TRENDS AND FUTURE DEVELOPMENTS
IN AEROSPACE MATERIALS

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ABSTRACT

This discussion treats the current state of the materials
trend and the developmental trends indicated for the period to
1970. Stresses and skin temperatures of manned vehicles can
be expected to increase as vehicle operations evolve kinet-
ically from Mercury orbital missions through Dyna Soar boost-
glide re-entry and eventual lunar re-entry. Many desirable
and promising materials for load-bearing and nonstructural
use under the natural and induced environments of aerospace
operations simply cannot be produced yet in the desired quan-
tities or shapes. Because of a lack of oxidation-resistant
alloys and suitable coatings for the refractory metals, their
use has been restricted to nonstructural applications. The
availability of structural-grade uniform alloy sheet is still not
optimum for molybdenum and columbium alloys. Tungsten
and tantalum alloy sheet of usable sizes is not generally avail-
able. The behavior under conditions of stress, temperature,
and oxidizing atmosphere is not too well understood and re-
quires considerable study. Behavior with coatings under these
conditions has not been investigated sufficiently to formulate
design concepts. Graphite is not currently available in the
necessary sizes or uniformity for immediate application as a
structural material; the need is shown for refractory carbide
development. Ceramics do not presently possess the requi-
site properties for immediate use.

A general evaluation of promising new materials includes
superalloys such as Nicrotung, Rene 41, Udimet 700 and Inco
717C. Projected improvements for refractory metals are ex-
amined, together with brief discussions of composites, plas-
tics, foams, metal fabrics, filament-wound structures, and
the use of metals as fuels. Coatings, elastomers, and adhe-
sives are discussed. Attention is also directed towards the
cryogenic behavior of both metals and nonmetals.
Introduction

Future aerospace operations -- through the sensible atmosphere into vacuum space and return -- will demand both the innovation of new materials and the refinement, adaptation, or combination of many currently available materials. The nature and scope of the aerospace mission will determine the performance and equipment specifications. The equipment requisites will, in turn, dictate the material requirements. The environmental parameters to be encountered -- and survived -- will vary with different types of missions, each of which will impose upon the vehicle a certain range of kinetic conditions.

The natural environments and the induced environments imposed by mission performance become interactive from the moment fueling of the vehicle stages commences. The degree to which vehicle operating loads, temperature gradients and heat flux, corrosion and oxidation, radiation effects, acoustic factors, and other considerations interact will vary in rate and amount with the type of operation. Figure 1 shows, for example, how projected average hot-side skin temperatures of manned vehicles can be expected to increase as operations evolve kinetically from Dyna Soar boost-glide to orbital re-entry and through lunar re-entry. Tactical vehicles may experience even higher deceleration maxima and heat flux.

This discussion treats the current state of the art for metals and nonmetals and the development trends indicated for the period to 1970. It is now obvious that meaningful materials data must be available before commencement of the engineering of spacecraft. Moreover, production technology for new materials generally lags from two to four years behind the technological advances made during development. Because of this, lead times for materials procurement must be extended. Many desirable and promising materials proved in research and development activities simply cannot be produced yet in the desired quantities or shapes.

An example can be seen in the case of the solar cells used in the Explorer VI and Pioneer V paddlewheel satellites. (1) Boron-diffused silica cells, coated with a 3-mil layer of filter glass were ordered from two sources. Sample batches worked well in the STL lab. But procurement of a sufficient number of these fragile cells that would meet quality control specs posed a serious problem. Both satellites were launched with only enough cells on hand, in each case, for a single, spare solar paddle. The two launches were seven months apart. As another example, the aus-formed steels developed in response to the demands for ultra-strength materials (2) are still in the
Figure 1. Temperature Trends for Manned Re-entry Vehicles.
SIXTH SYMPOSIUM ON BALLISTIC MISSILE AND AEROSPACE TECHNOLOGY

developmental stage; pilot work has not yet been translated into production requirements.

**Direction of Effort**

In an effort to examine current trends and future developments, it is instructive to contemplate briefly some of the past and present developmental trends. Almost without exception, surveys (3) have indicated that the most pressing needs are 1) more complete understanding of the space environment in which the materials must survive, and 2) comprehension of the nature of a specification before extensive materials development is undertaken. There have been instances of misuse of materials by designers, and cases in which programs were conducted at a high level of effort only to be abandoned eventually because the first statement of the problem proved to be erroneous. (4)

The design of re-entry vehicles in the 1950's is a case in point. Typical ways of expressing the characteristics required for nose cone materials were founded on the assumption of equilibrium conditions. By this postulation it could be shown how temperatures at, or exceeding, the melting point of any known material were to be expected. Exhaustive materials studies were initiated, but the problem was not resolved by this approach.

Concurrently, a critical appraisal of the thermal environment during re-entry led to the conclusion that transient heating was the design consideration. (4) Calculations of the magnitude of the heat pulse were verified by experimentation, (5) and a means of simulating the heat pulse was developed. With these test methods, it became possible to screen many promising materials and to utilize existing materials for the solution of the nose cone re-entry problem. (4)

A decade later, a somewhat similar problem is posed by the need for negotiating the aerospace environment. We do not yet understand the properties required of materials well enough to guide development programs. (4) All aspects of the space environment that could affect the behavior and performance of materials require clarification for the creation of evaluation techniques.

Considerable difference of opinion exists at this time as to the state of our materials efforts. While some highly regarded materials people feel that our programs are progressing fairly well and in the proper direction, others are of divergent opinion:

"There is wasteful work on exotic refractory metals and overlapping research activities in certain of the newer metal
applications... There are waves of fashionable research which, unfortunately, lead to insufficient research on older materials. "(6)

On the other hand, there is considerable evidence that the discovery, development, or adaptation of new materials could conceivably lead to a breakthrough that would advance markedly the state of the art in aerospace materials. The emergence of germanium helped advance the field of electronics. In certain specialized fields, titanium is providing the foundation for a whole new light metal technology comparable to that provided by aluminum. Zirconium has been transformed from a laboratory curiosity into a vital substance for atomic power technology. The entire nuclear program was founded on two metals: uranium, a relatively rare and unknown curiosity in the 1940's; and plutonium, an entirely man-made chemical element. (7)

Similarly, the design of a tailor-made material for some specific application holds both challenge and reward for the materials engineer. The revolutionary transistor depended upon the development of an appropriate semiconductor. Cubic boron nitride and the artificial diamond are the direct outgrowths of materials science. (2)

It is, then, obvious that activity is justified in both directions. Adaptation and/or combination of existent materials must be pursued vigorously. And the innovation of new special application materials must be encouraged. The level of effort in either direction will be determined largely by military and civilian aerospace mission requirements. It will be determined also by the development of evaluation techniques which are based on a broader fundamental understanding of materials and their behavior in complex aerospace structures and components.

At the current state of the art, three general approaches are being taken in the design of spacecraft to insure structural integrity. Materials people are seeking, first, to use refractory metals in areas of extremely high temperature, despite the relatively difficult fabrication problems. Certain desirable property improvements are indicated in figure 2 for the most readily available materials. The second approach seeks to devise cooling techniques through which temperatures can be maintained within the capabilities of superalloys or other alloys of lower melting point. (8) The third approach is to establish the vehicle geometry, maneuvering procedure, and operating regime—such as the Dyna Soar re-entry corridor—which permits temperature reduction to the degree where superalloys can be employed.
Refactory Metals

The application of refractory metals in both high-Mach-number aircraft and re-entry vehicles has been confined largely to discussion of temperatures between 2000°F and 4000°F, the corridor which is created by 5-degree and 50-degree re-entry angles of attack, respectively. Below 2000°F, the lighter weight superalloys are suitable; the heavier refractory metals can remain useful up to 4000°F to 5000°F.

For the stagnation area on a nose cone, re-entry temperatures of 4000°F-5000°F will require tungsten, tantalum, composites, and reinforced plastics. Here, heat resistance or heat dissipation is the primary requirement, with strength of only secondary consideration. Leading edges and other very hot areas of the structures will develop temperatures which can be accommodated by molybdenum or columbium in the primary structure. (8)

At present, only tungsten, tantalum, molybdenum, and columbium—and their alloys—remain for potential applicability for structures designed to operate above 2000°F. On a strength-to-weight basis, the lighter weights of columbium and molybdenum provide superiority to tungsten and tantalum in the 2000°F to 2500°F regime. Above this range, molybdenum and tantalum are comparable, with tungsten superior in all respects up to its useful limit of almost 4000°F. (8)

Lack of high temperature oxidation resistance is a critically limiting factor in the use of refractory metals. Columbium and tantalum are superior to tungsten in this characteristic. They are far better than molybdenum, which oxidizes so rapidly at 1700°F to 1800°F that its dense, bluish smoke literally obscures shop areas when the metal is being hot-worked. However, the oxidation rate of all four materials is too high to permit their use without a coating in re-entry vehicles. Inasmuch as re-entry conditions include the probability that temperatures created by the first bounce will be in the neighborhood of 4000°F, and since the limit of presently developed coatings is approximately 3000°F, great strides in coating improvements are necessary if the full potential of refractory metals is to be realized. (9) High priority experiments are underway with molybdenum disilicide coatings and other processes in connection with the Dyna Soar program.

Another significant design criterion that must be established for the individual vehicle and mission is the ultimate tension allowable, based on the temperatures encountered. Many mechanical properties of the refractory metals are presented in terms of the strain-hardened (cold-worked) condition. However, these strength levels may never be utilized, as the
Figure 2. Projected Improvements of Refractory Metals.

Temperature °F

1960

1965

1970

TEMPERATURE --

TRANSITION TEMPERATURE

RECRYSTALLIZATION

SHORT TIME SERVICE

LONG TIME SERVICE

COLUMBIUM

ALLOYS

MOLYBDENUM

ALLOYS

TANTALUM

ALLOYS

TUNGSTEN

ALLOYS
extreme heat of the first re-entry maneuver—even though it be of short duration—is sufficient to recrystallize the microstructure and reduce the allowable strength by as much as 50 percent. A molybdenum 0.5-percent titanium alloy, for example, can reach an ultimate tensile strength level of 115,000 psi, with 50 percent reduction by rolling. However, after a short exposure at 2580°F the ultimate strength in tension is less than 25,000 psi.

Thus, the magnitude of the high temperatures during the first re-entry bounce, for example, can completely recrystallize the thin gages in even a few seconds. Representative material thicknesses are 0.008 inch and 0.010 inch for the majority of applications.

Super alloys

It is in the temperature range of 1500° to about 2000°F that the nickel-base or chrome-base superalloys have been widely adopted because of their ability to withstand high stresses for sustained periods of time at these temperatures, and because superalloys are available in a wide variety of the required forms. This, together with the experience accumulated with these alloys, indicates that superalloys will become increasingly important in aerospace technology during the next few years. The refractory metals, as indicated previously, are still not in the large-scale production stage.

A significant expansion of the operating limits of superalloys has taken place with the development of more than a dozen new nickel-base and cobalt-base materials. Certain of these alloys are fabricable into sheet, while others are suitable only for precision casting.

The new nickel-base superalloys have much in common insofar as composition is concerned. All consist basically of a nickel-chromium solid solution, to which have been added various amounts of tungsten (8%), molybdenum (4 to 10%), and columbium (2%). The latter are used to strengthen the matrix solid solution and to participate in carbide formation. Except for Inconel "713 C," all the new nickel-base superalloys also contain appreciable amounts of cobalt, which increases the creep strength of precipitation-hardenable, nickel-base alloys; one (Unitemp 1753) contains 9.5 percent iron. Precipitation hardening, which contributes to the high-temperature strength, is brought about by the presence of aluminum (1.5 to 7.5%) and titanium (0.75 to 4%). Boron and zirconium are present in several of the newer superalloys and appear to have a beneficial effect on the high-temperature strength and ductility. In order for the alloys to be workable however, limitations have been placed upon the percentages of titanium, aluminum, zirconium, and boron present. (10)
Figure 3. Operating Temperature for 100-Hour Rupture Time and 15,000-psi Stress Level for Various Superalloys.
The new cobalt-base superalloys contain approximately 19- to 25-percent chromium; this, together with the carbon content, yields a high-strength base material hardened by a carbide-precipitation mechanism. Nickel is usually included in the alloys. At least one of the high-melting, carbide-forming elements such as tungsten, molybdenum, tantalum, and columbium is present in various amounts. Boron additions to the S-816 alloys have yielded improved high-temperature mechanical properties, while titanium is an important addition in the wrought alloys J-1570 and J-1650. (10)

Figure 3 illustrates how operating temperatures have been increased, based on a 100-hour rupture time at 15,000-psi stress. It should be noted that the properties of the casting alloys are for the as-cast condition, the condition in which they are normally used. Similarly, the workable alloys are delineated in the heat-treated condition. These representative properties are for illustrative purposes only.

High-Nickel Steels

The new 20- to 25-percent nickel iron alloys with steel-like crystal structures possess great potential for solid propellant casings and pressure vessel construction. These steels currently exhibit uniaxial yield strength approximating 280,000 psi; they also indicate a measurable toughness superior to that demonstrated by most of the presently employed high-strength steel.

High-Strength Titanium Alloys

Current and projected analyses of the alpha, alpha-beta, and beta of the titanium alloys indicate considerable promise for solid propellant casings. Effort is being extended on the improvement of solid-state structures concurrent with constituent modification for the purpose of refining microstructures, increasing the working strength, and improving weld ability. Heat treatments are also being studied which promise to improve mechanical properties that are not attainable at the present state of the art.

From the 190,000-psi tensile strength available from the present 6-aluminum/4-vanadium titanium alloy, it may be expected that 250,000-psi ultimate tensile strength can be developed from an all-beta titanium alloy in 1965, approximately 290,000 psi by 1968, and probably 315,000 psi by 1970.
High-Strength Aluminum Alloys

Recent investigations by Alcoa have resulted in the development of Cu-Mg-Zn alloy which exhibits strength-to-density ratios of the order of 1 million inches. (This, of course, is based on an ultimate tensile strength level of approximately 100,000 psi and a density of 0.10 pounds per cubic inch.) The alloy at present offers limited weldability. Further development effort will provide high weld-joint efficiencies and perhaps a 125,000-psi ultimate strength.

Coatings

In common with other metallic elements, W, Ta, Cb, and Mo display a considerable affinity for oxygen at elevated temperatures. Thus, the limiting factor in the case of most refractories is the availability of coatings which will protect the material from oxidation at high temperatures and from corrosion at room temperature. Development of such coatings will enable us to take advantage of the full useful strength ranges of refractory metals. Of the various techniques by which structural metals can be coated—namely, aluminum hot-dipping, metal spraying, electro-plating, electroless plating by chemical reduction, and vapor plating—it appears that coatings formed by vapor deposition might be particularly desirable because the temperature at which the coating is applied may be actually higher than that which the structure will reach in use.

For relatively narrow limits of radiation environment and internal heat generation loads, it has been possible to control the average equilibrium temperature within a closed vehicle (where thermal conduction and convection is negligible) by providing a surface of proper "color," or emission and reflection characteristics. Variations can be made to a limited extent in this color by the use of movable panels or vehicle orientation relative to radiation sources.

Thermochromic pigments, whose colors change with temperature, are known; a properly compounded mixture of such substances might automatically provide a control system. Alternatively, application of mechanical, electrical, chemical, or thermal signals to suitably sensitive colored materials could be made from within the vehicle.

The theory of the equilibrium temperature of a body in space as a function of radiation flux is well understood, and data are now being accumulated from satellites, space probes, and astronomical observations as to radiation flux patterns in the aerospace regime.
Development is required now of temperature control coatings with variable reflective and emissive characteristics for control of temperatures in orbiting vehicles containing variable heat generating devices. Such control should be maintained within the limits of $59^\circ$ to $86^\circ F$ through automatic or independently controlled variation of the reflective and emissive characteristics of the coating material. (11)

**Metal Fabrics**

The use of metal woven fabrics has interesting possibilities for aerospace applications. Wire mesh shows promise for spaceship antennas, solar collectors, re-entry structures, drag brakes, and certain inflatable, or expandable, structures.

For these representative applications, a maximum temperature of $1500^\circ F$ seems adequate at this time. One manufacturer selected Rene 41 as most promising, as considerable wire-drawing experience was available and fabrication methods were not radically difficult. It appears that metals such as Udiment 700 may replace Rene 41 in some applications as more fabrication experience is obtained with superalloys. (12)

Rene 41 wire of 0.0016-inch diameter has been woven into 200 x 200 count cloth (warp x fill count per inch) in plain, twill, and basket weaves. (This represents the finest weave, similar to percale sheet or dress shirt material.) Representative re-entry type tests have been conducted on these materials with suitable surface coatings. The tear strength of this woven cloth is greater than that of stainless steel shim stock of three times the cross-sectional area. The weave weighed approximately 13.60 ounces per square yard; this included a coating weight of 8.0 ounces per square yard applied to one side. The coating of a metal cloth may provide protection from oxidation. The coating material must have good adhesion to the basic material under static and dynamic conditions and good flexibility to facilitate packaging when required. Media such as metal powders, ceramic materials, powdered aluminum and antimony, carbon black, and iron oxide can be added to the base elastomers for improvement of high-temperature properties. (12)

Refractory metals may also find application in this area when properly coated. Recent experiments indicate that tungsten wire filaments or mesh can be protected against oxidation in stagnant or moving air at temperatures up to $3000^\circ F$ for periods as long as 20 minutes. This was achieved by applying a multilayer coating of chromium, silicon, and rhodium. It has been suggested that further improvement can be made if complete diffusion alloying, bonding, and melting of the surface coat is achieved over the entire length of the specimen. (13)
<table>
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<th>Metal</th>
<th>Energy Content (1000 BTU/LB Oxide)</th>
<th>Oxide Sublimation or Boiling Temp (°F)</th>
<th>Molecular Weight of Cooled Product</th>
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<tr>
<td>Hydrogen</td>
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<td>212</td>
<td>18</td>
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<tr>
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<td>4220</td>
<td>30</td>
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<td>Silicon</td>
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Figure 4. Metals As Fuels.
Metal Fuels

The use of metals as fuel constituents has received considerable attention in recent years. Figure 4 shows the more important metals which may be used as fuels. Of particular interest are the lighter metals including lithium, beryllium, boron, magnesium, and aluminum. Although none has the heating value of hydrogen, some compounds of boron and hydrogen have been developed as fuels that have better handling properties than either hydrogen or the elemental metal. A major difficulty with the boron-hydride class of fuels is the high fusion and vaporization temperatures of the oxide, resulting in liquid condensation in the working temperature range. This condensation can have a deleterious effect in the thrust produced by these fuels when burned in rocket motors. (5)

The use of aluminum as a component of solid rocket fuels is now making possible the production of fuels with appreciably improved specific impulses. However, high molecular weight such as exhibited by aluminum oxide is not a desirable characteristic of a working propellant. Thus, the lighter metals lithium, beryllium, and boron, and the hydrides of lithium and boron must be considered as solid-propellant constituents. (5)

Foamed Materials

Foamed plastics have demonstrated their high potential for aerospace applications. These polymers may be carried to the deployment location in compact, powdered form and expanded to many times the original volume without any increase in weight. In addition to the considerable rigidizing qualities, the foams offer promise as a micrometeorite attenuant; they can serve as ablating heat shields and may prove useful as high-energy impact absorbents or vehicle bumpers. One application features double-wall construction, with foamed materials sandwiched between; the inner wall serves as the load-bearing member. The foam-in-place systems are favored, additionally, because of their ability to be foamed within, or outside, the vehicle in space after launch. Polyurethane resins capable of being "heat-triggered" to foam after a period of suspended animation at low temperatures are receiving major attention. Polyvinyls, polyesters, epoxies, silicones, and phenolics have been designated for evaluation.

Translucent Beryllium Oxide

Translucent beryllium oxide is one of the more promising aerospace materials. Original interest in this ceramic was
created by its application to nuclear reactors. More properly known as polycrystalline dense beryllium oxide (BeO), this material has properties which make it desirable for use as a neutron moderator or reflector in high temperature reactor cores. BeO is second only to graphite as the best heat conductor of all non-metals. The material is being considered for numerous aerospace applications in which ceramic structural material would be subjected to high temperatures occurring simultaneously with high heat fluxes. The refractory properties of dense BeO and its resistance to corrosion in a gaseous environment make the material attractive for use as nozzles and other components in rocket motors.

The transparency of BeO to microwave transmission, combined with its strength at high temperatures and its resistance to thermal shock, make it particularly suitable for radome applications. BeO appears to be somewhat superior to alumina in this application because it has three to four times the resistance to thermal shock while having equivalent strength and electrical properties.

The resistance of BeO to corrosion by liquid metals suggests potential uses in various metallurgical processing operations such as the vacuum melting of refractory metals.

**Whiskers**

Fine single-crystal filaments, commonly referred to as "whiskers", are synthesized from various inorganic refractories and can attain high elastic strengths approaching 4 million psi, with correspondingly high modulus of elasticity levels.

The use of whiskers in reinforcement of certain organic materials can produce composites with mechanical strength levels five times greater than the strength of fiberglass reinforced plastics. The problems associated with the mass production of whiskers are complex, as is the subsequent fabrication into composite components. It is estimated that commercial production of whiskers suitable for reinforcements in both organic or metallic matrices may not be achieved until the late sixties. The potential, however, is so great that increased effort must be expended to devise methods of synthesizing defect-free long whiskers. It should be emphasized that only those crystallites which exhibit the highest strengths and elastic moduli are useful; no increase in strength occurs in the composite unless the modulus of elasticity of the fiber reinforcement exceeds that of the matrix.

Some progress has been made in the development of techniques for mass producing Al₂O₃ whiskers. Fibers of other substances such as B₄C, SiC, ZrO₂, and MgO are also under consideration.
Composite Materials

An interesting trend is seen in the development of synthesized composite materials based on structural plastics. These materials exhibit lightness, are thermally insulative, and have low erosion rates—characteristics which, for example, suit them admirably to rocket nozzle applications. The materials are basically structural plastic substrates covered, in turn, with porous insulators and erosion-resistant coatings.

Composite systems which have been found to be optimum consisted of an outer refractory surface layer, then a very thin metallic film; next came a porous insulating inorganic layer, and finally a structural plastic base material. The properties of individual components of the protective surfaces have been studied in subsonic and supersonic high-temperature gas streams. With the aid of these experimental results, composite surfaces were formulated and subsequently exposed in the same high temperature environments. Results showed a significant lag in heat penetration into the substrate structural plastic during hyperthermal exposure. Tungsten-faced ceramics exhibited desirable performance characteristics in high-temperature reducing atmospheres; nickel-coated zirconia surfaces were optimum in high-temperature oxidizing environments. The principal problems encountered with the protective composite systems were developing suitable methods of fabrication, and preventing separation of laminates during exposure to temperatures up to 5400°F. (15)

Ablative PlasticChars

Research on ablative plastic chars has uncovered new information on their physical structure. New data on the chemical mechanism of the ablative process has also been revealed. One important ablative mechanism is that some plastics decompose into gases which undergo further decomposition into carbon and lower molecular-weight gases. This carbon is deposited in the surface region of the char, reinforcing it and making it more resistant to erosion. Results of this research are being used to synthesize new improved ablative plastics. (16)

Techniques have been developed for studying the microstructure of ablative plastic chars. One method consists of impregnating the porous char with plastic so that its structure is permanently rigidized in its asformed state. The impregnated char is surface-ground and polished, then magnified photographs of the surface are made. From the photographs,
Figure 5. Elastomer Applications.
information on cell structure—including cell diameter and wall thickness—are being obtained. These data are then correlated with ablation performance and materials constructions. Investigation of ablative plastics and composites in simulated propulsion combustion gas environments has provided insight in promising materials constructions and revealed new concepts of thermal protection. Plastics containing vitreous silica fibers oriented normal to the gas flow have outstanding resistance to erosion. Phenolic resins with high carbon content and high cross-linking appear most promising. The concept of using highly gasifying plastics upstream of the throat section in nozzle specimens has been found in exploratory work to have considerable promise.

New concepts in low-erosion-rate plastic composites for re-entry environments have been investigated. One promising material, containing carbon fiber reinforcement had extremely small dimensional loss and good surface and shape retention after exposure in a 15,000°F air plasma stream. (15)

Elastomers and Compliant Materials

Elastomers are classified generally by characteristics of elasticity as contrasted with their degree of brittleness. Higher temperature and shorter exposure trends continue in elastomer applications. Present organic elastomers are useful for approximately 100 hours at 500°F and for several hours at 600°F. Inorganic composite seal materials show promise for use at 1000 degrees, but lack the high degree of resilience and ease of deflection desired in an ideal seal material. (See Figure 5.)

High temperature adhesion studies of the better heat resistant elastomers (namely resin-cured butyl, fluoroelastomers, silicone rubbers) with the new wholly aromatic polyamide fiber (HT) have been very encouraging. Preliminary evaluations have shown this elastomer-fiber combination to be superior with regard to high temperature performance (temperature range from 350°F to 550°F) to previously available elastomer-nylon, glass or wire cord combinations. Such improved fiber-reinforced elastomer systems would be extremely useful in applications such as flexible connectors, fuel containers, tires, etc. Improved fluoro-elastomer and silicone rubber compounds have been developed which are resistant to temperatures of 600° to 1000°F for short-time exposures of five minutes or less. (17) These elastomeric materials may prove especially useful under re-entry regimes.
Plastics Development

Efforts are being directed toward synthesis of improved lightweight, thermally resistant insulating materials for propulsion system applications and use on manned hypersonic vehicles. Present effort is directed toward conversion of polymers--with and without reactive filters--to refractory species. New resins with higher carbonization efficiency, and inorganic polymers with molecular backbones of elements other than carbon also appear promising. Semi-rigid ablative plastics with improved resistance to rupture and crack formation appear to have potential for propulsion environments. (See Figures 6 and 7.)

Organic and Inorganic Adhesives

The increasing needs for high-strength, temperature-resistant structural adhesives require increased activity in the field of inorganic materials as a source for component materials. Principal current investigations are centered on ceramic, cermet, inorganic polymers, and metallo-organic type base materials and combinations thereof. A temperature of 2000°F is considered as the target. For less severe requirements in the range of approximately 700°F, investigations are under way on two promising organic polymer systems--polyisocyanurates and polymeric chelates.

Research programs on the heat-stabilizing effects of various metallic oxides as additives to adhesive formulations has resulted in an adhesive which displays target tensile shear strength (1000 psi) in short-time (10-minute) exposures to 600°F and 750 psi after 200 hours at 600°F.

A two-part, low-pressure, ambient-temperature-curing adhesive system based on an epoxylated glycerine-modified, amine-cured novolac epoxy was developed to meet prime target strength and pot life requirements. One contractor's concept of using metallic chromates as filler material was an entirely new approach to the problem of overcoming a heretofore general susceptibility to salt spray exposures of epoxy resin-based adhesive metal-to-metal bonds. Adhesives of this type are of particular need in the field repair of flight vehicle structures where the thermosetting adhesives are not at hand.

Inorganic nonpolymeric (ceramic type) adhesives have been developed which in metal-to-metal bonds on stainless steel adherents display mean tensile strength values of nearly 2000 psi at room temperature and close to 1000 psi at 800°F. Sandwich panels with core facings of stainless steel are showing substantial flexure and edgewise compression strengths.
Figure 6. Plastic Materials for 0.1-Hr Service.
Bonds have been prepared with Iconel X as the adherent metal, that display room-temperature tensile strengths in the order of 1800 psi, with no appreciable weakening at temperatures to 1100°F. Work is continuing along various approaches to develop adhesives which can be adapted to bonding still higher-temperature-resistant metals such as refractories to provide structurally sound bonded composites.

Research efforts on adhesives will continue to be primarily directed toward attaining high temperature durability in metal-to-metal bonds. Based on the more promising developments to date in the field of inorganic nonpolymeric, ceramic type, adhesives, efforts will be continued in this area. However, work will continue also in exploiting the fullest capabilities of organic polymeric and metallo-organic systems as potential adhesives components.

Proper preparation of adherent metal surfaces prior to adhesive application has been shown to be a necessary and integral factor in the ultimate strength and durability of a bonded joint. This has been shown to be specific for both a given adhesive type and a given metal or alloy. Investigation of such factors are being made in direct connection with the individual adhesive research programs.

Particular emphasis in the investigations of ceramic-type adhesives will be placed on obtaining bonds with resistance to temperatures much higher than those required to mature or cure the bonds. This effort will include investigations of air-setting adhesives and a means of developing moisture absorption. Further research will be conducted toward developing formulations and processing techniques which will impart ductility and toughness—as opposed to brittleness—in the bonds.

**Filament Windings**

Recent studies in the field of materials have shown that large weight savings can be made through extensive use of filament windings as the basic structural material for aerospace structures, particularly pressurized components. Some of the structural advantages of filament winding are a high strength-to-weight ratio, corrosion resistance, and lack of creep at working stress. The pressure-vessel type structure can be wound in such a manner as to provide a ratio of allowable radial-to-axial stress. This allows efficient design for radial loads due to burst pressures and longitudinal loads resulting from both burst pressure and axial loads. This is possible because the filaments have uniaxial strength that can be oriented in any required geometric pattern. Engineering metals are essentially isotropic in behavior, and thus do not
Figure 7. Plastic Materials for 1000-Hr Service.
exhibit maximum efficiency in any particular orientation; for example, the longitudinal direction of cylindrical pressure vessels.

Many glass-reinforced plastics structures are stronger on a unit-weight basis than metals. But putting the reinforced composite together in such a way that the primary load-bearing members—namely the glass filaments—are used to maximum efficiency in the final structure is the aim of the filament winding technique.

The fact that the individual filaments are primarily loaded only unidirectionally in tension makes it possible to design structures of maximum efficiency. For example, in cylindrical pressure vessels, the ratio of hoop stress to longitudinal stress acting in the wall is 2:1.

In metal pressure vessel design, the benefit of the sphere over the cylinder is that the same stress is present in both directions. In designing cylinders in metal, although the longitudinal stress is only one-half the hoop stress, the wall thickness must be designed to withstand the hoop stress. Consequently, since metals are essentially isotropic in strength, the product of operating pressure and volume capacity (PV) per unit weight of material is less in the cylinder than in the sphere for a given peak stress. (18)

In filament-wound cylinders, however, the reinforcement is so oriented and proportioned that the hoop strength of the cylinder wall is actually twice the longitudinal strength.

Most of the work performed to date on the larger, irregularly shaped, wound structures has been through developmental trial and error. One of the largest primary structures yet produced by filament winding was a 950-pound propellant tank 8 feet in diameter and 17 feet long.

An extremely interesting material, from the material engineer's standpoint, is a filament-oriented prepreg material. The purpose of the material is to combine the preorientation of filament inherent in filament winding with the shape flexibility inherent in molding flat prepreg reinforced plastics.

This material is made by winding impregnated glass roving on a cylindrical mandrel in a predetermined helix. The cylindrical structure thus produced is then slit axially, flattened and molded, or the resin can be B-staged. The material can be molded by bag or matched metal techniques.

At present, conventional E-glass in the form of roving is by far the most commonly used reinforcement in filament winding. But improvements in both type and form of reinforcement promise future property improvement, as well as increased versatility in the process. Development interest is now centered on higher modulus glass reinforcement.
<table>
<thead>
<tr>
<th></th>
<th>Filament Laminate</th>
<th>Cylinder Design Values</th>
<th>Sphere Design Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hoop</td>
<td>Longitudinal</td>
<td></td>
</tr>
<tr>
<td>GLASS STEEL</td>
<td>200</td>
<td>140</td>
<td>315</td>
</tr>
<tr>
<td>STEEL</td>
<td>450</td>
<td>140</td>
<td>93</td>
</tr>
<tr>
<td>GLASS STEEL</td>
<td>210</td>
<td>47</td>
<td>105</td>
</tr>
<tr>
<td>STEEL</td>
<td>70</td>
<td>158</td>
<td></td>
</tr>
</tbody>
</table>

**Ultimate Tensile Strength, 1000 PSI**

- Glass Steel: 200
- Steel: 450
- Glass Steel: 140
- Steel: 140
- Glass Steel: 315
- Steel: 93
- Glass Steel: 210
- Steel: 47
- Glass Steel: 70
- Steel: 158

**Tensile Modulus of Elasticity, 10^6 PSI**

- Glass Steel: 10
- Steel: 29
- Glass Steel: 70
- Steel: 20.3
- Glass Steel: 235
- Steel: 13.5
- Glass Steel: 6.6
- Steel: 3.5
- Glass Steel: 10.2

**Total Elongation, %**

- Glass Steel: 2.0
- Steel: 1.6
- Glass Steel: 2.0
- Steel: 1.6
- Glass Steel: 2.0
- Steel: 1.6
- Glass Steel: 2.0
- Steel: 1.6
- Glass Steel: 2.0

**Density, LB/CU IN.**

- Glass Steel: 0.92
- Steel: 0.283
- Glass Steel: 0.077
- Steel: 0.077
- Glass Steel: 0.209
- Steel: 0.077
- Glass Steel: 0.209
- Steel: 0.077
- Glass Steel: 0.209

**Strength-Weight Ratio, 10^6 IN.**

- Glass Steel: 2.17
- Steel: 1.59
- Glass Steel: 1.82
- Steel: 1.51
- Glass Steel: 1.21
- Steel: 1.0
- Glass Steel: 0.60
- Steel: 0.50
- Glass Steel: 0.91
- Steel: 0.75

Figure 8. Comparison of Steel Versus Glass Reinforcement for Filament Winding.
For higher temperature applications, high silica and quartz fibers could be useful. Unfortunately, high silica fibers such as Refrasil have only about one-fourth the strength of E glass. Quartz fibers, although somewhat stronger, are extremely expensive; namely, about $60 per pound. For long-term, high-temperature applications, E glass is satisfactory for use with any of the resin systems developed to date. (Of possible future interest also are yarns made of ceramic fibers.)

High-strength metal filament (0.004 to 0.005-in. diameter wire) reinforcement provides substantial increases in strength and modulus, as shown by the strength data and design values shown in Figure 8. However, strength-weight ratios are still lower than those obtainable with glass.

One of the most recent developments in metal wire for reinforcement is a 575,000-psi high carbon steel wire in diameters of approximately 0.004 inch. Although this strength level improves strength-weight ratios, ratios are still not so high as those of glass-reinforced structures. (18)

Metals at Cryogenic Temperatures

Because of the behavior of certain materials at low temperatures, the selection of materials for use in forthcoming liquid hydrogen propellant missile systems presents a challenge to the engineer. First generation Atlas and Titan I missiles are built of structural and nonstructural materials for service at temperatures as low as -300°F. The second generation liquid propellant missiles will utilize materials at temperatures as low as -423°F. Although the temperature variation between LH₂ and lox is not too great, the difference in materials properties can be significant.

From the dearth of data available, it appears that certain structural materials now in use should be satisfactory at LH₂ temperatures. Others that can be used at lox temperatures appear less satisfactory for service at the lower LH₂ temperature range. (19)

The effect of cryogenic temperatures on materials properties varies with the alloy content, microstructure, and the condition of the alloy. Behavior of an alloy at cryogenic temperatures is also considerably dependent on design configuration and geometry. The designer is faced frequently with decreased toughness in a metal which becomes increasingly notch-sensitive at lower temperatures. In general, the strength of metals increases as the temperature decreases. But along with this increase in strength is a corresponding decrease in ductility. The strength properties attained at low temperatures are usually desirable with, however, an unwelcome tendency toward brittle behavior.
<table>
<thead>
<tr>
<th>TEMP, °F</th>
<th>$F_{tu}$, KSI</th>
<th>$F_{ty}$, KSI</th>
<th>$E$, $10^6$ PSI</th>
<th>NOTCHED, $F_{tu}$</th>
<th>NOTCHED TENSILE RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROOM</td>
<td>72.3</td>
<td>60.5</td>
<td>10.0</td>
<td>101.0</td>
<td>1.40</td>
</tr>
<tr>
<td>-110</td>
<td>75.2</td>
<td>64.8</td>
<td>10.1</td>
<td>103.0</td>
<td>1.37</td>
</tr>
<tr>
<td>-321</td>
<td>83.2</td>
<td>74.4</td>
<td>11.3</td>
<td>105.0</td>
<td>1.26</td>
</tr>
<tr>
<td>-423</td>
<td>93.2</td>
<td>82.0</td>
<td>10.6</td>
<td>99.6</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Figure 9. Results of Tensile Tests on Notched and Unnotched Specimens of 7079-T6 Aluminum Alloy Billet.
The principal type of brittleness encountered at low temperatures is attributed to ductile-to-brittle transition behavior. This, fortunately, is unique to certain metal systems. The transition temperature may be defined as that range below which the metal fractures with little or no plastic deformation. Another cause of brittleness, primarily in ferrous base alloys, is attributed to metallurgical phase transformation. Figures 9 through 12 show that certain alloys show particularly good behavior to temperatures as low as -423°F.

Certain design applications are dependent on materials which do not exhibit the ductile-to-brittle transition. These include aluminum and austenitic stainless steel alloys. The cold-worked aluminum alloys, 5052-H38 and 5456-H38, and the precipitation-hardenable 2024-T6 alloy have been used with considerable success at temperatures as low as -423°F. AISI 301-XH stainless steel has exhibited similar advantages. (19)

The alpha titaniums also show exceedingly good promise for low-temperature designs, with considerable experience available on Ti-5Al-2.5Sn. An alpha-beta type titanium alloy has been fabricated for LH₂ containment by one manufacturer.

When consideration is given the behavior of nonmetals at cryogenic temperatures, it is noted that, compared to metals, the nonmetals demonstrate poor low-temperature ductility. (See Figure 13.)

Measurement Techniques

In seeking to develop materials and evaluate them for use over periods up to three or four years in aerospace environments, activity will include determination and study of normal physical properties, along with optical and electrical properties as applicable. Tests must be devised from which long-life properties can be predicted from short-time tests. Key experiments on test vehicles to correlate test results in simulated environments with actual aerospace results are also under way.

Considerable study is required to determine and/or develop the necessary instrumentation best suited to measure and telemeter changes in characteristics of materials during long-time flight in aerospace environments. This will provide a means for a limited number of key experiments which can be used for validating results from simulation tests.

Most effects on materials have been predicted from simulated environmental tests on the ground, or from measurements on the environment and prediction of probable effects on materials. One available method that can be adapted is based on the change in electrical resistance with the change.
<table>
<thead>
<tr>
<th>TEMP, °F</th>
<th>$F_{tu}$, KSI</th>
<th>$F_{ty}$, KSI</th>
<th>$E$, $10^6$ PSI</th>
<th>NOTCHED, $F_{tu}$</th>
<th>NOTCHED TENSILE RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROOM</td>
<td>269.0</td>
<td>225.0</td>
<td>28.4</td>
<td>344.0</td>
<td>1.28</td>
</tr>
<tr>
<td>-110</td>
<td>281.0</td>
<td>239.0</td>
<td>30.6</td>
<td>349.0</td>
<td>1.24</td>
</tr>
<tr>
<td>-321</td>
<td>319.0</td>
<td>278.0</td>
<td>30.6</td>
<td>269.5</td>
<td>0.85</td>
</tr>
<tr>
<td>-423</td>
<td>332.0</td>
<td>--</td>
<td>30.4</td>
<td>199.0</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Figure 10. Results of Tensile Tests on Notched and Unnotched Specimens of AISI 4340 Steel Bar.
<table>
<thead>
<tr>
<th>TEMP, °F</th>
<th>F_{tu}, KSI</th>
<th>F_{ty}, KSI</th>
<th>E, 10^6 PSI</th>
<th>NOTCHED, F_{tu}</th>
<th>NOTCHED TENSILE RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROOM</td>
<td>141.0</td>
<td>129.0</td>
<td>15.5</td>
<td>161.0</td>
<td>1.14</td>
</tr>
<tr>
<td>-110</td>
<td>167.0</td>
<td>156.0</td>
<td>15.9</td>
<td>193.0</td>
<td>1.16</td>
</tr>
<tr>
<td>-321</td>
<td>223.0</td>
<td>212.0</td>
<td>16.7</td>
<td>253.0</td>
<td>1.13</td>
</tr>
<tr>
<td>-423</td>
<td>267.0</td>
<td>260.0</td>
<td>19.4</td>
<td>234.0</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Figure 11. Results of Tensile Tests on Notched and Unnotched Specimens of Annealed 6AL-4V Titanium Alloy Sheet.
<table>
<thead>
<tr>
<th>TEMP, °F</th>
<th>$F_{tu}$, KSI</th>
<th>NOTCHED, $F_{tu}$</th>
<th>NOTCHED TENSILE RATIO</th>
<th>TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROOM</td>
<td>185.0</td>
<td>205.0</td>
<td>1.11</td>
<td>42% COLD WORK</td>
</tr>
<tr>
<td>-320</td>
<td>293.0</td>
<td>249.0</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>-423</td>
<td>289.0</td>
<td>238.0</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>ROOM</td>
<td>224.0</td>
<td>241.0</td>
<td>0.94</td>
<td>62% COLD WORK</td>
</tr>
<tr>
<td>-320</td>
<td>316.0</td>
<td>301.0</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>-423</td>
<td>323.0</td>
<td>303.0</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>ROOM</td>
<td>298.0</td>
<td>217.0</td>
<td>0.73</td>
<td>78% COLD WORK</td>
</tr>
<tr>
<td>-320</td>
<td>367.0</td>
<td>290.0</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>-423</td>
<td>423.0</td>
<td>241.0</td>
<td>0.57</td>
<td></td>
</tr>
</tbody>
</table>

Figure 12. Results of Tensile Tests on Notched and Unnotched Specimens of Cold Rolled 301 Stainless Steel.
<table>
<thead>
<tr>
<th>LAMINATE</th>
<th>TEMPERATURE</th>
<th>ULTIMATE TENSILE, PSI</th>
<th>TENSILE MODULUS, PSI</th>
<th>STRENGTH/WEIGHT, INCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHENOLIC GLASS</td>
<td>77</td>
<td>56,300</td>
<td>2.7 x 10^6</td>
<td>8.45 x 10^5</td>
</tr>
<tr>
<td>(COAST F-120-14)</td>
<td>-320</td>
<td>95,400</td>
<td>3.0</td>
<td>1.4 x 10^6</td>
</tr>
<tr>
<td>POLYESTER GLASS</td>
<td>77</td>
<td>57,000</td>
<td>2.9 x 10^6</td>
<td>8.55 x 10^5</td>
</tr>
<tr>
<td>(U.S. POLYMERIC C)</td>
<td>-320</td>
<td>95,400</td>
<td>3.0</td>
<td>1.43 x 10^6</td>
</tr>
<tr>
<td>SILICONE GLASS</td>
<td>77</td>
<td>38,800</td>
<td>2.8 x 10^6</td>
<td>5.81 x 10^5</td>
</tr>
<tr>
<td>(COAST F-130-14)</td>
<td>-320</td>
<td>76,800</td>
<td>2.8</td>
<td>1.15 x 10^6</td>
</tr>
<tr>
<td>EPOXY GLASS</td>
<td>77</td>
<td>60,700</td>
<td>2.9 x 10^6</td>
<td>9.1 x 10^5</td>
</tr>
<tr>
<td>(COAST F-150-14)</td>
<td>-320</td>
<td>107,500</td>
<td>4.3</td>
<td>1.61 x 10^6</td>
</tr>
<tr>
<td>POLYESTER GLASS</td>
<td>77</td>
<td>41,800</td>
<td>3.2 x 10^6</td>
<td>6.27 x 10^5</td>
</tr>
<tr>
<td>(181 SELECTRON 5003, WADC REPORTS 5662)</td>
<td>-320</td>
<td>70,000 ULTIMATE COMPRESSION</td>
<td>3.7 x 10^6</td>
<td>1.05 x 10^6</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>42,500</td>
<td>3.6 x 10^6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-320</td>
<td>58,250</td>
<td>4.0 x 10^6</td>
<td></td>
</tr>
</tbody>
</table>

Figure 13. Properties of Structural Plastics at Cryogenic Temperature.
Figure 14. Materials Characteristics.

- Aluminum
- Magnesium
- Beryllium
- Steel Alloys
- Vanadium
- Titanium
- Tantalum
- Molybdenum
- Graphite
- Carbides (TiC)
- Reinforced Plastics
- Glass
- Borides (ZrB₂)
- Oxides
- Nitrides (ZrN)
- Cermets
- Single-Crystal Fibers

- Melting Temperature
- Maximum Serviceable Temperature
- Room Temp. Strength
- Uniaxial (Uniaxial)
- Compressive (Compressive)
- Transverse (Transverse)

Values in psi:
- 60,000
- 80,000
- 100,000
- 120,000
- 130,000
- 150,000
- 170,000
- 190,000
- 210,000
- 230,000
- 250,000
- 285,000
- 300,000
- 330,000
- 360,000
- 400,000
- 500,000
- 600,000
- 700,000
- 800,000
- 900,000
- 1,000,000
- 1,200,000
- 1,400,000
- 1,600,000
- 1,800,000
- 2,000,000
in cross section of a wire or metal film. Using the corrosometer technique, even microscopic changes caused by erosion, corrosion, or electromagnetic radiation could be detected. Sputtering, ionization, sublimation, or vaporization are several of the deteriorative mechanisms that could be measured by this technique. (20)

**Cushioning Materials**

Vehicles designed for lunar operations will require materials with shock-absorbing and/or vibration-damping characteristics. Such materials will be designed to protect occupants and instrumentation from high-g forces during soft and hard landings on the Moon. Transmissibilities of the order of 2 or less and cushion factors of approximately 2 or less for resilient materials will be needed. For crushable (bumper) materials, energy absorbing qualities of the order of 1000 foot pounds per pound or greater are desired.

Currently, the best crushable materials available have an energy absorbing capacity of 5000 foot-pounds per pound at an impact velocity of 27 feet per second. Present materials have cushioning factors of the order of 3 and transmissibility of approximately 3.5. (21)

**Shielding Materials**

The need exists for development of shielding materials for various types of radiation, including gamma, neutron, Van Allen, and cosmic types which can serve also as load-bearing materials.

Current thinking devoted to methods for developing materials to provide neutron shielding is centered on heavy metal hydrides. These materials combine most of the essential properties but are thermally unstable and lack sufficient strength. Lead tungsten, depleted uranium, and tantalum are of interest for gamma attenuation, but these oxidize at high temperatures. Some of the rare earths have good neutron capture ability, but the cost to date is prohibitive. (22)

**Summary Statement**

It is apparent from the foregoing that material technology must be acquired within the next four years to make possible the development of ultra-high-strength metals, nonmetals, and composites that exhibit the near ultimate in theoretical strength and strength-to-weight characteristics. In order to facilitate such development, a broader fundamental understanding must be gained in the very near future concerning the
nature of the aerospace environment in which the materials must survive serviceably. Definite establishment of the aerodynamic, thermodynamic, and electrical properties of the hypersonic flow environment would, for example, delineate very definite materials engineering approaches. The representative materials listed in Figure 14 indicate generally the serviceability at the current state of the art.

This report represents a general survey and integration of industry efforts in certain materials areas only. For this reason, and for proprietary considerations attendant upon specific materials recommendations, no attempt is made to arrive at conclusions.

Acknowledgements

The authors are especially grateful for the cooperation of the Materials Advisory Board Panel, National Academy of Sciences, National Research Council, Aerospace Industries Association, and the Air Research and Development Command WADD Materials Central. Many of the illustrations and certain portions of the text material were adapted from work accomplished originally by these organizations.

References


239

