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Requirements of Capsule Materials*

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ABSTRACT

The requirements of capsule materials for radioisotope heat sources are demanding particularly for space applications where the requirements often exceed current materials capabilities and knowledge. The present day heat sources utilizing alpha-emitting radioisotopes are in effect moderately high temperature pressure vessels, which for reasons of safety, should, with high reliability, contain the fuel in a multitude of hostile environments. Consequently, the capsules are generally multilayered structures with each layer having a definite function relative to the operating conditions and probable environments.

One may classify the capsule material requirements as follows: those resulting from (a) the radioisotope fuel and its form, (b) operating conditions such as temperature and life, (c) anticipated and potential environments, e.g., launch accidents, space vacuum, and reentry, and (d) mutual compatibility and stability considerations, arising from capsule materials selection. These

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requirements will be discussed with regard to current practice, materials knowledge, and future needs. The discussion will be biased toward space applications since the materials problems encountered seem more exacting and less facile in those applications. The lack of knowledge concerning materials behavior for long periods of time (greater than 5 years) at the service temperatures of radioisotope heat sources is a serious problem and this frequently has led to materials selection based on availability of limited information rather than on the basis of potential promise of materials such as refractory metals. Future service temperature requires that materials other than superalloys be extensively explored for radioisotope capsule applications.

INTRODUCTION

Snap 3B was a signal achievement as it initiated the use of radioisotope electrical power generators in space. Since the June 29, 1961, launch of SNAP 3B7, which is still producing power, the design concepts of the generators are basically unchanged. However, the materials used for the capsule, the energy converter, and throughout the generator have changed and are still changing in rather dramatic but not surprising ways. The potential use of thermionic conversion units presages even greater changes in the materials technology and requirements. What has already started in capsule technology is that increasing temperature and life requirements have started a trend away from nickel or cobalt based superalloys to refractory metals and noble metal alloys. In time dispersion-strengthened alloys, fiber eutectic alloys, composite alloys, and ceramics may prove advantageous for capsule structures. In many ways, the increasing sophistication of the materials used in capsules is analogous to jet engine turbine bucket development over the past twenty years.

The capsule and the radioisotope fuel it contains is the heart of the system since it is the source of energy. The function of the capsule is to contain the radioisotope in a usable form during operation and to minimize safety hazards associated with the radioisotope fuel. The latter capsule function, and the design ramifications thereof, are critically dependent on the mission safety philosophy, i.e., fuel dispersal, intact reentry, intact through impact, or post impact

integrity. The current and potential future requirements for capsule materials for space applications are reviewed here. The need to extend present materials capabilities for the relatively long service life and high reliability required for space uses is stressed as vital.

MATERIALS REQUIREMENTS

The requirements for capsule materials are dependent to a large extent on the intended use of the radioisotope power generator. This applies for terrestrial and biomedical applications as well as the space applications considered here. The capsule materials requirements may be arbitrarily categorized into four areas. First there are requirements that are a direct result of the radioisotope fuel and its chemical form. For example, with a gamma emitting radioisotope such as ^{60}Co , shielding may be a prime consideration; however, for an alpha emitting radioisotope such as ^{238}Pu shielding is a very minor consideration except in multi-kilowatt man rated systems. Helium gas containment or venting may be the dominant criteria. A second category of requirements are a consequence of the operating conditions, in particular temperature and service life. Thirdly, there are the requirements imposed by the operating environments and potential accident environments. The environments are of such paramount importance that they will be discussed in a separate session at this conference. In the accident environments, the prime concern is to insure safety and all other considerations such as reliable power generation are distinctly secondary. Fourthly, there

are requirements that are dependent on the materials selected to meet previous criteria; these include fabricability, mutual compatibility, and thermodynamic stability. In general the requirements for terrestrial use differ from those for space in that the normal and accident environments are much less severe for the terrestrial application from a materials standpoint. In addition, since weight is not a prime consideration for terrestrial applications, much larger safety factors may be used.

Because of the difficulties encountered in meeting the varied materials requirements, presently designed radioisotope capsules are generally multi-layered structures. The material for each layer is selected because it possesses one or more of the required attributes. Hence, a capsule may require five or six consecutive layers of materials across which good thermal conductivity is required. In Figure 1 is a schematic drawing of a hypothetical capsule which illustrates the principles involved and does not represent the capsule for any SNAP generator. The essential layers represented are: 1) capsule liner, 2) structural shell, 3) diffusion barrier, 4) oxidation resistant cladding, and 5) emittance and/or ablation coating. Chemical compatibility with the fuel is the selection criteria for a liner. The material selected for the structural shell is directed primarily by the operating conditions and secondarily by the environments. The selection also depends, in the case of alpha fuels, on whether the capsule is vented or unvented. The diffusion barrier is selected to

limit the interdiffusion between shells and hence is selected to improve the mutual compatibility and interface stability. An oxidation resistant cladding is often required because of the earth operating environment and the oxidation characteristics of the structural shell, particularly if the shell is a refractory metal alloy. An outer emittance and/or ablation layer may frequently be desired for self-evident reasons.

The situation I am describing is a rather exacting materials problem. The situation also calls for ingenuity and extension of current materials capabilities. In recent capsule designs the application of alloys such as T-111 and Mo-TZM represents the first use to my knowledge of refractory metals for long service life (~10,000 hours) under stress at reasonably high temperatures (>800°C). Other innovative uses of materials will no doubt follow as operating conditions require higher service temperatures and/or longer service lives. As we focus attention on the various categories of materials requirements, the need to extend current materials technology becomes more apparent.

First consider the requirements due the radioisotope fuel and its form. To date the alpha emitting fuels have been favored for space applications. However, cheaper fuels such as ^{90}Sr have been used for terrestrial applications. The release of helium from fuels such as PuO_2 and the resulting increase in internal gas pressure impose the need for creep strength on structural materials used in unvented capsules. This requirement will continue to exist until it

is demonstrated that helium can be reliably vented. Until such time, capsules for alpha fuels will probably continue to be pressure vessels. An exception might occur if the helium could be retained in the fuel itself.

Most of the alloys with high temperature capability were designed for service lives of the order of 1000 to 5000 hours or less. Accordingly, very little creep data exists beyond these anticipated service lifetimes. Capsule materials for an alpha emitting isotope such as ^{238}Pu ($t_{0.5} = 87.5$ yrs.) usually have service requirements of greater than 10,000 hrs and may extend for longer than 100,000 hours. In a recent capsule designed as a test vehicle for the Large Radioisotope Heat Source Capsule Program^{1,2}, see Figure 2, the requirement on the structural shell was that it should exhibit a creep strain of less than 1 percent in seven years where the capsule was designed for an operating life of five years and an operating capsule surface temperature of approximately 1100°C. The rationale for the creep strain limitation of 1 percent in seven years was that capsule integrity could be assured with some confidence over that strain and time interval. It also assumed that the capsule would be launched within a year after encapsulating the $^{238}\text{PuO}_2$ fuel. The candidate materials for this capsule structural shell were columbium and molybdenum alloys, T-111 and Ta-10% W. In this case T-111 was picked because of superior creep strength and excellent impact resistance. This particular test capsule was intended for use in generating materials data applicable to the NASA

Brayton Cycle demonstration, however, it should be noted that capsules for a new generation of thermoelectrics, i.e., Si-Ge and cascaded thermoelectrics, will have the requirement for similar operating times and temperatures.

With beta and gamma emitting radioisotopes, the need for creep strength in the structural material diminishes. Instead, the question of providing gamma shielding and impact strength in the capsule arises. Tungsten and its alloys are candidate materials that meet these criteria and also have high temperature utility.

The chemical activity of radioisotope fuel forms requires that chemical compatibility between the radioisotopic fuel and the capsule be provided. This problem can be particularly severe as the fuels often chemically attack potential capsule materials in localized areas such as grain boundaries and weld zones. In general, compatibility can only be established by isothermal experiments run at the temperatures of interest. For example, limited results are now available from compatibility tests of PuO_2 , Po, GdPo, Cm_2O_3 , SrTiO_2 , Pm_2O_3 , Tm_2O_3 , and Co; this work is still in progress at Mound Laboratory, Oak Ridge National Laboratory, Battelle Northwest Laboratory, and Savannah River Laboratory. Materials such as Pt, Pt/Rh alloys, Ta, and Ta/LOW are current candidates for liner materials for use with PuO_2 . Changes in the fuel form and its characteristics, such as purity, will modify the chemical interaction with the container or liner materials. Since the fuels are often incompatible with the

structural material, capsules are designed with a liner whose function is to provide primary containment of the fuel. The liner material is selected from compatibility considerations and is not required to contribute significantly to the overall strength of the capsule.

The requirements, due to the operating conditions, are straightforward. The primary considerations are the operating temperature and desired lifetime. These requirements basically modify the requirements for adequate creep strength and fuel-capsule compatibility just discussed. As temperature and lifetime increase, the demands on capsule materials become more exacting. Hence, as thermoelectric technology moves from PbTe to higher temperature thermoelectric materials, such as Si/Ge alloys, then presently used, nickel and cobalt based superalloys become marginal.

The environmental requirements are less well defined. This simply reflects a lack of knowledge of the severity of many accident situations and of the behavior of materials in abnormal or extraterrestrial environments. Even the anticipated environments are difficult to define. The predictable requirements from anticipated environments for space use include pre-launch atmospheric effects (e.g., oxidation), launch abort, space vacuum, reentry and aerodynamic heating, capsule impact, and oxidation and corrosion in post impact environments. More detailed accounts of these environments will be presented in a later session. For the present, I merely want to indicate the ramifications of these environments on capsule materials requirements.

The prelaunch atmospheric effects are negligible when the capsule structure has inherent oxidation resistance. One reason for this is that capsule surface temperatures when in air are roughly $1/2$ to $2/3$'s of the equilibrium surface temperature when operating in space vacuum. Thus, for service temperatures within the capability of Haynes-25 or Hastelloy-N prelaunch oxidation effects are insignificant. Capsule structural shells fabricated from refractory metals require protection prior to launch. In many cases it is preferable to provide this protection by cladding the capsule with a noble metal alloy. This cladding also provides oxidation protection for reentry and post reentry conditions and selection is usually based primarily on these conditions.

The environments related to launch abort such as pad fires (fireballs) and explosions, premature reentry, etc., essentially demand an extension of the normal environment requirements. For example, in launch pad fires and fireballs the capsule should not release fuel by melting or structurally degrade to a significant degree. In an explosion, the capsule should be capable of withstanding the explosive force without rupture. In addition, it should be resistant to shrapnel penetration. The aerodynamic heating in a premature reentry has a different profile than normal reentry but the materials requirements are very similar in that the capsule should be highly resistant to thermal degradation and melting.

Vaporization losses and changes in surface condition in space vacuum are causes of concern. Therefore, capsule materials that are

exposed to space vacuum should have very low vapor pressures (less than the vacuum pressure of space) at the operating temperatures. In general, it is difficult to offset this requirement by providing a positive pressure of inert gas within the generator because of potential leaks and micrometeoroid penetration. Vaporization losses of constituents and the breakdown of normal surface oxides in space could potentially have deleterious effects on the creep resistance. While there is no direct evidence related to this, it is known that surface active agents can drastically alter the deformation and creep characteristics of many materials reputedly by alteration and removal of the surface oxides³⁻⁶.

The requirement for capsule materials varies depending on the reentry conditions, e.g., ballistic coefficient, reentry angle, etc., and upon the safety philosophy involved, i.e., intact reentry, intact impact, and dispersal. For example, in a dispersal capsule the objective is to breach the capsule at very high altitude and effect a wide dispersal of the fuel. The capsule breach may be designed to occur from capsule melting at a localized hot spot. For either intact reentry or intact impact, the objective is to minimize capsule structural damage due to reentry heating. Therefore, the capsule structural material must have a melting point sufficiently high to preclude weakening both by general melting and melting of any of the alloy phases. Secondary recrystallization and exaggerated grain growth effects may be important but they have not been a major concern.

Capsule impact requirements seem to be becoming increasingly important. The reason is recent efforts to insure that capsules retain their integrity through and post impact. The rationale is that if the fuel is contained through impact, the fuel is relatively safe. Release well after impact is likely to occur at relatively slow rates and there is a reasonably high probability against any gross fuel release. Also, the probability of atmospheric resuspension of the fuel is greatly reduced. This discussion is germane to alpha emitting fuels that are stable in air and probably does not apply to fuels such as ^{210}Po , ^{90}Sr , or ^{60}Co . For these latter isotopes total containment on earth is highly desirable, therefore capsule integrity well after impact is a necessity unless the capsule can be effectively buried in acceptable locations such as ocean depths.

Impact resistance is of great importance, but this characteristic can not be reliably predicted. Typical impact velocities are in the range of 100 to 600 feet per second. It is generally considered that the most severe condition is for impact on granite, hence most capsule impact testing is against granite. The capsule temperature at time of impact and the effects of the thermal and stress history of the capsule complicate the situation. The capsule should absorb the energy of impact by deforming without fracturing. The capsule structural material should exhibit good impact resistance in an aged condition, see Figure 3, 4, and 5. Lack of notch sensitivity and good ductility seem to contribute to this characteristic.

Protecting the capsule in post impact environments is difficult at best. Cladding and coating layers tend to abrade or strip away during impact. This has been experimentally observed for Pt/Rh claddings up to 40 mils thick⁷. Greater strength and hardness in the cladding is needed, but it is difficult to provide. A capsule lying on the ground or totally immersed in water (either fresh or sea) will maintain a temperature much reduced from the steady state operating temperature in space because of improved thermal transfer. Therefore, in this situation a refractory metal capsule structural shell might have appreciable life. The Ta/Hf alloys may be useful in this regard since they have a limited degree of oxidation self protection if sufficient Hf is present.

Corrosion in sea and fresh water and stress corrosion are also of concern. Paucity of data regarding these effects makes it difficult to assess the material requirements. Capsule burial with resulting soil corrosion is another area in which it remains difficult to determine the materials needs, see Figure 6. The capsule temperatures vary depending on soil type. A buried capsule that reacts with the soil to form a molten slaglike mass may represent a method of safe containment of radioisotopes.

One must also consider individual material stability, interaction of materials in various layers, and possibility of significantly modifying the materials by interdiffusion across interfaces. The severity will depend on the materials selected, but to the extent feasible instabilities should be avoided. This is vital where the

structural shell is concerned. Formation of Laves phases in cobalt base superalloys, pick-up of interstitial contaminants by refractory metals, and formation of new phases, particularly embrittling intermetallic compounds, can all have dire consequences during service, reentry, and impact. An example of potential problems from diffusion is Pt diffusing into a Ta base alloy. Formation of any of the several known Ta/Pt intermetallics could potentially degrade a Ta alloy structural shell. For problems such as these, an indicated solution is to provide diffusion barriers to minimize problems across materials interfaces. Stable oxides such as Al_2O_3 and ThO_2 are being considered for this purpose.

Finally, the problem of fabricability has to be taken into account. Formability and weldability are vital practical requirements. Capsules are relatively complicated to fabricate and this is further complicated by the presence of the radioisotopic fuel during assembly and weld closure. Thus, formability and weldability assume greater importance than usual.

In summary, the materials requirements are manifold. High temperature strength, creep resistance, high strain rate ductility, oxidation resistance, chemical stability, resistance to environmental effects, high melting point, phase stability at high temperature, and impact energy absorption are vital characteristics of materials selected for the structural shell of radioisotope capsules for space use. Since it is unusual to find these characteristics to an acceptable degree in a single material, capsules are generally multilayered. Each layer

provides for one or more of these materials needs. Terrestrial capsules have less stringent requirements than space capsules because the environmental effects are less varied and are more predictable and greater safety factors may be employed.

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Figure Captions

1. Schematic of hypothetical radioisotope fuel capsule for space applications. The capsule is for alpha emitting radioisotopes and illustrates a multilayered approach to capsule design and materials selection.
2. The Large Radioisotope Heat Source Capsule. The cross section gives the materials layers and dimensions. The inner liner is .020" Ta -10% W, the outer liner is .020" Ta -10% W; the structural shell is .127" tantalum alloy T-111; the diffusion barrier is .002" alumina; the oxidation cladding is Pt-10% Rh; the emittance coating is .004" iron titanate. A shock mitigating structure is incorporated which is a honeycomb structure of Ta -10% W.
3. Cross section of a spherical capsule designed by Hittman Associates. The structural shell is Haynes-25. The liner material is Ta -10% W. Capsule assembly is also indicated. This capsule designed has been extensively impact tested at Sandia.
4. Spherical capsule after impact onto granite. The capsule was in an unaged condition; the nominal capsule temperature at impact was 260°C; the impact velocity was 452 feet per second. The apparent capsule integrity was confirmed by subsequent post impact examination.
5. Spherical capsule after impact onto granite. The capsule had been aged 1000 hours at 816°C; the nominal capsule temperature at impact was 260°C; the impact velocity was 374 feet per second.

6. Burial test of the Snap 27 capsule. The capsule temperature exceeded 1374°C; the total burial time was 48 hours; the soil was bentonite.

TYPICAL RADIOISOTOPE FUEL CAPSULE
CENTERLINE TEMPERATURE $> 800^{\circ}\text{C}$, OUTER WALL TEMPERATURE $> 600^{\circ}\text{C}$

D67-15686

SPHERICAL CAPSULE ASSEMBLY

D67-15673

SNAP 27 BURIAL TEST