ITEM 7
Pyrolytic Technology

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Pyrolytic deposition and densification equipment and “technology” as follows:

(a) “Technology” for producing pyrolytically derived materials formed on a mould, mandrel or other substrate from precursor gases which decompose in the 1,300 degrees C to 2,900 degrees C temperature range at pressures of 130 Pa (1 mm Hg) to 20 kPa (150 mm Hg) including technology for the composition of precursor gases, flow-rates and process control schedules and parameters;

Nature and Purpose: Pyrolytic deposition is a high-temperature process used to deposit a thin, dense coating of metal or ceramic onto a mold or mandrel in order to form a part. It also can be used to coat another material in order to achieve strong adhesion and bonding between the coating material and the underlying surface. The purpose of these processes is to improve the ability of the coated or densified items to survive the extreme environments in which critical rocket system parts operate.

The general procedures and methods used to create pyrolytically derived materials and their precursor gasses are widely known. However, specific formulae, processes, and equipment settings are usually empirically derived and considered proprietary trade secrets by industry. Controlled data (technology) may take the form of technical assistance including instruction, skills, training, working knowledge, and consulting services. Technology may take the physical form of blueprints, plans, diagrams, models, formulae, engineering designs and specifications, and manuals and instructions written or recorded on other media or devices such as disk, tape, and read-only memories.

(b) Specially designed nozzles for the above processes;

Nature and Purpose: Nozzles for pyrolytic deposition direct an unreacted gas to a surface on which deposition is desired. The nozzles must be movable or located so they can cover the entire surface within a chemical vapor deposition (CVD) furnace at high temperature and pressure.

Produced by companies in

- France
- Germany
- Russia
- United States

Method of Operation: Nozzles used in CVD furnaces deliver cold, unreacted gas to the surface being treated. The gas must be both unreacted so that the coating occurs on the intended surface rather than on the inside of the nozzle, and close to the surface to be treated so that the surface and not the walls of the furnace get sprayed. A nozzle is like a paint spray gun, which must be close to the part being painted.

Typical Missile-Related Uses: These nozzles are required parts of pyrolytic deposition equipment used to make critical, high-heat-tolerant parts such as rocket nozzles and reentry vehicle nose tips.

Other Uses: These nozzles are used to make high-heat-tolerant parts for jet engines.

Appearance (as manufactured): Nozzles for CVD furnaces are designed to tolerate high furnace temperatures either by construction from very high-temperature-resistant material such as graphite or by water-cooling. Nozzle dimensions are approximately half the width of the furnace. Small nozzles are typically made of graphite because it is inexpensive, easily replaced, and lightweight (approximately 0.5 to 2.5 kg). Larger nozzles for production furnaces are often made of metal, require water cooling, may have integral attachment flanges, and weigh upwards of 25 kg.

Nozzles are made in varying lengths, which depend on the size of the furnace and the surface. The larger, more complex, water-cooled nozzles are up to 1.5 m long, with their tubular portion 20 cm in diameter. However, because some portion of most nozzles is custom designed, there is no standard shape or size.

Appearance (as packaged): Packaging for the nozzle and pyrolytic deposition equipment is suitable for preventing damage to a highly durable pipe with somewhat fragile valves and fittings. Typically, several nozzles are shipped together in well protected packaging separate from any large furnace shell.

(c) Equipment and process controls, and specially designed software therefor, designed or modified for densification and pyrolysis of structural composite rocket nozzles and reentry vehicle nose tips.

Nature and Purpose: Specialized equipment and process controls are essential for the densification and pyrolysis necessary to produce structural composites used for rocket nozzles and reentry vehicle nose tips. Specially designed software often is required to operate the equipment and/or control the processes to produce these structural composites. Manufacturing items from this type of material usually requires cycling through various process conditions such as high temperature and/or pressure. Precise control of the conditions during the cycles and their timing is key to ensuring acceptable results. This subitem also includes documentation (technical data) of the various process conditions needed to produce these materials.

Method of Operation: Equipment, process controls, and software for densification and pyrolysis are used throughout the manufacturing process for structural composites to handle, process, and finish the material and the resulting products (i.e., rocket nozzles and RV nose tips).

Typical Missile-Related Uses: This equipment, process controls, and software are used to produce structural composites (including carbon-carbon items) used for rocket nozzles and reentry vehicle nose tips.

Other Uses: These items are also used for diffusion bonding of metals, in powder metallurgy, and for treating metal components.

Appearance (as manufactured): The equipment resembles other manufacturing equipment but can include smaller (research size) items. Process controls can take the forms of technical data such as paper, magnetic, or other media. Specially designed software is usually indistinguishable by visual inspection from commercially available software and can take the form of computer disks, CD ROMs, etc.

Appearance (as packaged): Larger pieces of equipment may be shipped as components, while smaller items may be shipped assembled. These items are usually shipped in crates or on pallets in a similar manner to other industrial equipment. Process controls (including technical data) are shipped like other information on paper, magnetic, or other media. Software can be transferred on disks, CD ROMs, etc., or over networks. Software and technical data may be included in the shipping containers with its respective equipment.

Notes to Item 7:

(1) Equipment included under (c) above are isostatic presses having all of the following characteristics:
- (a) Maximum working pressure of 69 MPa (10,000 psi) or greater;
- (b) Designed to achieve and maintain a controlled thermal environment of 600 degrees C or greater; and
- (c) Possessing a chamber cavity with an inside diameter of 254 mm (10 inches) or greater.

Produced by companies in

- France
- Germany
- Russia
- United States

Nature and Purpose: Isostatic presses are used to infuse carbon into a porous carbon preform of a rocket nozzle or reentry vehicle nose tip under great pressure. This process, referred to as densification, fills up and virtually eliminates voids in the preform and thereby increases the density and strength of the treated object.

Method of Operation: The object to be processed is placed in the appropriate chamber and lowered into the hot zone of the furnace. All water and electrical connections are made and all process instrumentation is connected before the lid is lowered into the furnace and sealed. As the object is heated, it is subjected to great pressure until the proper densification has been achieved. Reaction products are removed by internal plumbing so they do not come into contact with the electric heaters and cause them to short.

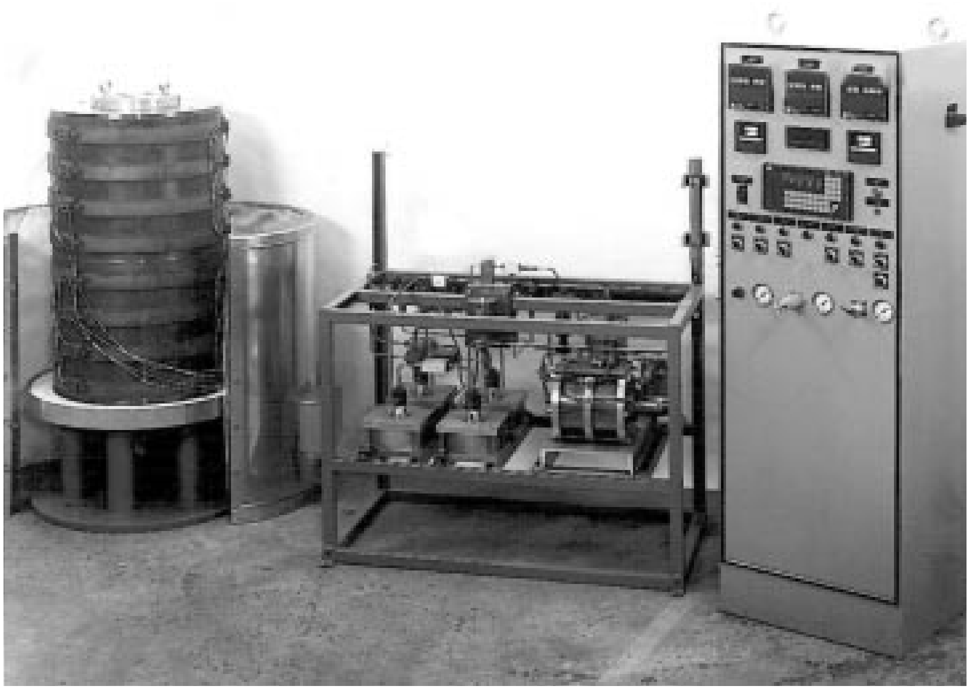

Photo Credit: A Handbook for the Nuclear Suppliers Group Dual-Use Annex. *Report No. LA-13131-M (April 1996).*

Figure 7-1: A laboratory-sized isostatic press showing its three main components: pressure chamber, pressure generator, and control console.

Typical Missile-Related Uses: Isostatic presses are used in making nose tips for reentry vehicles and nozzle inserts for rocket motors.

Other Uses: These presses are used in diffusion bonding of similar metals, diffusion bonding of dissimilar metals to form laminates (silver-nickel-silver or copper-stainless), and provision of seamless joints. They are used in various powder metallurgy applications. They are also used to improve the quality of metal castings and forgings by hydrostatically forcing defects to close and bond shut.

Photo Credit: Engineered Pressure Systems, Inc.

Figure 7-2: Two removable high-pressure closures, showing holes for hoses or pipes.

Appearance (as manufactured): Isostatic presses intended for densification are specially modified to operate while a pyrolysis reaction is occurring. A typical laboratory-size system has three main components: a pressure chamber, a high-pressure generator, and a control console, as shown in Figure 7-1. The pressure chamber is usually a vertical, thick-walled cylinder with a removable, high-pressure closure, or plug, at the upper end. Two examples are shown in Figure 7-2. They are water-cooled and have attachments for hoses or pipes. The press may be surrounded by an energy-absorbing shield, shown partially removed on the left of Figure 7-1. This shield may be engineered at the plant where the system operates and often involves installing the chamber belowground. The pressure chamber also has an isolation chamber and plumbing to be sure that gas from the process zone is removed from the exhaust and does not flow to the heater zone.

The high-pressure generator uses air to drive a large piston connected directly to a smaller piston, which pressurizes the gas used in the chamber. These simple pumps operate at pressure ratios between 10 and 1000 and are available with maximum pressures up to about 1,400 MPa. The piston-and-cylinder mechanisms of the pressure intensifiers can be seen in the high-pressure generator system pictured in Figure 7-1.

The control console has an instrument panel with typical industrial temperature and pressure control and recording instrumentation, as shown in the right of Figure 7-1. The console usually includes a computer and a keypad for entering data required to control the operation of the press. Isostatic presses can be quite large. A top and side view, respectively, of two different presses are shown in Figures 7-3 and 7-4. Notice the thick-walled pressure vessel and the large threaded plug in Figure 7-3. Another isostatic press is shown in the background of Figure 7-5.

Appearance (as packaged): The components of an isostatic press system are likely to be shipped separately and assembled at the final work destination. Packaging varies with the requirements of the purchaser, but wooden pallets and crates with steel banding and reinforcement are common. Two wooden crates containing components of an isostatic press system are shown in Figure 7-6; a different crate for a similar press is shown in Figure 7-7. Larger chambers are very heavy because of the thick walls and may be packaged in a cylindrical wooden crate with wide steel banding, as shown in Figure 7-8.

Additional Information: The distinction between a normal hot isostatic press and one modified for use in pyrolytic densification is that decomposition does not occur in the former and does in the latter. To avoid the carbon deposition on the heaters, which would otherwise cause an electrical short, the heater chamber for densification has plumbing connections and controls to pipe carbon decomposition products directly from the heated zone out to gas handling equipment.

Photo Credit: A Handbook for the Nuclear Suppliers Group Dual-Use Annex. Report No. LA-13131-M (April 1996).

Figure 7-3: A very large isostatic pressure vessel and threaded plug.

Photo Credit: Engineered Pressure Systems, Inc.

Figure 7-4: Side view of a large isostatic press.

Photo Credit: Engineered Pressure Systems, Inc.

Figure 7-5: An isostatic press in the background, surrounded by a light, metal frame.

Photo Credit: A Handbook for the Nuclear Suppliers Group Dual-Use Annex. *Report No. LA-13131-M (April 1996).*

Figure 7-6: Shipping crates for an isostatic press.

Photo Credit: Engineered Pressure Systems, Inc.

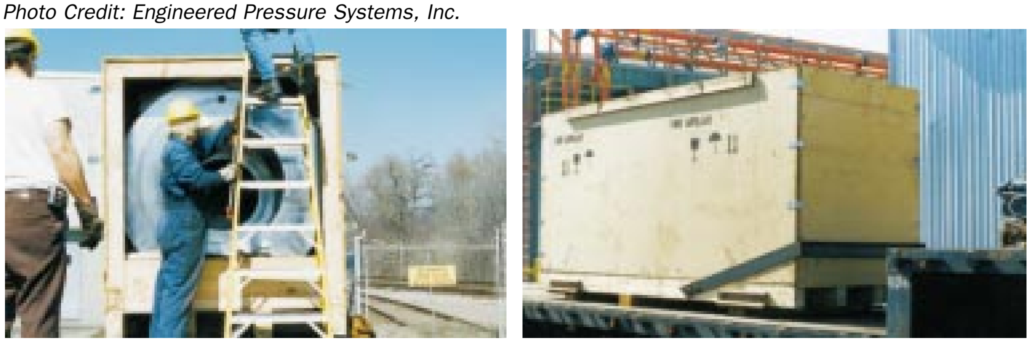

Figure 7-7: Alternative shipping crate for an isostatic press.

Figure 7-8: Shipping crate for a very large isostatic press.

Photo Credit: A Handbook for the Nuclear Suppliers Group Dual-Use Annex. *Report No. LA-13131-M (April 1996)*

Note
(2) Equipment included under (c) above are chemical vapour deposition furnaces designed or modified for the densification of carbon-carbon composites.

Produced by companies in

- France
- Germany
- Russia
- United Kingdom
- United States

Nature and Purpose: CVD furnaces are used to infuse carbon into a porous carbon preform of a rocket nozzle or reentry vehicle nose tip. This process, referred to as densification, fills up and virtually eliminates voids in the preform and thereby increases the density and strength of the treated object.

Method of Operation: CVD furnaces use either isothermal or thermal-gradient processes for densification. The object to be processed is placed in the appropriate chamber and lowered into the hot zone of the furnace. All gas, water, and electrical connections are made, and all process instrumentation is connected before the lid is lowered into the furnace and sealed. The process sequence of heating and supplying the deposition gases is automated, but furnace operators follow the part development through view-ports built into the furnace walls.

Typical Missile-Related Uses: CVD furnaces are used to make lightweight carbon-carbon rocket nozzles and nose tips. Carbon-carbon pieces are light and strong, and can increase system performance.

Other Uses: CVD furnaces are used in coating optics, some medical instruments and components (e.g., heart valves), and cutting tools; in coating and polishing precision surfaces; and in making semiconductors.

Appearance (as manufactured): CVD furnaces are large, double-walled, cylindrical vessels with gas-tight closures. Typical CVD furnaces are large because they house an internal heat zone, electrically driven heaters, and insulation. Furnaces smaller than 1.5 m in height and 1 m in diameter are considered laboratory scale and are barely able to process a single nose tip or rocket nozzle insert. Process production sizes are larger than 2 m in height and 2 m in diameter. These furnaces have several ports: at least one large port for power feeds, others for instrumentation, and, when temperatures are measured by optical or infrared pyrometers, one or more view-ports.

They are double-walled so that they can be water-cooled during operation. Power cables are large and may also be water-cooled. The actual retort is housed inside the furnace and is heated by a graphite induction or resistive heater to temperatures of up to 2,900°C. Two typical furnaces, without lids in place, are shown in Figure 7-9. An induction power supply with heavy, water-cooled connections between the power supply and the smaller of the two furnaces is also shown. The induction coil, retort, and silicon steel shunts, which prevent inductive coupling to the furnace wall, are shown in Figure 7-10. A typical production setup of CVD furnaces consists of several components, as shown from left to right, in Figure 7-11: an impregnation

Figure 7-9: Two small CVD furnaces and an induction power supply.

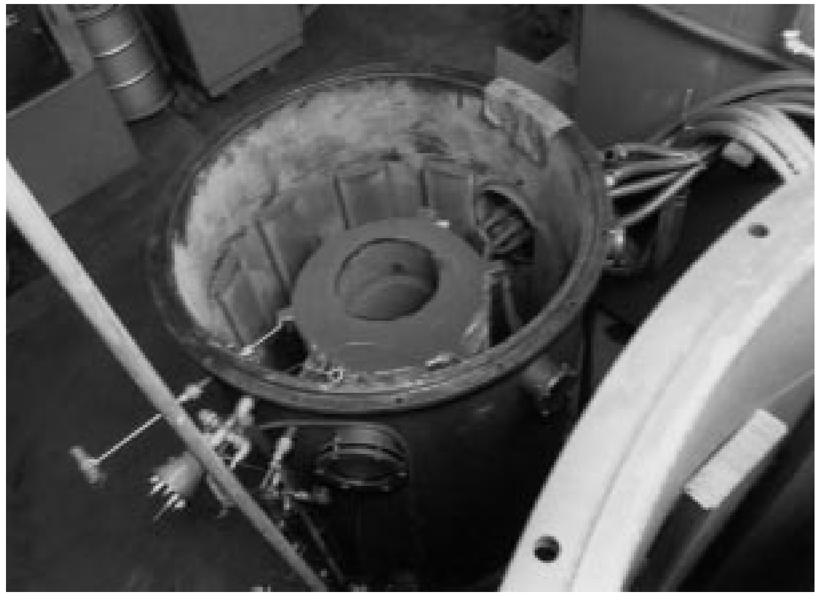

Figure 7-10: Inside of a small CVD furnace showing the retort, heaters, and insulation.

Photo Credit: Alliant TechSystems, Inc.

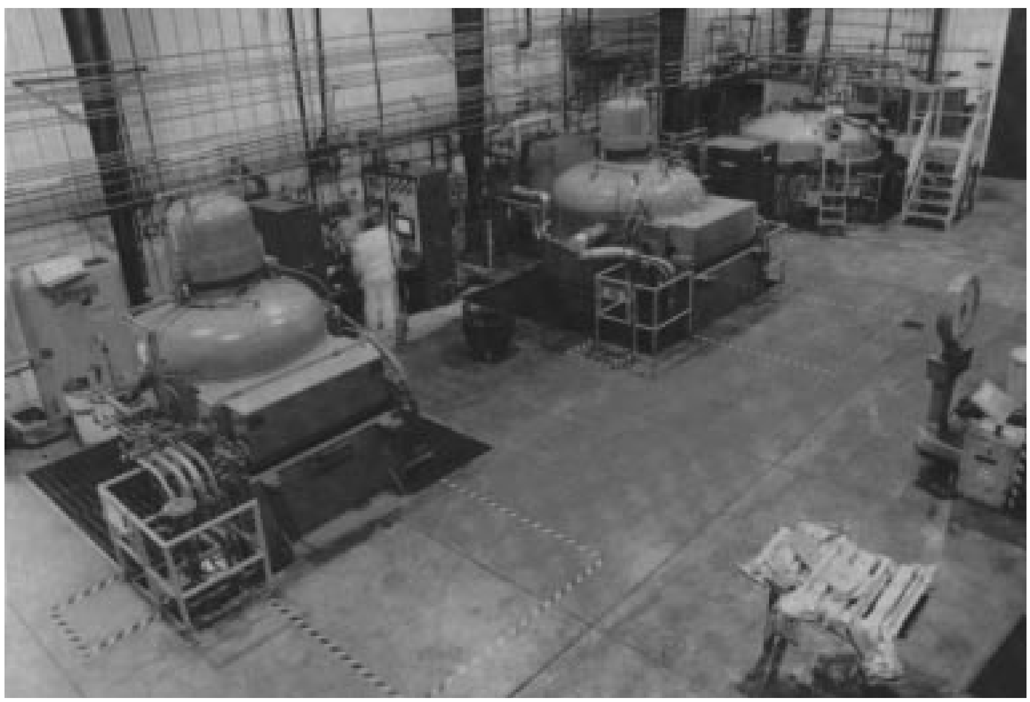

Figure 7-11: A typical production setup for carbon-carbon or ceramic matrix nose tips and nozzles.

vessel for adding a liquid resin to the preform; instrumentation and control panels; a pressure-carbonization furnace with a 69 Mpa capacity; and a CVD furnace for pyrolytic deposition of carbon from a gas.

Appearance (as packaged): Packaging consists of pallets and crates for each part because of the large size and weight of the equipment. The large lids, the power supply, and the body of the furnace often have built-in lift points or rings to help move and assemble them.