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Materials for Astronautic Vehicles\*

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#### SUMMARY

The nature of the environment in outer space and its significance for materials of construction of astronautic vehicles are considered.

The most advanced experience with heat-resisting engineering materials has been gained in gas turbine applications. The potential developments towards higher operating temperatures of alloys based on iron, nickel and cobalt are approaching exhaustion. The next stage may use the higher melting point metals, especially molybdenum, columbium and tungsten, non-metallics such as carbon and ceramics, or combinations of metals and ceramics. The refractory metals are capable of stressed service at 2500°F. (1370°C.) and higher, if means of protection against oxidation can be found. On the same condition graphite can be used for much higher temperatures.

For the ballistic missile, ablation of surface layers on the nose cone offers the best prospect of successful heat-dissipation. The ablating material may be an organic material, e.g. synthetic resin, or a ceramic compound. For longer spells at high temperatures, as in satellites on re-entry, the alternatives are thermal insulation by non-metallic surface coatings, and skins of metals having very high melting points. Coatings which provide insulation and protection from oxidation are provided as flame-sprayed ceramic oxides, especially alumina and zirconia, or ceramics reinforced by a refractory metal grid attached to the base metal.

The major technical difficulties in applying the refractory metals to service at very high temperatures arise from their reactivity with ambient gases, especially oxygen, and their tendency to brittleness at low and moderate temperatures.

Characteristics of materials which acquire special importance in astronautic applications are: thermal conductivity, specific heat, latent heat of fusion and evaporation, coefficient of thermal expansion, reactivity at high temperatures, sensitivity to irradiation, creep strength and resistance to high fatigue stresses at high temperatures and mechanical properties at low temperatures.

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#### Introduction

The materials specialist, and the metallurgist in particular, has become accustomed in this generation to finding himself in the position where the pace of engineering progress is dependent on his success in developing improved materials. In an earlier age the change from timber to iron in the construction of ships was not a condition for a revolutionary change in water-borne transportation, nor did it effect any immediate transformation. In heavier-than-air aviation the spruce wood of which the first aircraft frames were built served very well for the same purpose in highly efficient aeroplanes for many years after metal construction had been widely adopted. But as the ambitions of the engineer have driven him to attempt ever more onerous tasks the record shows, from time to time a pause, indicating an exhaustion of the capabilities of the existing materials for structural or automotive components. Then a metallurgical obstacle is overcome, and engineering achievement bounds forward again. We have seen this in the steam turbine and, more dramatically, in the gas turbine. In the field of nuclear energy the same story is familiar. It need not be a cause for surprise, therefore, if in this new adventure into astronautics materials are found to play a vital role.

#### Conditions in Outer Space

In order to assess the demands which astronautics will make in this direction we must first consider the nature of the environment in which astronautic vehicles will operate and the working conditions which this imposes on the materials of structure and propulsive unit.

The features of outer space which appear to merit consideration in this connection are the extremely high vacuum, low temperatures, solar radiation, cosmic rays, X-rays and electrons, meteoric bombardment, and ionised and dissociated gases.

At altitudes of 100 to 1,000 km. (62 to 620 miles) in the orbits of satellites the static atmospheric pressures are expected to be in the range 10<sup>-7</sup> to 10<sup>-10</sup> mm. Hg. Further out into space the atmospheric pressure will be almost absolute zero. A consequence of these extremely low pressures which might not have been foreseen is that sliding friction between metals becomes very high, doubtlessly because of the absence of sufficient oxygen to renew an oxide film and thus to prevent "cold welding" between the metallic surfaces. Dry, non-volatile, lubricants such as molybdenum disulphide and graphite suggest themselves for service under these conditions.

In outer space the mean equilibrium temperature of a body which is not a source of heat is said to be about 3°K, i.e. -270°C. or -454°F. The characteristics of metals to which one would give attention in judging their suitability for service at these temperatures are the electrical properties, as super-conductivity may be attained, and the mechanical properties. As regards the latter, experiments in cryogenic laboratories do not lead to the expectation that all metals will become brittle at the low temperatures. In the case of those metals in which a transition from high to low shock-resistance occurs at a temperature in the "terrestrial" range, e.g. around 0°C., 32°F., the tendency to brittle fracture must be expected to become more marked at lower temperatures. This includes the metals having body-centred cubic crystal structures: iron and ferritic alloys, molybdenum and the other metals of very high melting points.

At the mean distance between Sun and Earth (150 x  $10^6$  km.;  $93 \times 10^6$  miles) the total radiation energy falling perpendicularly on a unit area is 7.38 B. Th. U./sq.ft. (1860 cals./sq.m.) per minute. This intensity of heating cannot be said to impose any serious difficulty or limitation in the use of the materials which the engineer is accustomed to employ on Earth.

Cosmic rays are a stream of electrically charged atomic nuclei at energy levels of  $10^{17}$  to  $10^{18}$  e V, equivalent to 0.5 ft. lb. (0.68 joules) per particle. Opinions differ as to the hazard they present to human astronauts, but their effects on structural materials are not likely to be appreciable. The same may be said of the auroral X-rays and electrons. Cosmic rays, X-rays and electrons would penetrate normal metallic and non-metallic skins with complicating effects on electronic apparatus within the vehicle. This would not become a matter of concern to metallurgists unless they were asked to provide screening against the radiation. As far as can be seen general screening by heavy metals would be precluded on account of the weight penalty.

Meteoric bombardment introduces a more likely cause of mechanical damage to the structure. Fortunately the probability of meteoric particles of disconcerting momentum hitting a satellite is very low, assuming that by navigation the orbits of known comets and meteoric showers are avoided. The larger the meteorite, the less probable is a collision. On an area of 1,000 sq.ft. (93 sq.metres) an impact from a meteorite of 0.16 in. (4 mm.) diameter would only occur on average once in 250,000 years, and from a particle of 0.024 in. (0.6 mm.) diameter once in 20 years. A duralumin skin of 0.04 in. (1 mm.) thickness would stop meteorites up to 0.06 in. (0.16 mm.) diameter: a collision with such a particle would occur once

in  $2\frac{1}{2}$  years. The risk of penetration of the skin by meteorites is therefore very small. Abrasion by cosmic dust is more probable and roughening of the skin from this cause would almost certainly change the emissivity, with possibly significant effects on the temperature equilibrium in the vehicle.

Ionisation and dissociation of gases would imply enhanced chemical activity with oxidisable metals and organic compounds, but the probable magnitude of this effect is not regarded as serious in respect of structural materials.

#### Induced Environment

Turning from a survey of the physical features of the regions into which the astronautic vehicle will enter, let us consider the effects which the motion of the vehicle in this environment will impose upon its materials of construction.

First there are the stresses and high temperatures within the propellant components, rockets, plasma jets or other engines. Assuming that design, construction and operation have succeeded in meeting the demands in this domain, the vehicle in flight is subjected to mechanical and thermal loads the magnitudes of which are intimately related to its flight path and velocity.

It would appear that in respect of those loads which are calculable from the specified masses and accelerations, the designer is not faced with a major difficulty. The acceleration during take-off in an Earth-launching may be in the order of 10 g. Vibratory accelerations of up to 40 g with frequencies of 5 to 2,000 cycles per second have been mentioned, but these again have not been found to be a cause of profound concern, possibly because of their very brief duration. Acoustic noise of great intensity will generally be in evidence at, and immediately following, launching. Values of 180 dB are spoken of: account would certainly have to be taken of this factor as a significant contributor to fatigue-inducing forces.

#### Effects of High Temperatures

In the foregoing brief review of the regime in which astronautical vehicles must voyage much is a matter of conjecture, but in one direction there can be no doubt about the magnitude of the problem arising in the selection of materials. This is in the temperature which will be attained by the skin and structure of the vehicle. It is this portion of the vehicle to which I wish to pay most attention, but it may be useful to refer

first to the conditions in the propulsion system, since historically it is in this department that the metallurgist has won most of his experience of stressed components operating at high temperatures.

Considering the conventional chemical rocket motor, high gas temperatures are necessary for efficient operation. The specific thrust is directly proportional to the square root of the absolute gas temperature in the combustion chamber. It is not possible, however, to take full advantage of the solid propellants available, because of the limitations of the nozzle materials. With liquid propellants it is generally feasible to provide forced convection cooling for the nozzle, and its inner surface can be protected with a film of propellant. Abrasion by aluminium oxide particles, originating in the aluminium sometimes included in the propellant, aggravates the difficulty in finding a nozzle material for solid propellants capable of surviving without appreciable loss of contour for the required period of about 30 seconds. Present-day wall temperatures at the throat of the exhaust nozzle with liquid propellants are, in fact, of the order of 1800°F. (1000°C.) but 2700°F. (1500°C.) is not thought to be an overambitious forecast of attainment in the fairly near future. With uncooled nozzles, as in the case of solid propellants, the temperature is limited only by the capacity of the material and the increase in throat area which can be tolerated.

The major part of our experience in approaching these temperatures in stressed components has been gained with the blades and guide vanes of gas turbines. Here continued service for periods reckoned in hundreds or thousands of hours has to be assured, so that creep resistance and fatigue strength at the elevated temperature and under the operating stresses are the decisive criteria in selection of the materials to be used. Capacity to withstand thermal shock is also essential. Metallurgists have reason to be proud of the success with which these requirements have been met.

The stress required to produce rupture in creep in 100 hours is a good working basis for a first order evaluation of materials for gas turbine blades and vanes. Figure 1 shows how far we have been able to go with the three groups of materials which have been the foundations of all heatresisting alloys to reach quantity production up to the present time. These are the alloys of iron, nickel and cobalt. If we assume a working stress of 20,000 lb./sq.in. (14.1 kg./sq.mm.) we see that the maximum service temperatures are: for iron-based alloys 1480°F. (804°C.), for colbalt-based 1750°F. (954°C.), and for nickel-based 1800°F. (982°C.). Reducing the stress to 10,000 lbs./sq.in. (7 kg./sq.mm.) would increase

these limits by about 100°F. (53°C.). It is conceivable that alloying with trace elements, dispersion hardening by oxides and special melting techniques might add another 150°F. (83°C.) to the permissible temperature level, but it would still fall short of the rocket-nozzle requirements.

As the demand moves to higher operating temperatures beyond the capabilities of the well-known trio of iron, cobalt and nickel it is natural to look to materials of higher melting point. Among metals this means those falling in the portion of the Periodic Table shown in Figure 2: vanadium, columbium (niobium), tantalum in the fifth group; chromium, molybdenum and tunsten in the sixth group; rhenium in the seventh. To complete the list of metals having melting points exceeding 3180°F. (1750°C.) we might add zirconium, hafnium, ruthenium, osmium, rhodium, iridium, platinum. Figure 3 shows the principal physical properties of eleven of these metals.

#### Non-metallic Refractories

If we can dispense with certain properties characteristic of metals, such as good conductivity for heat and electricity, and toughness (i.e. absence of brittleness), some non-metallics of very high melting point come into the picture. These are notably graphite and a large family of ceramics. The softening range and melting points of a number of these highly refractory materials are shown in Figure 4. This also indicates the combustion temperatures of three liquid propellant combinations: oxygen-kerosene, nitric acid-kerosene and hydrogen peroxide-hydrazin hydrate.

Not many of the materials included in the list have been tested under actual rocket motor conditions. Graphite, particularly when coated, has given good results. It has the great advantage that, as shown in Figure 5, its strength increases as the temperature rises to  $4500^{\circ}$ F. ( $2500^{\circ}$ C.), and it is to be noted that its density is only 0.063 lb./cu.in. (1.75 gm./cc.). For some limited short-time, expendable applications unprotected graphite may be suitable, but its use for missions involving longer times and re-usable systems must await further developments. Among such developments showing promise are impregnation of graphite with silicon carbide, (see Figure 6) and coating with silicon carbide, molybdenum silicide and silicon nitride.

Another interesting technique which has been applied to produce rocket nozzles is that of "slip-casting" cermets, tungsten and molybdenum.

In this process the material is in the form of very fine particles, from 1 to 2 microns in diameter. The powder is suspended in an aqueous medium and the mixture is poured into a porous shaped mould, just as in ceramic practice. The "green" casting is sintered at a very high temperature. By this means nozzles up to 90 lbs. (41 kg.) in weight have been produced and they have given lives of up to 3 minutes under very severe conditions. The main difficulty with this process is achieving the desired accuracy of form, since there is a large change in volume on sintering the green slip casting. In the green state the casting may typically have a density 60 per cent of the bulk value and this rises to 90 per cent on sintering.

#### Refractory Metals

Figure 7 presents in summary form the up-to-date position in the development of the refractory metals and their alloys, expressed in terms of their tensile strength/density ratio at elevated temperatures. At the higher temperatures these curves all relate to tests made in vacuum or in an inert atmosphere, leaving for later consideration the vital question of oxidation.

Subject to a satisfactory solution being found for the problem of oxidation, it is evident that molybdenum-base and columbium-base alloys are capable of serious engineering service at temperatures up to 2500 F. (1370 C.), while tungsten and rhenium have possibilities at even higher temperatures. Other evidence suggests that tantalum should be included with tungsten and rhenium in this highest category of refractory metals. In 100 hour creep tests the stress to rupture of the best molybdenum alloy at 2500°F. is about 20,000 lbs./sq.in. (14.1 kg./ sq.mm.). It is expected that columbium-base alloys may not quite reach this figure, but that tungsten-base alloys will exceed it. Tungsten has another complication, however, : in the unalloyed metal there is a transition from the ductile to the brittle condition as the temperature falls below 500 F. (260 C.). This introduces difficulties in fabrication and in operation. Columbium, for its part, suffers from a different disadvantage in its low modulus of elasticity, E. At ordinary temperatures E is about 15 million lbs./sq.in. (10,540 kg./sq.mm.), compared with a figure for steel of 30 million lbs./sq.in. (31,620 kg./sq.mm.) and the value falls to less than one half of this at high temperatures. Offsetting this low elastic modulus to some extent in a comparison with other refractory metals is the relatively low density of columbium 0.3 lbs./ cu.in. (8.5 gm./cc.).

Of all the high-melting point metals molybdenum has been studied the most intensively. It is one of the few "strategic" metals which are native to North America and the U.S. Government agencies have invested heavily in research programmes aimed at its exploitation. The metal possesses many technical features which fully justify this attention. Specially notable are its high melting point (4750°F., 2620°C.) and its high modulus of elasticity (47 million lbs./sq.in.; 33,046 kg./sq.mm.). Its two major drawbacks are brittleness at low temperatures and high susceptibility to attack by oxygen. The low temperature brittleness appears to be essentially a question of extreme sensitivity to oxygen contained in the metal. The best hope for an amelioration in this respect lies in the attainment of a still higher degree of freedom from the interstitial elements oxygen, nitrogen and carbon and in heat treatment to diminish the concentration of these elements in the grain boundaries.

The poor resistance of molybdenum to oxidation arises from the characteristics of its oxides. On exposure of a cleaned surface of molybdenum to the air an oxide coating, probably a mixture of MoO<sub>2</sub> and MoO<sub>3</sub>, already begins to form at 480 F. (250 C.). As the temperature is raised the coating thickens slowly, but above 1290 F. (700 C.) the volatility of MoO<sub>3</sub> causes oxidation to progress much more rapidly. MoO<sub>3</sub> also melts at a low temperature, 1460 F. (795 C.), and this circumstance also seriously impairs the resistance of the metal to oxidation.

An immense amount of research and development has gone into the attempts to find reliable means of protecting molybdenum from oxidation so as to permit something more nearly approaching a full exploitation of its mechanical potentialities at high temperatures. Methods investigated include coatings based on chromium, silicon, nickel, precious metals, ceramic and refractory oxides. It is impossible to refer to these in detail here. The common shortcomings of such protective coatings are either that their own melting points are too low to match the capability of the molybdenum, or that they are too brittle. A programme of treatment which is reported to have given adequate protection to molybdenum gas turbine blades for service at 2000 F. (1100°C.) is: coating with electroplated chromium-nickel plus flamesprayed nickel-silicon-boride plus a cladding of Nichrome V plus flamesprayed cobalt-chromium-tungsten-boride. In the case of simple coatings of molybdenum disilicide, MoSi,, which can be produced by diffusion of silicon into the surface of the molybdenum, the greatest risk is cracking of the brittle silicide, but if this hazard is survived the protective effect is gradually lost by diffusion of molybdenum metal into

the coating and conversion of the silicon into silicon oxide, SiO.

Columbium does not suffer the handicap of volatile, easily fusible oxides, and for periods of service measured in hours some of its alloys can be used at temperatures in the range 2000 to 2500°F. (1090 to 1370°C.) without a protective coating.

The oxidation resistance of tungsten can be improved by alloying, but for applications at temperatures above 3000°F. (1650°C.) it would appear that a protective coating will be indispensable.

Rhenium, which on present evidence offers no prospect of becoming available in large quantities, has only poor resistance to oxidation at high temperatures. Next to tungsten its melting point (5740°F., 3170°C.) is the highest of any metallic element. Rhenium is difficult to work because of its hot shortness, but it may find a valuable application as an alloying addition to molybdenum; 30 per cent rhenium in molybdenum greatly improves the ferming properties.

Figure 8 shows the relative susceptibilities of some refractory metals to oxidation in flowing air at 2000°F. (1090°C.): molybdenum is the most seriously affected. Figure 9 gives an idea of the oxidation rate of columbium at 1470°F. (800°C.) in comparison with that of commercial Nichrome. This figure also illustrates what can be achieved by alloying: addition of 4.86 per cent of chromium has made columbium as resistant as iron to oxidation at 1470°F.

#### Temperatures attained on Re-entry

Having briefly surveyed the constructional materials available for high temperature service based on the refractory metals, let us see how the temperature likely to be encountered by the skin of astronautic vehicles on re-entering the Earth's atmosphere may correspond to the capabilities of our resources.

Orbiting about the Earth is attainable at a speed of about 18,000 m.p.h. (approximately Mach No. 24) and escape from the Earth's gravitation requires a speed of about 24,000 m.p.h. (approximately Mach No. 32). Re-entry speeds for ballistic missiles may be in the region of 10,000 to 20,000 m.p.h. (11,500 to 23,000 f.p.s., 16,000 to 32,000 km.p.h.). The nose cone of an intermediate range ballistic missile (I. R. B. M.) re-enters the atmosphere from 300 to 400 miles (480 to 640 km.) travelling at about 10,000 m.p.h. (16,000 km.p.h.). In the case of an

inter-continental ballistic missile (I. C. B. M.) the peak altitude may be at 600-800 miles (960 to 1,280 km.) after which the nose cone plunges towards the Earth at a final speed of 15,000 m.p.h. (24,000 km.p.h.). On the ascent the missile gains speed only slowly and is beyond most of the atmosphere before reaching speeds much exceeding the speed of sound (Mach 1 or 740 m.p.h. (1185 km.p.h.) at sea level). On the return journey the nose-cone accelerates as it descends towards the atmosphere from peak altitude, and as it moves into increasingly dense air a shock wave appears at about 60 miles (96 km.) altitude. Behind this shock wave gas temperatures of 15,000 F. (8,300 C.) or more are generated. This is higher than the temperature of the radiant surface of the sun. Deceleration forces of 20 to 50 g may be imposed on the structure as atmospheric drag increases.

The nose cone for an I.C.B.M. encounters far higher temperatures and decelerations than the I.R.B.M., the heat flux increasing roughly as the cube of the velocity.

In a satellite re-entry, the vehicle is travelling initially along a path nearly parallel to the Earth's surface. This is in contrast to ballistic missiles, for which, as they enter at steep angles, the period of overheating and deceleration is relatively short. Typical trajectories are illustrated in Figure 10. The re-entry speed of the satellite may be somewhat greater than that of an I. C. B. M., say 17,000 m.p.h. (27,400 km.p.h.). The flight-path of the satellite is under control, however, and the angle of re-entry will probably be held to less than 5 from the horizontal. By this means the maximum temperature and the deceleration forces are maintained at much lower values, although the heating period is considerably longer. In the case of the satellite, therefore, the designer is concerned mainly with insulation of the interior, as the temperatures and structural loads will be much easier to handle.

At the very high speeds of re-entry with which the astronautical engineer inevitably must deal, there is obviously a major problem in disposing of the energy content of the re-entry body in some way which will not result in the destruction of the vehicle. The energy content of an I. C. B. M. is about 10,000 B. Th. U./lb. (1,145,000 cal./kg.), which is more than enough to vaporise completely any known structural material. A continuous heating rate of 100 B. Th. U./sq.ft./sec. (270,000 cal./sq.m./sec.) will melt an inch (25 mm.) thick plate of steel in about 2 minutes.

Figure 11 illustrates the rate at which heat may be transferred from

the air to the body surface at varying heights and speeds. The curves show the maximum heating rate to be expected for a fully developed turbulent boundary layer and for body surface temperature equal to the ambient air temperature. The graph gives a good indication of the tremendous heat potential available.

The maximum temperature during the phase of aerodynamic heating is, of course, in the boundary layer, as shown in Figure 12. By aerodynamic skill in design most of the kinetic energy can be dissipated in air compression taking place through the shock wave system when the body has a blunt high-drag configuration. For a very blunt body over 99 per cent of the energy could be dissipated in this manner, leaving less than 1 per cent to be accommodated by the re-entry body mass. At a flight velocity of 23,000 f.p.s. (25,261 km.p.h., 15,700 m.p.h.) surface heat transfer for a nose radius of 4 ft. (1.2 m.) is about 20 B. Th. U./sq. ft./sec. (54,000 cal./ sq.m./sec.) at an altitude of 300,000 ft. (91,000 m.) above the Earth's surface; about 800 B. Th. U. /sq. ft. /sec. (2,160,000 cal./sq.m./sec.) at 100,000 ft. (30,000 m.): and about 2070 B. Th. U./sq.ft./sec. (5,600,000 cal./sq.m./sec.) at 60,000 ft. (18,000 m.). Several techniques and materials are available which will effectively absorb 100 B. Th. U./lb. (11,500 cal./kg.) and these data therefore indicate the envelopes of speeds and heights within which flight paths of astronautic vehicles must operate on re-entry into the Earth's atmosphere.

Figure 13 is one form of the "Corridor of Flight" diagram which has become familiar in writings on the subject of aerodynamic heating effects at very high speeds. Altitude is plotted vertically and velocity horizontally. The upper curve is the boundary of height/speed combinations in which nor-stalling flight is possible. At higher speeds and lower altitudes than correspond to this boundary continuous flight is possible but as the flight path moves further away from the stalling boundary the intensity of aerodynamic heating increases, i.e. the temperature in the boundary layer rises at lower altitudes and higher velocities. The data in this Figure show equilibrium stagnation temperature curves relating to the leading edge of a re-entry boost glider. The upper curve refers to a leading edge radius of 1 inch and it shows that in a vehicle following this path the stagnation temperature at the tip of the leading edge would be 2660°F. (1460°C.). If the same vehicle had a leading edge radius of 3 in. the stagnation temperature would be about 2260°F. (1240°C.). The two lower curves illustrate conditions with a 1 in. radius leading edge following paths at higher

speeds and lower altitudes. It is seen that temperatures of 3280°F. (1800°C.) and 4090°F. (2250°C.) are attained. The stagnation temperatures are higher than the actual temperature reached in the material of the leading edge, and this latter may be 200°F. to 400°F. (110°C. to 220°C.) lower than the stagnation temperature.

Between the limiting condition where low velocity and high altitude prevent the combined lift and centrifugal force from overcoming the weight of the vehicle, and the area where, on account of high speed and low altitude, temperatures exceed those which the vehicle can endure, is the "corridor" where continuous flight can proceed. Figure 14 shows typical flight paths of high speed vehicles. It is seen that the two ballistic missiles pass through the corridor into the area where excessive temperatures are developed. The satellite and glide missile are shown as following flight paths which do not pass out of the corridor, except for slight excursions of the satellite into the "too high - too slow" region. The aim of the materials specialist is to put into the hands of the engineer the means of shifting the lower wall of the corridor of continuous flight in the direction of higher permissible temperatures.

#### Materials for Re-entry Temperatures

A variety of methods may be adopted to this end. We have referred already to those which are within the sphere of the aerodynamicist and designer, and we should now consider what can be done by the judicious selection and application of materials to cope with the large heat-flux which will pass to the critical parts of the outer surface of the vehicle.

The lowest re-entry speed of interest is probably that for a lowaltitude satellite, about 26,000 f.p.s. (17,700 m.p.h., 28,500 km.p.h.). Re-entry velocities after a coasting trip from the moon approach 36,000 f.p.s. (24,500 m.p.h., 39,400 km.p.h.). There is little likelihood of re-entry vehicles from powered space flights exceeding 50,000 f.p.s. (34,000 m.p.h.; 54,700 km.p.h.) for the passenger-carrying vehicles. The total heat generated during re-entry may be expected, therefore, not to exceed 50,000 B.Th.U./lb. (5,725,000 cal./kg.) of vehicle weight.

#### Heat Sinks

One way of dealing with this heat is to provide a sufficient mass of material to absorb it, without suffering an intolerable loss of strength and certainly without melting. If copper were used as such a "heat sink"

it could absorb 150 B. Th. U. per lb. (17,200 cal./kg.) during a rise in its temperature from about 60°F. (15°C.) to a figure close to its melting point 1980°F. (1084°C.).

The heat sink capacities of some materials which might be used are :-

	Copper	Alum - inium	Molyb- denum	Tungsten	Beryll- ium	Graphite
Heat required						
to raise to melting temperatu B. Th. U./	ire.	280	420	770	1600	4100 (Vapor- isation)

Figure 15 compares the merits as heat sink material of seven metals and alloys. The curves show the total heat input per unit of surface area which nose-cones of the names materials will accept during re-entry before the surface temperature has risen to 80 per cent of the melting point. The temperatures at various depths below the surface in a steady-state condition are given. It is seen that there is no advantage in having a thickness of metal greater than 1 in. except in the case of copper, where a 2 in. (5 cm.) thickness can be used with benefit.

#### Ablation

Another way is to make use of the phenomenon of "ablation". In this the surface of the nose is made of a material which will melt or vaporise under the intense heating to which it is exposed. The molten or vaporised material is carried away from the skin in the air stream. Very large quantities of heat can be absorbed in the process of fusion and evaporation. As examples, plastics absorb 1,000 to 5,000 B. Th. U. per lb. (114,500 to 572,500 cal./kg.) and graphite (vaporising) something in the order of 10,000 B. Th. U. per lb. (1,145,000 cal./kg.). These figures indicate how much greater is the heat absorbing potential of the ablation technique than that of the heat sink.

For successful operation in a nose-cone an ablating material must possess good resistance to thermal shock, and an ability to sustain dynamic and static stresses of fair magnitude. A serious disadvantage

of the ablation principle is that it necessarily involves a change during flight in the contour of the nose of the vehicle. This will almost certainly modify the aerodynamic characteristics of the body and it is important that the removal of material by ablation should proceed with sufficient regularity to avoid producing asymmetry in the geometry of the vehicle.

For most effective ablation a material should have low thermal conductivity, a high melting point, high specific heat and high latent heats of fusion and evaporation. The first requisite is low thermal conductivity, since otherwise the temperature gradient between the surface of the skin and the inner portions of the structure will not be sufficiently steep to maintain a suitably low temperature within the casing and the damage by fusion or excessive softening will penetrate too deeply. The thermal conductivities of some high melting oxides and other non-metallic refractories are shown in Figure 16. These disclose a rather wide variation: in some the thermal conductivity is of the same order as that of heat-resistant metallic alloys such as Inconel (chromium 15 per cent, iron 5 per cent, nickel remainder). A careful examination of all the physical properties is therefore necessary in selecting a material for an ablative application: good thermal insulating properties are indispensable.

An attractive feature of ablation as a means of heat dissipation is that the rate of melting or volatilisation adjusts itself automatically to the rate at which heat is transferred to the surface. Meteorites found on the Earth give a useful indication of the relative merits of ceramictype skins and metallic. Stoney meteorites appear to be in relatively good shape and are smooth when recovered, whereas those of iron and iron-nickel alloys are badly pitted and eroded. In cooling by ablation very high surface temperatures, for instance 20,000°F. (11,000°C.), can be contemplated. At these temperatures chemical bonds are broken, with absorption of large quantities of heat. As an example, the dissociation of molecular hydrogen into atomic is accompanied by an absorption of 100,000 B.Th.U. per lb. (11,500 cal./kg.) of hydrogen. The high effective heat absorption from ablation is enhanced by the fact that the vapour and decomposition products from the ablated material tend to block the input of heat from the boundary layer.

#### Non-ablating Casings

It is obvious that the process of ablation cannot be allowed to continue for prolonged periods, since the loss of material from the skin would eventually entail excessive mechanical damage to the body. Ablation is

therefore appropriate for ballistic missiles, in which the time of exposure to very high temperatures is short. For such cases as the orbital-glide manned vehicle, where the skin may be expected to be at a temperature above 2,000°F. (1090°C.) for as long as 30 minutes, a durable non-expendable skin has to be provided. For this vehicle about 80 per cent of the structure is required to be in the form of sheet. It is here that the metals of very high melting point present their strongest claims. The nose-cone and the leading edges of wings or other control surfaces are the portions of the vehicle where the maximum temperatures are experienced. On the leading edges these may be in the order of 3,000°F. (1650°C.).

If an entirely metallurgical solution to the problem, (i.e. for stressed components to withstand operating temperatures in excess of 2,000 F. (1090 C.) for, say, 30 minutes), had to be provided, now or in the immediate future, one would think first of chromium, or a chromium-base alloy. The operating temperature in that case would have to be limited to 2100°F. (1150°C.), or in specially favourable circumstances, 2300 F. (1260 C.), on account of the serious falling away in mechanical strength with rise of temperature in this region. The resistance to oxidation of chromium is good, but the melting point 3380°F. (1860°C.) is uncomfortably low in relation to the specified working temperature. There would be some cause for apprehension because of the susceptibility of chromium to attack by nitrogen, but it may soon be possible to counter this by a natural film, resistant to nitriding and generated from an alloying addition. Subject to the restrictions mentioned, chromium-base alloys could be used without an externally-applied protective coating.

For immediate application at temperatures beyond the capacity of chromium, molybdenum, protected from oxidation by one of the methods mentioned earlier, is the only metal available in the required form. An indication of the great advance in mechanical strength at the temperatures now under discussion which molybdenum offers over the best of the currently used alloys is given by comparing the stress producing rupture (in 100 hours at 1830 F. (1000 C.)) in Nimonic 100 (the most recent addition to the Nimonic series) of 6,000 lbs./sq.in., with the corresponding value for molybdenum alloyed with 0,45 per cent titanium, namely 48,000 lbs./sq.in. Figure 18 extends this comparison to a number of other heat-resistant alloys up to 2,000 F. (1090 C.).

Looking to the not too distant future, perhaps five years ahead, it may well be that columbium alloys, coated, will take the place of molybdenum,

chiefly because columbium has a considerably lower density and the problem of protecting it from rapid oxidation at high temperatures is not so formidable.

#### Ceramic Coatings

Although it is a natural ambition of the metallurgist to find a purely metallurgical solution for the problem of materials associated with the re-entry of astronautical bodies into the Earth's atmosphere, enough has been said already to show that for the most extreme conditions of heat in an oxidising atmosphere in the present state of the art recourse must be had to non-metallics, at least as a protective coating on the surface of the metal.

A coating may be considered solely as a barrier between the metal and the reactive hot ambient atmosphere, without appreciably reducing the temperature of the metal, or it may be employed as a thermally insulating device with the object of preventing the underlying metal from being heated to a temperature at which its mechanical properties become seriously impaired and the rate of oxidation becomes unduly rapid.

The coatings which have been mentioned in connexion with the protection of molybdenum against oxidation fall within the first category. They include metallic coatings such as rolled-on, or electrodeposited, cladding of chromium alloy, "cemented" coatings produced by diffusing silicon and chromium into the surface, and thin coatings of ceramic enamels. Where there are severe limitations in respect of dimensions, as in turbine blades, only thin coatings, e.g. 0.020 in. (0.5 mm.) thick can be used. Ceramic coatings can be applied in these thicknesses by spraying in an oxy-acetylene flame or by a detonation device which propels the coating particles on to the metal surface at high velocities. The ceramic materials with which there has been most experience in this application are alumina and zirconia. The properties of these coatings are shown in Figure 19.

These flame-sprayed coatings are generally not thicker than 0.08 in. (2 mm.). This limits their insulating capabilities, but greater thicknesses can be employed by incorporating reinforcing media, such as wire mesh of steel or molybdenum, fibres of ceramic material or short lengths of molybdenum wire randomly oriented in the ceramic matrix. These reinforced ceramic coatings can be built up to a thickness as great as 1 in. Figure 20 shows the effect of these types of coating in insulating the metal skin (nickel alloy 0.05 in. thick) to

which they had been applied and which was exposed to an oxyacetylene torch flame. It will be seen that with a reinforced coating 0.136 in. thick (3.5 mm.) the steady-state temperature of the metal was reduced from about 2100°F. to 1600°F. (1150°C. to 870°C.).

It was reported on 8th April, 1959 that the nose-cone of a Thor-Able missile fired from Cape Canaveral, Florida, and recovered from the South Atlantic after a 5,000 mile test, was made of "reinforced ceramic".

In another type of protective layer alternate layers of molybdenum metal and aluminium oxide are applied to the metallic surface by flame-spraying. Figure 21 shows a cross-section. These multilayer laminated coatings are reported to have withstood exposure to 3000°F. (1650°C.) for over 18 minutes. Their insulating properties are so good that a molybdenum-alumina coating of 0.050 in. (1.2 mm.) thickness on a fibreglass dome 0.04 in. (1 mm.) thick preserved the dome from burn-through in the exhaust flame of a rocket motor.

It has been proposed to approach this problem of alleviating the working conditions for the metallic skin and structure of the re-entry vehicle by providing, outside the main metallic body, insulating slabs, 1 or 2 in. (25 or 50 mm.) thick, held in position by an expendable outer skin. This skin might be a metallic mesh, or a layer of fused silica. If something of this kind proved practicable it would become possible to use conventional materials of modest heat-resisting capacity, e.g. stainless steel or even aluminium alloys, for the skin and structural elements of the vehicle. It must be said, however, that none of the available effective insulating materials, of sufficiently high melting point, appears to have the degree of toughness (i.e. freedom from brittleness) or resistance to thermal shock to encourage the hope that it could survive the conditions to which it would be exposed as the outer component of an astronautical vehicle.

#### Temperature Effects in Outer Space

The foregoing discussion has been devoted mainly to the problems stemming from the intense aerodynamic heating on re-entry into the Earth's atmosphere and the very high temperatures which this develops in the skin of the vehicle. This emphasis is justifiable as long as it is assumed that the body is to be recoverable on the Earth. Kinetic heating is negligible at altitudes greater than 100 miles (160 km.) above the Earth's surface and the temperatures likely to be experienced on the

surface of a satellite in outer space are not more extreme than those now catered for in manned aircraft designed for speeds of Mach. 2.

At satellite altitudes radiation is the prime source of external heating. How much heat enters the vehicle depends upon surface emissivity and absorptivity, both of which are functions of temperature as well as surface conditions. Surface coatings on satellite skins exempt from re-entry requirements are designed for a maximum reflection and the maintenance of reflecting properties. On the Vanguard satellite (Figure 22) the magnesium skin, 0.028 in. (0.7 mm.) thick, was plated with gold for corrosion-prevention and to improve adhesion of subsequent coatings. Chromium was next applied, followed by a layer of silicon monoxide, which prevents diffusion of chromium into the fourth layer, aluminium. The aluminium reflects the radiant heat. The aluminium was protected by a silicon monoxide coating. The total thickness of these coatings was only a few millionths of an inch.

The Explorer had a stainless steel nose striped with a white reflecting paint pigmented with zirconia, the stripes covering 85 per cent of the surface. The external temperature of Explorer was reported as ranging from -13°F. (-25°C.) to +167°F. (+75°C.), while the internal temperature varied between 50 and 86°F. (10 and 30°C.). An estimate of the temperature cycle at the surface of a satellite skin of titanium 0.02 in. (0.5 mm.) thick insulated internally, in orbit at 300 miles (488 km.) with an orbit time of 1.5 hr. in an orbital plane containing the Earth-Sun line, gave a maximum temperature of about 390°F. (200°C.) and a minimum of -148°F. (-100°C.). This range is quite sensitive to changes in absorptivity and emissivity of the surface. The figures just quoted are for an absorptivity of 0.8 and an emissivity of 0.4, giving an A/E ratio of 2. If A can be lowered to 0.14 and E raised to 0.97, for instance by using a magnesia surface, the amplitude of the temperature cycle is diminished to a variation from +32°F. (0°C.) to -202°F. (-130°C.).

The lowest temperatures encountered in astronautical flight are not likely to introduce serious complications in the application of metallic materials. For most metals the strength is enhanced as the temperature is reduced, even down to the temperature of liquid helium, 4.2 K (-451.8 F., -268.8 C.), but metals which exhibit a transition from the ductile to the brittle state on falling temperatures in the normal terrestrial regime remain brittle at very low temperatures. Elastic moduli increase by about 10 per cent as the temperature decreases to 90 K. (-300 F., -183 C.).

With few exceptions the tensile strength of all face-centred cubic

(e.g. copper and aluminium, as shown in Figure 23) and hexagonal (e.g. magnesium) metals increases considerably below room temperature: their ductility and yield strength do not change greatly. For bodycentred cubic metals the yield strength increases markedly as the temperature is reduced, and the fracture eventually becomes brittle, with little or no plastic deformation, at some temperature below room temperature. Metals in this category are: iron and ferritic steels, columbium, chromium, molybdenum, tantalum, vanadium and tungsten.

#### Structural Efficiency

Second only to the requirement that the vehicle must survive in a viable condition the vagaries of its intended journey, is the necessity for lightness. When the very high temperatures associated with re-entry do not have to be reckoned with, the selection of materials for astronautic vehicles does not raise any questions which have not already come under consideration in connexion with manned aircraft. Strength-weight ratios, fatigue properties, moduli of elasticity, forming qualities, sensitivity to temperature, coefficients of thermal expansion and cost are among the factors, familiar to discussions of aircraft structural materials, which come into account for astronautical vehicles. Thus alloys based on magnesium, aluminium, and titanium and precipitation-hardening stainless steels vie with each other in keen competition. At temperatures up to about 212 F. (100 C.) the choice is largely influenced by the particular type of structural loading involved, which decides whether, in relation to density, tensile strength or elastic modulus is more important. These features are illustrated in Figures 24 and 25. For moderately elevated temperatures, say in the region of 750 F. (400 C.), there is at present in progress a most interesting struggle between the precipitation-hardening stainless steels and titanium alloys, some aspects of which are seen in Figure 26.

One metal, the merits of which have not yet been exploited in aircraft, is beryllium, although it has been known for a long time that it possesses certain characteristics which are very attractive for strong, stiff, light structures. These are low density, high modulus of elasticity, high strength/weight ratio, good thermal properties for a heat-sink application, i.e. high specific heat and high melting point (for a light metal) and reasonably good retention of strength at elevated temperatures, e.g. 1200°F. (650°C.). The high ratio of elastic modulus to density is particularly striking: in all other structural metals the density increases approximately in linear proportion to the modulus, giving a ratio: E(million lbs./sq.in.)/d(lbs./cu.in.) of about 100. This is true for

instance for aluminium, magnesium, steel and titanium. For beryllium, however, the ratio is 670. The metal is therefore attractive for structural uses where resistance to compressive buckling is important.

Beryllium would enable substantial weight saving to be achieved in comparison with precipitation hardening steel and titanium alloys up to temperatures of 1000° . (540° C.).

The shortcoming of beryllium which prevents its use in airframes and similar structures is its directional brittleness. By carefully controlled rolling of compacted, extruded beryllium, adequate ductility (e.g. 30 to 40 per cent elongation) can be achieved in the plane of the sheet, but in the short-transverse direction, i.e. across the thickness of the sheet, the ductility is very low. This appears to be an inherent characteristic of the crystal structure of the pure metal, possibly connected with the axial-ratios of its hexagonal space lattice. In spite of many attempts to overcome this deficiency no success has been achieved. It may be that the special value which beryllium would have for structures of astronautic vehicles will provide the stimulus required for a new attack on this baffling metallurgical problem.

#### Acknowledgements

Realistic study of astronautic engineering is of such recent beginning and the speed of development is so rapid that the writer reviewing the status of the materials available for use in this subject must draw his information from current technical publications, unclassified research reports and personal communications. I mention in the bibliography some recent publications which I have found usefully informative. I have also been fortunate in receiving up-to-date information and assistance from a number of friends. Without implying their approval of any views expressed in this paper, I would like to thank Dr. E. Epremian of the Metals Research Laboratory, Union Carbide and Carbon Corporation, Mr. F. S. Badger of Haynes Stellite Company, Kokomo, Indiana, Professor N. J. Grant of Massachusetts Institute of Technology, Captain I. E. Maxwell of Pergamon Press, Dr. G. L. Miller of Murex Ltd., and my colleagues Professor A. J. Kennedy and Mr. S. W. Greenwood in the College of Aeronautics, Cranfield, for their help.

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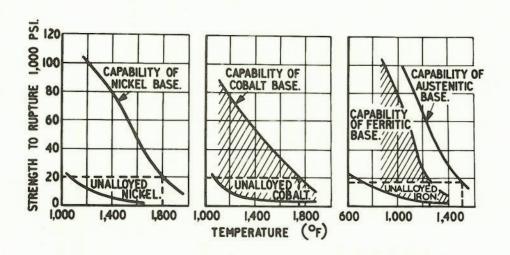


FIG. 1 100 HOUR CREEP RUPTURE CAPABILITIES

GROUP	3	4	5	6	7	8	9	10
-								
2								
3	13 Aluminum							
4	21 Scandium	22 Titonium	23 Vanadium	24 Chromium	25 Manganese	26 Iron	27 Cobalt	28 Nickel
5	39 Yttrium	40 Zirconium	41 Columbium	42 Molybdenun	43 Technetium	44 Ruthenium	45 Rhodium	46 Palladium
6	57 Lanthanum	72 Hafnium	73 Tantalum	74 Tungsten	75 Rhenium	76 Osmium	77 Iridium	78 Platinum
7	89 Actinium			hs, Cerium	58 to Lut	etium 71		

FIG. 2 PERIODIC TABLE SHOWING THE LOCATION OF THE ELEVEN LESS COMMON METALS

Physical Property	Cb	Cr	Hf	Ir	Mo	Os	Re	Ta	v	W	Zr
Unit cell	bcc	bcc	cph	fcc	bee	cph	cph	bce	bcc	bcc	cph
Dimension a, A	3.300	2.8848	3.195	3.831	3.140	2.730	2.760	3.296ª	3.028	3.158	3.231a
Dimension c, A			5.052			4.310	4.458				5.148ª
Density, g. per cu. cm.	8.6a	7.20	13.2ª	22.5a	10.2ª	22.5ª	21.0	16.6	6.1 <sup>a</sup>	19.3	6.50a
Melting point, OC.	2415	1890 <sup>a</sup>	2220	2454	2620	2850	3170	3000a	1885	3400	1855
Specific heat, cal. per g. per °C	0.065	(0.11)	0.035	0.031	0.065	0.031		0.036ª	0.120	0.034	0.066
Thermal coef. of expansion, per °C. x 106	7.1	5.0 <sup>a</sup>	6.2	6.8	5.45	6.6	6.7 <sup>b</sup>	6.5	8.3	4.45 <sup>b</sup>	5.7ª
Thermal conductivity, cal/ sq.cm./sec./OC./cm.		0.16		0.141	0.349		0.17	0.130		0.399	0.21
Electrical resistivity, ohm- cm. x 10 <sup>6</sup>	13.1	12.8	34.0	5.3	5.17	9.5	19.0	12.4	23.3	5.48	43.0 <sup>a</sup>
Temp. coef. of electrical resistance, per C. x 10 <sup>4</sup>	39.5	30 <sup>a</sup>	44.0	39.0	47.0	42.0	3.11	38.2	28.0	48.2	44.0
Magnetic mass susceptibility, cgs. x 10 <sup>6</sup>	2.2	3.3ª	0.42	0.133	0.093	0.052	0.29	0.84	5.0	0.32	1.3
Vapor pressure at indicated temperature, µatm. per C.		2740 1800			0.0034		0.71	$0.92 \times 10^{-9}$	0.059	$4 \times 10^{-5}$	0.0054

a An average of several values.

FIG. 3. SOME ROOM-TEMPERATURE PHYSICAL PROPERTIES OF ELEVEN METALS (Data Compiled from Various Published Sources)

b Measured between 20 and 500 °C.

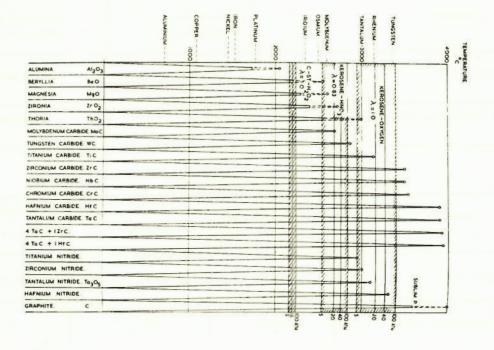


FIG. 4. SOFTENING RANGE AND MELTING POINTS OF SOME RE-FRACTORY MATERIALS

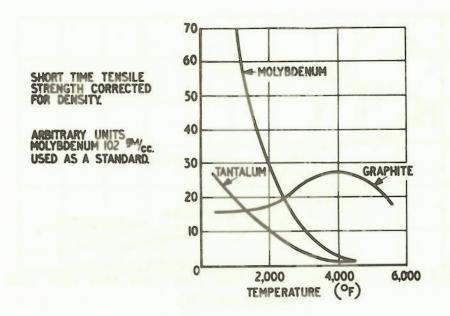


FIG. 5 TENSILE STRENGTH/DENSITY vs TEMPERATURE

Sample		Density m/c.c.	Average Rupture Strength p.s.i	
Graphite "A"		1.75	5,400	
30/70 Graphite + SiC impre	gnation	2.75	12,100	
	Arc Flam	ne Test		
Sample	Arc Flam Apparent temp.F	Time in secs.	Weight loss,	
Sample  Graphite "A"	Apparent	Time		

FIG. 6. COMPARISON OF GRAPHITE WITH A GRAPHITE CARBIDE

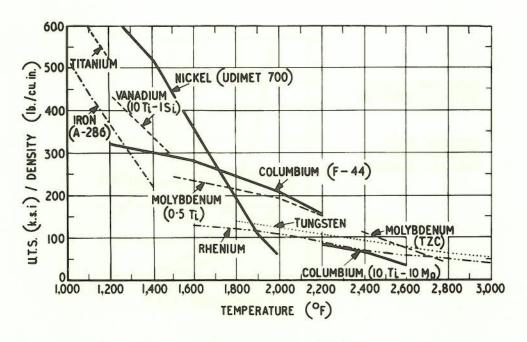


FIG. 7. TENSILE STRENGTH/
DENSITY RATIO OF REFRACTORY
METALS AT ELEVATED TEMPERATURES

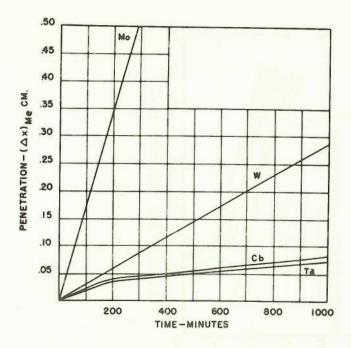


FIG. 8 PENETRATION vs TIME CURVES AT 2000°C

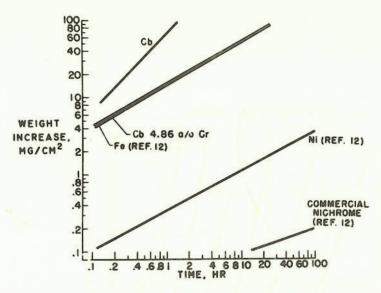


FIG. 9 COMPARISON OF OXIDATION RATES IN AIR AT 800°C OF COLUMBIUM AND A COLUMBIUM-CHROMIUM ALLOY WITH OTHER METALS AND ALLOYS

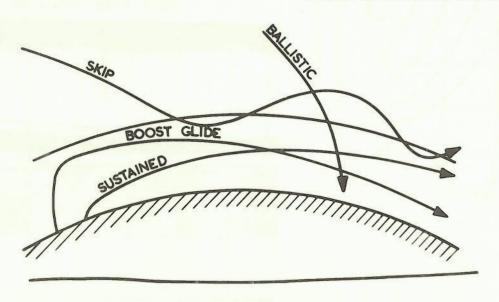


FIG. 10 TYPICAL TRAJECTORIES FOR HIGH-SPEED VEHICLES

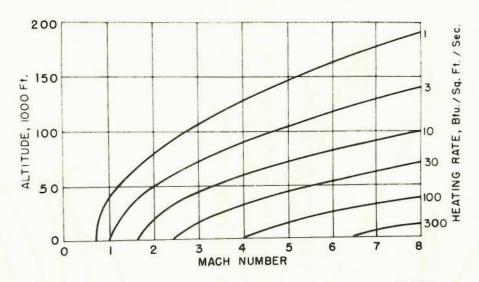


FIG. 11 MAXIMUM HEATING RATE AS A FUNCTION OF ALTITUDE AND MACH NUMBER

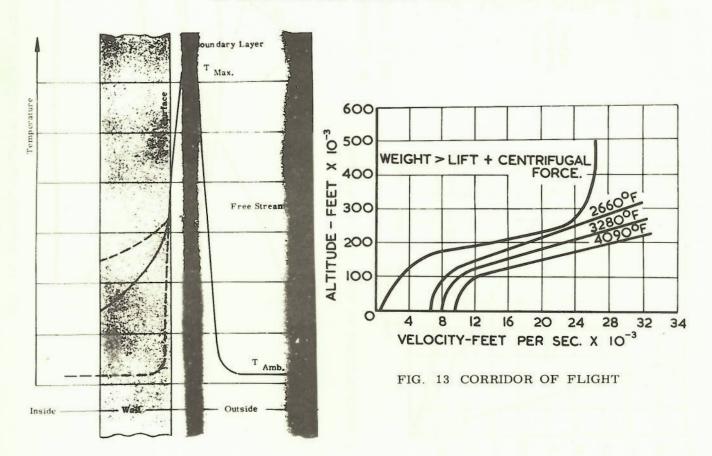


FIG. 12 REGION OF HEAT EXCHANGE BETWEEN ENVIRONMENT AND SKIN MATERIAL

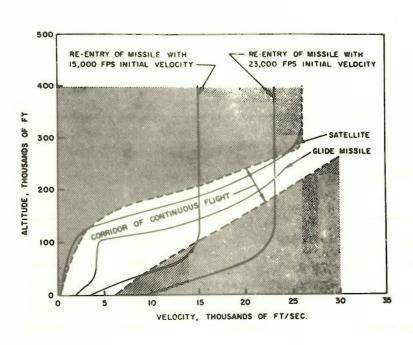


FIG. 14 REPRESENTATIVE HYPERSONIC FLIGHT PATHS

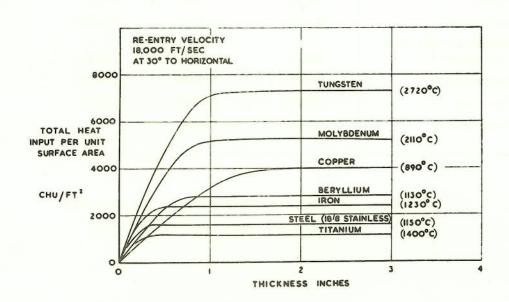


FIG. 15. HEAT ABSORPTION
PROPERTIES OF SOME METALS
USED AS HEAT SINKS

	Thermal Conductivity (cals./sec./cm. <sup>2</sup> /°C.)				
Material	100°C	at 400°C	1000°C		
Alumina	0.072	0.031	0.015		
Beryllia	0.525	0.222	0.049		
Spinel	0.036	0.024	0.014		
Thoria	0.025	0.014	0.008		
Zirconia (stab.)	0.0047	0.0049	0.0055		
Mullite	0.015	0.011	0.010		
Porcelain	0.0041	0.0042	0.0045		
Zircon	0.016	0.012	0.010		
Cordierite	0.0053	0.0050	(0.005)		
Titania 4.1 per cent porosity	0.011	0.009	0.008		
Spodumene	0.0026	0.0028	0.0033		
Fireclay	0.0027	0.0029	0.0037		
Fused Silica	0.0038	0.0045	-		

FIG. 16. THERMAL CONDUCTIVITY VALUES FOR OXIDES AND RELATED COMPOUNDS

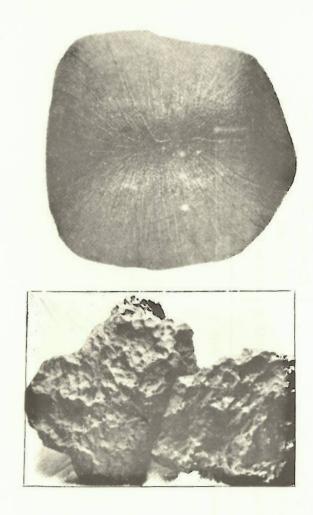


FIG. 17. STONEY METEORITE (TOP)
AND IRON METECRITE

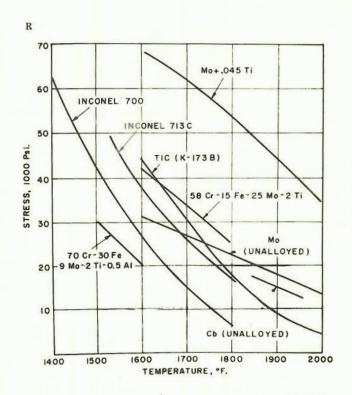


FIG. 18 STRESS-TO-RUPTURE IN 100 HOUR FOR SOME POTENTIAL HIGH TEMPERATURE MATERIALS

PROPERTY	ALUMINA (ROKIDE A)	ZIRCONIA (ROKIDE Z)
Composition	98.6% Al <sub>2</sub> O <sub>3</sub>	98% ZrO <sub>2</sub>
Density, lb. per cu.in.	0.115	0.187
Thermal drop through 0.030 in. at steady-state melting temperature  Maximum service temperature	6°F. per 0.001 in.	8°F. per 0.001 in 4200°F.
Thermal conductivity*, B.Th.U. per hr. per sq.ft. per in. per F. at 1000 to 2000°F.	19	8
Emissivity, 1000 to 2000 F.	0.3 to 0.4	0.3 to 0.4
Thermal expansion coefficient, 70 to 2550°F.	43 x 10 <sup>-7</sup> per °F.	64 x 10 <sup>-7</sup> per °F
Coating thickness range	0.005 to $0.100$ in.	0.005 to 0.060 in.
Porosity	8 to 12%	8 to 12%
Hardness and abrasion resistance	Very high	High
Thermal shock resistance	Excellent	Good
Resistance to vibration and flexing	Very good	Good
Application cost per sq.in. per 0.001 in.	0.8 to 1.0 <b>d</b>	$1\frac{1}{2}$ to 2 &

<sup>\*</sup> Calculated from thermal drop data

FIG. 19. PROPERTIES OF FLAME-SPRAYED CERAMIC COATINGS

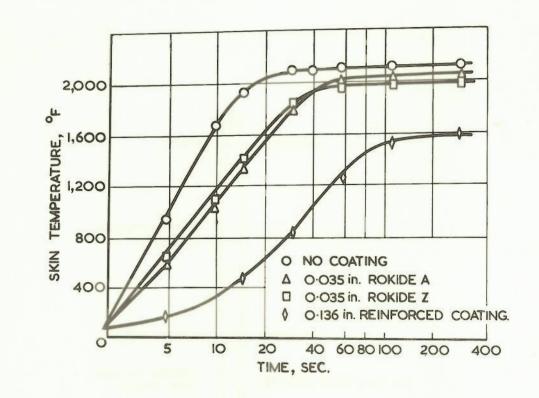




FIG. 20. INSULATION PROPERTIES OF CERAMIC COATINGS ON NICKEL ALLOY SKINS

FIG. 21 MULTILAYER COATING CROSS SECTION. FOUR LAYERS OF MOLYBDENUM (DARK) SANDWICH THREE LAYERS OF ALUMINA (LIGHT)

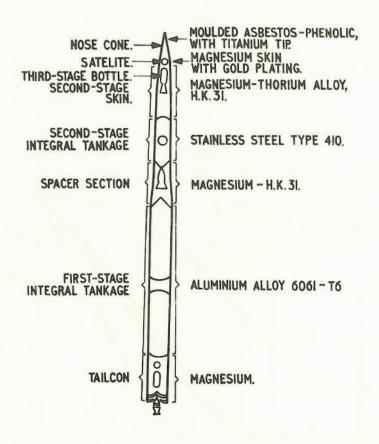


FIG. 22 VANGUARD SATELLITE WITH LAUNCHER

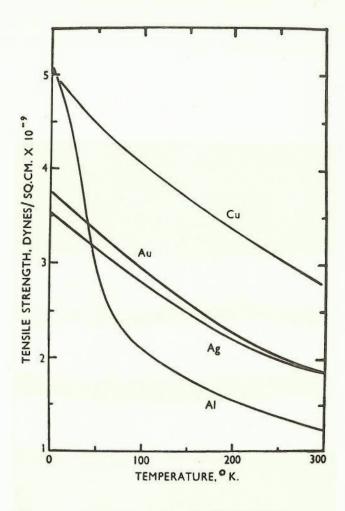


FIG. 23. TENSILE STRENGTH OF SOME METALS AT LOWER THAN ROOM TEMPERATURE

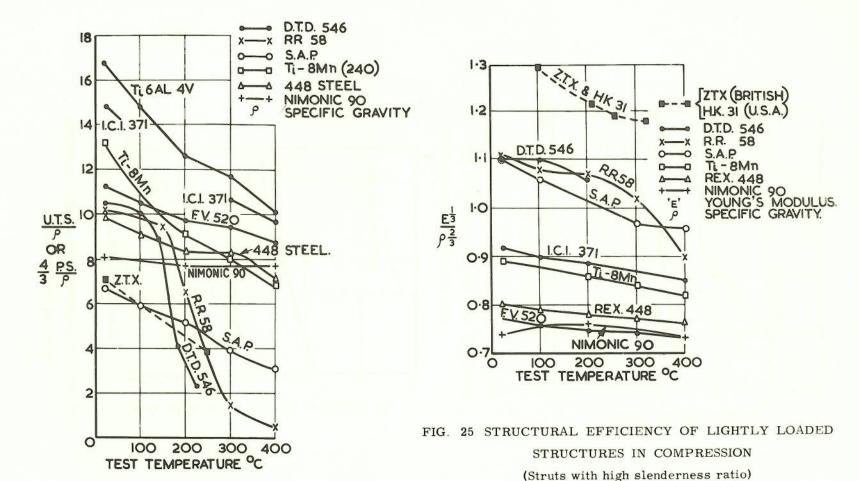


FIG. 24 STRUCTURAL EFFICIENCY IN TENSION