

MATERIALS FOR ENERGY CONVERSION SYSTEMS

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Space flight with its tremendous extension of attainable altitude, observable areas, and communication capabilities within compressed time periods promises to provide the ability for important changes in our civilization. Unmanned exploration was initiated with Sputnik and the some 30 satellites which followed. Manned travel in cislunar space has recently become a demonstrated capability. Both the Soviet Union and the U.S. have launched unmanned Sun and solar planetary probes. By the mid-1960's we expect to move from exploration to utilization of the space environment for purposes such as navigation, mapping, weather observation, reconnaissance, communication and air traffic command and control with both unmanned and manned vehicles.

In all the above applications, power is required to accomplish any intended task or combination of tasks. The power will most probably be electrical and must be reliable over long time periods, light weight, reasonably efficient, and economical. The energy conversion process, by various techniques, converts a relatively narrow band of the energy spectrum into useful energy for power.

However, regardless of the conversion cycle being considered by the aerospace engineer, whether it be: thermoelectric, thermionic, fuel cell, solar cell, photovoltaic, mechanical-dynamic, magneto gas plasma-dynamic, the materials used, determine the ultimate feasibility, efficiency, longevity and reliability.

The materials research and development efforts of several scientific and engineering disciplines provide direct capability and impetus to developments in energy conversion processes and systems. The nature of the Directorate of Materials and Processes research and the state of the art in some pertinent areas will be discussed. Our effort has been concentrated on synthesizing and developing into useful form, materials with potential for broad usage, and in the characterization of the mechanical, thermal, optical, and electrical properties over wide temperature ranges of environment. Studies in refractory metal alloys, ceramics, graphite, surface coatings, high polymers, and techniques for measuring thermophysical properties of solids and fluids are of particular interest.

Let us examine some of the facets of applied research as they bear directly on the energy conversion process.

The temperature levels of materials for the mechanical aspects of dynamic systems indicate a range of requirements from modest levels (500° - 800°F) to temperatures in excess of 2000°F with the higher temperature relating to high power output at low weight-to-power ratios. Materials can be chosen from limiting thermal and dynamic stress data. Design fluid containment, rotating parts, and some materials for the gamut of temperatures are shown in figure 1. However, the strength-weight-temperature curve lacks an important ingredient - the time factor. The long life requirements dictated a necessity for reliable data at 10,000 hours. Figures 2 and 3 show estimates of the strength-weight ratio and creep to yield ratio for the 10,000 hour period. These estimates, especially at the higher temperatures (above 1000°F), are based on meager amounts of stress-rupture and creep data and at times up to 1000 hours, with up to 100-300 hours

at 2000°F. Obviously, an increase in the amount and duration of time data would greatly increase confidence in use of the high temperature materials and insure a more reliable design of minimum weight.

The transfer of thermal energy and its conversion to mechanical power are accomplished by heat transfer and working fluids. These two functions may require different, or the same fluids with the latter preferable where feasible. The vapor pressure chart (figure 4) shows fluids which are being used and being considered for use. The significant fact is that internal pressure and stability considerations have led to the use of metallic materials which are liquid in the -40° to 400°F range. Extensive effort is being devoted to characterization and critical review of the physical and thermodynamic properties in the liquid and vapor state of these materials and certain elements and salts.

The use of these materials, however, produce containment problems—compatibility with tubing and system components. The compatibility of materials and working fluids is one of the more serious problems requiring careful and diligent attention. Compatibility problems may be divided into three major categories—corrosive attack, erosion, and fouling. The chart (figure 5) describes the relationship.

The rate of corrosive attack on metal surfaces by non-aqueous inorganic liquids may vary significantly with flow rate if the slowest step in the corrosion process is the rate at which the solute diffuses through the liquid boundary layer. On the other hand, the corrosion rate may be independent of the flow rate if the slow step is the rate of dissolution of the solid or the rate of diffusion of the solid phase. Iron-mercury typify the first of these cases and iron-sodium and iron-molten salt are representatives of the latter.

In certain instances, the net thermal gradient mass transfer of pure metal phase from a hot zone to a cold zone may proceed by way of formation of an intermediate compound. For example, sodium oxide dissolved in liquid sodium may react with iron in a hot zone to form an iron-sodium-oxygen compound. This compound may revert to sodium oxide and iron in a cool zone and thereby cause a net transport of iron, resulting in intergranular corrosion and blockage of tubes and orifices.

In the case of the liquid alkali metals, the presence of dissolved oxygen or oxide (and dissolved nitrogen or nitrides in the case of lithium) increases fluid corrosion activity. This enhancement of corrosion activity may result from compound formation as noted above, or it may reflect the surface fluxing ability of dissolved oxide. The problem may be minimized by starting with an initially clean fluid in a clean system, or by cold trapping oxide contaminants as solid oxides.

Static compatibility data are shown in figure 6 for rubidium and lithium. The usefulness of the refractory metal alloys is apparent and the compatibility problems of joined areas in contact with the liquid metal environment are obvious.

Collection and efficient utilization of absorbed energy and rejection of unused heat to a heat sink are important design considerations of many energy conversion systems. The surface properties of materials are important facets of both energy absorption and rejection. Solar radiation offers a virtually inexhaustible source of energy, and all space flights, except very short ones, to date have been powered by the direct photovoltaic quantum conversion of solar energy using silicon solar cells. The newer systems under study, e.g. thermoelectric, thermionic, and turbine drives, are dependent upon the thermodynamic conversion of energy from a source heated by solar irradiance or nuclear energy. Fundamental to these systems is an energy receiver having high absorption in the spectral

range from 0.3μ to 2.0μ (which include about 94 percent of the solar energy) and having low radiation loss over the range of operating temperatures. This combination of requirements are direct functions of the receiver surface optical properties. To achieve high thermodynamic efficiency in a power system, a large temperature differential between heat input and heat rejected is required.

High absorption of solar energy is readily obtained. However, reradiation of this energy, and this becomes significant at high temperatures, becomes the chief loss of power. There are several approaches to overcoming the reradiation problem and achieving the desired balance of surface optical properties -- namely, high solar energy absorption with low emittance. The Directorate of Material and Processes is exploring the use of "interference" coatings to obtain selective energy absorption on the so-called dark mirror concept. To get selective energy absorption, the coating system must have high absorption for short wavelength light and high reflection (low emittance) for long wave length light. The coating consists of extremely thin films of metals deposited alternately with a dielectric film. About 90 percent absorption can be obtained in a three-layer film. Figures 7 and 8 show the percent of solar energy absorbed and percent reradiated of a silicon monoxide-aluminum-silicon monoxide coating on an aluminum substrate at 600°K . The high degree of energy absorption and low energy loss by reradiation show the efficiency of this system. Development of stable coating systems, chemically inert, non-volatile, and with low diffusion into substrates at high temperatures are required.

What of the other side of the coin? Systems using fluid heat transfer must eventually reject heat by radiation to the infinite sink of space through a radiator. For a given temperature, the amount of heat radiated is directly proportional to the emissivity. The desired characteristic is high emissivity at as high a temperature level as is compatible with the system design and the radiator material. The total normal emissivity of some of the oxidized metallic surfaces can be enhanced by the application of coatings. A recent design study indicated that a condenser radiator made of Hastelloy tubing and beryllium fins and operating at a fluid temperature of 1500°F would be 30 percent lighter with an emissivity $E = 0.9$ as compared to an $E = 0.5$. Directorate of Materials and Processes has obtained emissivity data on a great many materials. Coatings which enhance emissivity often have been a by-product of other research rather than a direct effort in this area. Coatings for refractory metal alloy oxidation protection are an example. The emissivity of these special coatings and oxides after long use at high temperatures and under high vacuum is an unknown and uncertain quantity.

Since the most desirable choice of materials for a given conversion application is often highly dependent upon subtle variation in properties, great emphasis has been placed on developing suitable techniques for measuring these properties over wider ranges of temperature. Measurement techniques for extreme conditions continue to be studied and much useful data continue to accumulate. However, only recently has there been a concerted effort to obtain, collate, critically review, and catalog these data. Several reports have been issued recently containing physical properties on a great variety of solid, liquid, and gaseous materials. The properties include density, thermal conductivity, heat capacity, thermal expansion, vapor pressure, heat of sublimation, electrical conductivity, Seebeck coefficient, emissivity, and transmittance. Such data, when readily available, greatly assist in firming up the heat transfer, optical, and electrical characteristics that might be expected of a system components. Plots typical of this data are shown in figures 9, 10, 11, 12, 13 and 14.

Some interesting considerations appear from such compilations. At about 2000°F, we have reached a limit in the usefulness of known magnetic materials. We can add the time ingredient to vapor pressure data by application of theoretical considerations and arrive at estimates of the loss of materials at temperature and in a vacuum — an important consideration in thermionic devices which employ high temperature cathodes. Tables 1 and 2 illustrate this point.

In summary, we have indicated through specific example where current research in several materials disciplines is providing direct and indirect support to various facets of the energy conversion process. Areas which require continued research emphasis and new research have also been indicated.

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TABLE 1 LOSS OF POTENTIAL CATHODE MATERIALS BY VAPORIZATION		
MATERIAL	T _{min} - °K	VAPORIZATION RATE AT T _{min} - cm/yr
TANTALUM	3010°	13
TUNGSTEN	3310°	54
RHENIUM	3630°	1.97 × 10 ³
NIOBIUM	2910°	92
MOLYBDENUM	3100°	2.94 × 10 ³
URANIUM CARBIDE	2330°	2

T_{min} - MINIMUM TEMPERATURE REQUIRED FOR EFFICIENT CATHODE OPERATION

TABLE 2 EVAPORATION OF METALS AND SEMICONDUCTORS IN HIGH VACUUM				
ELEMENT	TEMPERATURE (°F) AT WHICH EVAPORATION IS			MELTING POINT °F
	10 ⁻⁵ cm/yr	10 ⁻³ cm/yr	10 ⁻¹ /cm yr	
Se	120	180	240	430
Te	260	350	430	840
Mg	260	350	460	1200
Li	300	410	530	370
Al	1020	1260	1490	1220
Be	1140	1300	1540	2340
Cu	1160	1400	1650	1980
Si	1450	1690	1970	2580
Pd	1490	1720	2020	2840
Ti	1690	1960	2280	3140
Pt	2120	2440	2840	3240
Zr	2340	2740	3150	3360
Mo	2520	2960	3450	4700
C	2780	3050	3400	6600
Ta	3250	3700	4200	5400
Re	3300	3700	4200	5700
W	3400	3900	4500	6100

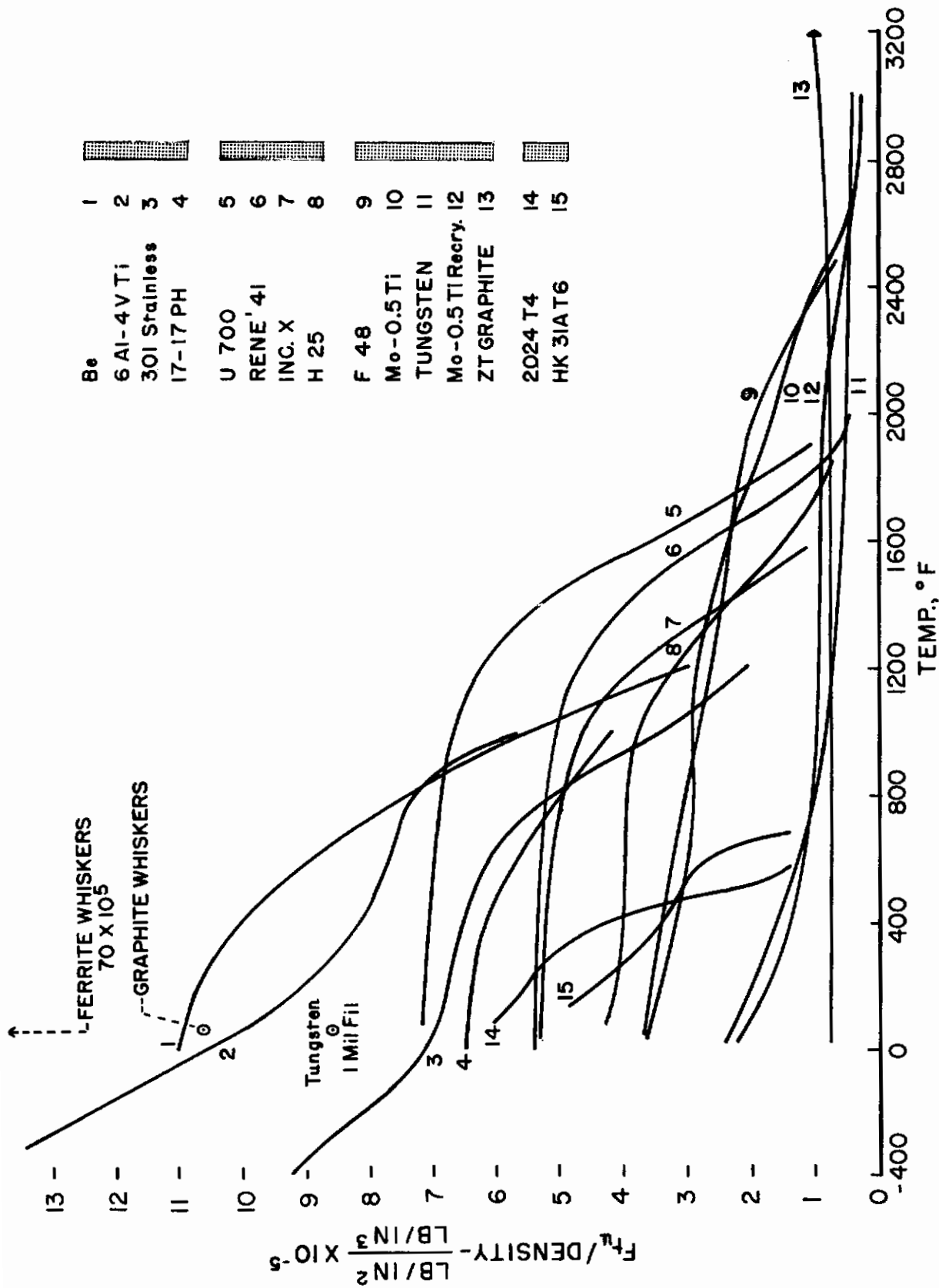


Figure 1.

STRENGTH-TO-WEIGHT RATIOS FOR 10,000 Hr.

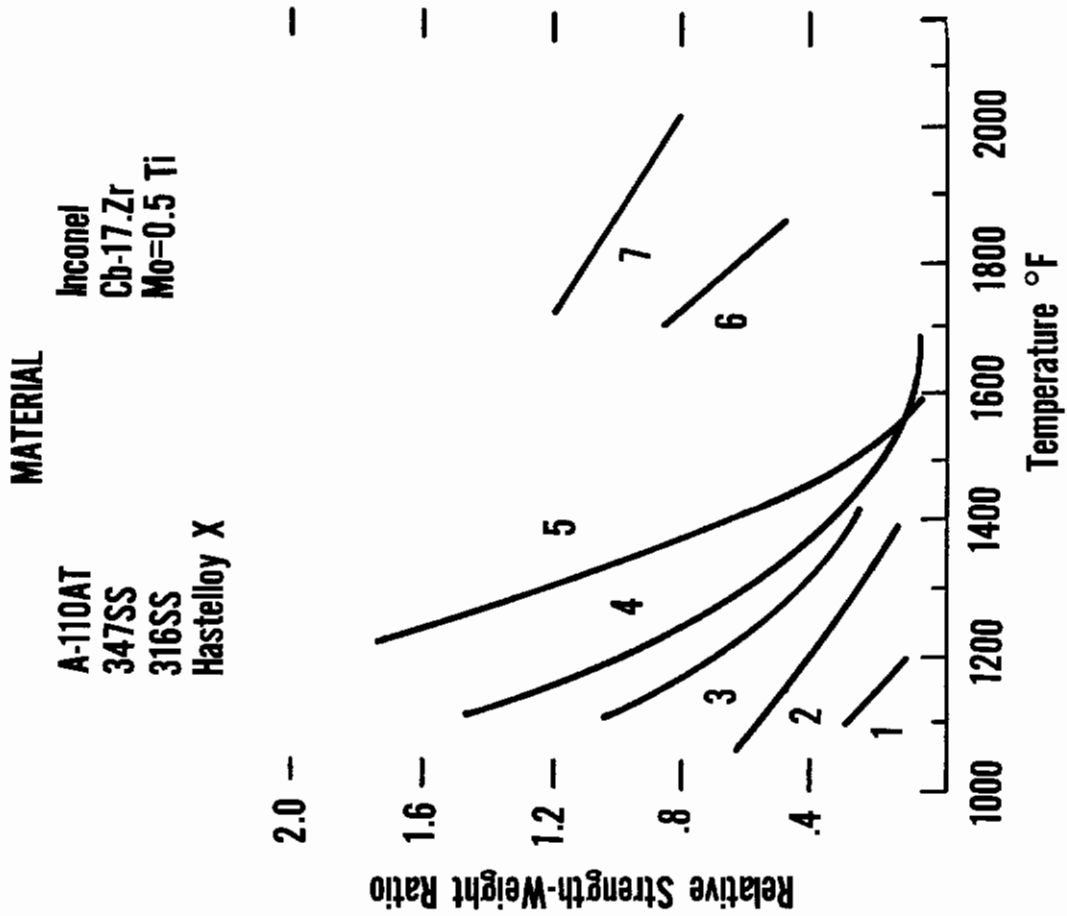
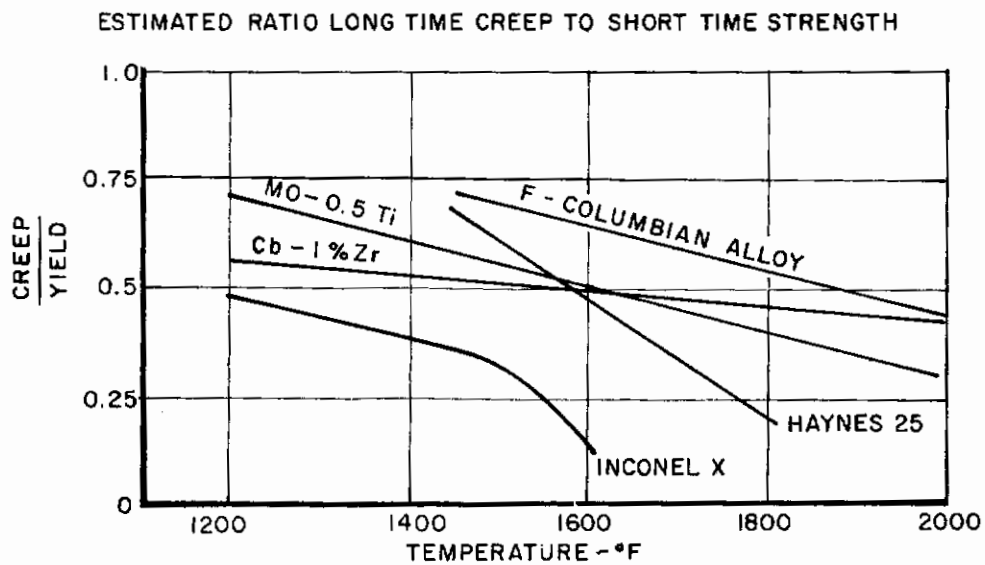


Figure 2.



NOTE:

CREEP = STRESS RUPTURE VALUE AT 0.2% CREEP AT
n HOURS, WHERE n VARIES FROM 100 HRS.
TO 1000 HRS.

YIELD = STRESS VALUE AT YIELD STRENGTH.

Figure 3.

WORKING FLUIDS & COOLANTS

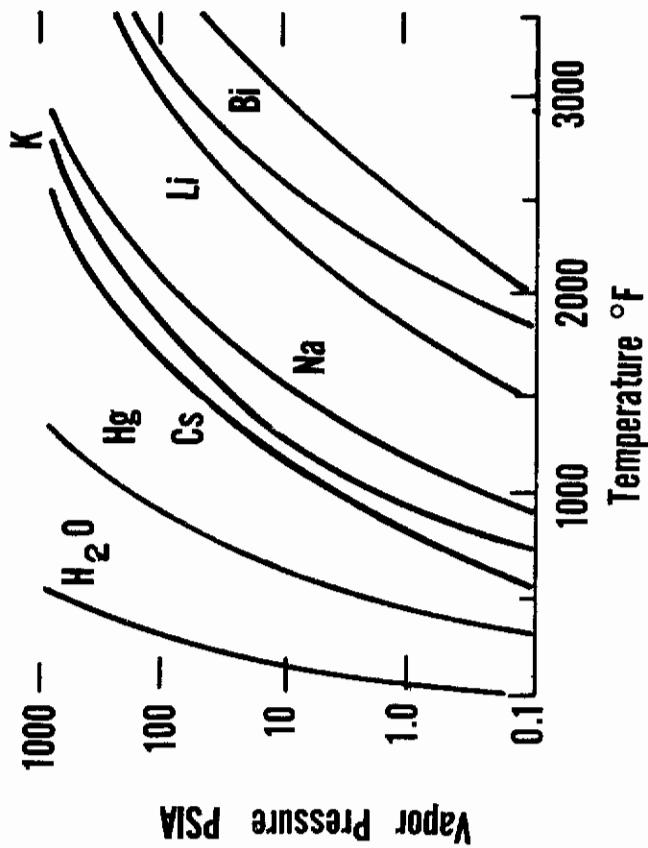


Figure 4.

MAJOR COMPATIBILITY PROBLEMS IN THE FLUID CYCLE

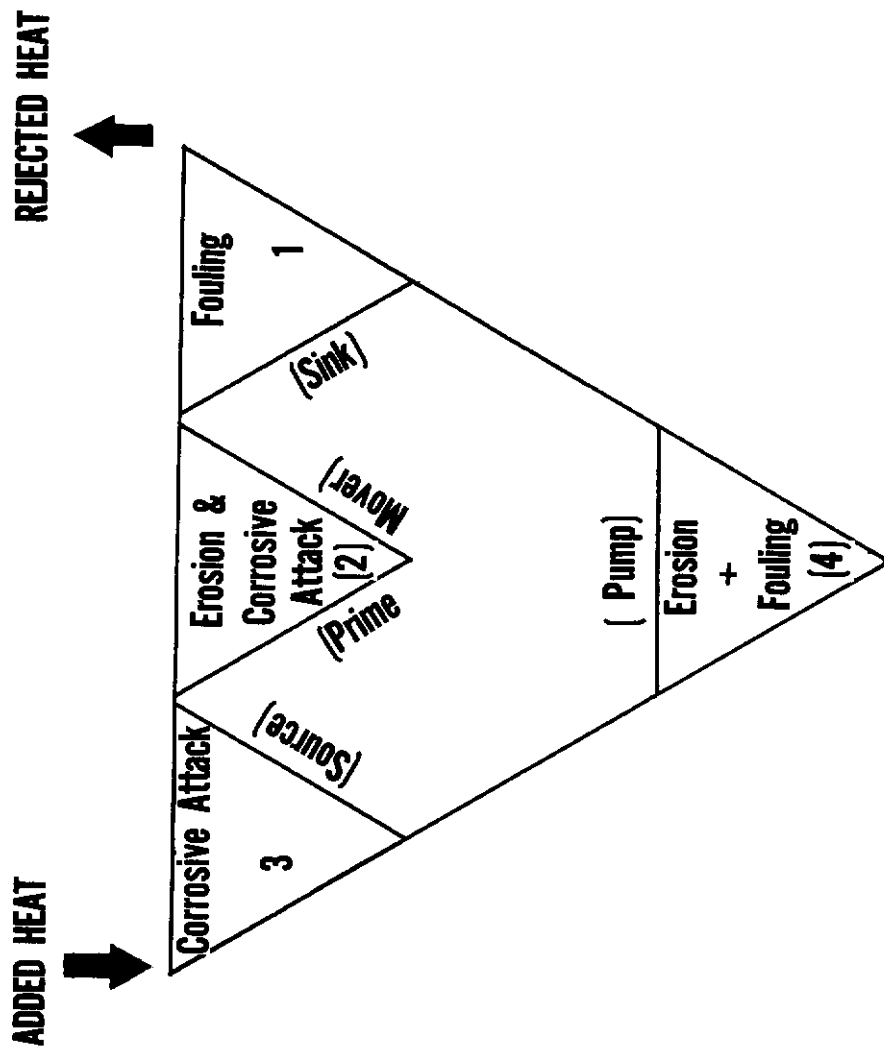


Figure 5.

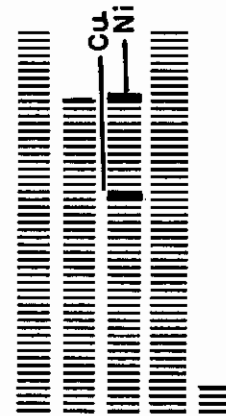
MATERIALS COMPATIBILITY WITH LIQUID RUBIDIUM

Temperature °F In Hundreds
0 2 4 6 8 10 12 14 16 18 20 22 24 26

Ferritic Stainless Steels 400 Series
Austenitic Stainless Steels 300 Series
Low Iron High Nickel Inconels
Pure Iron



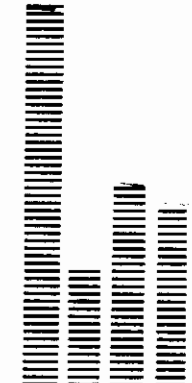
Cobalt And High Cobalt Alloys (Stellites)
Beryllium
Nickel, Copper And Their Alloys
Titanium And Vanadium
Zirconium



Molybdenum
Columbium
Tungsten



Brazing Metals Ni-Mn, Ni-Mo, Ni-P
Silver Brazing Alloys
Noble Metal Brazing Alloys Pt, Pd, Etc.
Aluminum And Aluminum Alloys



Aluminum Oxide
Beryllium Oxide
Graphite (Mono-Metal System)



Figure 6a.

MATERIALS COMPATIBILITY WITH LIQUID LITHIUM

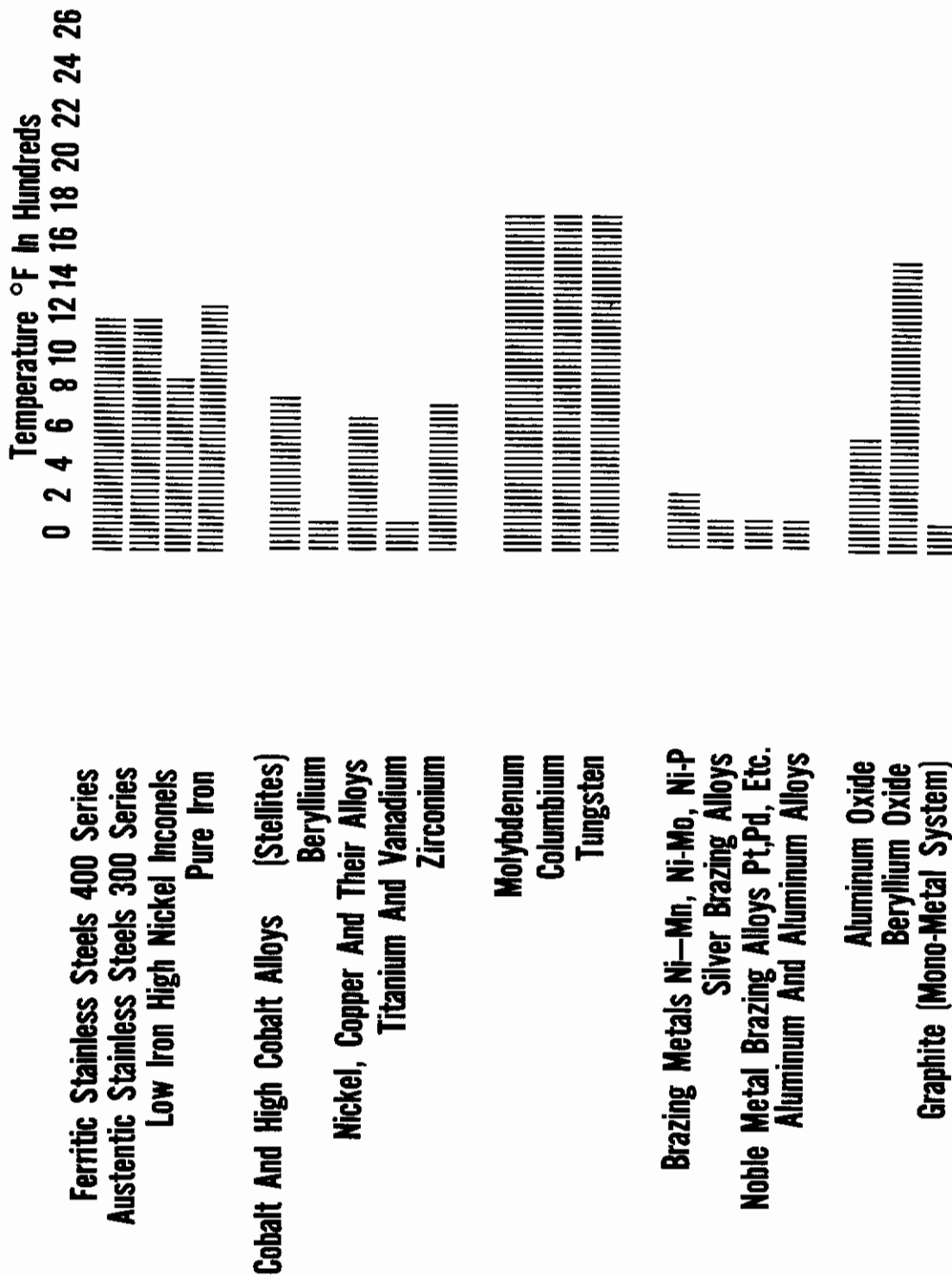


Figure 6b.

THE SOLAR ENERGY ABSORPTION OF THE DARK MIRROR COATING

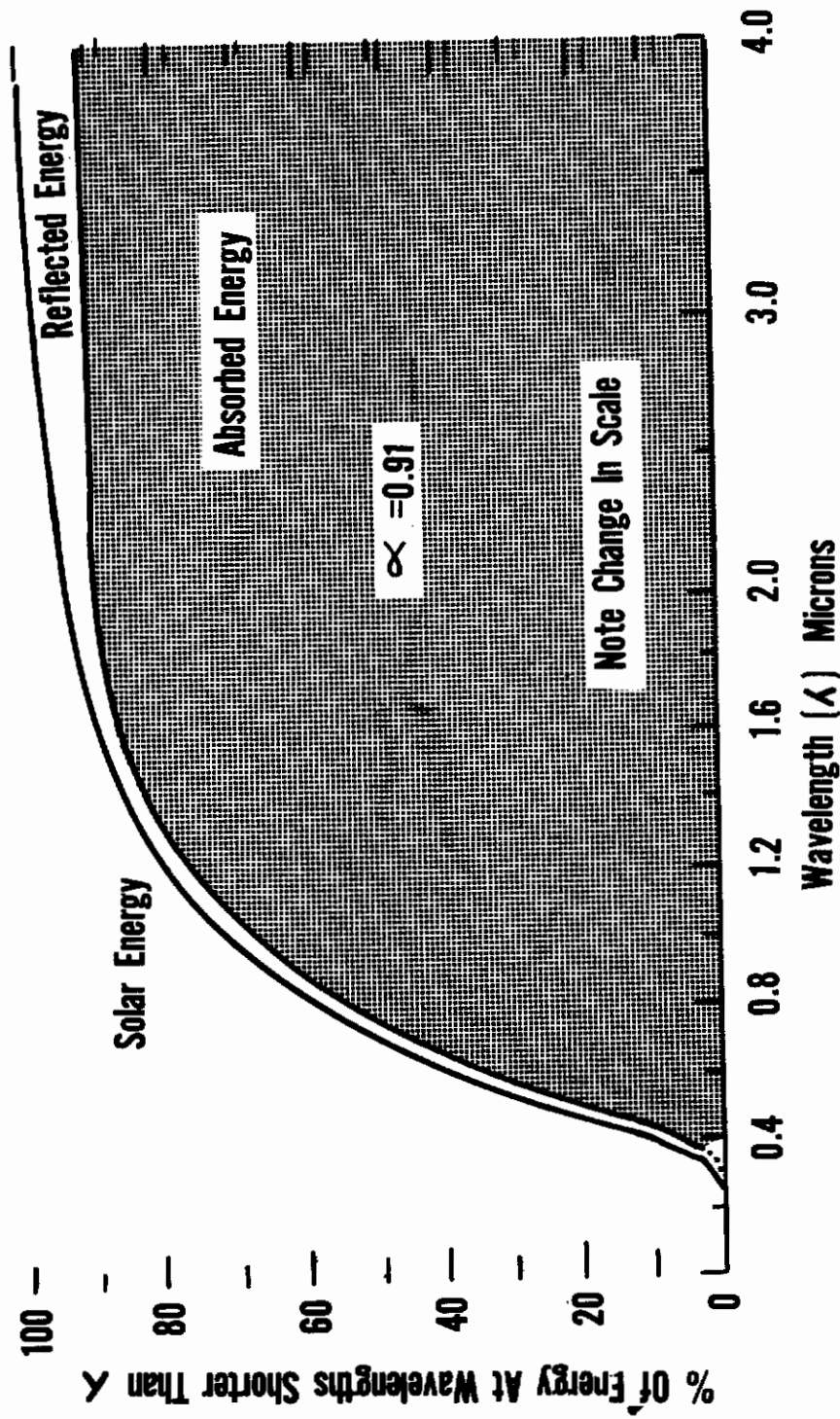


Figure 7.

THE INFRARED ENERGY ABSORPTION (OR EMITTANCE) OF THE DARK MIRROR COATING

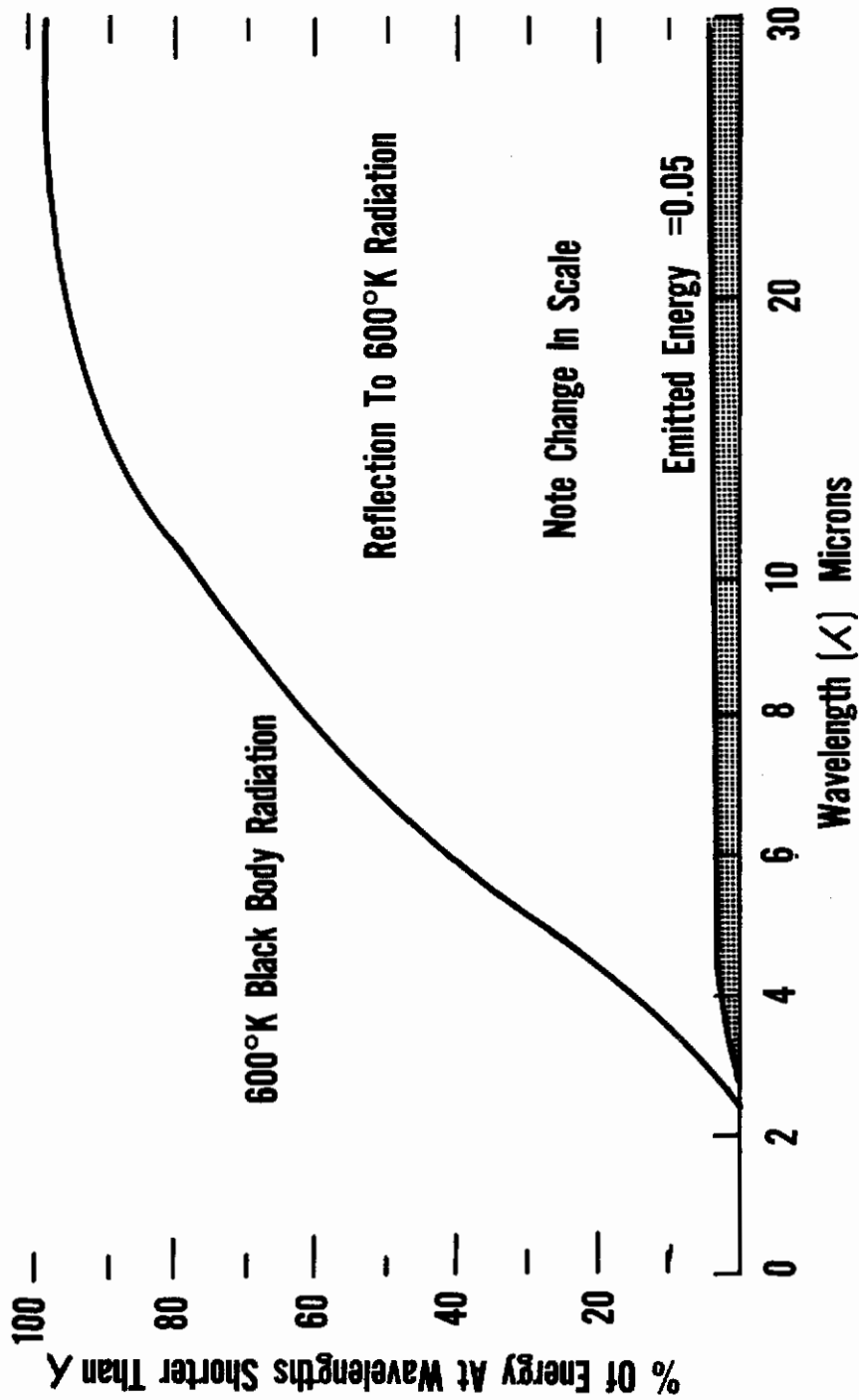


Figure 8.

TOTAL NORMAL EMISSIVITY VS. TEMPERATURE

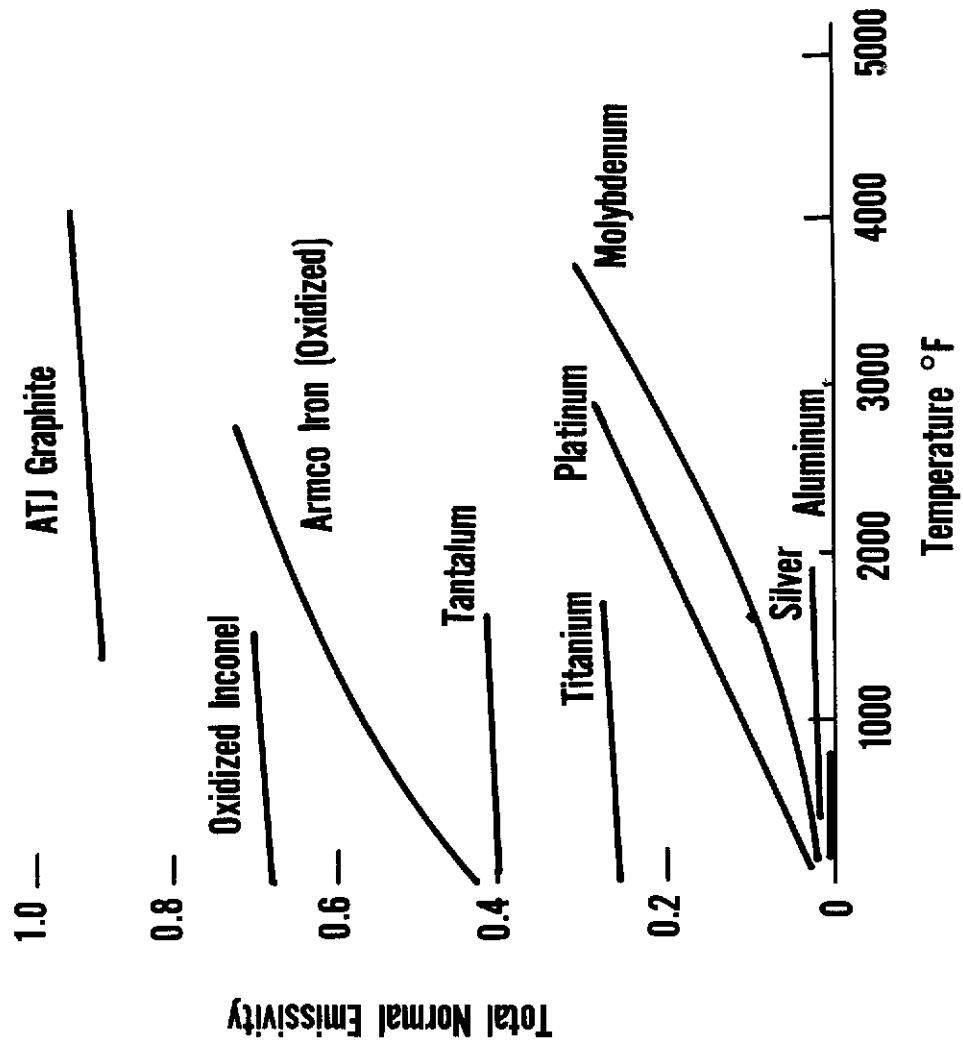


Figure 9.

TOTAL NORMAL EMISSIVITY VS. TEMPERATURE OF VARIOUS REFRACTORY MATERIALS

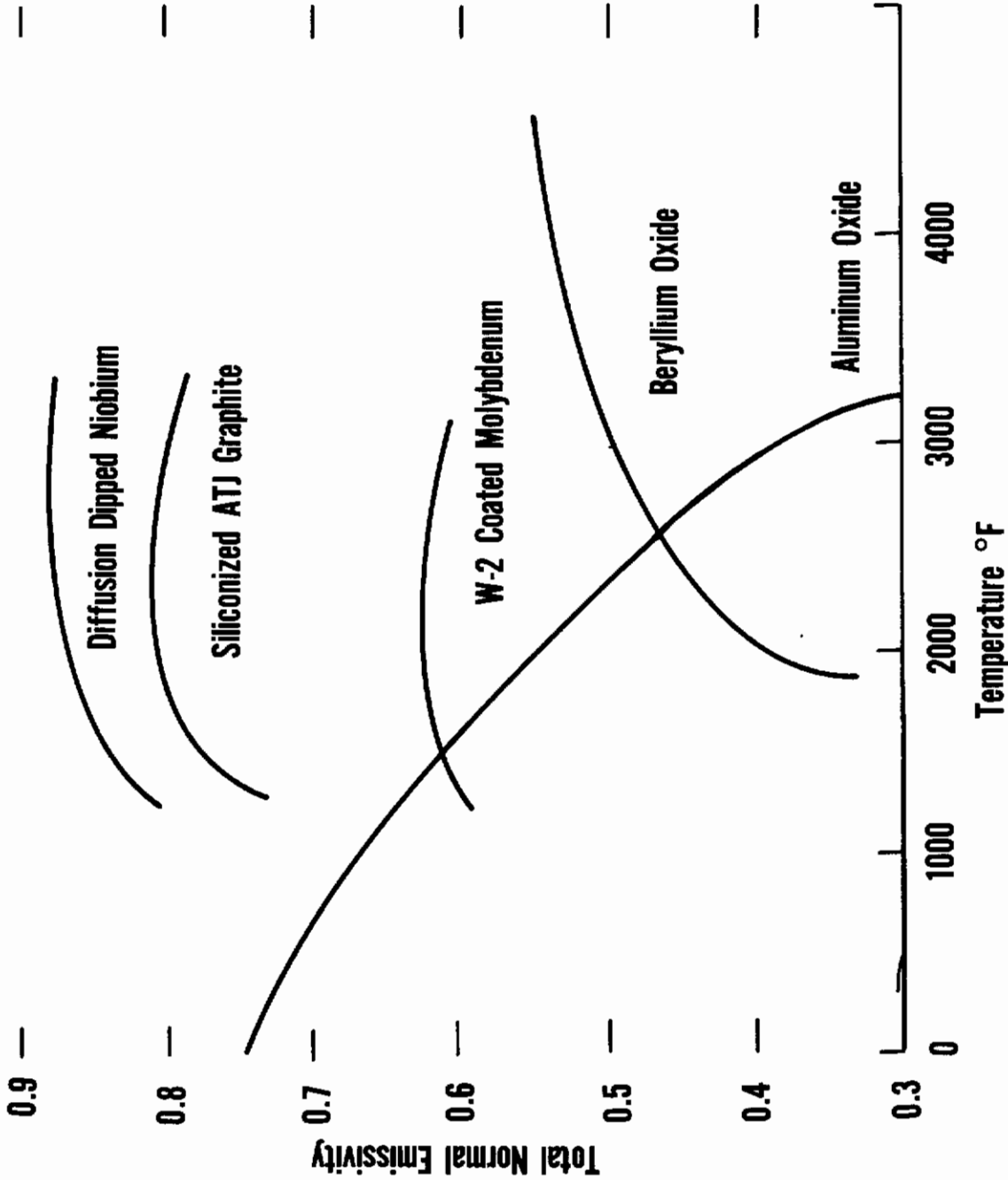


Figure 10.

LINEAR EXPANSION VERSUS TEMPERATURE

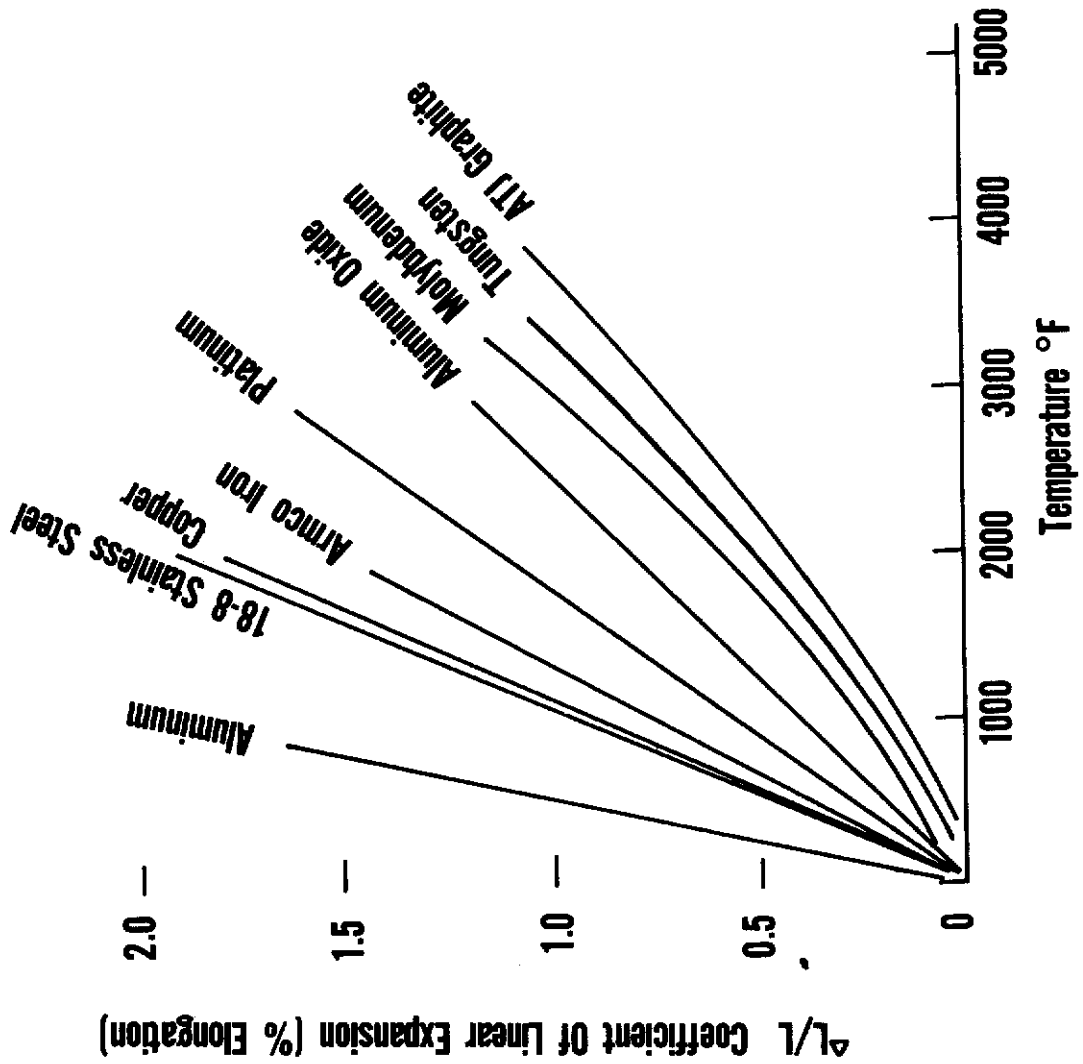


Figure 11.

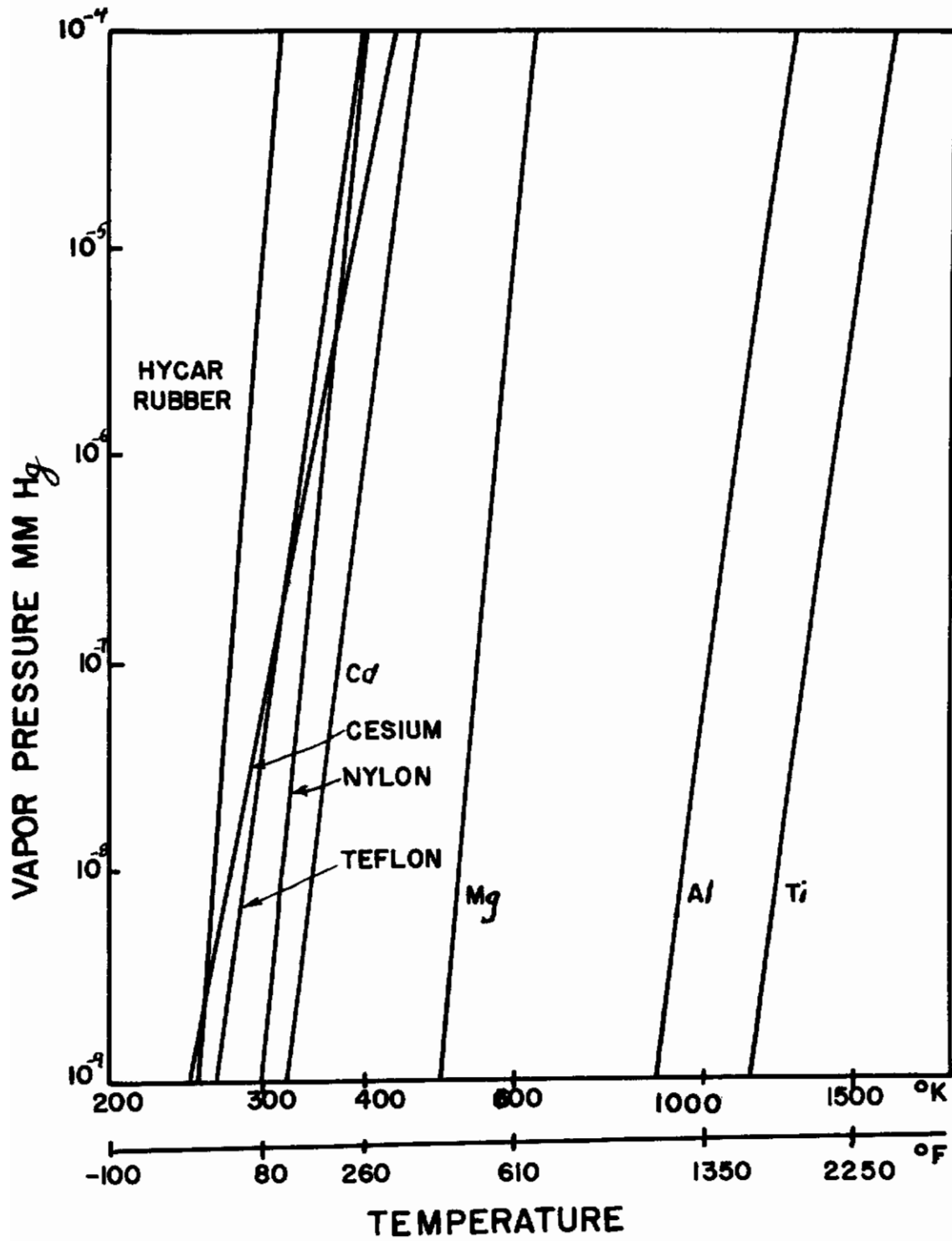


Figure 12.

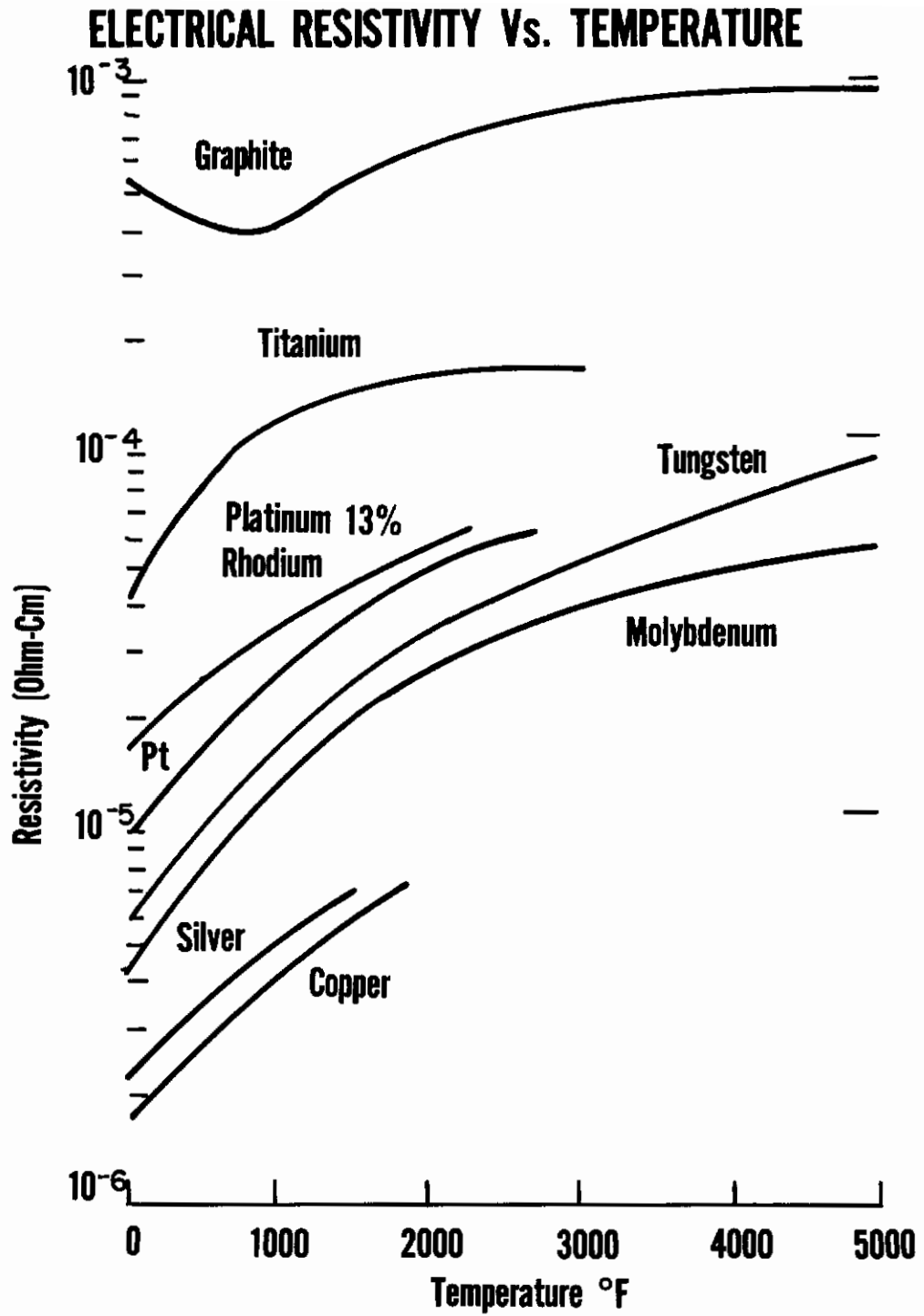


Figure 13.

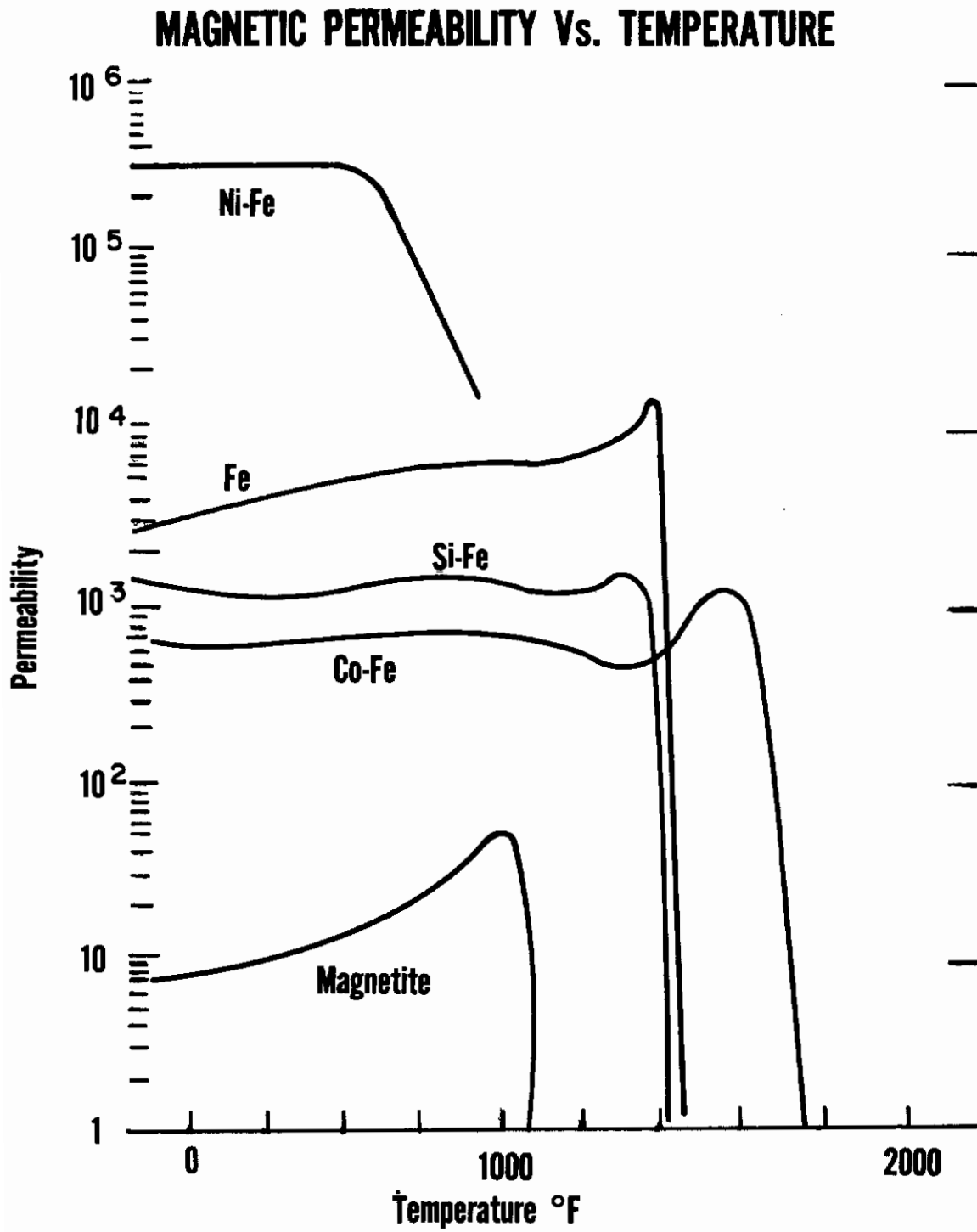


Figure 14.