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MATERIALS PROBLEMS IN CHEMICAL LIQUID-
PROPELLANT ROCKET SYSTEMS

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With the advent of the space age, new adjustments in technical thinking and engineering experience are necessary. There is an increasing and extensive interest in the utilization of materials for components to be used at temperatures ranging from -423° to over 3500° F.

This paper presents a description of the materials problems associated with the various components of chemical liquid rocket systems. These components include cooled and uncooled thrust chambers, injectors, turbine drive systems, propellant tanks, and cryogenic propellant containers.

In addition to materials limitations associated with these components, suggested research approaches for improving materials properties are made. Materials such as high-temperature alloys, cermet, carbides, nonferrous alloys, plastics, refractory metals, and porous materials are considered.

INTRODUCTION

Liquid rocket engines, complex systems which vary in materials requirements, are influenced by a host of factors which include propellants used and performance requirements. It is difficult to generalize on the materials problems without reference to specific components and systems. In the past years, considerable research and development have taken place with varied monopropellant and bipropellant systems. It is necessary in the interest of brevity to limit this discussion to some pertinent materials problems relating to major components in chemical liquid rocket engines. Examples of presently developed systems are

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**Title, Unclassified.
(1) the Titan propulsion system using liquid oxygen and RP-l, (2) the
Bomarc propulsion system utilizing type III-A fuming nitric acid and
JP-X, and (3) the second-stage Vanguard propulsion system utilizing
type I-A fuming nitric acid and unsymmetrical dimethyl hydrazine.

To obtain improved performance, future liquid rocket engines will
undoubtedly require the use of oxidizers such as fluorine, nitrogen
tetroxide, and liquid oxygen with such fuels as ammonia, hydrogen, and
other exotic fuels. This will undoubtedly increase the combustion gas
temperatures which the materials of construction must withstand and, in
some cases, increase storability and handling problems. Table I indi­
cates some of the potential future propellant combinations and their
theoretical combustion temperatures. It may also be pertinent to indi­
cate that rocket industry research and development efforts in materials
and processes have been primarily (1) in the evaluation of the mechanical,
physical, and chemical properties of commercially available materials to
provide design criteria, and (2) in the establishment of reliable proc­
essing procedures. Theoretical and basic research findings are applied
wherever possible to improve the state of the art. Discussion of mate­
rials problems will therefore reflect design concepts and processing
limitations.

**THRUST-CHAMBER ASSEMBLY**

**Uncooled Chambers**

Uncooled chambers operate under unsteady-state thermal conditions
in which temperature equilibrium is not attained. Heat is transferred
to the inner wall of the chamber from the combustion gases and is absorbed
by the metal. The temperature of a given point within the chamber wall
varies with the time of exposure. Operating temperatures of uncooled
chambers are limited mainly by the high-temperature materials used.
However, metal chambers can be made to withstand higher temperatures by
the use of a refractory liner. Thus, refractory materials are used in
uncooled-thrust-chamber interior walls and throat areas in either cast
or formed bodies and as coatings or both. The metal structures support
the refractories and carry the applied loads.

The principal problem encountered with uncooled units, aside from
erosion of the lining, is premature overheating of the metal casing
brought about by localized overheating and breakdown of either component
of the composite lining-insulation wall or development of gas passageways
behind the lining (usually related to overheating). The problem has been
controlled principally by lining design (e.g., heavier walls, geometric
design to minimize thermal-shock effects to the lining, etc.), selection
of lining and insulation materials, and injector pattern design.
In the selection of refractory materials for uncooled-thrust-chamber liners, the following parameters are considered: (1) resistance to thermal shock, (2) refractory properties, (3) low specific gravity, (4) oxidation and corrosion resistance, (5) erosion resistance, and (6) thermal conductivity.

Some of the most promising high-temperature refractory materials for thrust-chamber lining applications include: graphite and carbon, silicon-carbide-coated graphite, silicon carbide, silicon carbide bonded with silicon nitride, zirconium boride, and graphite plus silicon carbide bodies. Of these materials, the graphite and the silicon-nitride-bonded silicon carbide have found the widest usage. Graphite's superior resistance to thermal shock, great refactoriness (volatilization point, 6600°F), low specific gravity, (1.6 to 1.7), and machinability has always made this material one of the most attractive refractories for airborne powerplants. However, its high affinity for oxygen at relatively low temperatures seriously limits its use in applications where highly oxidizing conditions may exist. Also, the erosion resistance of graphite is low. With the development of silicon carbide and silicon nitride coatings applicable to graphite, its utility has notably increased through improved resistance to erosion and oxidation.

Silicon carbide bonded with silicon nitride, unlike most molded refractories, essentially retains its original molded dimensions in kiln firing and thus permits dimensional stability without attendant shrinkage problems for precision parts. Its resistance to thermal shock is less than graphite-bearing refractories, but some control is possible through section design (shape and size). Being more resistant to gaseous erosion and almost infinitely more resistant to oxidizing acids than graphite, this material has found considerable use as a lining media for repetitive firing applications with liquid propellants. The specific gravity of the material (2.7 to 2.9) and manufacturing limitations on minimum wall thicknesses limit the size of the unit which can be made on a competitive weight basis. Typical properties of this material are given in table II.

A mixture of silicon carbide and graphite has proven to be a promising combination for lining use. One combination shows very good resistance to fuming nitric acid oxidizer injector streaking. Although the material will disintegrate when immersed in acid, it resists attack under oxidizer streaking conditions by the development of a continuous protective coating, formed from additives in the body, as a high temperature is reached. This material also has exhibited good thermal-shock resistance and has a specific gravity between graphite and silicon carbide.

Silicon carbide (100 percent) shapes, a new promising material, can now be produced with a higher melting or softening point than silicon-nitride-bonded silicon carbide. Ninety-five percent of the theoretical density of silicon carbide (3.17) can be produced in this product (KT
silicon carbide), but, because of the need for lightweight materials having the greatest possible resistance to thermal shock, the introduction of more porosity in the material may be advantageous. Zirconium boride, another relatively recently developed material, is next to graphite in refractoriness, having a melting point of 5540° F. It is extremely heavy, expensive, and difficult to manufacture, all of which limit its use to small components. The resistance of zirconium boride to thermal shock has been found to be rather low as compared to the other materials mentioned. Recent tests of the cermets LT-1 and LT-2 (60% W, 25% Cr, 15% Al₂O₃) show promise for use as small nozzles. Cermets have not received much attention in the past as lining materials because of their high specific gravity, cost, and critical material content.

It may be noted that the oxide ceramics (alumina, magnesia, and zirconia) have not been mentioned. Although the oxides, with few exceptions, have a low thermal conductivity (6 to 18 Btu/sq ft/hr/°F in. at 2200° F), a desirable property for lining materials, as compared to the noted carbides (109 to 113') and graphite (>600), the oxides have limited thermal-shock resistance and are difficult to form in close tolerances in any but small shapes. The mean coefficient of thermal expansion per °F (to 2500° F) is higher for oxide ceramics (14x10⁻⁷ to 89x10⁻⁷) than for the carbides (29x10⁻⁷) or graphite (22x10⁻⁷).

Erosion and high-temperature breakdown of refractories are usually interrelated. This has been particularly noted in liquid-propellant thrust chambers where strong oxidizing atmospheres are possible. Some observers believe eroding is more often the result of an erosion-corrosion process rather than the erosion alone. In solid-propellant engines, where chamber pressures are usually higher than in liquid-propellant engines and solid particles of material may be ejected, eroded surfaces of graphite appear coarse and abraded. In liquid-propellant engine chambers in areas of known oxygen-rich atmospheres, the eroded surface of the graphite is fairly smooth. It, therefore, appears that erosion of the materials is affected by the composition, solids content, and velocity of the gases.

New concepts of thrust-chamber designs using refractory linings are not numerous. An interesting and potentially promising concept which has had only limited investigation is the combination of a refractory lining and a regeneratively cooled chamber. This probably would be most applicable to the smaller sizes of units (less than 1000-lb thrust). The temperatures resulting from higher impulse propellants are obviously more difficult to contain for either the uncooled or cooled type of unit. Insertion of a refractory between the chamber gases and the metal walls of the coolant passages to give lower metal temperatures should provide a much higher reliability factor than would be possible otherwise. However, this concept does not provide for design simplicity or weight reduction.
Because of its high stress-rupture and other high-temperature properties, molybdenum can be considered as a future potential structural material for the outer liner where radiation from a hot outer shell is not important or can be tolerated. Problems relative to joining (welding and brazing) and surface coating (to prevent surface oxidation) require that molybdenum undergo state of art development to ensure its reliability for this application.

Another concept for uncooled units, which has not been investigated to any extent for liquid-propellant engines but has been used successfully in solid-propellant units, concerns lining the walls with reinforced plastics, glass, quartz, or asbestos in combination with ceramic throat inserts for single fired units. While the excellent insulating qualities of the plastic components are attractive, erosion of the plastic could be expected, therefore requiring thickness loss allowances. Promising results have also been obtained with liners fabricated from a cellular or skeleton ceramic impregnated with plastic resins. Lightweight transpiration-cooled ceramic or cermet materials may also be worthy of future development.

Test samples fabricated from tungsten metal which were evaluated for jetavator application showed excellent erosion resistance to 5500°F when placed in the exhaust of a solid-propellant rocket engine operating with high solids content in the exhaust gases. Further evaluation is needed of the possibility of the application of a tungsten metal coating over graphite and other substrates. Such coatings might provide high erosion resistance in nozzle inserts under conditions of liquid-propellant oxidizing exhaust atmospheres with high velocity and high specific heat.

Cooled Chambers

Cooled thrust chambers may be constructed by using a double wall or formed assembled tubular design. Parameters for both types are essentially similar. The strength-density ratio is an important consideration to minimize weight of chambers. Materials with high thermal conductivity tend to alleviate hot-spot difficulties. The material must be able to resist coolant corrosion or the buildup of a corrosion product surface film which would interfere with coolant heat transfer on one surface. It also must resist the corrosive-erosive action of high-velocity combustion gases on the opposite surface. The material must have excellent formability characteristics and must be readily welded or brazed. The materials must be available in forms and with dimensional tolerances that are economically and expeditiously usable for the design. All these requirements are considered and compromised when materials are selected for specific, cooled-thrust-chamber designs and heat-transfer requirements. Some materials which have been utilized are 304 stainless steel,
17-7PH and AM-350 stainless steels, Haynes 25 cobalt-base alloy, and 5052 and 6061 aluminum alloys. Each has had its peculiar set of difficulties.

Some of the material and process problems encountered with cooled thrust chambers have been: (1) areas of localized overheating, often to the melting point, that is, hot spots; (2) reduction of chamber wall thickness by the erosion-corrosion action of high-velocity hot exhaust gases; (3) welding of thin wall tubes without excessive drop through, which would restrict internal fluid flow and disrupt cooling; (4) lack of facilities of sufficient size to braze large-size thrust chambers; and (5) excessive tubing tolerances, which result in fabricating problems associated with maintenance of proper braze joint tolerances.

A destructive hot spot exists when the material of the chamber wall cannot rapidly distribute local heat concentration over a wider area. Melting or structural change occurs. Figure 1 illustrates a thrust chamber in which failure occurred in a localized overheated hot spot. As indicated in figure 2, a hot-spot fracture may show a similarity in microstructure to a thermal-fatigue crack. There is also some evidence of intergranular oxidation. Similar failures have also been observed which were definitely stress-rupture in nature. Increasing the melting point of the wall material is one solution. Increasing thermal conductivity will help. Aluminum, with a low melting point of approximately 1200°F but with higher thermal conductivity than the common elevated-temperature service alloys, has been successfully utilized for cooled thrust chambers. However, as indicated in figure 3, the erosion-corrosion action of high-velocity hot exhaust gases can result in reduction of tube wall thickness and burn-through. Figure 4 shows a Vanguard aluminum alloy thrust chamber in which erosion-corrosion of the chamber walls has been overcome to some extent by the application of a tungsten carbide coating by means of the Linde Flame Plate Process. This provides an erosion-resistant adherent coating with high melting point and good thermal conductivity, and, thus, the advantages of the aluminum alloy (low density, high thermal conductivity, and high corrosion resistance) are retained.

Figure 5 shows the interior surface in the convergent section of an uncoated aluminum alloy thrust chamber in which tube wall thickness reduction and subsequent fracture and localized melting occurred after repeated firings. Figure 6 shows the interior surface appearance of an aluminum alloy thrust chamber coated with tungsten carbide to increase the operating life of the assembly. Coating thickness is of the order of 0.004 to 0.005 inch. Molybdenum, with a melting point of 4760°F and high thermal conductivity, may be used in the future for cooled chambers when reliable joining techniques with acceptable joint efficiencies and suitable coatings to provide oxidation resistance have been developed.
Tubular design thrust chambers introduce fabricating difficulties: first, in procuring tubing in the material, dimensions, and tolerances desired; second, in the forming of the tube to provide the necessary internal shape; and, third, in joining a large number of such tubes together in the shape of a thrust chamber. Manual welding and brazing have been utilized to join the tubes together. Limited welding development has been undertaken. Figure 7 shows a setup for welding of an aluminum alloy chamber. Brazing offers advantages of improved productivity, lower costs, less time to fabricate, and elimination of tube wall burn-through during joining. Molten salt dip brazing has been demonstrated successfully on 6061 aluminum tubular chambers. Large facilities for molten salt dip brazing are not presently available. The primary limitation of this joining procedure is largely tolerance control. Furnace brazing in pure, dry hydrogen has been demonstrated successfully on large-size 347 stainless-steel tubular chambers (fig. 8) using nickel-base brazing alloys. Problems encountered with furnace brazing of stainless-steel tubular chambers are: (1) tolerance control and (2) large surface area which requires low dew point to prevent formation of surface oxides with resultant interference in wetting with the braze alloys. Some difficulty has been experienced in hydrogen-furnace brazing of alloys containing aluminum or titanium such as 17-7PH and Inconel X. The aluminum or titanium in the alloys makes them highly susceptible to formation of tenacious surface oxides which prevent obtaining satisfactory braze joints. Extremely low dew points, -100°F or lower, or iron plating of the tube exterior surfaces have proved successful solutions to this problem. Vacuum brazing may be required for future assemblies. Automatic welding is another applicable joining technique.

Transpiration cooling may offer some promise in maintaining cooled-thrust-chamber wall temperatures within the useful range of available commercial materials. Materials problems of such designs, if any, are not known at this writing. However, the forming and joining characteristics of porous metals need exploration. Problems may exist with this cooling system with respect to corrosion products or foreign matter clogging the pores which may require evaluation in respect to specific propellants and systems.

Presently available materials permit operating temperatures of 1200°F to 1300°F for cooled thrust chambers. Here also, the use of molybdenum alloys as a future potential inner liner material may extend the operating temperatures for cooled thrust chambers to 1800°F dependent on successful state of art developments previously mentioned.

Injectors

Thrust-chamber injectors, whether for cooled or uncooled chamber designs, have the same problems. Generally, the passages and numerous
small orifices are drilled into a thick disk. Hence, it is extremely important that injector material be easily machinable. Drilling without burrs is a problem since deburring is impractical at many stages in the operation. Frequently, one of the propellant components is extremely corrosive and in passing through the injector could dissolve nonmetallic inclusions and disrupt flow characteristics. Nonmetallic inclusions have also caused considerable machining difficulty. A great deal of care in procuring highly clean material is necessary. In two phase alloys a different problem has been encountered in heavy plate, that of internal lamination. Both problems, however, involve a means of determining non-destructively the quality and soundness of the raw material to be used in fabrication. Completely satisfactory inspection techniques and standards have not been established for most materials of interest. Ultrasonic inspection shows promise.

A possibility exists for reducing the time of fabrication and cost of drilling numerous small holes. Brazed assemblies offer a promise of cost reduction possibilities in which an easy-machining aluminum alloy is bonded to a high-strength steel.

TURBINE DRIVE SYSTEMS

Turbines

Turbine drive systems utilize the energy of hot combustion gases to produce useful mechanical or electrical energy through pumps, gears, alternators, and so forth. The turbine wheel is one of the most critical components in the system. Materials for turbine wheels must possess a high strength-density ratio in both tension and compression, low creep rate, and high rupture strength over a wide temperature range (1300° to 2400° F) and generally for times up to 10 hours. High thermal conductivity and low thermal expansion are desired to give high thermal-shock resistance. Corrosion resistance to the combustion gases and microstructural stability under the conditions of stress and temperature for the service life are necessary. The material must be capable of being machined, cast, or pressed, economically, to the desired shape. Figure 9 presents the yield strength of various elevated temperature alloys considered for use in turbine wheels as a function of temperature. The alloy systems can be grouped according to their base element, hardening element content, and the temperature at which rapid overaging occurs with a resultant large strength decrease. These groupings, when compared to gas generator gas temperatures, define the alloy systems to be considered. High rotational speeds are characteristic of most turbine drive systems. Hence, turbine-wheel material density is significant in defining the stress levels attained and, for all airborne systems, weight (i.e., density) is an important design consideration. It is therefore valuable
to compare materials on a strength-density ratio basis as has been done in figure 10. A considerable portion of the interest in utilizing titanium-carbide-base (TiC) cermet in turbine wheels is due to the low density of the materials.

Cast cobalt-base alloys, such as Haynes 31, and forged and machined precipitation hardenable iron-base austenitic alloys, such as Discaloy, have been used. Increased strength and operating temperature requirements presently dictate use of alloys such as Modified Discaloy, Inconel 713C, René 41, and other new nickel-base types. Titanium-carbide-base cerments and molybdenum alloy wheels have been given serious consideration.

One of the problems encountered in turbine wheels is cracking at the root of the buckets due to insufficient ductility in the material to relieve thermal stresses resulting from thermal gradients during thermal cycling (fig. 11). The immediate problem in the evaluation of materials for turbine wheels in rocket-engine auxiliary power systems is the lack of tensile, creep, and stress-rupture data under conditions of rapid heating and suddenly applied loads for short-cycle, short-life operation. Recently initiated ultrashort-time tensile and creep tests have been predominantly concerned with airframe materials and requirements. Consequently, the materials and typical cycles of interest applicable to turbine wheels remain unexplored. Much work has been done by the NASA and others to provide an understanding of the behavior of brittle materials. There is still an inadequate understanding of the behavior of some of these materials, such as cermet, under the transient startup conditions of large thermal gradients experienced in turbine wheels. A satisfactory criterion relating the thermal-shock resistance of a material to turbine-wheel design parameters is necessary. Molybdenum alloys, which may be the only commercially available materials for service above 2000°F, have not been evaluated in section sizes of interest, which is quite necessary for all systems strengthened by strain hardening. However, ductility of molybdenum as well as its high density must be considered. Similarly, the oxidation behavior of molybdenum and the characteristics of oxidation-resistant coatings for molybdenum have not received attention for short-life applications. Bucket contours are machined from the forged blank in many designs. Large quantity production necessitates process development to reduce the amount of machining required. Mechanically attached buckets, composite designs utilizing cast bucket segments and forged disks, and forged-in rough bucket shapes for small-diameter turbine wheels are approaches which have not been developed or thoroughly evaluated.

An entirely new concept, applicable to satellite vehicles, must now also be considered. This is extremely high temperature (3500°F) long life (to 10,000 hr) turbine wheels. There is presently no basis for designing to such requirements. Alloy systems with engineering properties that could operate under such conditions have not been achieved.
Bearings

Another critical component is bearings. Bearings are presently lubricated with oil, fuel, or oxidizer, dependent upon the system. A problem exists with turbine bearings that is related to turbine-wheel temperatures. As wheel temperature increases, the problem of maintaining bearing temperatures to below 700°F becomes increasingly difficult. This is particularly true of high-speed highly loaded bearings. Studies are necessary to evaluate and develop bearing materials for unlubricated operation throughout the operating temperature range of the components, very high in turbine bearings to very low in subzero fluid pump systems. An independent but related study is necessary to evaluate and develop lubricants which can withstand operating temperatures ranging from low to high. Dry-film bonded graphite, sulphides, nitrides, and carbides are considered as possible lubricants. Cold-worked 300 series stainless steels, cermets, cobalt-base hard-surfacing alloys, and molybdenum are considered as possible future bearing materials.

Gas Generators

Another critical subassembly in turbine drive systems is the gas generator. It is generally considered that service temperatures for gas generators are lower for monopropellant systems than for bipropellant systems. However, service temperatures as high as 2400°F have been obtained with normal propyl nitrate monopropellant. Two significant problems are: (1) The gas generator body may be exposed to an exterior atmosphere different from the interior atmosphere, and (2) the fabricating processes are not as readily adaptable to alloys being considered for future high-temperature service. An interior reducing atmosphere and an exterior oxidizing atmosphere present problems when the body material is not resistant to one or the other. Among available materials, Haynes 25 cobalt-base alloy has provided best service for temperatures to 2200°F with Hastelloy C as second choice.

Nozzle erosion-corrosion has occurred with several elevated-temperature service alloys. This phenomenon is not understood, and, therefore, predictions of material behavior cannot be reasonably made. Further investigation is required. In many hot gas systems utilizing carbon-containing fuels, coking occurs as a result of combustion at less than stoichiometric ratios, a limitation imposed because of the necessity of keeping component operating temperatures below specific values. Coking alters and plugs gas passages and erodes surfaces. Materials capable of higher temperature operation would permit efficient combustion and eliminate coking.

Future use will require the evaluation of molybdenum alloys, tungsten, and cermets for gas generators. However, a more extensive study of the
effects of processing, forming, and joining protective coatings on material properties will be required. Such processes as drawing, spinning, tube forming, rolling, and joining are not as advanced for molybdenum as forging and require further investigation.

Pumps

Pumps are characterized by complex housings and complex machined impellers. The major problems with housings are weight and casting quality such as low ductility and porosity. Weight reduction dictates the use of 355 and 356 aluminum casting alloys. Normal porosity can generally be corrected by the use of suitable impregnants such as plastics, petroleum derivatives, waxes, water glass, or other chemicals. Vacuum and pressure impregnation are two accepted methods used, with vacuum considered as the superior one. However, when service conditions require use with cryogenic or highly oxidizing propellants, the commercially available impregnants do not provide satisfactory service because of one or both of the following reasons: (1) The impregnant is reactive with the propellant, and (2) differences in contraction between casting and impregnant result in unreliable sealing.

Development of processes is necessary to permit alloys with higher yield strength and high ductility, free from gases, to be cast into complex shapes. Such developments might include vacuum pouring or casting in an inert gas atmosphere and the use of ultrapure aluminum alloys (very low in iron and other impurities). Reduction of interstitial dissolved gases in the higher strength alloys through vacuum or improved degasification techniques may provide improved porosity-free high-yield-strength castings. Structure variations may also be improved through pouring temperature control, mold selection, and use of chills. Successful development of casting techniques which improve ductility and eliminate porosity when applied to pump housings will avoid the problem of loss of pressure tightness and increased bursting pressure. The same techniques if extended to the casting of impeller shapes will minimize costly time-consuming machining operations.

A major problem with pumps for acid service is corrosion, which may exist in such forms of attack as galvanic corrosion, crevice corrosion, fretting corrosion, and salting.

Galvanic corrosion is produced by the placement of dissimilar metals in intimate contact with each other, or in close proximity, both in the presence of an electrolyte such as acid. The most obvious and efficient solution is to avoid dissimilar metals in this configuration or to use
those metals that are of approximately equal potential on the galvanic scale. The use of dissimilar metals in pump assemblies is a result of the variation in materials required to satisfy service conditions of the component parts, such as bearings, shafts, pump housings, and so forth. The separation may be physical in nature (space) or may be accomplished by utilizing insulating spacers (nonmetallic, corrosion-resistant materials).

Crevice corrosion is caused by the action of concentration cells between closely adjoining surfaces acting to restrict or prevent the replenishment of oxygen in the affected area. The result is localized, excessive attack ultimately causing failure of the (usually) pin-hole type. The use of corrosion-resistant shims or spacers or redesign of the component to eliminate crevices is recommended.

The problem of salting is especially serious in components utilizing aluminum as a material of construction. With most oxidizing propellants, corrosion produces crystals of aluminum salts that bridge the gap between mating parts. Some of these salts are extremely hard, and scoring of smooth surfaces and damage to seals result from mechanical operation. When bound parts are broken loose, the assembly may operate satisfactorily or may fail during the next run. The causes of the salt formations have not been definitely established, but certain factors are believed to contribute. (1) Acid composition has been demonstrated to influence corrosion rates of materials, and the formation of corrosion products alters the composition by changing the dissolved solid content of the acid. (2) The type of materials in the components influences the species of dissolved ions in the acid and will govern the quantity of dissolved solids. (3) Galvanic effects and dissociation of the acid associated with close fitting parts tend to accentuate the corrosive effects and locally increase the concentration of dissolved solids to augment the salting problem. (4) Idleness of the fluid system causes stagnation of the propellant in crevices and in areas of close-fitting parts. This stagnation then permits dissociated products to accumulate. Further, the dissociation products tend to accelerate corrosive attack. During corrosion, metallic ions are taken into solution, which results in the precipitation of nitrate salts after the salt solubility limits have been exceeded.

The use of at least two methods of preventing or minimizing salting is immediately obvious, although they have not been shown to be completely satisfactory. First, the isolation and substitution of materials in close-fitting components could be effected to reduce the effect of galvanic couples and the resultant rapid corrosion. Second, the corrosive attack by dissociated acid ions may be reduced by flushing the system after use or by introducing storage solutions during periods of inactivity or both.
Another major problem with pumps, both for acid and liquid oxygen and other cryogenic propellant service, is seals. Some general properties which must be evaluated to determine the suitability of nonmetallic materials for use as seals with any propellant include changes in tensile strength, elongation, volume, hardness, flexibility, stiffness (at low temperature if appropriate), and compression set. As an example, should excessive swell occur to an O-ring on exposure to a propellant, an increase in friction would occur on a moving seal, and some extrusion from the O-ring groove may occur which would cause tearing and disintegration of the seal. Even though disintegration of the ring did not occur, the increase in friction would drastically alter the operating characteristics of the mechanism. In addition, any adverse effects the materials themselves may have on the propellant must be carefully noted. Recent investigations of various rubbers and plastics for use in contact with ethylene oxide indicate these materials polymerize the propellant which results in a slightly cloudy appearance or in some instances a complete solidification of the fuel. Complete evaluations are required, and a full knowledge of exact operating conditions is extremely important.

Fuming nitric acid systems are notorious for their corrosive action on nonmetallic materials. Such systems employ Teflon, Kel-F, and Kel-F elastomer because of their greater resistance to chemical attack. However, Teflon is noted for its poor resistance to cold flow and cannot be placed under high loading and still maintain a seal. Kel-F plastic, if plasticized (for greater resiliency), rapidly becomes hardened because of leaching out of its plasticizer by the acid. Kel-F elastomer, the only fuming-nitric-acid-resistant rubber, gradually swells, softens, abrades, and delaminates with use in a sliding seal. It has often taken a set while installed in an O-ring groove and assumes a square instead of a round cross section. Naturally, the life of such a seal is limited and requires frequent replacement.

PROPELLANT TANKS

Propellants are stored in tanks and may be fed to the injector by pumps or by pressurized gas. The most critical problems exist in those tanks which must withstand high pressures. One of the principal criteria for selection of material for tankage is based on the propellant employed. At present, 17-7PH and type 410 stainless steels have been widely used for acid service, pure aluminum and selected aluminum-clad alloys for hydrogen peroxide, and austenitic stainless steel or other face-centered alloys for liquid-oxygen service. Parameters generally considered in the selection of the material are (1) corrosion resistance, (2) decomposition of the propellant, (3) strength-density ratio, and (4) fabricability.
The types of corrosion problems generally encountered are intergranular and stress corrosion cracking. Some materials, such as cold-worked 304 stainless steel, normally a corrosion-resistant material, are sensitized when welded and will exhibit intergranular corrosion in the weld and heat-affected zones when exposed to fuming nitric acid. Intergranular corrosion is manifested by a preferential attack at the grain boundaries. Intergranular corrosion occurs because of electrochemical potential differences between grain body and the adjacent grain boundary. Such differences result, according to one theory, from the precipitation of carbides and other constituents, leaving anodic areas which are degraded by electrochemical action, as in galvanic corrosion. Another theory postulates lattice strain differentials between grain and grain boundary. Control of carbide precipitation through addition of stabilizing elements such as columbium or titanium is one method of combating intergranular corrosion. Another approach is to anneal after welding, size permitting. Development of ultrasonic or other cold-welding techniques for application to tankage fabrication would eliminate sensitization in the weld zone and thus provide control of carbide precipitation.

Type 410 stainless steel, in certain heat-treated conditions, is subject to rapid failure by stress corrosion cracking upon exposure in a stressed condition to acid (fig. 12). Stress corrosion cracking occurs under conditions of static tensile stress in conjunction with exposure to a corrosive. The stress may be either applied or residual. A peculiarity of stress corrosion cracking is that almost any metal will be subject to this failure in certain specific environments; but the same set of conditions which causes cracking in one metal will not necessarily affect another. Although it can generally be expected that the static tensile stresses causing failure are close to the yield strength of the material, there have been failures at stresses much below the yield stress. These probably are the result of local stress raisers, in the form of mechanical notches, corrosion pits, or intergranular corrosion, which cause concentration of the stress to the point where cracking occurs. Figure 13 indicates the effect of fuming nitric acid temperature and imposed stress level on the time to failure for type 410 stainless steel heat treated to two temper conditions. It is believed that increasing acid temperature increases the rate of formation of the initiating crack. It is also believed that the effects of increasing imposed stress level are: (1) acceleration of the corrosion which produces the initiating crack, (2) increase in the rate of growth of the crack to a critical length, and (3) decrease in the critical crack length necessary for fracture. In 410 stainless steel it is believed that the microstructural changes responsible for the drastic reduction in impact strength, general corrosion resistance, and secondary hardening observed in the 700° to 1000° F temper temperature range also are responsible for the
sensitivity to hydrogen embrittlement reported and stress corrosion observed. Further basic studies are necessary to determine the mechanism and qualitative effect of factors inducing stress corrosion cracking and hydrogen embrittlement.

Corrosion and its effects can be controlled for long periods of time by the addition of inhibitors. (Hydrofluoric acid is an inhibitor in fuming nitric acid.) As a result of research and development, it was possible to establish optimum inhibitor concentrations for white and red fuming nitric acids as well as to determine the effect of storage time on corrosion resistance. Figure 14 shows the effect of hydrofluoric acid additions to white and red fuming nitric acid in reducing the corrosion rate of 347 stainless steel and 6061-T6 aluminum alloy. Corrosion rates expressed as a thickness loss in mils (thousandths of an in.) penetration per year are converted from weight loss by means of the following formula:

\[ R = \frac{19.31 \Delta W}{dAt} \]

where

- \( R \) corrosion rate, in./yr
- 19.31 conversion factor
- \( \Delta W \) weight loss due to corrosion, g
- \( d \) density of alloy tested, lb/cu in.
- \( A \) surface area of test specimen, sq in.
- \( t \) immersion or exposure time, hr

Long-time storage material and propellant compatibility testing are needed. Retaliatory missiles must be in a state of readiness at all times, which could mean the requirement that tanks be operable after long storage, fully loaded with propellants, and possibly highly stressed. The stress corrosion and hydrogen embrittlement sensitivity of potential tank materials should be determined in pressure vessel tests.

For minimum weight designs, particularly for pressurized gas systems, increased material strength is required. No weldable aluminum alloy of strength comparable to 7075 exists. The high strength of precipitation-hardenable stainless steels cannot be used in pressure vessel design.
because of brittleness at high strength levels. Higher strength materials at subzero temperatures may possibly be attained by use of strain-hardening austenitic stainless steels. This technique has been established with 300 series stainless steels on a laboratory scale.

Having attained higher strength level materials, the problem of retaining the strength through assembly or obtaining the strength after assembly remains. Existent commercial joining techniques involve high temperatures which reduce the strength of strain-hardened materials to varying degrees. This necessitates heat treating to obtain the high strength levels desired and introduces many fabrication problems because of inadequate facilities to handle large-size components (tank diameters to 100 in.). Cold-joining techniques such as ultrasonic welding require evaluation and development to utilize this potential process for putting together high-strength subassemblies.

A greater understanding of the brittle behavior of metals at high strength levels is necessary. Vacuum melting is believed to be beneficial in that internal notches arising from nonmetallic inclusions or gases would be reduced. Vacuum-melted alloys need to be more thoroughly compared to alloys produced by standard commercial practice. In this connection, there is also the problem of establishing standards for acceptance and the means of inspecting material. Raw material must more nearly approach perfection when maximum attainable strength and reliability are the goals.

Many high-strength steels become embrittled during conventional cleaning operations. There is need to investigate ultrasonic methods as a substitute to avoid such embrittlement. In the past, it has been difficult to adapt such equipment to the cleaning of large fabricated hardware.

Frequently, rigidity requirements limit gage reduction that could be obtainable from increased strength. To obtain weight savings, the feasibility of hollow-core construction (honeycomb, tube skin) requires establishment.

CRYOGENIC PROPELLANTS

Introduction

One of the earliest oxidizers utilized in liquid-propellant rocket engines and still extensively utilized is liquid oxygen, a cryogenic fluid. Interest in cryogenic fluids of lower boiling temperature than liquid oxygen is increasing. At the liquid-oxygen temperature, \(-297^\circ F\),
the number of materials of construction which have useful engineering properties is very limited. Several for which data are available are shown in figures 15 and 16. Considerable data exist for metals and alloys at temperatures to -320°F. Information of a general nature indicates face-centered cubic lattice structures retain considerable ductility or experience increased ductility at such temperatures, whereas body-centered cubic lattice structures, though increasing considerably in strength, suffer transition from ductile to brittle fracture characteristics. Although a limited amount of work has been done in the investigation of the behavior of metals and alloys at lower temperatures, to -423°F for liquid hydrogen, the information obtained is not sufficiently extensive to provide adequate engineering design data. Extrapolation of data in these temperature ranges is dangerous, though no more so than at any other temperature when extrapolations are made without adequate knowledge. Certain materials experience microstructural changes which have accompanying deleterious effects on mechanical properties. Martensitic microstructures, as obtained in carbon and low alloy steels and in martensitic stainless steels (400 series), are brittle at low temperatures. This characteristic behavior of this class of materials eliminates a large number of alloys with considerable design and fabrication history from consideration for low-temperature use. The ductile materials such as monel, nickel, and annealed austenitic stainless steels have low strength-density ratios and therefore are not the most desirable for lightweight design. Available information, therefore, merely indicates the following general types of alloys which may have application for low-temperature service: the stable iron- and nickel-base austenitic alloys and aluminum alloys.

Some of the major problems encountered in liquid-oxygen systems will be discussed briefly to provide a better understanding of the degree of difficulty which can be expected with lower temperature systems.

Liquid-Oxygen-Systems Problems

A major problem with moving contact surfaces in liquid oxygen is lubrication. Lubricants of the normal liquid and grease types cannot be used in liquid-oxygen systems because of the chemical reactivity and ignition hazards involved. It is necessary to use an inorganic, noncombustible, dry-film lubricant for such applications. However, dry-film lubricants may not function properly below -80°F. Heaters are frequently employed to maintain operating temperatures above -80°F. Such an arrangement adds to the complexity of the design and contributes considerable weight to the system.
Another major problem with lubricants is seals. In valves there is a need for a satisfactory lubricant compatible with both the rubber O-ring and the propellant. Normal liquid or grease lubricants are not compatible with oxygen. The lubricants of this type which are compatible (normally fluorocarbons) have a deleterious effect on the O-rings employed. Dry-film lubricants have been attempted but do not possess the necessary lubricity with rubber surfaces. There is also need for a nongalling thread lubricant. A recent tentative specification required a resistance of 70-foot-pound impact loading for such a lubricant. After considerable investigation it was found that only one such lubricant was commercially available, and in recent tests the vast majority of lots failed to meet the specification requirements. The fluorocarbon lubricants, nevertheless, are among the most impact-resistant materials available as shown in table III. However, these materials, when under high shear loading in contact with fresh aluminum surfaces, exhibit a strange phenomenon, detonation with great violence. Naturally, these materials, which are otherwise highly desirable lubricants, cannot be used under high shear loading with aluminum.

Metal seals offer some promise for use in liquid oxygen. To obtain adequate seals, the use of metals with too wide a differential in coefficient of expansion must be avoided, such as austenitic stainless steel and aluminum alloys in the same assembly. Frequently, it may be desirable to use a low-expansion alloy, such as Invar, for certain component parts. However, data on the expansion characteristics of Invar and related alloys are frequently unavailable for temperatures lower than -100°F.

Liquid-oxygen tanks have been fabricated using conventional techniques and low-strength material or material conditions. Welding has been extensively employed. The evaluation of material and welds at cryogenic temperatures is best based on bend ductility and impact-strength test results. Information on the bend ductility (angle at which fracture occurs) at cryogenic temperatures is not available. The angle at which fracture takes place in the bend test is influenced by the manner in which the outer fibers of the test specimen elongate. An analysis of the distribution of the elongation over a fixed gage length, measured in increments of 0.1 inch and referenced to the angle of fracture, may provide a better means of evaluating the ductility of welds at cryogenic temperatures. Considerable impact-strength data at cryogenic temperatures are available for unwelded alloys. Impact-resistance data for welded materials are generally lacking. What is available, however, indicates that considerable importance must be attached to the choice of parent alloy for welded design, choice of filler metal, and the fabrication operations following welding. Figure 17 indicates the effect of welding and various post-weld heat treatments on the low-temperature
impact resistance of an unstabilized and a stabilized grade 300 series austenitic stainless steel. Data on the unwelded parent material in the annealed condition are included for comparison. Sensitization and ferrite formation in the weld result in dangerously low impact values even in the stabilized grade (3 to 10 ft-lb at -320°F). Data for aluminum alloys indicate very low impact resistance in weld joints made with the most widely used filler metal composition, 4043. A study of the effect of exposure to cryogenic temperatures on weld joint properties in all materials of construction is necessary.

On the basis of available limited data and commercial joining processes, tanks for liquid oxygen would have to be constructed from annealed austenitic stainless steels, annealed nickel-base alloys, or aluminum alloys. Increased wall thickness, due to low yield strength values for these alloys, results in increased weight. The use of heat-treated ferritic steels or precipitation-hardened semi-austenitic alloys for higher yield strength design values is not practical because of a transition from ductile to brittle behavior at subzero temperatures. High yield strength values have been obtained through the use of cold-worked iron-, nickel-, and cobalt-base materials. However, a thorough investigation of the effect of exposure to liquid-oxygen temperatures on these classes of cold-worked materials has not been made and requires determination. Normal fusion welding methods are not suitable for strain-hardened materials. To maintain adequate strength in joints and permit full utilization of the capabilities of the limited number of alloys available, other methods of joining must be developed. Here again, development of ultrasonic welding techniques or application of resistance or seam fusion welding at extremely rapid rates merits investigation to reduce the extent of the heat-affected zone. Increased yield strength values may also be obtained through the use of precipitation-hardened austenitic alloys, such as A-286 and the newer nickel- and cobalt-base heat-resistant alloys. These types of alloys can be fusion welded prior to the precipitation heat treatment. However, investigation of the properties at cryogenic temperatures for both parent metal and welded joints for these alloys in the aged condition is necessary since no such data are presently available.

Liquid Fluorine

Fluorine is the most powerful oxidizing agent known, reacting with practically all organic and inorganic substances. Only inert gases, a few complete fluorinated compounds (Teflon, etc.), and metals which develop stable fluoride surfaces can be used to handle fluorine. In addition to the extremely difficult problems of chemical reactivity, liquid fluorine, with a boiling point of -305°F, imposes the same limitations on materials as liquid oxygen. The same general classes of materials would be useful: austenitic iron- and nickel-base alloys,
aluminum alloys, copper and copper-base alloys. All rubbers are attacked to some extent with increasing brittleness, cracking, and surface hardening.

Utilization of liquid fluorine will require an extensive study of materials compatibility and development of nonmetallic materials if existent design concepts are retained. Unique design approaches can alleviate some problems. Much increased emphasis on fabricating process utilization and development would be necessary with any design.

Liquid Hydrogen

Liquid hydrogen holds the same position in the fuel class as liquid fluorine holds in the oxidizer class. The probability of use of liquid hydrogen as a fuel increases as the need for higher energy propellants increases. However, a different set of problems exists. Problems of handling liquid hydrogen arise predominantly from the extremely low boiling point, -423°F. Chemical reactivity will be less significant.

A general problem of concern to engineers is the almost complete lack of engineering data describing materials behavior at -423°F. Available data on the properties of metals and alloys at liquid-hydrogen temperatures have been obtained from a limited number of specimens and thus indicate trends only. Properly evaluating and selecting materials for use with liquid hydrogen require much investigation. For example, cold-worked 300 series stainless steels, applicable at liquid-oxygen temperatures, may experience martensitic transformation near -423°F with a very sharp decrease in ductility and impact strength and may thus eliminate an entire promising class of materials from consideration. The degree of cold work to produce this transformation should be determined. Similar studies are necessary for other metastable austenitic systems and even for austenitic systems thought to be unquestionably stable. Such alloys as cold-worked Haynes 25 and A-286, with or without aging, and aged A-286 should be studied. The effect of manufacturing and fabrication variables on properties should be determined. Seemingly unimportant composition variations could result in significant property differences. Investigators have urged extreme caution and recommend against extrapolation of low-temperature data, even from -320°F, to liquid-hydrogen temperatures. Unknown reactions may occur and rapidly change the applicability of a material.

The exceptionally low temperatures will increase the mechanical and physical property deficiencies of nonmetallic materials in general. There is a very great deficiency in experimental data concerning what changes actually occur in materials at these temperatures. Recent studies have been made on adhesives at temperatures below -320°F. Bond strength data indicate that the adhesives may be feasible for construction
purposes. Since at present there is no knowledge of this application, adhesive and adhesive filler systems must be investigated. Lubricants may present a serious problem. Liquid lubricants and greases will probably be inadequate at liquid-hydrogen temperatures since they become hard and solid, break up, and form a debris of nonlubricating matter. Dry-film lubricants will need investigating for service at these temperatures.

CONCLUDING REMARKS

Rapid adjustments to the new space age are inevitable. The specific, present indications of such adjustments are: increasing, extensive interest in an extremely broad range of operational temperatures (-423°F to 350°F), a significant recognition of the necessity to reduce component weight to minimums, a continuing trend toward very large size systems, and the recognition that our defensive effort must be at least capable of instant, retaliatory attack. These adjustments place a tremendous burden upon those responsible for materials and process application and development because of the vast unexplored areas which must be mapped if the technology is to remain abreast of the requirements of design. For example, the temperature range within engineering experience for the past half century will probably be considerably extended in less than a decade. The greatest single need, therefore, is to extend our knowledge of the behavior of engineering materials, metallic and nonmetallic.

ACKNOWLEDGEMENTS

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Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, June 3, 1959
## TABLE I. - SOME THEORETICAL PERFORMANCE VALUES FOR SPECIFIC PROPELLANT COMBUSTIONS

[Bipropellant systems.]

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Fuel</th>
<th>Mix ratio, Oxidizer/Fuel</th>
<th>Combustion temperature, °F</th>
<th>Chamber pressure, lb/sq in</th>
<th>Specific impulse, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>Ammonia</td>
<td>2.9</td>
<td>7512</td>
<td>300</td>
<td>295.5</td>
</tr>
<tr>
<td>Fluorine</td>
<td>Hydrogen</td>
<td>9.42</td>
<td>8072</td>
<td></td>
<td>371</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Aluminum</td>
<td>1.32</td>
<td>6000</td>
<td></td>
<td>276</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Ammonia</td>
<td>1.25</td>
<td>4834</td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Hydrogen</td>
<td>2.89</td>
<td>3886</td>
<td></td>
<td>345</td>
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<tr>
<td>Hydrogen peroxide</td>
<td>n-Octant</td>
<td>5.10</td>
<td>4095</td>
<td></td>
<td>230</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>Methyl alcohol and hydrazine hydrate</td>
<td>2.54</td>
<td>3934</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>Nitrogen tetroxide</td>
<td>Hydrogen</td>
<td>11.5</td>
<td>5610</td>
<td></td>
<td>279</td>
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<tr>
<td>White fuming nitric acid</td>
<td>JP-4</td>
<td>4.7</td>
<td>5000</td>
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<td>229</td>
</tr>
<tr>
<td>Red fuming nitric acid (16% NO₂)</td>
<td>Hydrazine</td>
<td>1.16</td>
<td>4728</td>
<td>242</td>
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</tr>
<tr>
<td>Property</td>
<td>Value</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>----------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity, Btu/hr/sq ft/in./°F</td>
<td>113.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistance to thermal shock</td>
<td>Very good</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compressive strength at -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>20,000 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700° C</td>
<td>20,000 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000° C</td>
<td>25,500 psi</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1350° C</td>
<td>21,500 psi</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1500° C</td>
<td>11,900 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Tensile strength at -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>3,500 psi</td>
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<td></td>
<td></td>
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<tr>
<td>700° C</td>
<td>3,500 psi</td>
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<td>1000° C</td>
<td>4,500 psi</td>
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<td>1350° C</td>
<td>3,700 psi</td>
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<td></td>
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</tr>
<tr>
<td>1500° C</td>
<td>1,900 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus of rupture at -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>5,500 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700° C</td>
<td>5,500 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000° C</td>
<td>7,000 psi</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1350° C</td>
<td>5,900 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500° C</td>
<td>3,000 psi</td>
<td></td>
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<td></td>
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<tr>
<td>Elastic modulus at -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° C</td>
<td>17.0×10^6 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700° C</td>
<td>16.0×10^6 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000° C</td>
<td>9.5×10^6 psi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>2.87 g/cc</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Porosity</td>
<td>6.0 to 10.0%</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Coefficient of thermal expansion:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25° to 200° C</td>
<td>3.26×10^-6 in./in./°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>25° to 400° C</td>
<td>3.76×10^-6 in./in./°C</td>
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<tr>
<td>25° to 600° C</td>
<td>4.07×10^-6 in./in./°C</td>
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<tr>
<td>25° to 800° C</td>
<td>4.29×10^-6 in./in./°C</td>
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<tr>
<td>25° to 1000° C</td>
<td>4.47×10^-6 in./in./°C</td>
<td></td>
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</tr>
<tr>
<td>25° to 1250° C</td>
<td>4.69×10^-6 in./in./°C</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Specific heat, Btu/hr/lb/°F</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0° C</td>
<td>0.137</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1100° C</td>
<td>.297</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>1400° C</td>
<td>.372</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractoriness</td>
<td>Does not have a melting</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>point, but dissociation of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si₃N₄ takes place at 1900°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>and of SiC at 2600°C</td>
<td></td>
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### TABLE III. - LIQUID-OXYGEN - LUBRICANT IMPACT SENSITIVITY

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Type</th>
<th>Maximum safe impact load, ft-lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha Molykote, Grade Z</td>
<td>Molybdenum disulfide</td>
<td>59.2</td>
</tr>
<tr>
<td>Hooker, Fluorlube FS (Foreshot)</td>
<td>Fluorocarbon</td>
<td></td>
</tr>
<tr>
<td>Hooker, Fluorlube S (Standard)</td>
<td>Silicon</td>
<td>10</td>
</tr>
<tr>
<td>Union Carbide Carbon, Fluorothane G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow Corning DC-4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow Corning DC-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow Corning DC-11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow Corning DC-33 (Light)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning DC-33 (Heavy)</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Dow Corning DC-41</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning DC-234S</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning DC-510</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning DC-550</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning DC-710</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning Valve Seal &quot;A&quot;</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Dow Corning Pneumatic Grease #55</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>General Electric Versilube F-50</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>General Electric Versilube G-500</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Metco Valve Lube</td>
<td>? Contains lead carbonate</td>
<td>10</td>
</tr>
<tr>
<td>Rectorseal #15</td>
<td>? Contains graphite</td>
<td>10</td>
</tr>
<tr>
<td>Gato High Pressure Thread Lube</td>
<td>?</td>
<td>10</td>
</tr>
<tr>
<td>Key Absolute Type B (MIL-T-5542)</td>
<td>?</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 1. - Interior of Haynes 25 thrust chamber in which failure occurred by thermal fatigue in hot-spot area indicated by arrow.
Microstructure in area of thermal-fatigue crack shown above. X75. Arrow indicates thrust-chamber interior surface at hot spot. Metal temperature differential between hot-spot area and adjacent cool metal may be as great as 1000°F.

Figure 2. - Thermal-fatigue crack in Haynes 25 thrust chamber in hot-spot area shown in figure 1.
Figure 3. - Forward view of acid-cooled thrust chamber showing tube-wall-thickness reduction and burn-through as a result of erosion-corrosion action of high-velocity hot exhaust gases.
Figure 5. - Interior surfaces in convergent section of uncoated aluminum alloy thrust chamber. Lettered areas indicate regions of reduced tube wall thickness with subsequent tube fracture and regions of localized tube wall melting.
Figure 6. - View looking through throat toward injector of interior surfaces of aluminum alloy thrust chamber coated with tungsten carbide (dark surface appearance). Coating extends from near injector to aft of throat.
Figure 7. - Development setup for welding of aluminum alloy thrust chamber.
Figure 8. - Thrust chamber of 347 stainless steel ready for brazing in pure, dry hydrogen furnace atmosphere using nickel-base brazing alloy.
Figure 9. - Comparison of elevated temperature yield strength of heat-resistant alloys.
Figure 10. - Comparison of heat-resistant alloys on basis of yield strength-density ratio.
Figure 11. - Root cracks in turbine buckets.
Figure 12. - Typical examples of stress corrosion cracking in 410 stainless steel heat treated to a high strength level and exposed to fuming nitric acid while stressed to a high level.
Figure 13. - Time to failure by stress corrosion cracking of 410 stainless steel exposed to fuming nitric acid as affected by acid temperature, imposed stress level, and material heat-treat condition.
Typical rates based on immersion for one month at 180°F

Corrosion rate calculated by formula:

\[ R = \frac{19.31 \cdot \Delta W}{dA t} \]

where

- \( R \) = corrosion rate, in./yr
- 19.31 = conversion factor
- \( \Delta W \) = weight loss due to corrosion, g
- \( d \) = density of specimen, lb/cu in.
- \( A \) = surface area of specimen, sq in.
- \( t \) = immersion time, hr

Figure 14. - Corrosion rates of 347 stainless steel and 6061-T6 aluminum exposed to 180°F liquid fuming nitric acids for 30 days.
Figure 15. - Strength of materials at very low temperatures.
Figure 16. - Effect of very low temperatures on ductility.
Figure 17. - Impact resistance at very low temperatures.
This paper provides a detailed review of the materials problems encountered in chemical liquid-propellant rocket systems and points out possible promising avenues for solving these problems.

1. Cooling - Rockets (3.10.5)
2. Alloys, Heat-Resisting (5.1.4)
3. Ceramics (5.1.5)
4. Plastics (5.1.6)
5. Protective Coatings (5.1.9)

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