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THIN REFRACTORY FILMS ON FUSED SILICA CRUCIBLES

Ultramet

J. Grady Sheek and Richard B. Kaplan

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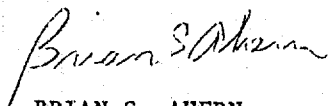
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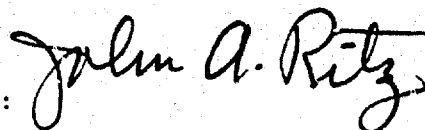
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The ability to control unwanted impurity levels during electronic device fabrication is essential to establishing the desired properties and quality for device reliability. Conventional production processes must be painstakingly monitored to ensure against contamination, and are vulnerable to the introduction of impurities at many stages. One source of impurities is the containment vessel for the melt. In this program, Ultramet demonstrated the feasibility of fabricating inexpensive, high-purity crucibles by an innovative application of chemical vapor deposition (CVD), which typically produces materials with impurity levels of 2.5 ppm. By depositing thins, pore-free refractory films on the interior surfaces of fused silica crucibles, contamination protection equal to or better than that of expensive monolithic freestanding crucibles can be provided.					
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1.0 INTRODUCTION

This is the final technical report submitted by Ultramet, 12173 Montague Street, Pacoima, CA 91331, to the Air Force Electronic Systems Division, Hanscom AFB, MA, 01731-5000, under SBIR Phase I contract no. F19628-87-C-0144. The period of this contract was from 1 June to 1 December 1987. The principal investigator was Richard B. Kaplan. The contract technical monitor was Dr. Brian S. Ahern (RADC/ESM).

The primary objective of this program was to develop a process for depositing very thin, ultrahigh-purity coatings of silicon carbide (SiC), niobium nitride (NbN), titanium diboride (TiB₂), iridium, and boron nitride (BN) onto the interior surfaces of vitreous silica (SiO₂) crucibles by chemical vapor deposition (CVD). This objective was achieved; it now is possible for relatively inexpensive crucibles with a thin, high-purity refractory coating to replace monolithic free-standing crucibles.

2.0 BACKGROUND

The Strategic Defense Initiative (SDI) and other programs will drive the development of optics in the years and decades to come. Containment for the melts used in producing optical quality glasses must, by necessity, be inert with respect to the melt and free of impurities, as an impurity level in the ppm range is sufficient to distort optical properties. At present, when an inert container for a melt is needed, it is fabricated entirely of that same material, usually at great cost. Many containment materials, such as platinum, iridium, and rhenium, are very costly from a material standpoint alone, without regard to the fabrication costs. Ceramic crucibles are generally slip cast, dried, and then sintered. Slip casting is an expensive process, and there are numerous opportunities for the introduction of impurities.

3.0 PHASE I TECHNICAL APPROACH

The primary objective of this Phase I program was to develop a process for depositing thin refractory coatings on the interior surfaces of glass crucibles by chemical vapor deposition (CVD). These crucibles then could be used in place of monolithic free-standing crucibles made entirely of the same, often expensive, material.

3.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) has been used to produce coatings 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 is done on an atom-by-atom basis, impurity levels are typically less than 0.1% and densities are 99.9%. The CVD process utilizes a gaseous compound of the element to be deposited, which is then 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 coated, 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 1. In this case, a boron nitride (BN) coating is being deposited on a crucible. Boron trichloride (BCl_3) and ammonia (NH_3) are fed into the reaction chamber. The gases then pass over the substrate (the crucible), which has been heated to deposition temperature by the induction coil. At the crucible surface, the

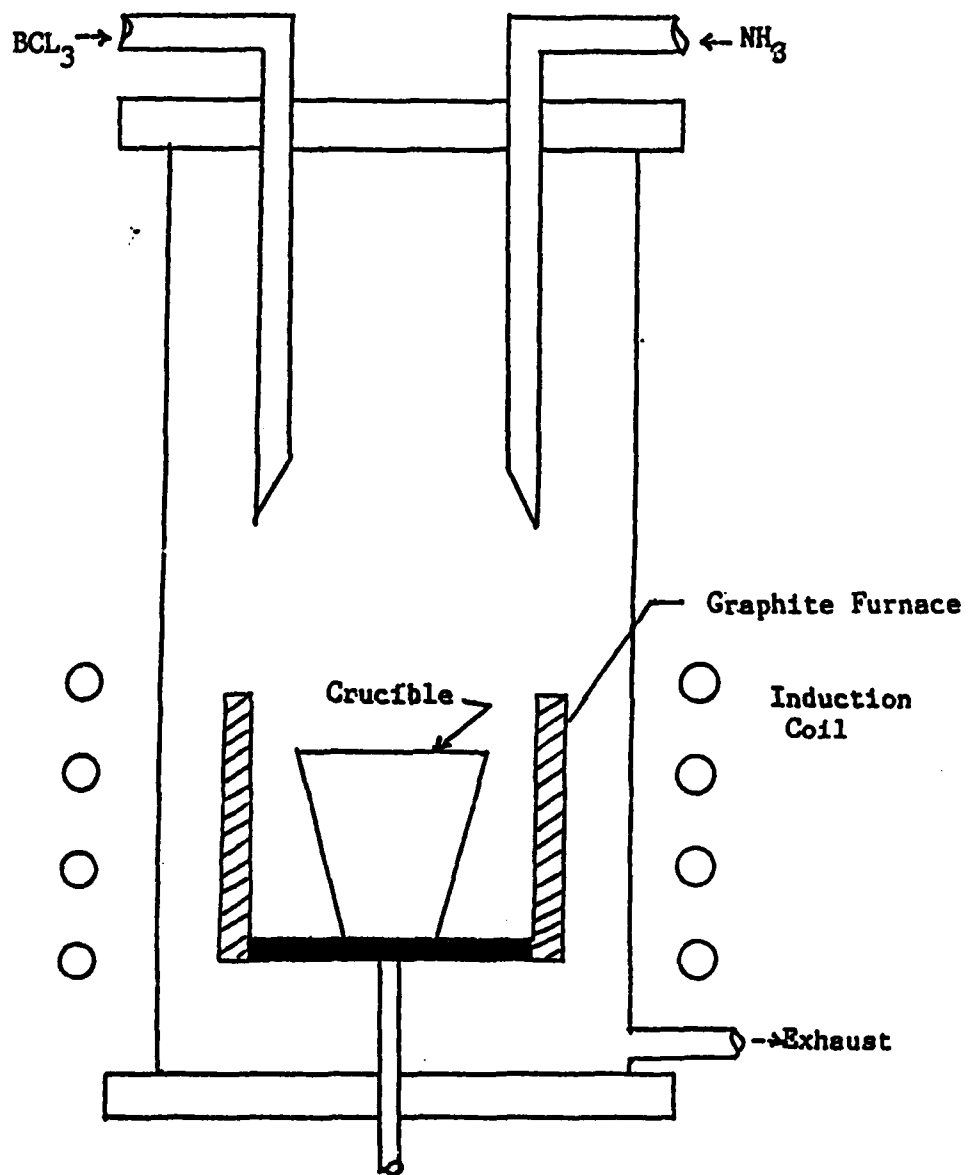


Figure 1. Schematic of Reaction Chamber

BCl_3 reacts with the ammonia, with BN depositing on the crucible and HCl passing out the exhaust.

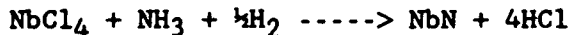
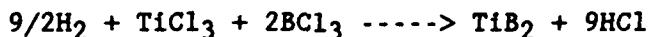
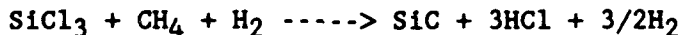
The ability to achieve extraordinary purity in CVD deposits is the result of three stages of purification in the overall process, analogous to triple distillation. First, in the chemical process of preparing the starting compound from bulk metal, impurities tend to be left behind in the unreacted metal or taken off in the other reaction products. Second, in the volatilization of the plating compound, less volatile components are left behind or condense, while more volatile compounds tend to escape. Third, in the decomposition or reaction stage, the pressure and temperatures are optimized for the wanted species; impurities are less likely to deposit and tend to go out the exhaust. The original application of CVD was to purify refractory metals, e.g. the Van Arkel-de Boer iodide process for titanium and zirconium purification. Ultramet has specialized in CVD for 18 years, and has considerable experience in the deposition of a wide variety of metals, ceramics, and compounds for coating, infiltration, and structural purposes.

3.2 Proposed Approach

By depositing a very thin, high-purity coating of the desired material on the interior surface of a vitreous silica crucible, crucibles can be fabricated at a fraction of the cost of a monolithic, free-standing crucible.

Based on previous experience at Ultramet in coating glass, it was decided to etch the smooth internal surfaces of the crucibles prior to deposition. This can be accomplished by two techniques. The first technique uses a hydrofluoric acid (HF) solution poured into the silica crucible and left to sit for five minutes, after which the acid is poured off and the crucible is rinsed thoroughly with water. The second technique, used here, utilizes a low-pressure sandblast to pit or roughen the surface of the crucible. In both cases, a roughened surface is desired, in order to promote good mechanical bonding between the substrate and the coating.

Figure 2 shows a schematic of the apparatus used to coat the silica crucibles. The crucibles are placed into the graphite furnace, which is heated inductively and in return heats the crucible by radiation; the graphite is necessary for induction heating because the glass crucibles are nonconductive. The following deposition reactions were investigated:



Iridium is deposited in a different manner than the process depicted in Figure 2. Iridium acetylacetonate (Ir ac-ac), a chelated compound, is volatilized and decomposed inside the crucible at a relatively low temperature. A typical apparatus for this type of deposition is shown in Figure 3. The probable reaction for the deposition of $\text{Ir}(\text{ac-ac})_2$ is as follows:

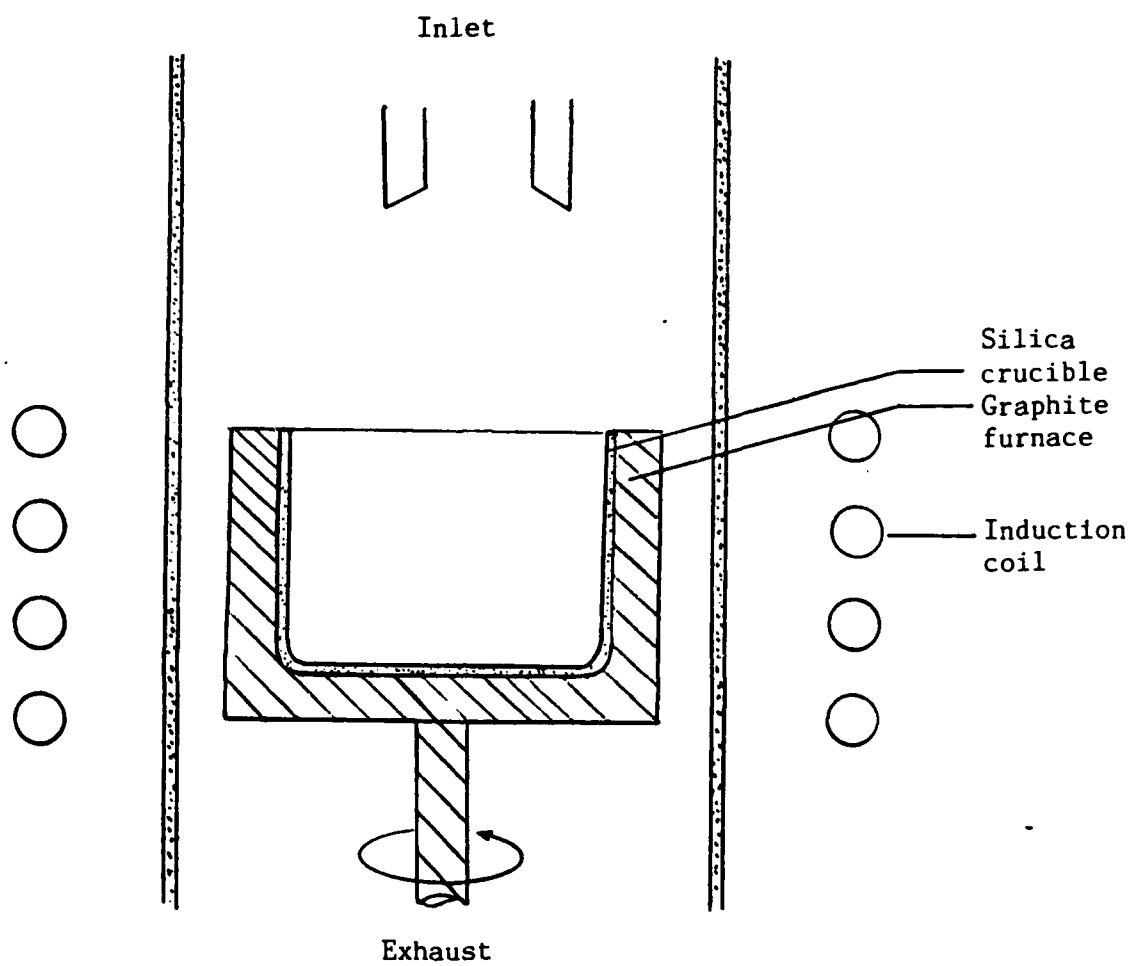


Figure 2. Crucible Coating Apparatus
(SiC, NbN, and TiB_2)

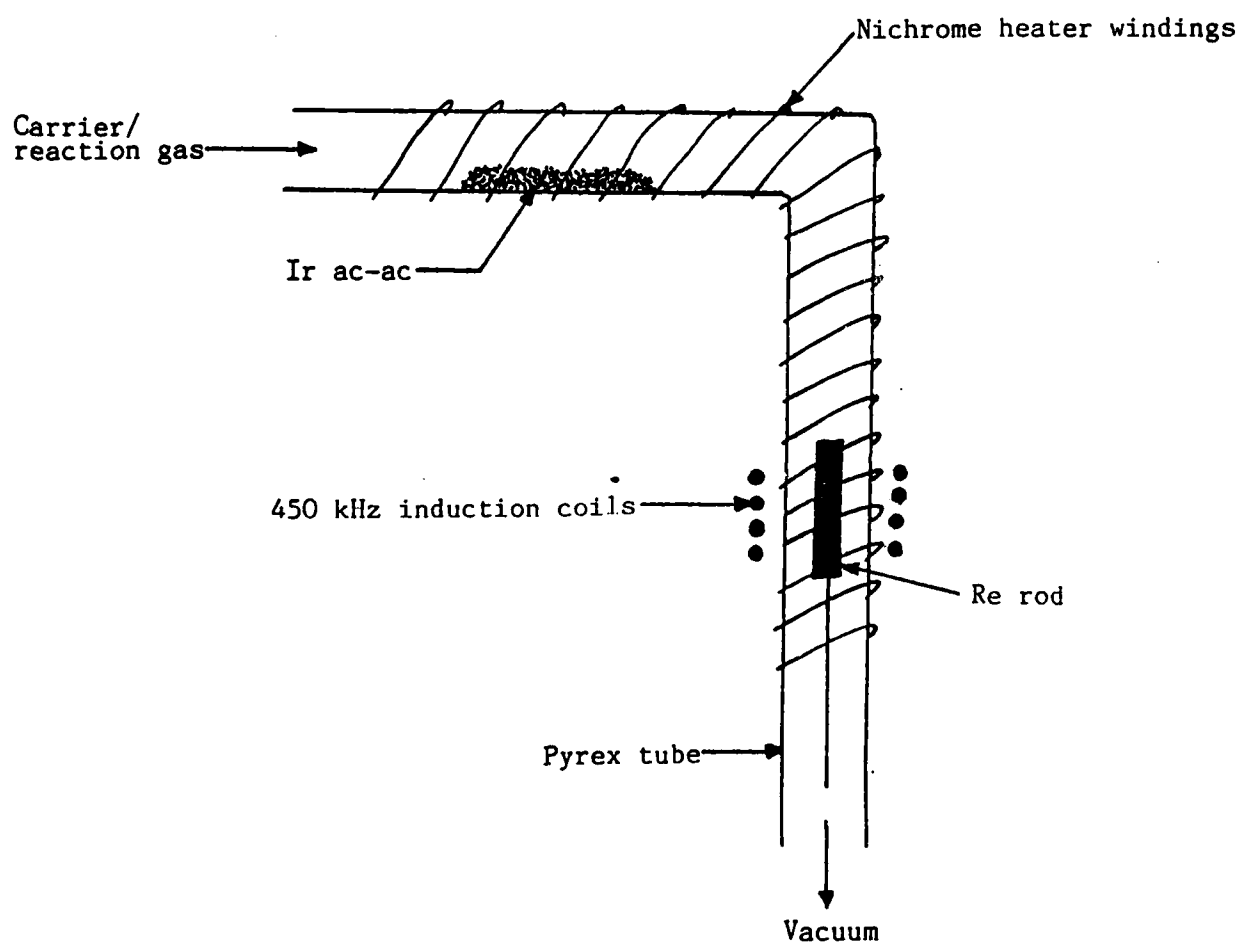


Figure 3. Schematic of CVD apparatus for iridium



As the Ir ac-ac is volatilized, a stream of carrier/reaction gas passes over the ac-ac bed and carries the vapor to the substrate. The substrate (crucible) is heated to a temperature sufficient to decompose the ac-ac and thus cause the deposition of iridium on the exposed surfaces.

4.0 PHASE I RESULTS AND DISCUSSION

4.1 Crucible Coatings

Deposition parameters for silicon carbide (SiC), niobium nitride (NbN), titanium diboride (TiB₂), boron nitride (BN), and iridium were established using graphite crucibles. Table I shows the deposition runs conducted in an attempt to optimize the reactions. The purpose of optimizing CVD reactions is to minimize intrinsic stress, refine grain size, promote interdiffusion to improve bonding, and maximize stoichiometry to eliminate lattice defects. In all the reactions under investigation, the factors which govern film growth, nucleation, grain size and epitaxial characteristics, stoichiometry, and crystallinity are the temperature of deposition, the degree of supersaturation, and the partial pressures of the reactive gases.

Intrinsic stress is caused by the incorporation in the growing film of interstitial and substitutional impurity atoms, vacancies, and dislocations, and by lattice mismatch between the film and substrate. The degree of intrinsic stress depends strongly on the method of film deposition. Highly stressed films are more susceptible to thermal shock and corrosion, and are more prone to adhesion failure. Intrinsic stress can be controlled to a great degree by control of the CVD conditions, helping to offset the inherent thermal stresses resulting from any thermal expansion mismatch between the coating and substrate.

Grain growth can be controlled by using compounds which alter the nucleation sites. Properly used, these compounds can produce very fine grain size and greater uniformity of coating.

The silica crucibles were supplied by the contract technical monitor; they were 6 cm diameter by 6 cm deep.

4.1.1 Silicon Carbide

Silicon carbide (SiC) was deposited by thermally decomposing methyltrichlorosilane (MTS). An SiC-coated crucible with a coating thickness of about 0.5 μm was fabricated; it was examined for coverage by shining a high-intensity light on the interior surface and examining the exterior surface for light transmission. The coating appeared to have good uniform coverage with good adhesion. The sample then was delivered to the contract monitor.

4.1.2 Niobium Nitride

Niobium nitride (NbN) was deposited by the decomposition of niobium tetrachloride (NbCl₄) and ammonia. The NbN-coated crucible was examined for uniform coverage in the same manner as that used for the SiC sample. It too had good coverage and adhesion. It then was delivered to the contract technical monitor.

4.1.3 Titanium Diboride

Titanium diboride was deposited by the hydrogen reduction of titanium trichloride (TiCl₃) and boron trichloride (BCl₃). The TiB₂ coating was

Table I. Summary of Deposition Runs

Materials	SiC	NbN	TiB₂	Ir	BN
Runs using graphite crucibles	2	2	2	-	-
Runs using silica crucibles	2	1	2	1	-
Runs using silica tubes	-	-	-	-	11

examined for coverage in the same manner as the SiC and NbN prior to delivery to the contract monitor. This coating system also had good coverage and adhesion.

The adhesion assessments for these SiC, NbN, and TiB₂ coated crucibles were based on visual inspections: no blistering of the coating or areas of the coating pulled away from the crucible walls.

4.1.4 Iridium

An iridium-coated crucible also was fabricated. It was not sent as a deliverable, however, due to some discoloration, the reason for which has not yet been ascertained. This discoloration is brown in color and covers about 10% of the area of the crucible.

The iridium coating also had a number of pinholes in the upper third of the depth of the crucible. These pinholes were discovered by shining a high-intensity light on the interior surface of the crucible in a darkened room; observation of the exterior surfaces of the crucible then showed several holes in the coating. The coating also had some blistering in one place, an area covering about one-tenth of the inside surface area. This blistering was not obvious, however, until about ten days after the coating was deposited. After the blistering occurred, acetone was poured inside the crucible and it was scrubbed lightly. This resulted in a slight amount of material being removed from the blistered area.

The iridium coating, for the most part, looked very good. The discoloration mentioned previously is not visible from the outside of the glass crucible; this means that the discolored area does not extend through the thickness of the coating and most likely is on the inside surface only.

4.1.5 Boron Nitride

The primary focus of this program was on boron nitride (BN) coatings. BN was deposited by reacting boron trichloride (BCl₃) with ammonia (NH₃) in accordance with the following equation:



Eleven runs were made to establish deposition parameters for BN, using quartz tubes approximately 20 cm long as substrates. BCl₃ and nitrogen were used as reactant gases for the first run. This resulted in a gray-colored coating, which was determined to be elemental boron. The ten succeeding runs were made using ammonia as the nitrogen source gas. This resulted in a white deposit, which initial indications suggest is BN; however, chemical analysis still is pending. The last three tubes coated had full coverage on the interior surfaces, although the coatings were not entirely uniform.

Figure 4 depicts complicated glassware to be coated with BN, and the graphite furnace used for the BN deposition process, although this particular glassware was not coated; the uniformity of the coatings on the quartz tubes used to establish BN deposition parameters was judged unsatisfactory to coat this complicated glassware.

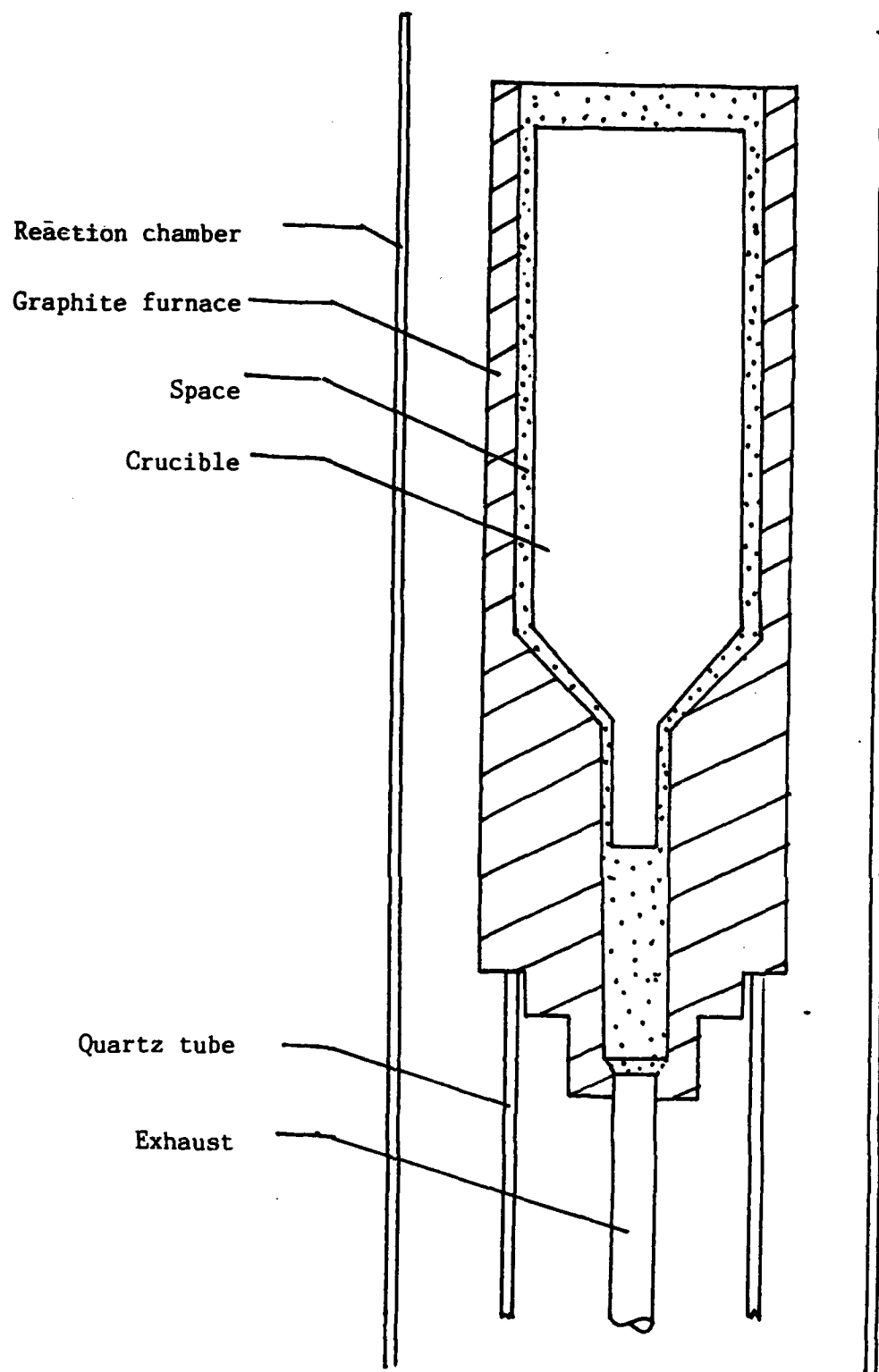


Figure 4. Schematic of Apparatus for Coating Glassware with Boron Nitride

4.2 Adherence Testing

In order to evaluate the adherence of the coatings to silica, samples of SiC, NbN, and TiB₂ were prepared as described previously on silica flat plates. Figure 5 shows the coated flat plates used for adherence testing.

A Sebastian II adherence tester was used to test coating adherence. In this process, a "pin" is affixed to the coating by epoxy cement; the pin then is pulled by the machine until failure occurs. The tester measures the force required to pull the coating from the substrate.

Unfortunately, adherence measurements could not be made due to the weakness of the silica surface. Failure occurred in the glass (silica) substrate in all cases; the coating never was pulled away from the substrate without concurrent substrate failure.

The sandblast surface treatment caused microcracking of the surface and resulted in failure prior to any measurable load being applied by the adherence tester. The coatings seemed to adhere to the silica, because a layer of glass was pulled away along with the coating on all samples tested.

4.3 Metallography

Figure 6 shows cross-sections of the coated flat slides (SiC, NbN, and TiB₂ coatings, respectively). Figure 6A shows the SiC/silica interface. The coating is fairly consistent, but a chip of glass that was coated around can be seen. This is consistent with what was seen in the adherence testing.

Figure 6B shows the NbN coating, which seems to be very adherent. While the TiB₂ (Figure 6C) appears thicker and displays a columnar growth pattern, it appears to have pulled a layer of glass off the substrate, as evidenced by a gap between the coating and the substrate. This also is in agreement with the adherence testing.

The cross-sections of the coated flat plates show a tight interface between coating and glass. The SiC and TiB₂ plates show the damage caused by the sandblasting; this is seen clearly in the TiB₂ plate, where the coating has pulled up layers of glass.

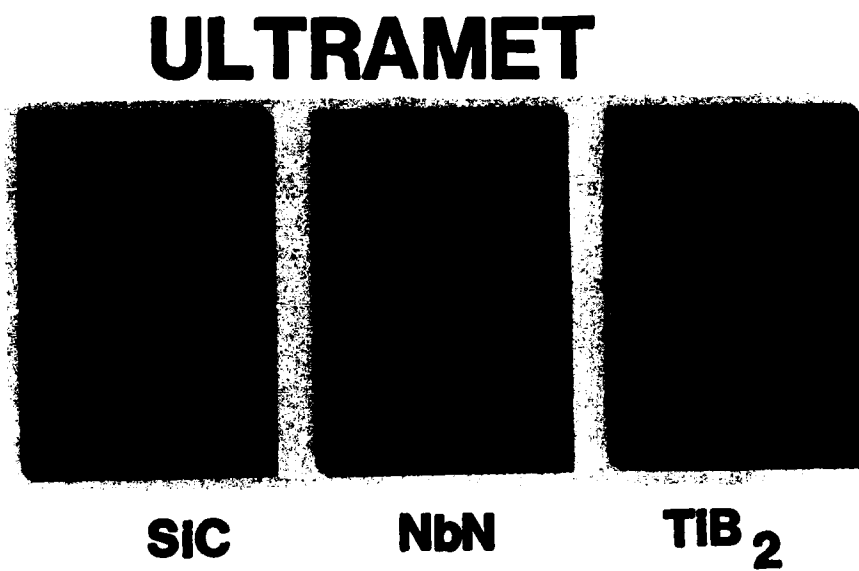


Figure 5. Coated Flat Plates Used for Adherence Testing

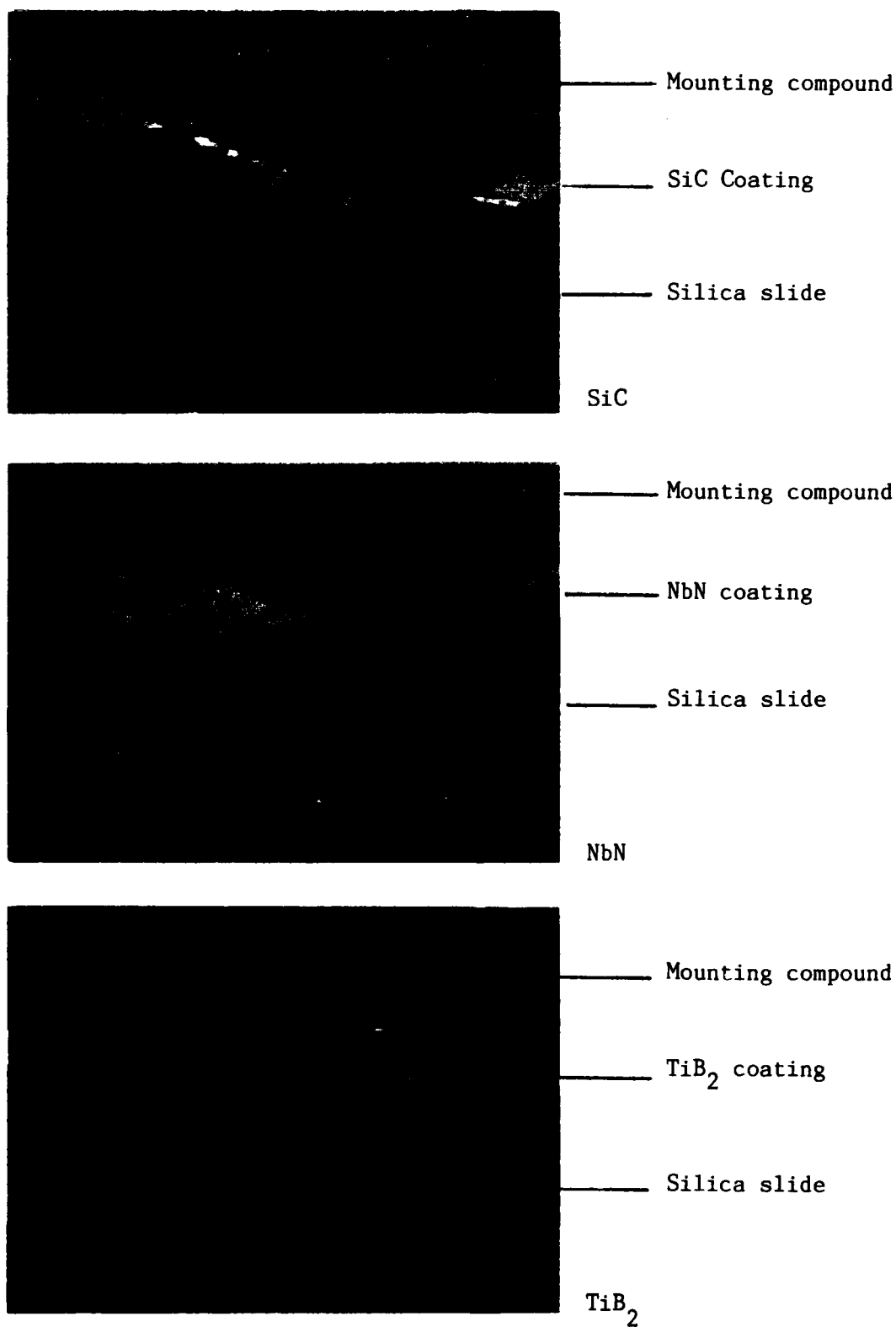
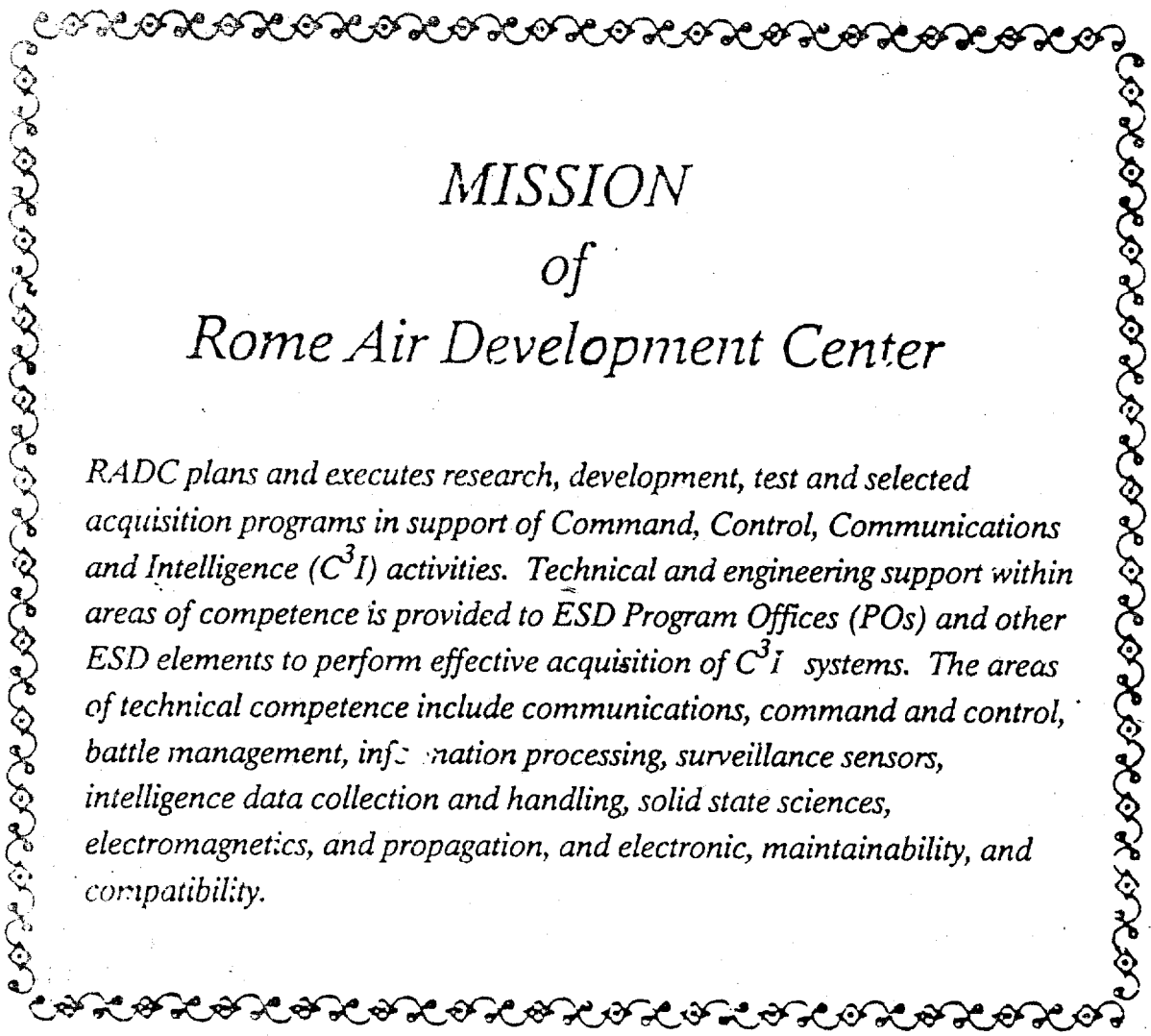


Figure 6. Cross-sections of various coatings on silica slides (all 200x)

5.0 CONCLUSIONS AND RECOMMENDATIONS

The technical objectives of this Phase I program were met: a process has been developed for producing thin coatings of SiC, NbN, and TiB₂ on silica crucibles. The time and resource constraints of a Phase I program did not allow for optimization of the iridium coating system on crucibles. Surface treatment of the glass crucibles, to increase coating adhesion, must be more gentle in order to alleviate microcracking; acid etching should be used instead of sandblasting. Work remains to be done on coating long cylinders with BN.

Interest shown by several major laboratories warrants an extensive study of BN coatings on glassware, and a Phase II effort is strongly recommended. Phase II should consist of optimizing the BN coating and developing plans for scaling up to high-output, low-cost production of BN-coated glassware.



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