TID-11429

Lade 4210 (Full paper)

MASTER

ore / AC

9/7/60

71933

MATERIALS PROBLEMS IN THE ROVER PROGRAM

by

Donald P. MacMillan

N-1

Los Alamos Scientific Laboratory
Los Alamos, New Mexico

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MATERIALS PROBLEMS IN THE ROVER PROGRAM

D. P. MacMillan

It appears to be true in the Rover program, as well as in the missile and aircraft fields, that improvement of design is placing increasingly severe demands upon materials. It is axiomatic that design can only accomplish what is permitted by the available materials. In the design of nuclear powered rocket engines there are of course material problems connected with not only the fuel element but also reflector, structural material, control mechanism, and other items. However, attention will be focused herein on the principal and most unique areas, i.e., the nature of problems in fuel element development.

The nuclear rocket engine which will be considered is a reaction motor in which energy is generated in solid fuel elements and transferred to a gaseous working fluid. The simplest measure of performance is specific impulse of the propellant. This is roughly proportional to the square root of absolute temperature and inversely proportional the square root of mean molecular weight of the reaction fluid passing through the nozzle. It is therefore inescapable that every effort should be made to develop fuel elements to withstand the highest possible temperature. The strong dependence of

$I \sim \sqrt{\frac{T}{M}}$

specific impulse on molecular weight also dictates that the reaction fluid shall be hydrogen, or largely hydrogen. The use of a reducing gas establishes the character of the chemical interactions of propellant and fuel elements and sets the nuclear rocket apart from air breathing devices.

The number of elements and compounds remaining solid, from which one may choose materials for fuel elements, decreases rapidly (Fig. 1) as temperature is increased so that, for example, a total only about fifty remain solid above 2500°C. Furthermore, there is vastly less information available about these materials than about the materials commonly used at more modest temperatures.

The extremely refractory materials fall into three groups. The first consists of a few metals, notably tungsten, molybdenum, and tantalum. A second class consists of a single member, graphite, which though not strong compared to metals at more ordinary temperatures, retains its strength and actually reaches a maximum at about 2700°C, above which temperature it rapidly becomes plastic. This is in strong contrast to the behavior of metals which steadily weaken from room temperature to the melting point. Fig. 2, Ref: 1, shows the dependence of compressive strength of some graphites on temperature. A third group of refractories includes carbides, borides, oxides, and nitrides of some of the elements of Groups 4-B, 5-B, and 6-B of the periodic table. These compounds of such elements as zirconium, niobium, and molybdenum

are by no means familiar substances like steel and aluminum, but are materials about which the most elementary properties are just being measured.

At ordinary temperatures the design engineer is commonly concerned principally with the tensile strength and creep properties of the material he is using, but the problem is somewhat different at the higher temperatures encountered in a nuclear rocket engine. Since the life required of the reactor is measured in minutes rather than in hundreds or thousands of hours and because, in the interest of performance, temperature is pushed to the point where the materials become plastic, it is the creep properties which are of greatest importance. The tensile and compressive creep properties of some varieties of graphite have been measured at Los Alamos. Fig. 3, Ref: 2, shows that the tension creep rate increases with both temperature and applied stress. It is convenient to express stress as a fraction, $\frac{\sigma}{\sigma_B}$, where σ_B is the breaking stress and σ is any other value of stress. Fig. 4, Ref: 3, shows that similar effects occur under compressive stress. The measurement of properties of graphite is complicated by the anisotropy of the material which results basically from the anisotropy of the solid particles of filler material used in the manufacture of graphite.

Graphite used to be almost exclusively a tonnage material made principally for use as electrodes in the steel industry and as such its manufacture was not closely controlled. The

mechanical properties of small pieces of graphite have been studied quite a lot and have been found to be fairly uniform throughout the piece; however, in large pieces of stock the properties commonly vary quite substantially from point to point. Fig. 5 shows a cross section of a piece of 36 inch O.D. specially processed H4LM graphite cylinder which was sectioned as shown and the tensile strength determined in a number of regions. Strength perpendicular to the grain is labelled $\perp$ and parallel to grain labelled $\parallel$. It is evident that there is very substantial radial variation in strength and, if such material is to be used, the designer must make due allowance for the variation in strength.

Another problem in the use of graphite is the substantial statistical fluctuation in strength of samples which commonly reaches a standard deviation of 5-10% in the case of tensile and compressive strength. This is also illustrated by Fig. 5. No doubt flaws as well as brittleness of the material contribute to fluctuations in strength. If the probability of a part withstanding design stress must be extremely large, e.g., 99.9%, then the designer is forced to use a value of strength of material which is very significantly less than the average value. This contrasts with the more reproducible strength of the commonly used metals in the use of which the designer has only to take account of

comparitively small statistical variations in properties.

Graphite of large sizes is difficult to make flaw free to the degree that is commonly expected in metals. Cracks often occur in the manufacture of graphite and these are not always easy to detect in the stock. It is worth noting that another less well known class of defects also occurs. To learn something about the frequency of occurrence and character of these, an X-ray study was made of two pieces of graphite, one of which is shown schematically in Fig. 5. Where flaws were found the piece was sectioned to lay bare the flaw and thus find out more about the nature of the defects. Fig. 6 shows examples of two different kinds of flaws which were found in this piece of stock and the X-ray image of each may be compared with the photograph of the sectioned flaw. In one instance it appears that a fragment of some volatile material has disappeared during the processing of the graphite, leaving a void. In the second case there appears to have been a region whose properties were unlike the bulk of the graphite so that the X-ray inspection showed it as a region of low density. Fortunately, graphites intended for scientific use are becoming more common and properties better controlled and high quality material easier to obtain.

In a chemical rocket, energy is generated in the burning gases, while if need be the walls of the container are kept at a lower temperature. This is not the case in a heat exchanger type of nuclear rocket where energy is liberated in

solid fuel elements and then must be transferred to the working fluid. Since fuel elements must be of appreciable thickness to sustain mechanical loads, a large temperature gradient is developed even if the material is of good thermal conductivity. This results in a limitation of surface temperature if the centerline temperature of the part must be kept below some arbitrary limit such as the melting point. As a result of this problem, measurement of thermal conductivity of material in the temperature region above 2000°C is needed. The conductivity of graphite is of course dependent upon the density of the material and the type of binder and filler used. The thermal conductivity, like other properties of graphite, is anisotropic. The thermal conductivity of ceramic materials varies within wide limits and often depends strongly on temperature within the range of temperatures encountered.

The compatibility of fuel element materials with the hydrogenous working fluid must also be investigated. This is complicated by the necessity for having fissionable material in the fuel element so that at the very least a ternary system must be dealt with. Measurement of dependence of corrosion upon the conditions of temperature, gas flow, pressure, etc., requires that an apparatus be set up to simulate the conditions encountered in a rocket engine and to control and measure these conditions. The energy density required of a rocket

engine in order to lift itself and its load against gravity is not commonly appreciated. The high energy density in a rocket engine makes electrical heating of test samples a problem so that even using power of the order of 1000 KW the size of sample that can be heated is suprisingly small. Apparatus for testing materials under conditions which simulate the environment found in nuclear rocket engines is necessary. In this, for example, the dependence of rate corrosion of graphite by hydrogen on temperature can be measured. Corrosion of graphite by hydrogen becomes appreciable at about 1500°C and increases rapidly with rising temperature. To measure corrosion, hydrogen is heated to some desired temperature in an electrically heated preheater and then passed over a test specimen which is separately heated to whatever temperature is desired relative to the gas. Fig. 7 shows some typical test coupons which demonstrate that corrosion is appreciable even in five minutes.

A great deal of study of the physical properties of the refractory metals is needed. The properties of greatest interest include the creep characteristics as well as strength. A substantial contribution to knowledge of these properties has been made recently at the Los Alamos Scientific Laboratory for tungsten and molybdenum. The creep-rupture behavior of commercial powder-metallurgy tungsten rod was studied in the

temperature range 2250 to 2800°C (Ref. 4). The logarithm stress versus logarithm rupture time for tungsten rod is shown in Fig. 8 and is found to be linear. Here, as in other physical property determinations for nuclear rocket application, it is noteworthy that times of interest are short compared to the hundreds or thousands of hours familiar in, for example, ferrous metallurgy. The dependence of creep rate on stress is shown in Fig. 9. It is found that at a given temperature, the logarithm of rupture time is a linear function of the logarithm of the initial stress. The investigators went on to other correlations including determination of Larson-Miller parameter (Fig. 10) and study of the Zener-Holloman temperature compensated creep rate parameter. It was found that the Larson-Miller parameter, Z , is a linear function of the logarithm of initial stress. A similar study of creep rupture behavior of commercial powder metallurgy molybdenum rod was made in the temperature range 1600 to 2500°C where the effects of temperature, stress, and grain growth were investigated.

Obviously, if a metallic fuel element is to be made, a fissionable material must somehow be contained in it. This leads to the necessity of studying such items as mechanical properties and phase diagrams of at least binary systems if for example uranium is to be contained in a refractory metal. Since uranium does not have a very high melting point (1133°C)

compared to desired operating temperatures, one may resort to using a compound of the fissionable material but this also brings complications resulting from the fact that substantially any element with which uranium forms a stable compound will also react with the refractory metal. This necessitates study of ternary phase diagrams which at best is rather difficult and time consuming.

The refractory metals, like the more familiar ones, recrystallize when held at high temperature for a protracted period. Restraint of crystallization of tungsten by incorporation of 1 or 2% thorium dioxide is familiar from manufacture of thoriated tungsten filaments. Here the interstitial material blocks the grain growth somewhat so that the metal will withstand a temperature several hundred degrees higher before recrystallization sets in. Fig. 11 shows molybdenum foil doped with light element material to restrain grain growth. This was effective for a 20 minute test at 1800°C, as can be seen from the fibrous structure of the metal after test. However, a sample is also shown which was heated to 2200°C for 20 minutes. Here restraint of crystal growth had completely broken down and the sample consists of only two grains. The weakening of metals by recrystallization makes their utilization more difficult.

Two of the refractory metals, tantalum and niobium, absorb hydrogen and are thus embrittled. The hydrogen is absorbed in

the temperature range of a few hundred degrees centigrade but not at higher temperatures. This leads to difficulties in utilization of these metals.

The third class of highly refractory materials may be somewhat loosely called ceramics. Of course, the usual ceramics, based on silicates, are not refractory enough for application as fuel element material in a nuclear rocket. The principal materials of interest are the carbides, oxides, borides, and nitrides of Groups 4-B, 5-B, and 6-B of the periodic table. In general, these compounds are characterized by brittleness and inferior thermal conductivity, with the result that problems of fabrication, resistance to thermal stress, and strength of parts present formidable problems. There is rather little known about even elementary properties of most of these substances and it is not uncommon to find gross misinformation in the literature. The situation is complicated by the fact that these substances do not display fixed composition like familiar materials from elementary chemistry such as H_2O and $NaCl$ in which the ratios of different kinds of atoms in a compound are as small fixed integers. Instead, the composition of these interstitial compounds is substantially continuously variable and with variation in composition there is variation in properties. One of the most important activities in this field is investigation of the phase diagrams of the systems of interest. One of the

greatest difficulties is to obtain pure compounds for study. It is generally not sufficient to order a compound by name from a supplier as one would order a pound of some common chemical with confidence that the composition will correspond to the label.

If a fuel element is to be made from some of these ceramic materials, uranium must somehow be contained in it. This makes it necessary to study the phase diagrams of at least ternary systems. Furthermore, the desired operating temperatures of fuel elements are so high that substantial evaporation occurs and since it is more the rule than the exception that different atomic and molecular species have different evaporation rates, it follows that the composition of these materials changes and with this changes occur in physical properties such as strength and thermal shock resistance, as well as melting point. Study of these materials generally involves measuring their composition, and this in itself is not easy because analytical methods for these substances are often difficult or not fully worked out.

The measurement of temperature where an object can be seen is usually most satisfactorily done with an optical pyrometer. However, in the numerous instances where temperature at a blind spot must be measured, one commonly resorts to a thermocouple. Certainly in the case of a nuclear reactor which cannot easily be approached by human beings, there is

a need for thermocouples which will operate above 2000°C in contact with whatever environment may prevail. This is particularly difficult, for example, where the thermocouples must come in contact with graphite. Most metals react with carbon to form carbon-rich eutectics whose melting point is disappointingly low, far lower than the melting of the pure metallic carbide. The best thermocouple so far developed for this application is tungsten versus tungsten containing 25% rhenium (Ref. 6). An additional problem in the use of thermocouples is to obtain adequate electrical insulation, since the electrical resistance of most materials decreases rapidly in contact with graphite at temperatures above 2000°C. Boron nitride is often useful in this application.

Environmental testing of materials under conditions simulating all but the radiation field can usually be accomplished using electric heating. Materials under test can be given a total irradiation equaling that expected in a rocket reactor by irradiation in a reactor such as MTR or ETR. However, even such reactors as these fall short of the dose rate of a rocket reactor by one or more orders of magnitude. Altogether the most satisfactory method of assessing performance of materials under environmental conditions is to carry out material tests in the rocket reactors themselves. This necessitates recovery of samples from the reactor after com-

pletion of the test. To accomplish this, a large hot cell has been built at the Nevada Test Site. After completion of the reactor testing, the reactor, which is mounted on a specially designed railroad flatcar, is brought to the disassembly building. The hot cell as seen from the large entrance door is shown in Fig. 12. Equipment includes a high capacity overhead manipulator carried on a bridge crane (not yet installed when the picture was made), two General Mills side wall manipulators and a pair of Argonne Model 8 manipulators. The latter, of course, are intended for only such things as repair of the larger manipulators and handling small pieces of material. The hot cell is overlooked by several windows, from any one of which the larger manipulators can be operated. After gross disassembly of the reactor has been accomplished in the large hot cell, examination of parts of the reactor can be continued in detail in two smaller hot cells in the building, where, if desired, small samples can be cut out for further examination at Los Alamos.

The investigation of material properties in the temperature region above 2000°C is in a comparatively primitive state at present and the progress of reactor design in this field depends upon improvement of our knowledge of materials just as does improvement in design of vehicles placing less severe demands upon temperature.

REFERENCES

1. Some Mechanical Properties of Graphite in the Temperature Range 20° to 3000°C, Paul Wagner, Allen R. Driesner, E. A. Kmetko, P/702, Vol. 7, page 379. Second International Conference (Geneva) 1958.
2. High-Temperature Properties of Graphite, II. Creep in Tension. Paul Wagner, Allen R. Driesner and Larry A. Haskin.
3. High-Temperature Mechanical Properties of Graphite, I. Creep in Compression. Paul Wagner and Allen R. Driesner.
4. Short Time Creep-Rupture Behavior of Tungsten 2250°C to 2800°C, W. V. Green. Trans. Met. Soc. of AIME, 215, Dec. 1959, p. 1057.
5. Short Time Creep Rupture Behavior of Mo at High Temperature, W. V. Green, M. C. Smith and D. M. Olson, Trans. Met. Soc. of AIME, 215, Dec. 1959, p. 1061.
6. Thermocouples for Use in Carbon Atmosphere, M. R. Nadler and C. P. Kempter, to be published.

NUMBER OF ELEMENTS AND BINARY COMPOUNDS
WHOSE MELTING POINT IS GREATER THAN $T^{\circ}\text{C}$

Figure 1

Ultimate compressive strengths of graphite as a function of temperature. 1. H4LM, parallel to grain; 2. H4LM, perpendicular to grain; 3. CK, parallel to grain; 4. LDH ($1/8 \text{ g/cm}^3 \text{ U}$), parallel to grain; 5. LDC ($1/4 \text{ g/cm}^3 \text{ U}$) parallel to grain.

Figure 2

EXPERIMENTAL TENSION CREEP CURVES SHOWING THE EFFECTS OF
STRESS (REDUCED) AND TEMPERATURE ON LDC GRAPHITE

Figure 3

CREEP CURVES SHOWING THE EFFECTS OF STRESS (REDUCED)
AND TEMPERATURE ON LDH GRAPHITE

Figure 4

|| = Parallel to grain

⊥ = Perpendicular to grain

○ Sample taken from top

□ Sample taken from bottom

Figure 5. Point to point variation in room temperature strength of 36 inch O.D. H4LM graphite

UPPER PICTURES: FLAWS FOUND BY X-RADIOGRAPHY
LOWER PICTURES: CROSS SECTIONS OF THE SAME FLAWS

Figure 6

Graphite test coupons about 1-1/4 x 3 inches.
Samples b and c were subjected to flowing
hydrogen for five minutes at 2600°C. Samples
a and d were untested.

Figure 7

ENGINEERING STRESS VERSUS RUPTURE TIME

Figure 3

Stress vs creep rate. Open points represent engineering stress vs linear creep rate; filled points represent true creep stress corresponding to minimum true creep rates.

Figure 9

Larson-Miller parameter, Z , vs engineering stress.

Figure 10

a

b

Light element doped molybdenum foil after
20 minutes at a) 1800°C b) 2200°C

Figure 11

Disassembly Hot Cell in MAD Building, Nevada Test Site,
as seen through entrance door.

Figure 12