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EXPLORING IN AEROSPACE ROCKETRY
5. MATERIALS

by William D. Klopp
Lewis Research Center
Cleveland, Ohio

Presented to Lewis Aerospace Explorers
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In the space program, materials can make the difference between success and failure. Some of the most important materials problems are associated with uncooled nozzles for both solid- and liquid-propellant rockets. Problems of crack propagation in large welded structures are also interesting, as is the development of lightweight, tough tank materials for containment of cryogenic fuels.

TYPES OF ROCKET ENGINES

In the liquid-propellant engine (fig. 5-1), liquid fuel, such as kerosene, is pumped by a turbine-driven pump directly into the combustion chamber. At the same time the liquid oxidizer, typically liquid oxygen at -297° F, is pumped through hollow passages in the walls around the engine before entering the combustion chamber. Injector nozzles spray fuel and oxidizer into the chamber where they are mixed and burned. The hot gaseous products are expelled through the nozzle to provide the propulsive thrust. The

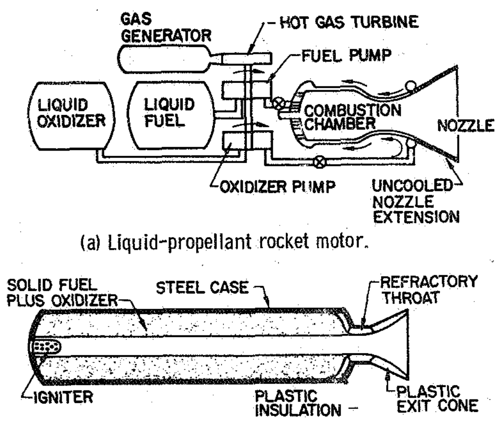


Figure 5-1. - Basic types of rocket motors.

*Head, Refractory Metals Section.

process of pumping the liquid oxygen through the lining of the nozzle and combustion chamber is called regenerative cooling. This is necessary because the materials, such as stainless steel, which are strong enough to be used safely have melting points significantly below the temperature of the combustion gases.

The liquid-propellant engine has a number of problems caused by clogged injectors or improper burning, such as screech (harmonic acoustic waves) and burn-through of the walls. However, these problems have been solved by improved design rather than through the use of advanced materials.

One version of the liquid rocket motor, which is planned for use on the Apollo mission, uses liquid fuels which are storable at room temperature. This type of fuel is unsuitable for regenerative cooling, and thus the engine must use heat-resistant materials in the combustion chamber and in the critical throat region of the nozzle. These pose a serious materials problem.

The solid-propellant rocket motor (fig. 5-1) employs a solid fuel-oxidizer combination rather than the more conventional liquids. Normally, the fuel, the oxidizer, and a bonding agent are mixed together in the liquid state, then cast to shape, and finally cured to a solid, rubbery mass. When heated to ignition temperature, the fuel and oxidizer combine at the surface to produce hot combustion gases which are expelled through the nozzle to provide thrust. Since in this motor no cryogenic liquids are available, regenerative cooling of the hot combustion chamber and nozzle is impossible. The ability of heat-resistant materials to withstand the extreme erosion and corrosion conditions in these hot regions is a limiting factor in the design and operation of solid-propellant motors.

HEAT-RESISTANT MATERIALS

Several types of material are potentially suitable for use in the critical throat region of uncooled nozzles. Many tests are employed to determine the best materials for a particular motor and a particular set of operating conditions.

The potentially suitable materials can be divided into two general classes, the refractories and the ablatives. The refractories, characterized by high melting points in the range 4000° to 6000° F, include such materials as tungsten, molybdenum, graphite, and certain oxides and carbides. These materials maintain their strength at high temperatures so that they are sufficiently tough.to withstand the erosive effects of the hot gas stream. During engine operation, the internal surfaces of throats and nozzles of these materials are heated to close to the temperature of the gas stream. This heat is absorbed by the material and dissipated by normal thermal radiation and convective cooling by the atmosphere on the outside.

In contrast to the refractories, the ablative materials are not high melting and tough. Instead, they absorb heat from the gas stream by chemical reactions as well as by melting and vaporizing. A typical ablative material is a composite called phenolic-refrasil. This material consists of a tape woven from silica glass fibers and impregnated with a plasticlike phenolic resin. The tape is wound on a mandrel to form the nozzle, which is heated under pressure to bond the tapes together with the phenolic resin. During use, the resin decomposes to form graphite and organic compounds which melt and vaporize (ablate). The silica tape also melts, absorbing heat in the process, and reacts with the graphite to form silicon carbide. The compound is fairly high melting and tough and imparts a certain degree of resistance to mechanical erosion to the nozzle. The ablative nozzles are cheap and easily fabricated and can be used in engines where the operating conditions are not so severe as to require the use of a tougher, refractory material.

MATERIALS EVALUATION

The selection of a material for the nozzle of a given motor designed to produce a predetermined thrust generally requires an experimental program to evaluate the candidate materials under the given conditions. The two major parameters measured during test firings are the temperature distribution in the nozzle and the gas pressure in the combustion chamber.

Figure 5-2 shows the temperature distribution profile in a refractory throat insert as a function of firing time. In the first few seconds of firing, the temperature of the

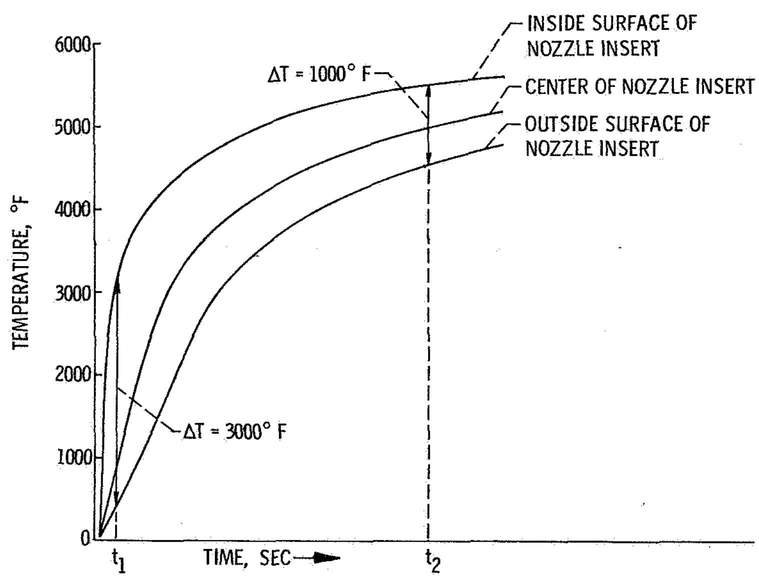


Figure 5-2. - Typical temperature distribution profiles in nozzle insert.

inside surface of the nozzle insert rises very quickly; it then begins to level off and approaches the flame temperature asymptotically. At the outside surface of the insert, the heat is supplied by conduction and the temperature rise is slower. This condition leads to a temperature difference of 3000° F between the inside and the outside surfaces at the start of firing, as indicated at time t_1. The difference decreases as firing proceeds, as at time t_2.

The large temperature differential between the inside and the outside surfaces just after ignition is a real problem with refractory inserts which are brittle when cold, such as tungsten, molybdenum, and the refractory oxides and carbides. The inside surface material tends to expand as it heats up, putting the outside surface in tension. Cracking of the nozzle can result if the material cannot deform plastically to relieve these stresses.

Typical pressure-time traces are shown in figure 5-3. These traces indicate the amount of material removed from the throat area by mechanical erosion and chemical

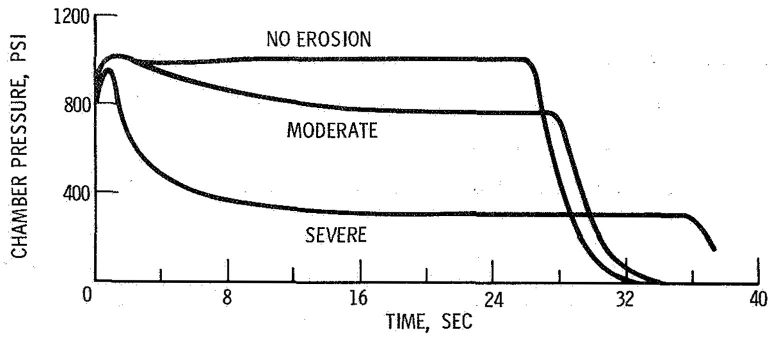


Figure 5-3. - Typical pressure-time traces for varying degrees of nozzle throat erosion.

corrosion during firing. As the throat becomes larger, the gaseous combustion products escape more rapidly and the pressure within the combustion chamber decreases. Thus, an erosion resistant nozzle material shows a relatively constant chamber pressure during the entire firing cycle, while a large pressure drop indicates severe erosion in the critical throat region.

The results of two experimental programs recently conducted at the Lewis Research Center offer an insight into the behavior of several nozzle materials in two different uncooled motors.

The first program used a small solid-propellant engine test facility to study the behavior of various types of throat insert materials under carefully controlled test conditions. The important characteristics of the engine were as follows:

Propellant	Arcite 368, a solid combination of fuel and oxidizer which burns to give entirely gaseous products
Flame temperature	Calculated to be 4700° F, an intermediate temperature for solid propellants
Chamber pressure, psi	1000, typical for solid-propellant engines
Burn time, sec	30
Nozzle throat diameter, in.	0.289

The appearance of several refractory and ablative nozzles after firing under these conditions is shown in figure 5-4.

The tungsten nozzle (fig. 5-4(a)) demonstrated excellent erosion and corrosion resistance. A pressure drop of about 10 percent indicated that slight erosion had occurred, probably by oxidation of the tungsten to form volatile tungsten trioxide. Although it is a brittle material at low temperatures, the tungsten did not crack because the walls were relatively thin and thus thermal stresses were relatively low.

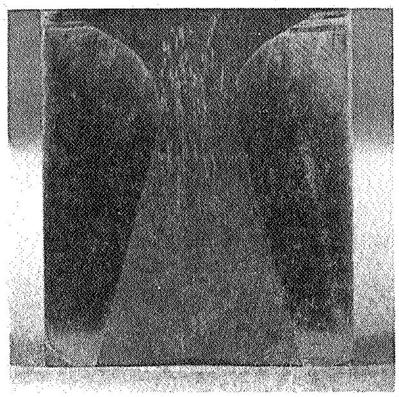
In contrast to tungsten, the graphite nozzle shown in figure 5-4(b) suffered considerable erosion and corrosion. The combustion chamber pressure decreased from 1000 to about 500 psi; this decrease indicated an unacceptably high loss of material from the throat area.

Figure 5-4(c) shows a nozzle of LT2, a cermet (ceramic-metal) material consisting of aluminum oxide (Al_2O_3) in a metallic tungsten-chromium matrix. Figure 5-4(d) shows a nozzle made of a ceramic compound, silicon nitride. Both of these materials showed good strength and corrosion resistance. There was no throat erosion, and chamber pressure during firing remained constant. Both of these materials, however, are quite sensitive to thermal shock and cracked severely on cooling after firing. Neither material is adequate under these conditions.

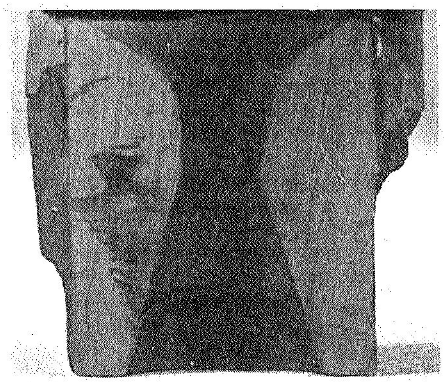
Two ablative nozzles are shown in figures 5-4(e) and (f). The darkened regions near the inside surfaces of these two nozzles indicate the depth of resin decomposition during firing. Both nozzles suffered high, though uniform, erosion. The 40-percent resin material in figure 5-4(e) showed a pressure drop from 1000 to 500 psi, while the 20-percent resin material showed a pressure drop from 1000 to 400 psi during firing. Both, of course, are unacceptably high pressure losses and indicate that these materials are unsuitable for this type of engine.

The results of this small-scale program indicated that for high-pressure solid-fueled engines, tungsten is preferable to the other materials tested, provided that thermal shock can be avoided when the engine is made larger.

A second study at Lewis illustrates how different engine conditions dictate the use of materials other than tungsten. The object of this study, the engines for the service module of the Apollo moon mission, uses liquid fuel which is storable at room temperatures. The nozzle material is ablative phenolic-refrasil for both the large main thrust



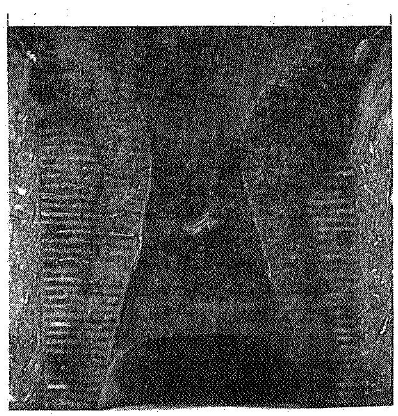
(a) Tungsten.



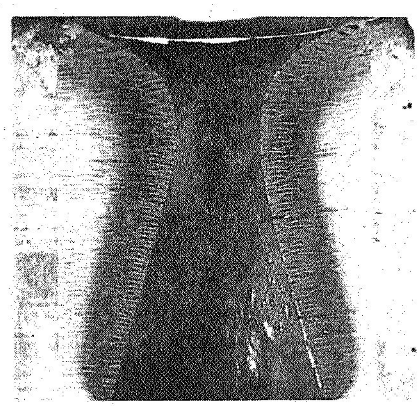
(b) Graphite. CS-26529

(c) LT 2.

(d) Silicon nitride.



(e) Phenolic-refrasil (40 percent resin).



(f) Phenolic-refrasil (20 percent resin).

Figure 5-4. - Nozzles of various materials after firing in small solid-propellant motor.

engine, which has an 8-inch throat diameter, and the smaller vector control engines, which have a 1-inch throat diameter. The operating conditions are moderate because the engine will be functioning only in a low-density atmosphere. The chamber pressure is expected to be less than 100 psi, flame temperature, 4000° to 4500° F, and total burn time, 700 seconds with several restarts.

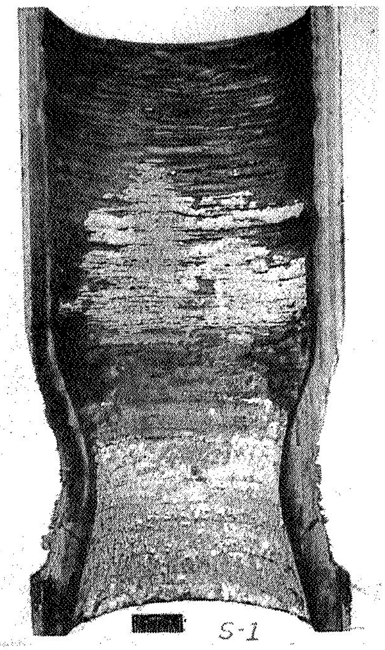
For these operating conditions, the ablative material appears adequate. However, possibly more thrust may be required of the engine, necessitating a higher chamber pressure or a higher flame temperature. Under these conditions, the adequacy of the ablative nozzle is marginal, and thus various alternative nozzle materials for both the 1- and the 8-inch-throat-diameter engines are being studied. The alternatives include other refractory metals and compounds, various types of reinforced refractory combination, and other ablatives.

Figure 5-5 shows several large- and small-diameter nozzles after being test-fired with the storable liquid fuel. Figure 5-5(a) shows an 8-inch-diameter nozzle of phenolic-refrasil ablative material after a 160-second firing. The nozzle has suffered relatively severe charring, and too much melting and running of the silica tape has occurred. A large-diameter nozzle such as this can tolerate more erosion from the throat region than a small-diameter nozzle.

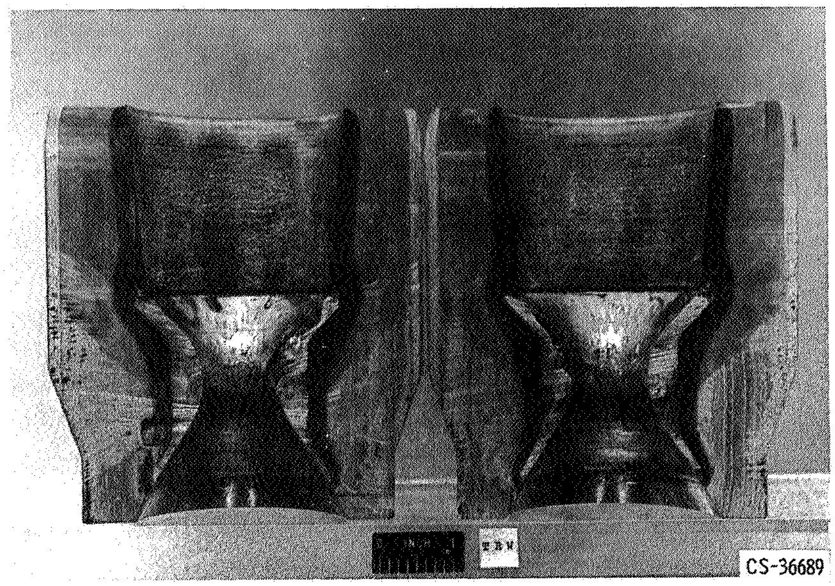
Figure 5-5(b) shows a molybdenum nozzle after firing for 47 seconds. This 1-inch-diameter nozzle has suffered severe erosion at the throat because of the highly oxidizing flame. Although molybdenum behaves similarly to tungsten, which was suitable for the less oxidizing flame of the solid-propellant engine described previously, molybdenum is a poor material for the liquid-fueled engine.

The throat insert which performed best is pictured in figure 5-5(c). This insert is made from sintered zirconia (ZrO_2) reinforced with tungsten-rhenium alloy wire. After a 734-second firing, the nozzle is still intact although beginning to deteriorate. It shows some erosion and cracking but appears adequate for at least 700 seconds of firing. Also visible in figure 5-5(c) are the graphite heat sink to reduce heat transfer from the throat insert to the ablative nozzle holder and a portion of the exit cone, which is also constructed of ablative material. Tests are continuing on this and similar materials.

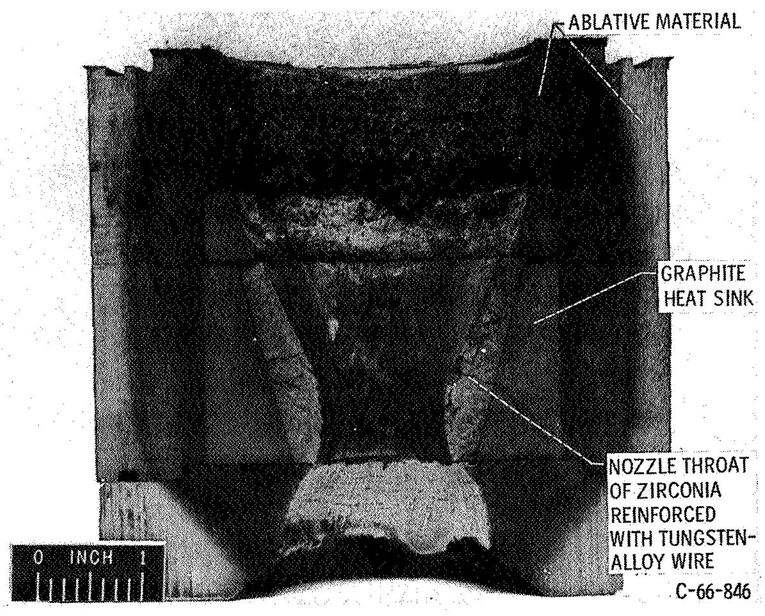
For a small solid-propellant rocket engine, a ceramic nozzle may be adequate. An example is the engine used by the Lewis Aerospace Explorers. It is designated type B-8-4 and has a short firing time of 1.4 seconds. After firing (fig. 5-6) the inside surface of the nozzle shows some erosion and also had a fused layer about 5 mils thick. Since silica melts at 3200° F, this suggests a flame temperature of approximately 4000° to 4500° F. The extent of throat erosion indicates a moderate pressure drop in the engine during the firing cycle.



(a) Ablative nozzle after firing for 160 seconds. Diameter, 8 inches.



(b) Molybdenum nozzle after firing for 47 seconds. Diameter, 1 inch.



(c) Composite tungsten alloy-reinforced-zirconia nozzle after firing for 734 seconds. Diameter, 1 inch.

Figure 5-5. - Nozzles of various materials after firing in storable-liquid-propellant motor.

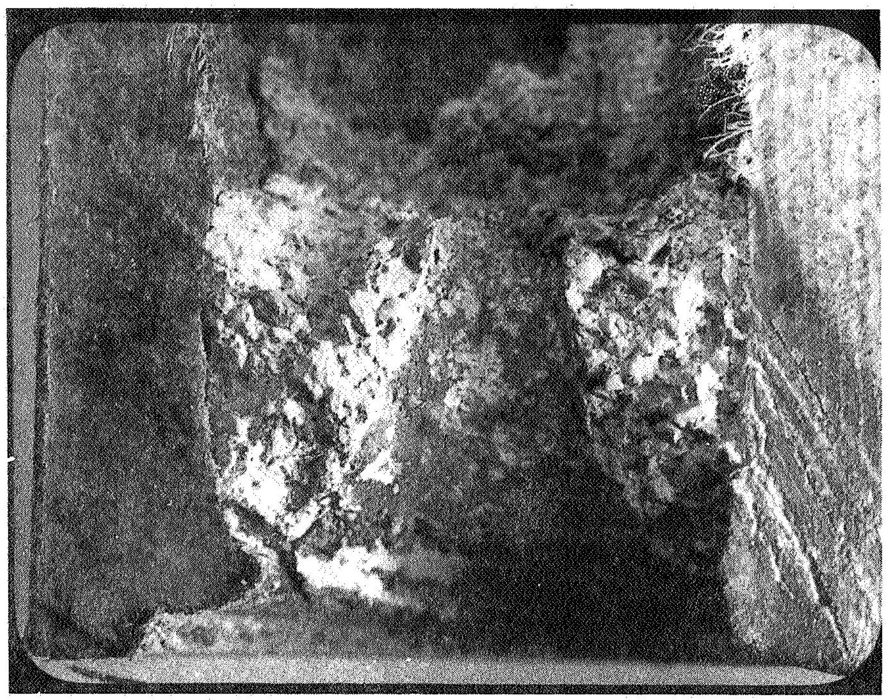
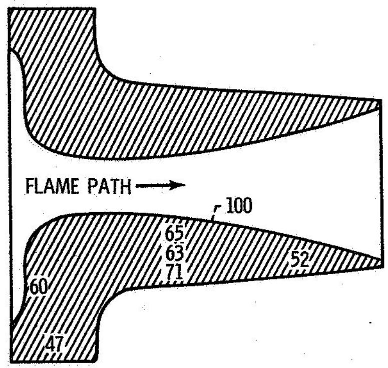


Figure 5-6. - Ceramic nozzle after firing for 1.4 seconds in solid-propellant model rocket engine, type B-8-4.

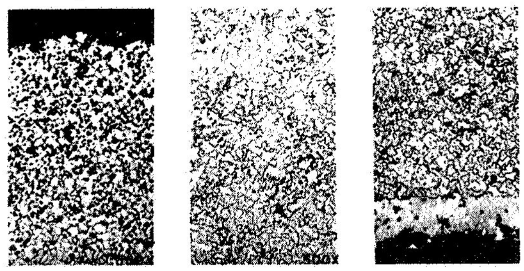
COMBINATION METHODS

Some rocket engines use a combination of refractory and ablative principles to achieve good heat-resistance in the nozzle. An example is the Polaris Missile, which is capable of being fired from a submerged submarine. This is a two-stage missile, with both stages being powered by solid-fueled engines. The first-stage engine burns for approximately 90 seconds with a combustion chamber pressure of 800 psi. The nozzle material for this engine is a refractory-ablative combination of a porous tungsten skeleton infiltrated with silver. The tungsten provides strength at high temperatures while the silver absorbs heat by melting and boiling. The drawing in figure 5-7 shows the extent of silver loss at various regions in the nozzle after firing. The silver loss reaches 100 percent near the hot inside surface and is 40 to 50 percent in the cooler areas near the external surface.

The second stage of the Polaris operates at a higher altitude and less total thrust is required. The chamber pressure for this engine is 200 to 300 psi, and because of the less erosive nature of the gas stream, graphite is a satisfactory nozzle material.



(a) Cross section showing percentage of silver loss at various locations during firing.



Inside surface Center section Outside surface

(b) Microstructure of silver-infiltrated tungsten after firing.

Figure 5-7. - Silver-infiltrated tungsten nozzle of type used in Polaris Stage I.

SUMMARY OF VARIABLES

Each of the important variables for engines requiring uncooled nozzles can range extensively as shown by the following summary:

Combustion chamber pressure, psi	$<$100 to about 1000
Temperature, $^{\circ}$F	About 4000 to 6500
Firing times, sec	About 60 to 700
Chemical nature	Combustion products may be reducing or oxidizing
Erosive nature	Solid-propellant combustion products may contain erosive solid particles, such as alumina
Fuel	Typical storable liquid fuel is NTO (nitrogen tetroxide) - Aerozine 50; typical solid fuel is polyvinyl chloride - ammonium perchlorate

The choice of material suitable for the various classes of engine is generally based on the extent of throat erosion during firing under simulated engine operating conditions:

Tungsten: Good erosion resistance but poor corrosion resistance; can be used as ablative by infiltrating with silver or copper

Molybdenum: Similar but slightly inferior to tungsten

Graphite: Fair erosion and corrosion resistance; usable in low-pressure engines

Ceramics and cermets: Good erosion and corrosion resistance, but subject to severe thermal cracking

Plastic ablative: Poor erosion resistance; light weight and low cost make it attractive for large, low-pressure nozzles where erosion is tolerable

ROCKET CASINGS

Other parts of rocket engines that new materials have improved are the casings for holding solid propellants and the tanks for liquid propellants. An example is the large steel casing for the 260-inch-diameter solid-propellant rocket which has been under development for several years as a low-cost backup vehicle for the more expensive and complicated liquid-fueled rockets that have powered all of our important space missions to date.

The rocket casing is constructed by welding together 3/4-inch-thick segments of high-strength steel. Structures such as this, however, are notoriously subject to premature brittle fracture, as demonstrated by costly losses of welded Liberty ships during World War II.

Such a failure occurred during proof testing of the first casing. This failure occurred at 56 percent of the intended proof pressure and, according to accelerometer measurements made during the test, originated at two welding flaws at the area indicated in figure 5-8. This figure shows the pieces from the casing laid out in a hangar where the cause of failure was under study. Once initiated, the cracks propagated rapidly and catastrophically through the entire structure.

In order to determine the influence of welding techniques on the structural integrity of the casing, the susceptibility of two types of welds to crack propagation was studied. The two types of weld investigated, a two-pass arc-weld and a multipass arc-weld, are shown diagramatically in figure 5-9. Steel specimens welded by the two techniques were then notched and fatigue-cracked to a predetermined depth by alternately stretching a small distance and releasing in order to simulate a weld flaw. The specimens were then pulled in tension to failure. These tests showed that the welds produced by the multipass welding technique were approximately three times stronger than those produced by the two-pass technique.

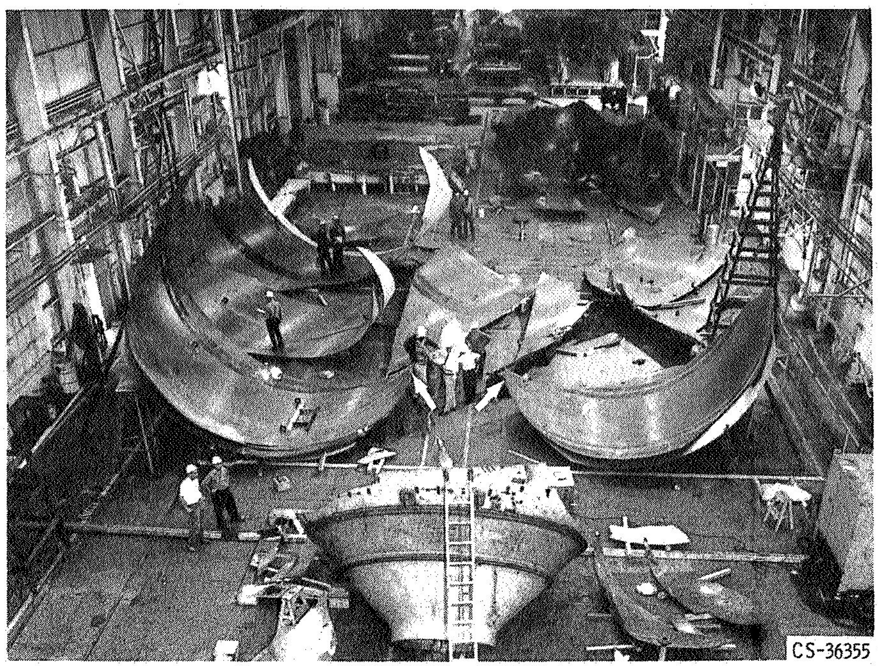


Figure 5-8. - 260-Inch-diameter rocket casing after failure during hydraulic proof testing. Arrows indicate weld flaw which caused failure.

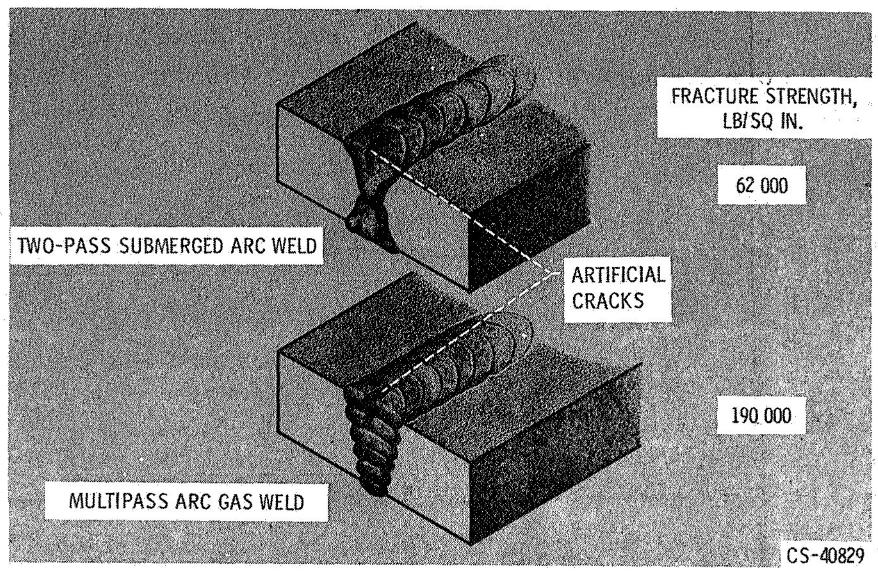


Figure 5-9. - Types of weld used in manufacturing 260-inch-diameter solid propellant rocket casings.

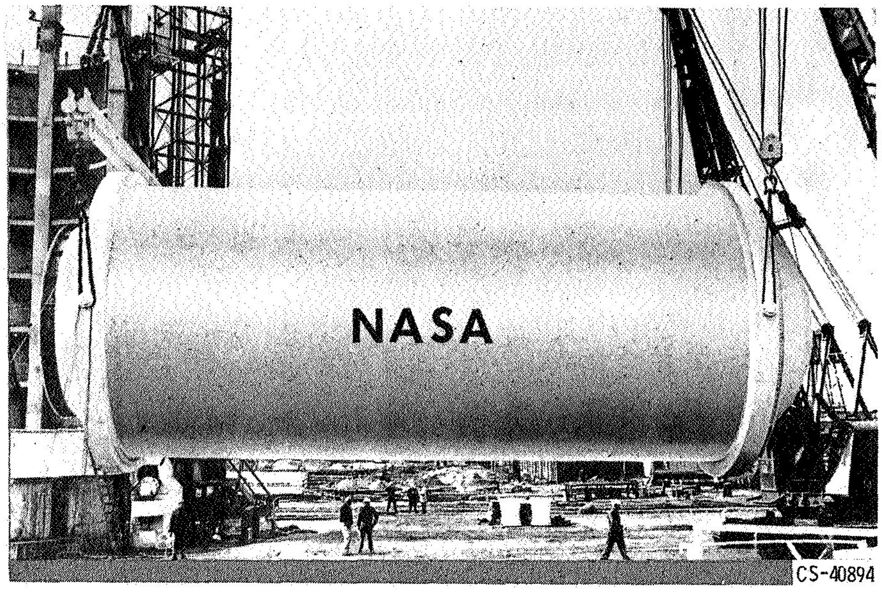


Figure 5-10. - 260-Inch-diameter casing manufactured with the use of multiple-pass tungsten-inert gas welding technique.

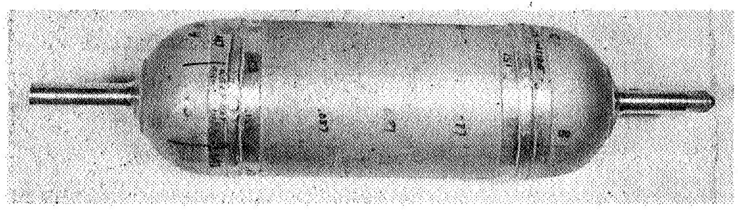
Figure 5-10 shows a second 260-inch-diameter casing which was welded by the multi-pass technique. This casing passed the hydraulic proof test and subsequently was successfully ground test-fired. This engine, incidentally, uses an ablative nozzle with an 89-inch-diameter throat. The chamber pressure is 600 psi and the flame temperature 5500° F with a 2-minute firing time.

The determination of the proper welding technique for the casing is an excellent example of the successful application of a modern laboratory technology, in this case the study of crack initiation and propagation, to the solution of an important manufacturing problem.

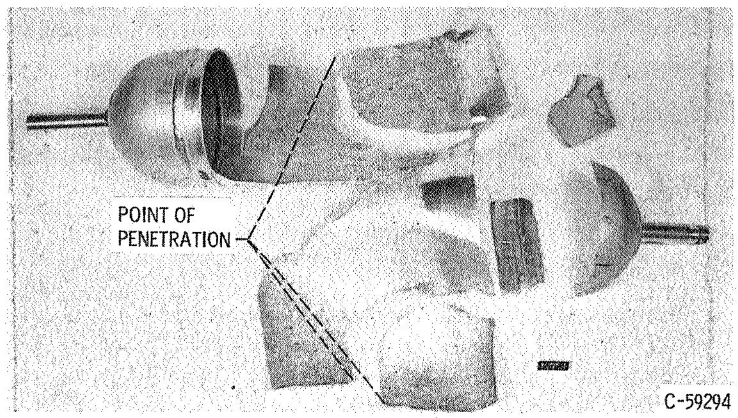
FUEL TANKS

The storage of cryogenic fuels is important to the success of post-Apollo missions. These trips will need large quantities of liquid oxygen and liquid hydrogen for long periods of time. This means not only adequate insulation to prevent excessive fuel losses through vaporization but also protection from damage by high-velocity micrometeoroids. Since much of the vehicle structure will consist of tankage, it must be as light weight as possible.

Although micrometeoroids are less common in space than was estimated several years ago, there are enough to constitute a potentially serious hazard. Most have very low masses, but, because of their high velocities (of the order of 17 000 miles per hour), their momentums are quite large.



(a) Before impact.



(b) After impact.

Figure 5-11. - Damage to water-filled aluminum tank resulting from impact by high-velocity projectile.

The damage resulting from impact of a high-velocity particle with a liquid-filled tank can be catastrophic. Figure 5-11 shows a metal tank which was filled with water and then hit with a high-velocity projectile. The extensive damage resulted not from the immediate shock of impact but from the high-energy shock wave created in the liquid as a result of the projectile passing through. The shock wave, on hitting the tank, literally tore the tank apart. Even more extensive damage occurs when the tank is filled with a cryogenic fluid such as liquid oxygen or liquid nitrogen since the toughness of the metal tank is reduced at low temperatures. Obviously, micrometeoroid impact into a metal tank containing a cryogenic fuel during a space flight could seriously damage or destroy the entire vehicle.

Several possible solutions to this potentially serious problem have been studied in the laboratory. For example, the tanks could be covered with a lightweight armor such as beryllium, which would reduce the probability of penetration by an impacting particle. Alternatively, the metal tanks could be protected by a "bumper," that is, a thin sheet of metal positioned a fraction of an inch outside of the tank. This would cause an impacting particle to fragment. Although the total momentum of the fragments would be the same as that of the original particle, the individual momentums would be lower; furthermore, the area of impact would be much larger and the probability of penetration would be significantly decreased. Both of these possible solutions have merit, but at the same time, both involve a significant weight penalty which can be measured directly in terms of reduced payload.

One attractive solution is to construct the tanks from plastic-bonded glass fiber material, which is both lightweight and shatter-proof. This is done by winding glass fibers into layers that are alternately oriented at 90° from each other and then impregnating and bonding them with an epoxy resin binder. Since the composite is permeable by the small hydrogen molecule, the inside must be lined with a layer of aluminum foil. The cylinder shown in figure 5-12 was filled with liquid nitrogen and hit with a high-velocity projectile. The cylinder contains a small hole where the projectile entered and another hole in the back where the projectile exited. However, the elasticity of the tank enables it to withstand the secondary, high-energy, shock wave in the liquid nitrogen. During space flight, the fuel in this tank would, of course, be lost, but damage to adjacent tanks and to the vehicle itself would be avoided. Thus, it appears that this material will be highly useful in our extended post-Apollo space missions.

Figure 5-12. - Damage to liquid-nitrogen-filled, plastic-bonded glass fiber cylinder resulting from impact by high-velocity projectile.

CONCLUDING REMARKS

In this chapter a few of the materials problems which directly affect and limit our space propulsion systems have been described. Of necessity, the discussion has emphasized the applied aspects of these problems and their solutions. It was impossible to cover the scientific and often more interesting aspects of the problems, such as the details of the oxidation behavior of refractory metals or the basic mechanisms of crack propagation. Furthermore, it avoided many other areas where materials properties are also limiting factors, such as the loops and radiators of self-contained systems for generating electric power in space. Development and selection of materials for these applications tax the ingenuity of the materials scientists.

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