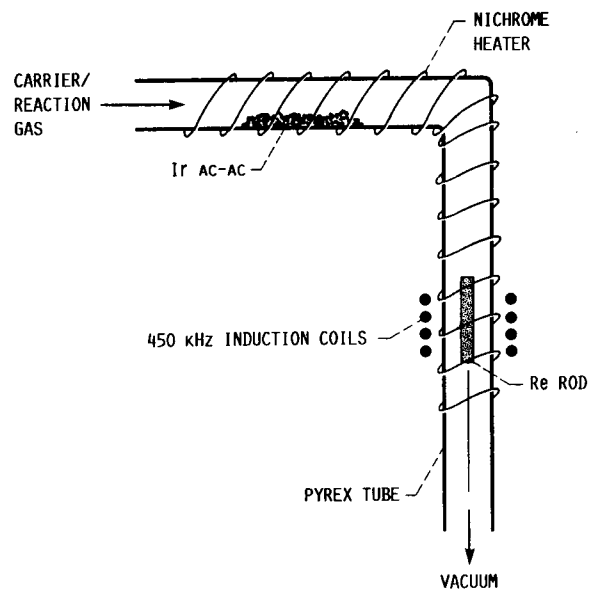


FIGURE 3. - CVD APPARATUS FOR IRIDIUM.

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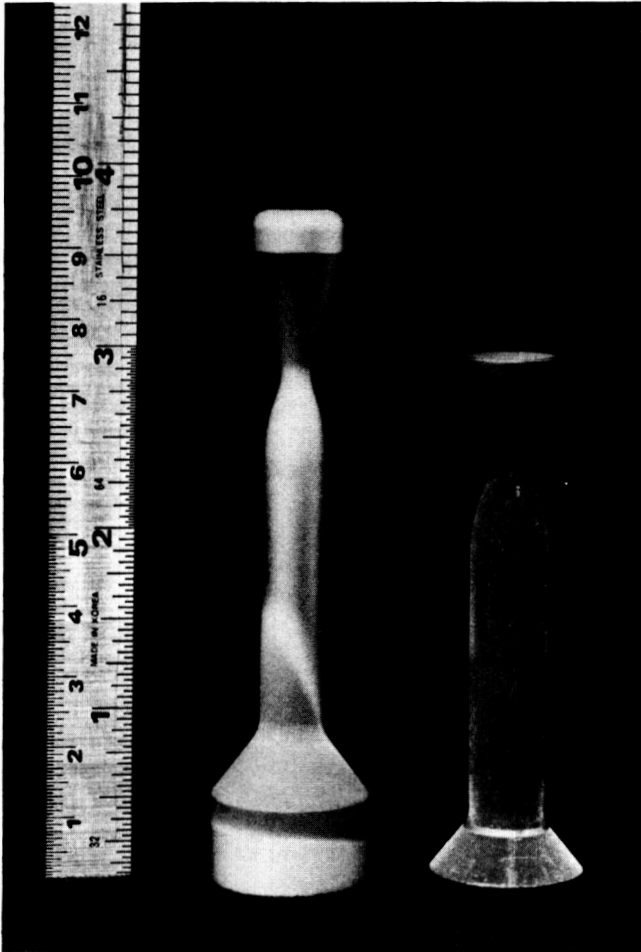


FIGURE 4. - 22-N (5-LBF) THRUSTER (RIGHT); MANDREL (LEFT).

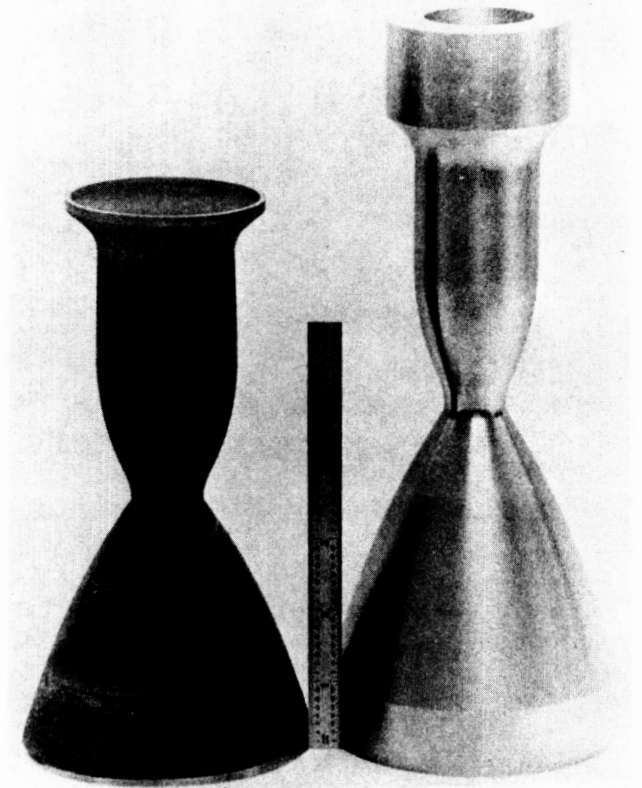


FIGURE 5. - 445-N (100-LBF) THRUSTER (LEFT); MANDREL (RIGHT).

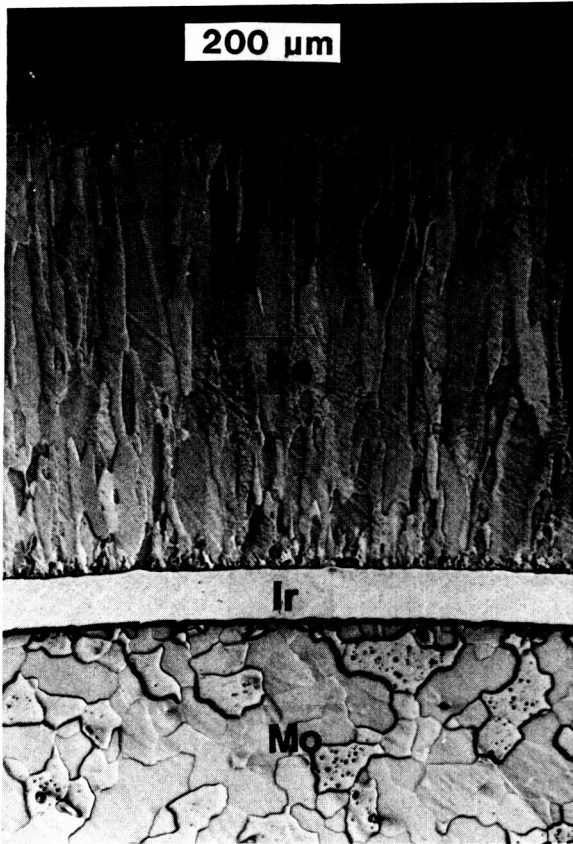


FIGURE 6. - LOW MAGNIFICATION MICROGRAPH OF SECTION AT INLET END OF 22-N (5-LBF) Ir/Re COATED Mo MANDREL.

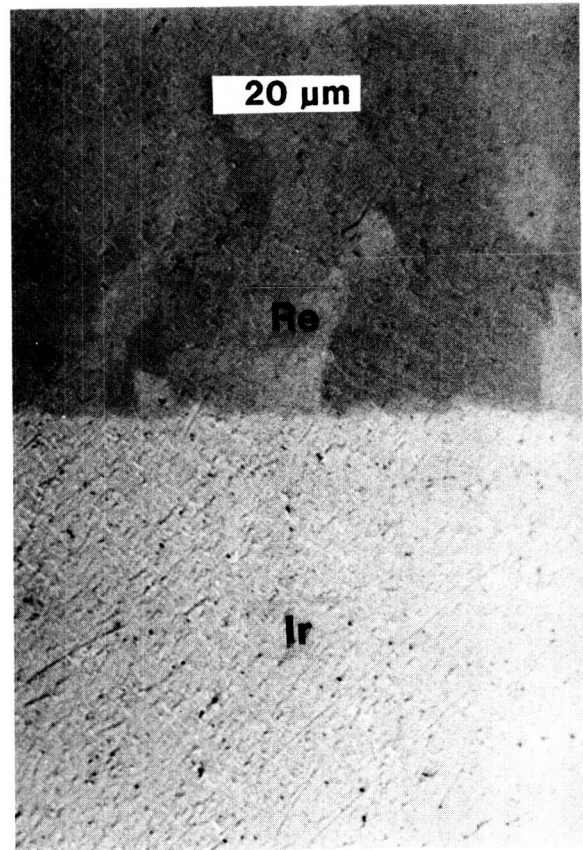


FIGURE 7. - HIGH MAGNIFICATION OF SECTION AT INLET END OF 22-N (5-LBF) Ir/Re COATED Mo MANDREL SHOWING Ir/Re INTERFACE.

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