

Advanced Stirling Duplex Materials Assessment for Potential Venus Mission Heater Head Application

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[Abstract] This report will address materials selection for components in a proposed Venus lander system. The lander would use active refrigeration to allow Space Science instrumentation to survive the extreme environment that exists on the surface of Venus. The refrigeration system would be powered by a Stirling engine-based system and is termed the “Advanced Stirling Duplex” (ASD) concept. Stirling engine power conversion in its simplest definition converts heat from radioactive decay into electricity. Detailed design decisions will require iterations between component geometries, materials selection, system output, and tolerable risk. This study reviews potential component requirements against known materials performance. A lower risk, evolutionary advance in heater head materials could be offered by nickel-base superalloy single crystals, with expected capability of approximately 1100C. However, the high temperature requirements of the Venus mission may force the selection of ceramics or refractory metals, which are more developmental in nature and may not have a well-developed database or a mature supporting technology base such as fabrication and joining methods.

I. Introduction and Design Requirements

Stirling technology has a long history of offering the potential for providing electrical power generation for various applications. It is an alternative to other power conversion technologies that are candidates for space application such as Brayton and Radioisotope Thermoelectric Generators. Most of the Stirling engine development efforts consider the heater head as the critical, life-limiting component. The heater head is typically a thin-walled cylindrical pressure vessel, and needs to be designed to withstand the stresses in the wall exerted by the internal pressure. Criteria for materials selection usually includes creep performance, fabricability, working gas containment, long-term stability, compatibility with other components as well as working fluids, ability to form a hermetic seal, and ductility/toughness. As will be discussed in more detail below, the envisioned Venus mission could require a heater head design life of as much as 20,000 hours at temperatures near 1200C. While nickel-base superalloys have long performed well in air-breathing turbine engines where temperatures can reach 1150C, typical aircraft engine component lives are on the order of 1000 hours. Terrestrial power systems such as nuclear power plants and land-based turbines are among the few systems where comparable, 15+ year lives at high temperature are expected. The Department of Energy has an existing database on materials for such use, although very few of those materials are capable of the extreme temperatures envisioned here. Designers must rely on extrapolation tools such as a Larson-Miller plot, which allows the extrapolation of creep behavior for alloys as a function of time and temperature combinations. Such extrapolations provide only semi-quantitative accuracy.

A range of materials and target temperatures have been considered over the last 25 years. In the 1980's and 90's, designs with heater head temperatures near 750-800C were investigated, with design lives reaching 60,000 hours. Several authors chose the cast superalloy IN713C (1), (2), (3) while others chose the wrought alloy Udimet 720 (4), (5). Some designs were targeted for even higher temperature operation, and in this case refractory metals were considered as prime choices (6).

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In the late 1990's, efforts to develop a flight-ready Stirling radioisotope generator accelerated. The emphasis on near-100% reliability for this effort resulted in a design that lowered risk by limiting temperatures and relied on well-characterized materials. This heater head was designed to operate at 650C, which led to the selection of IN718, a wrought superalloy with widespread use throughout the aerospace and terrestrial energy industries. It has excellent ductility, fabricability and weldability compared to the stronger superalloys. Also important was the extraordinary database available on IN718, where creep data from tests exceeding 20,000 hour lives was available in the literature. Technology development efforts were still needed to achieve flight readiness, particularly a need to define the optimum grain size for the ~1mm thick heater head, and an evaluation and optimization of various heat treating, brazing, and welding procedures. Bowman et al (7) built on this IN718 heater head design and determined that heater head temperatures of 850C were feasible for deep space missions at tolerable risk levels. They concluded that cast alloy Mar-M247 was the best choice over other wrought and cast materials surveyed. Mar-M247 thus represents the current state-of-the-art for the heater head, and has been designed to allow Stirling operation at 850C for up to 17 years.

The materials selection efforts summarized in this paper are based on expected design requirements, although a variety of configurations are still under consideration. Essentially, two segments of the mission exist, "Transit" and "On Venus." Transit to Venus could take between 4 and 18 months. In some designs, the vacuum of space is allowed to exist outside of the heater head, whereas other options consider a protective/insulating cover gas. One option that would be very beneficial to heater head life would be if the operation of the Stirling engine can be "off" during transit, which would allow it to run perhaps ~200C cooler than during service on Venus.

The transit portion of the mission could be demanding, especially if a large pressure differential across the wall is created between the internal pressure from the working fluid and the external vacuum of space. An issue unique to high temperature vacuum exposures is that sublimation of some constituents of superalloys is significant at temperatures above 1000C. When on the surface of Venus, the environment changes dramatically. The atmosphere of Venus (9) consists of CO₂ and N₂ as well as SO₂ and other trace species, including HCl and HF. At a surface temperature of 460C and atmospheric pressure of 92 bar (9.2 MPa), the CO₂ is supercritical, i.e., liquid. These conditions are oxidizing and potentially corrosive. If the heater head is exposed to the Venus atmosphere, the external pressure of 92 bar acts on the heater head wall and can be either partially or fully balanced by the internal pressure of the working fluid. A protective cover gas is also possible on the surface of Venus.

With the Venus temperature determining the cold end of the heater head equal to 500C (773K), higher hot-end temperatures are required to achieve power conversion efficiency goals. To define the creep limit of candidate materials, we are using an estimate of the hoop stress in the wall of the cylindrical heater head. Some design flexibility exists here, in that increased wall thickness will compensate for lower material strength. This increases weight but also can influence engine efficiency through changes in both axial and radial heat conduction (8). Other sources for material stresses also exist, and may in fact exceed those due to the internal pressure. High bending stresses can develop from a combination of wall thickness variation, pressure, and axial temperature gradient along the wall. In addition, integration of dissimilar materials (for example a ceramic heater head and a nickel base heat exchanger) can result in stresses arising from different thermal expansion coefficients. The screening metric used here is to select materials with creep strengths of at least 70MPa combined with 10,000 hour lives.

Thermal conductivity may be an additional, first order constraint on materials selection. In general, low conductivity is desired to minimize conduction along the length of the heater head. However, in so-called "monolithic" heater head designs, high thermal conductivity may be required for transferring heat from the GPHS into the hot end of the heater head. This is especially true if the heater head wall thickness needs to be high to contain the pressure loads. Thus, thermal conductivity requirements are a complex function of the specific design and compromises among competing issues.

Finally, we considered the potential of heater head material failure during the temporarily high loads of re-entry in the Venus atmosphere during landing. The estimated forces during re-entry were provided by Dyson (10) as not to exceed 180g. A preliminary analysis was performed using a prototypical heater head oriented in the worst-case scenario by applying the g-forces laterally combined with internal pressure of 100 bar. For the purposes of calculating thermal stresses induced by different thermal expansion coefficients, the stress-free temperature in the current analysis was assumed to be the operating temperature. A simple steady-state temperature profile was used in

the current models given a constant 1300C hot end and 50C cold end. This analysis indicated that the g-forces would not exceed the material capability, even for the lower ductility refractory metals and ceramics. On some geometries with thin walls (1mm), the cold-end stresses were modestly high, but appeared to be easily handled by slight reinforcement of the cold end wall section. The stresses induced by the axial temperature gradient, combined with dissimilar materials with a CTE mismatch such as a ceramic heater head joined to an IN625 superalloy heat exchanger, could reach excessively high levels. Careful design will be needed to prevent the build-up of high thermal stresses in the heater head during the various manufacturing processes up through operation.

II. Environmental Attack of Candidate Materials

A. Corrosion and Oxidation on Venus

Corrosion and oxidation resistance is a key issue in selection of materials for this mission. This is a complex issue due to the fact that the materials will be exposed to high temperatures (550-1200C) as well as several possible different environments. These environments include low oxygen partial pressures (low PO₂ in He), supercritical CO₂ (S-CO₂) as either a cover gas or in the Venusian atmosphere, and the vacuum of space. In addition to the S-CO₂, the Venusian atmosphere contains SO₂ and trace amounts of the acids HF and HCL. The candidate materials discussed above fall into four categories: superalloys, intermetallic, ceramics, and refractory metals. All of these materials, except the ceramic alumina (Al₂O₃), rely on a thin, impervious oxide for protection. Most of the refractory metals would require a coating in order to form a protective oxide layer.

Typical oxide films are alumina (Al₂O₃) or silica (SiO₂). In oxygen or air, these films form in the desired dense form free of cracks and fissures. This protects the alloy or ceramic from corrosive species such as HCl(g), HF(g), and SO₂(g) which can be quite reactive even in very small quantities. HF and HCl will react at the oxide/alloy phase, forming volatile species which will degrade the alloy. SO₂ can form condensed phase sulfides, possibly liquid, which will also degrade the properties of the alloy. These general issues apply to the superalloys, intermetallics, and silicon-based ceramics. The first question is to evaluate the quality of protective oxide films which form in the S-CO₂ of the Venus environments since any cracks in the oxide film would provide penetration points for the corrosive species. The integrity of the oxide formed in these environments is not known due to the uniqueness of these environments.

The refractory metals such as Mo, W, Ta, and Re do not form thin, protective oxides, but rather oxidize rapidly via formation of non-protective oxides. Coatings are thus required, and commercially available coatings are proposed: R512E (Si-20Cr-20Fe) or other silicide-based candidates where silica functions as a protective oxide. The possibility of cracks and fissures in both the oxide and the coating needs to be considered as well as adherence of the coating to the refractory alloy.

B. Corrosion From Potential Working Fluids or Directly in the Venusian Environment

He-5 ppm O₂ is a primary option for the working fluid and/or cover gas to protect critical components. If the gas is contained in a leak-tight chamber, then the ppm-level oxygen is likely to be quickly consumed by reaction with most heater head candidates, and further reaction is precluded as long as the oxygen is not replenished. However, a continuous supply of even very low partial pressures of O₂ can be very detrimental to the refractory metals as well as the Si-base ceramics. Even the behavior of well-characterized superalloys is in need of experimental testing in this scenario, since for example, selective leaching of Cr or Mo could result, or, in the absence of a protective oxide film, the O₂ could diffuse into and oxidize reactive elements within the alloy or within grain boundaries degrading mechanical properties.

One option would be for the Stirling converter vessel to be pressurized with supercritical CO₂ (S-CO₂). Additionally, as stated above, the Venusian environment consists primarily of S-CO₂. Normally, CO₂ is an oxidizing gas. However, very little is known about the interaction of these candidate materials with S-CO₂ at elevated temperatures (1000°C and above). Recent studies related to the use of S-CO₂ for nuclear power generation have looked primarily at steels at 500-650C in S-CO₂. (11) (12) (13) These studies show the expected formation of Fe and Cr oxides, although in one case, carburization within the substrate was also observed. (12) Only one study has been performed as high as 1000C with two Ni-based alloys, MA754 for 500 hrs and IN-617 for 175 hrs. (14) For IN617, corrosion in the S-CO₂ environment resulted in the expected oxidation but accompanied by a deleterious internal grain boundary attack. For the candidate materials discussed above, whether a stable, protective oxide (Al₂O₃ or SiO₂) will be form, or whether deleterious carburization or grain boundary attack could

occur is unknown and requires additional research and testing. The presence of the SO₂, HF and HCL in the Venusian environment presents added complications and uncertainty to the material's behavior in the S-CO₂ environment. The formation of Al₂O₃ or SiO₂ films could provide adequate protection in these environments, but testing of the desired candidate material is required

C. Sublimation in Vacuum During Transit

The evaporation or sublimation of alloys into the vacuum of space is also a critical issue, especially for nickel base superalloys which contain Cr and Al that would be expected to sublime. The metal surface will recede based on the rate of sublimation and the surface activity of each subliming component of the superalloy. As the surface is depleted in the subliming elements, it will become enriched in the lower vapor pressure components, such as Mo, Ta, and W. The extent of this decrease depends on the sublimation rate and diffusional transport within the alloy. This problem can be modeled with commercial software. It depends, of course, on the level of vacuum and temperature. Even small amounts of residual oxygen may be sufficient to form a thin surface oxide which would limit sublimation. Some elements in the alloys, such as Mo, may form volatile oxides, which would actually enhance sublimation. The oxygen levels of the actual space environments need to be known in order to model these effects. Again, it is critical to know if the oxygen will be continuously replenished or not. However, a simplified analysis with several unverified assumptions was performed, and shows that the risk from sublimation is not especially severe. After 4 months exposure to vacuum at 850C, approximately 0.05 mm of a superalloy heater head wall would be depleted of Cr, with an expected loss of creep strength in this layer. At 18 months (850C), the depleted zone grows to 0.1 mm. These rates are significantly faster at 1100C, where a 3 month exposure could result in a ~0.4 mm depletion layer. There are several means to mitigate this potential damaging effect. In addition to the beneficial effect of residual oxygen mentioned above, pre-oxidation to form a protective scale, or the use of a He cover gas can also serve to reduce the sublimation effect.

D. Environmental Attack Summary

Despite the uncertainties in predicting corrosion resistance of the various materials, we still expect the nickel base alloys and ceramics to have a good chance for adequate behavior for the Venus ASD mission. Refractory metals would either need to be coated or be placed under a protective cover gas to survive. Vaporization of alloy components and resultant compositional changes is a potential risk, especially for superalloys during transit to Venus. Initial calculations show that the risk is not severe, but further modeling and some key experiments are proposed to assess the severity of this process. Considerable work is needed to turn these expectations into confirmed reliable behavior. The key issues center on the integrity of the oxide film and stability of the various interfaces: oxide/alloy, oxide/ceramic, or coating/refractory alloy. The integrity of the oxide formed in these environments is not known due to the uniqueness of these environments.

III. Candidate Material Types for Potential ASD Heater Head Application

A. Nickel-Base Superalloys

As was discussed in the Introduction, superalloys have been the major focus for heater head application. Specific alloys of IN718, IN713, IN738, Udimet 720, and MarM-247 are among alloys that have been identified in past studies. The most recent work was performed by Bowman et al (7) for ASRG space missions of up to 17 years and a heater head temperature of ~850C. They screened over 200 material candidates against these criteria: creep resistance, fabricability, He gas containment, long-term stability and compatibility, the ability to form a hermetic closeout seal, and ductility and toughness. Subsequent to screening based on existing literature data, Bowman et al. selected 5 alloys that were most promising to meet ASRG requirements – Udimet 720, IN738LC, IN939, MarM-247, and MA754, and performed additional creep testing. Mechanically alloyed MA754 appeared to be a promising candidate based on handbook data, particularly its superior long term creep strength. However, those properties are a result of an elongated grain structure, and only one grain orientation shows exceptional creep strength, and the weakest direction would be highly stressed in the thin wall of a heater head. Bowman's testing included transverse creep tests of MA754, and the resultant poor creep properties confirmed that ODS alloys are not preferred. Mar-M247 was thus selected for the ASRG heater head. Crucial to Bowman's selection of Mar-M247 was the adoption of non-fusion welding methods to integrate the heater head into the Stirling system. Solid state welding techniques, including brazing, friction welding, and diffusion bonding were adopted to achieve the required hermetic seals, thus allowing the higher creep strength of Mar-M247 to be utilized. Although the use of MarM-247 in the ASRG is limited to 850C, the current ASD application can benefit from shorter life requirements, thus allowing the temperature to grow to perhaps 1000C.

Figure 1 shows a summary of creep performance (for 1000 hr life) of several cast superalloys. (15) Note that creep strength is diminishing rapidly with temperature, and temperatures will need to be restricted to about 1000C if our proposed guideline of 70MPa/10,000 hour life is used as a threshold for consideration. Table 1 summarizes the creep data collected on potential alloys that may meet the 70 MPa/10,000 hour life requirement. Multiple sources for Mar-M247 creep data are shown in Table 1 to illustrate some of the property variability that is inherent to multiple batches, each with different processing history. In addition, a column titled “Longest Real Test” illustrates where significant extrapolation was needed. Several sources concur that Mar-M247 and a similarly advanced cast polycrystalline alloy from Canon-Muskegon (CM681) have creep properties approaching 70MPa at 1000C for duration up to 10,000 hours.

It is clear that Mar-M247 is at or near the best possible creep strength available in a conventionally cast form. However, there is one class of superalloys that could provide significant advances over this capability. Single crystal superalloys, produced by a directional solidification process, have been flying in jet engines for over 30 years. An early, first generation single crystal, PWA1480 is shown as the best performing superalloy in Figure 1. However, available data on this alloy is very limited, and extrapolation to the 10,000 hr life regime was not attempted. However, another 1st generation alloy, NASAIR100 (16) actually has data extending to 10,000 hrs, so extrapolation is not needed. This alloy shows 50% increase in creep strength over the best available Mar-M247 data, equal to 96 MPa, equally relevant for both time to rupture (Fig. 2) and 1% creep (Fig. 3).

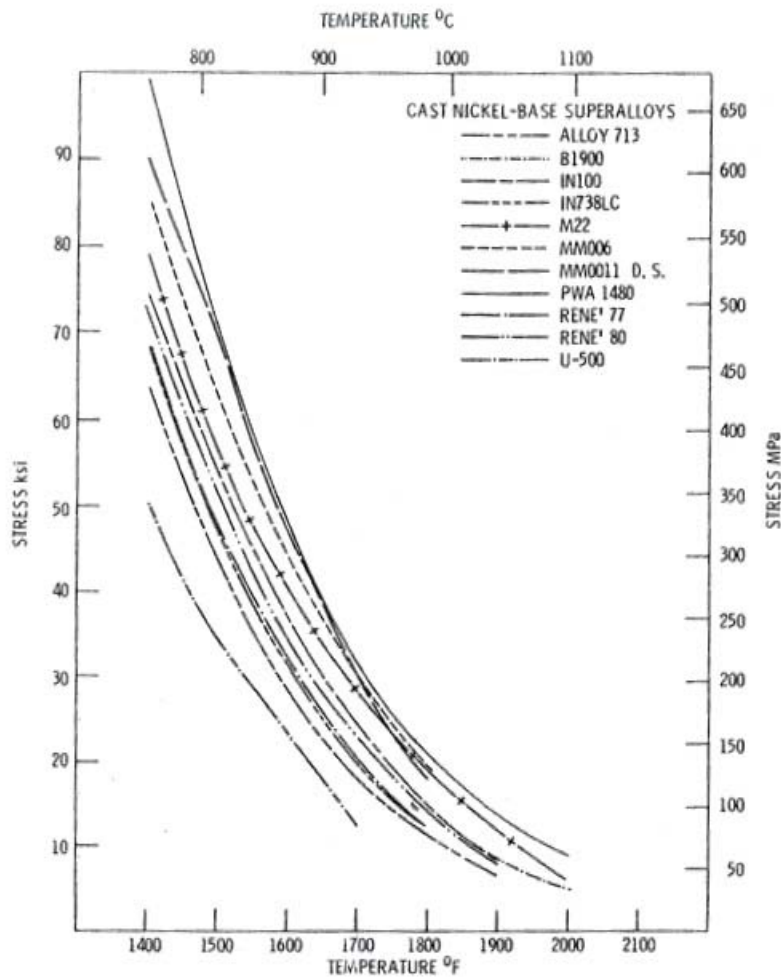


Figure 1. Creep summary plot for cast superalloys. Creep strength is reported as stress to produce rupture in 1000 hrs. (15)

Table 1. Candidate ASD heater head superalloy materials and predicted creep performance.

Alloy	Condition	Reference	1000C			1100C		
			Stress to 1% creep in 10,000 hrs	Stress to rupture in 10,000 hrs	Longest real test hrs	Stress to 1% creep in 10,000 hrs	Stress to rupture in 10,000 hrs	Longest real test hrs
Mar-M247	cast + HIP; large Grain size	Wood et al (17)	3 ksi		1000	< 1 ksi		
	Microcast + HIP; fine grains	Bowman (7)	-	< 1 ksi	500		< 1 ksi	
	Cast; large grains	Cannon Muskegon product literature, (18)	-	< 1 ksi			< 1 ksi	
	Cast + HIP Hub coarse grain?	Helmink et al (19)	-	9	500			
	Cast + HIP airfoil fine grain?	Helmink et al (19)	-	1				
CM681 LC	Cast + pseudo HIP	Cannon Muskegon product literature, (18)	9 ksi	9 ksi	1000		< 1 ksi	100
	Cast	Cannon Muskegon product literature, (18)	9	9 ksi	1000		< 1 ksi	
	Cast + HIP Hub coarse grain?	Helmink et al (19)	-	10	1000		1	
	Cast + HIP airfoil fine grain?	Helmink et al (19)	-	6	1000		<1	
NASAIR100	1st gen Single crystal	Nathal & Ebert, (16)	14	14	10000			
Rene N4	1st gen Single crystal	Ross et al (20)	-	14-17	10000			
Rene N5	2nd gen Single crystal	Walston (21)	-	16			<~7	
CMSX-4	2nd gen Single crystal	Erickson (22)	15	14	9000		<~5	

Table 1 (cont). Candidate ASD heater head superalloy materials and predicted creep performance.

Alloy	Condition	Reference	1000 C			1100C		
			Stress to 1% creep in 10,000 hrs	Stress to rupture in 10,000 hrs	Longest real test hrs	Stress to 1% creep in 10,000 hrs	Stress to rupture in 10,000 hrs	Longest real test hrs
Rene N6	3rd gen Single crystal	Ross et al (20)	-	18-19	10000			
EPM102	4th Gen Single crystal	EPM final report (23)	-	19-21	2600	~5	6-7	1000
LDS 1101	low density single crystal	MacKay et al (24)	-	18-20	1000		~6	1000
LDS 4583	low density single crystal	MacKay et al (25)	-				~10	

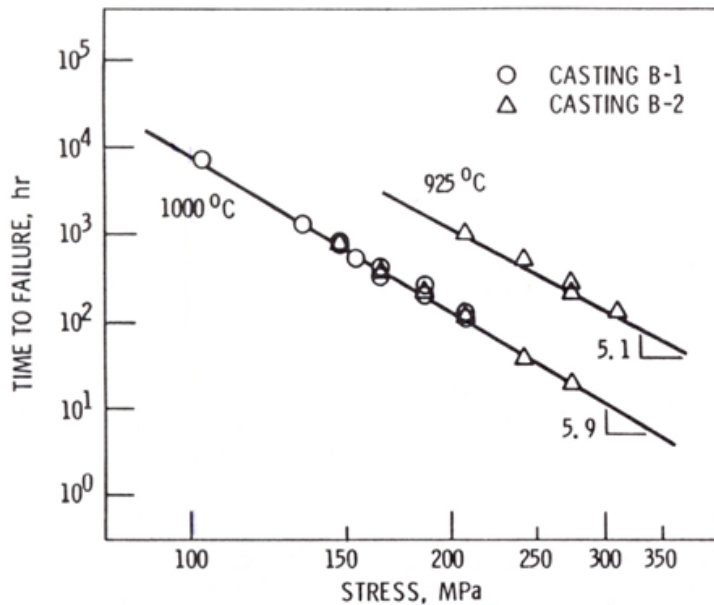


Figure 2. Creep data (time to rupture) for the first generation single crystal alloy NASAIR 100, with data extending to 10,000 hrs.

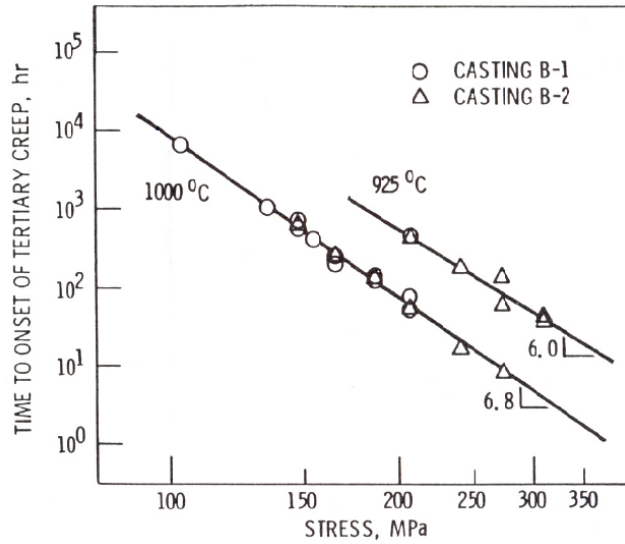


Figure 3. Creep data for the first generation single crystal alloy NASAIR 100, with data extending to 10,000 hrs. (This plot is for the time to the onset of tertiary creep, which closely approximates time to 1% creep).

Second and third generation single crystal alloys are also available and could potentially increase capability even further. Cannon Muskegon has developed CMSX-4 (22) and CMSX-10 (22) as 2nd and 3rd generation alloys respectively, and GE has similarly developed Rene N5 and N6 (21). All of these alloys are included in Table 1, although again we emphasize caution, especially at 1100 C, because of the degree of extrapolation required. Indeed, Ross et al (20) show that 1st Gen alloys may be better than 2nd Gen alloys at very long lives, as shown in Figure 4. However, Ross (20) still shows an advantage for 3rd Gen alloys even at long times. The data in Table 1 confirm useable performance to 1100C.

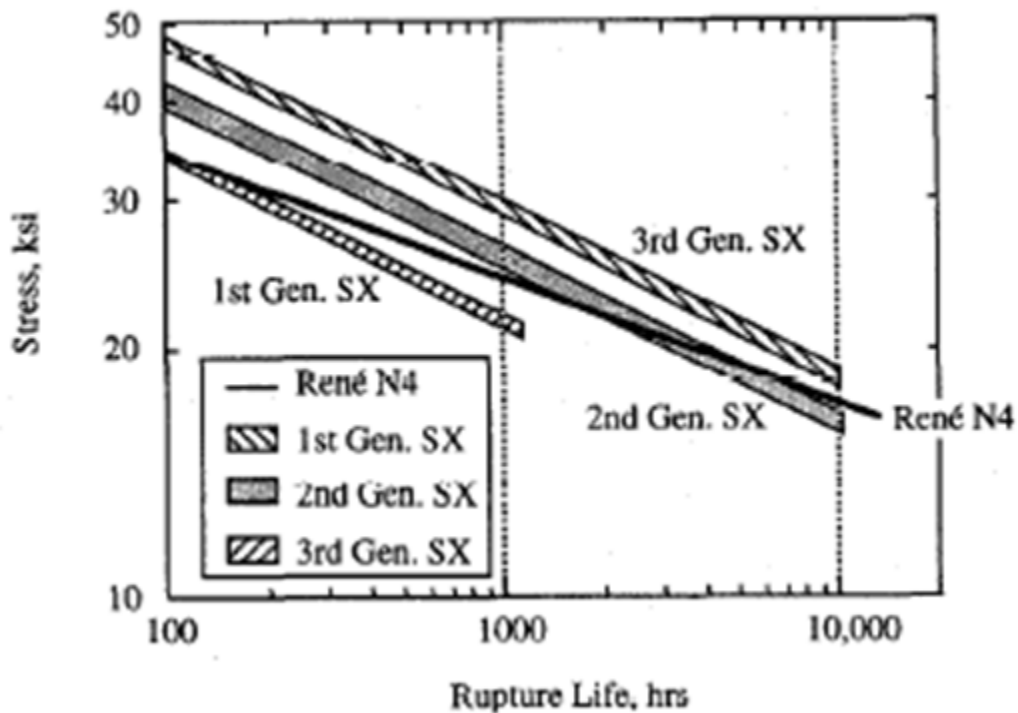


Figure 4. Long time creep data from Ross et al (20), showing how the 1st generation single crystal alloy Rene N4 starts to exceed the 2nd generation alloys at longer lives.

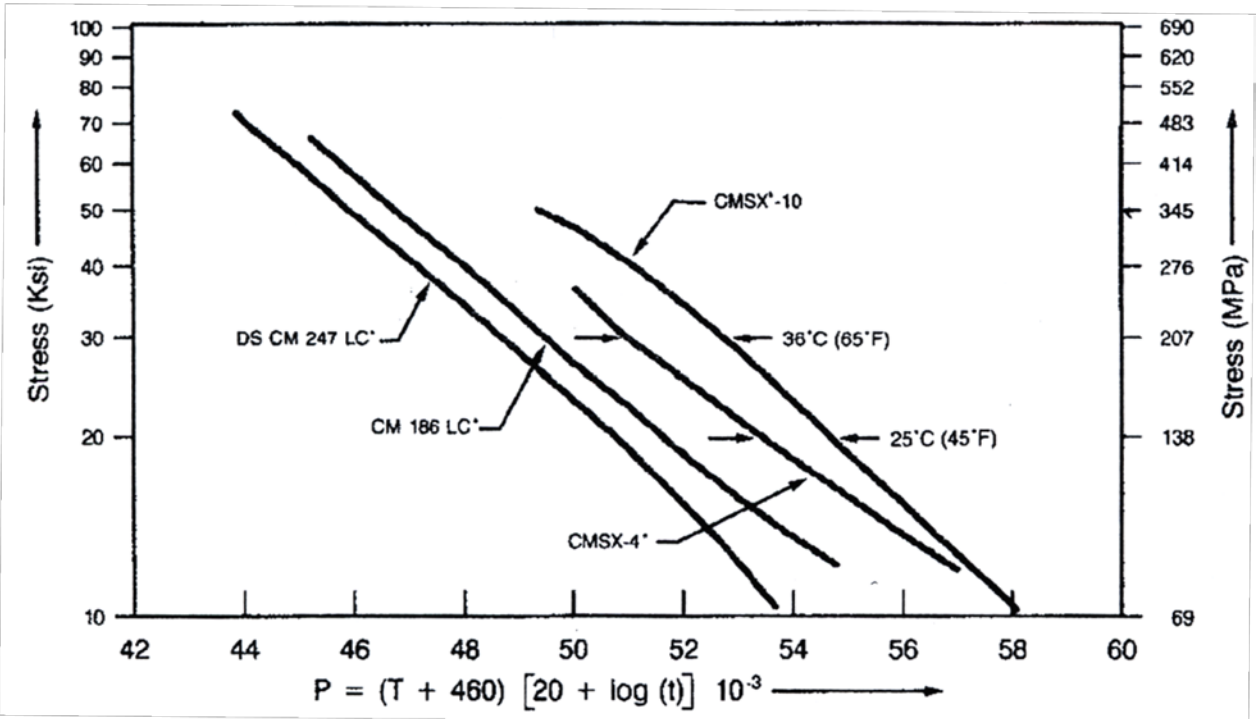


Figure 5. Creep data for CMSX-4 and CMSX-10 from Erickson (22).

Figure 5 (22) presents data in the form of time to 1 percent creep strain for CMSX-4 and CMSX-10. The creep strength of the CMSX alloys are roughly equivalent to GE's alloys, so alloy down selection may be based on other criteria such as commercial availability or environmental resistance. Rene N5 in particular is known as one of the most oxidation resistant structural alloys ever produced (26).

Fourth generation superalloy EPM102 was developed (27) and is shown in Figure 6. EPM102 has a very large advantage over N5 at 1000C but a much smaller (if any) advantage at 1100C, particularly when extrapolated to the 10,000 hour life regime.

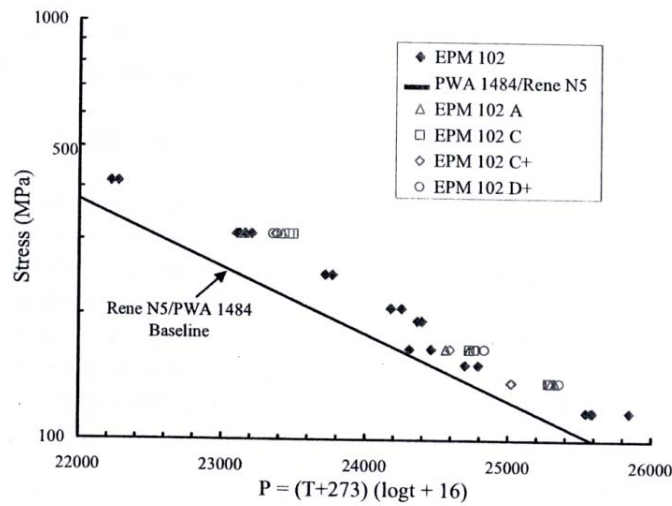


Figure 6. Creep data for 4th generation alloy EPM102, from Walston et al (27).

Additionally, MacKay et. al. (28) recently developed a suite of low-density (LDS) alloys to minimize the stresses induced in rotating components such as turbine airfoils. Figure 7 shows how the creep performance of several of

their alloys exceeds Rene N5. As summarized in Table 1, the LDS alloys display the best creep strengths at 1100C. In addition, their oxidation resistance exceeds both the 3rd and 4th generation alloys and is roughly equivalent to the gold standard for oxidation, Rene N5.

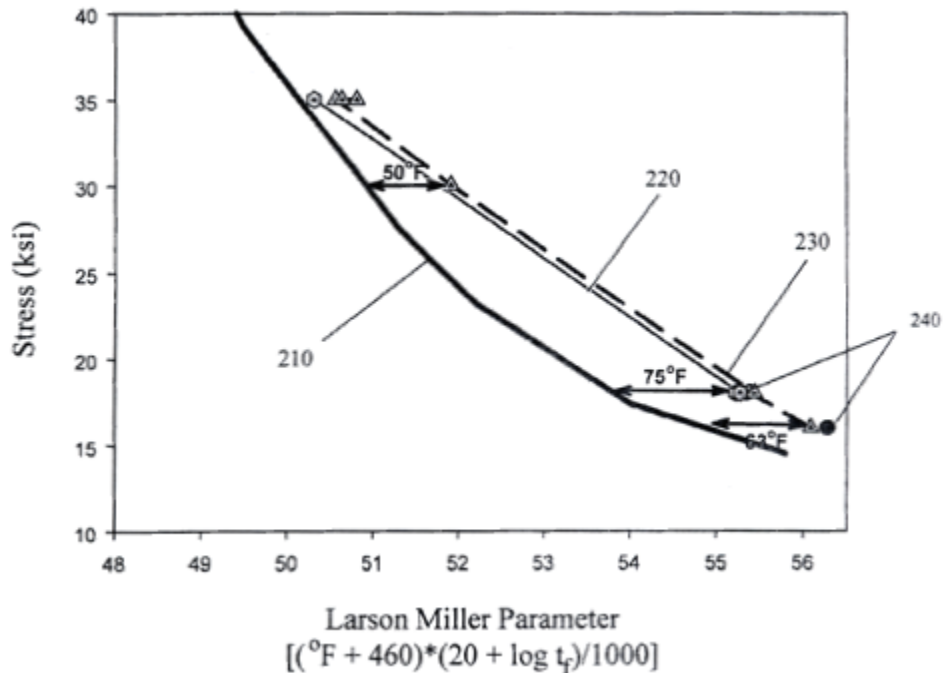


Figure 7. Creep data for low density single crystals from MacKay et al. The curves are labeled as 210: Rene N5; 220: EPM102; and 240: LDS1101.

Single crystals derive their improved creep performance from the lack of grain boundaries; they have essentially infinitely large grain sizes. They are processed via directional solidification and are usually grown in the <001> crystal orientation. Single crystals are known to have anisotropic properties, for example the elastic modulus can vary from 20Msi in <001> orientations to 40 Msi in <111>. Anisotropy in creep is also of concern, which would be manifested in a heater head as a circular cross section becoming elliptical as creep proceeds. However available data for CMSX-4 (29) show that this is not a large issue above about 950C. At lower temperatures, such as 750C, creep life can vary by 3 orders of magnitude as a function of orientation, but even the weakest directions would exhibit strengths above 600 MPa at 750C. So in summary, although anisotropy in mechanical performance is an additional complexity to design, it does not appear to be severe enough to eliminate single crystals from consideration. Turbine engine manufacturers deal with this complexity routinely. For the ASD mission, some testing as a function of orientation would still be required. One final comment on the creep strength summaries in Table 1 should be mentioned. If the life requirement for the ASD mission is reduced from 10,000 hrs, the stress capability of the alloys increases by a small but significant amount. In the case of LDS4583 at 1100C, the stress for a life of 5000 hrs is 84 MPa, which is 20% higher than the 70 MPa value for a 10,000 hr life. Similar 20% improvements could be expected for the other alloys in this table.

Manufacturing capability for large single crystals is not assured. Aircraft jet engine parts with incredibly complex geometries are routinely made into single crystals using lost wax investment shell molds. Although jet engine blades rarely exceed 20 centimeter lengths, single crystals blades over 60 centimeters long have been made for terrestrial power generation plants.

Summary and Recommendations

Superalloys exhibit excellent damage tolerance and can build on previous manufacturing experience from previous Stirling development activities. They have the potential to operate uncoated in the Venus environment, although this needs to be confirmed experimentally. The temperature limits to superalloys will be determined by creep strength, and the estimates in this section will need to be confirmed experimentally. It is expected that the

conventionally cast superalloy Mar-M247 could provide ~63 MPa creep strength for 10,000 hrs at 1000C, although several previously published studies did not achieve this high level. A small amount of testing to determine if CM681 can provide additional strength at 1000C may be of interest. The only realistic superalloys that are likely to achieve useful strengths at 1100C are the single crystals. Several different alloys have attractive creep strength, and the choice of specific alloys may be based on oxidation resistance, castability, or availability. The most promising alloys appear to be the LDS alloys, with about a 40% strength advantage over commercially available alloys. If increased engine efficiency drives the heater head design to even higher temperatures, consideration of ceramics or refractory metals will be necessary.

B. Ceramics

Ceramics are known for high temperature capability combined with low density and resistance to oxidizing environments. Ceramic matrix composites (CMC's) are receiving the most interest in the aircraft engine community because of their superior toughness compared to monolithic ceramics. However, most if not all CMC's achieve their high toughness via fibers that bridge matrix cracks, and they have multiple internal fiber/matrix interfaces with frequent porosity, which creates many pathways for the working fluid to permeate through the heater head wall. Unfortunately, the hermetic sealing requirements for the ASD heater head will not tolerate even small matrix cracks, and the first-matrix-cracking stress of CMC's is no better than the fracture strength of monolithic ceramics.

A variety of carbide and nitride ceramics have been investigated for application in heat engines. Much of the research was driven by Department of Energy (DOE) funding to reduce pollution and increase efficiency by increasing heat engine temperatures. Although some successes have occurred, cost, foreign object damage, and corrosion issues have interfered with commercial success. Due to the relatively high fracture toughness, *in situ* toughened silicon nitrides (30) were the material of choice for applications such as turbine vanes and turbochargers, however, more brittle materials such as alpha silicon carbide have been considered and components as complex as turbocharger rotors with integral blades have been manufactured and tested in demonstrator heat engines under programs such as Advanced Turbine Technology Applications (ATTAP) and Advanced Gas Turbine (AGT). The programs generally considered screening temperatures of 25, 1100, 1260, 1371C.

The result of these programs and efforts of organizations such as the American Society for Testing and Materials (ASTM) has been the development of substantially improved materials testing and design methods. Some successful applications of glasses and ceramics in NASA flight hardware include the Orbiter and International Space Station (ISS) windows, the Orbiter liquid oxygen turbo pump bearings (31), and ISS Fluids and Combustion Facility windows (32). Large ceramic components, such as turbine combustors have been made from monolithic (33) and composite ceramics (34).

Besides commercial availability, the nominal structural requirements for ASD requires consideration of creep or crack growth mechanisms along with oxidation and sublimation. Other factors are thermal conductivity and fracture toughness, which tend to be low at elevated temperatures. Currently, several silicon carbides and aluminas are commercially available for high temperature application; however, the only silicon nitride available for high temperature application is SN282.

From a chemical compatibility and density standpoint, silicon nitrides, silicon carbides, and aluminas are likely candidates. Alumina suffers from poor thermal conductivity, low fracture toughness (~3 MPa√m), and low thermal shock resistance. Thus nitrides and carbides will be emphasized in the following paragraphs. The terms "silicon nitride" and "silicon carbide" are general and include many versions (e.g. hot pressed, reaction bonded, gas pressure sintered). The properties of silicon nitride and silicon carbide can vary greatly, particularly with the amount and type of intergranular grain boundary phase. For example, the fracture toughness can be increased from ~4.5 to 12 MPa√m by increasing and elongating the grain size. This can lead to anisotropic thermal conductivity, strength, and fracture toughness when the starting powder is extruded. Similar modifications of silicon carbide have been made, increasing toughness from 2.7 vs 4 MPa√m. Table 2 gives a property range summary. The wide range of properties is due to the wide range of porosity, purity, and grain size that has been produced. Tables 2 and 3 imply that ceramics are structurally applicable to an ASD heater head. Low fracture toughness is an issue for many ceramic systems, and any ceramic would need detailed assessments to verify that the damage tolerance meets mission requirements. More detailed properties are given below to help evaluate the usefulness of ceramics and what systems might be pursued.

Thermal Conductivity

The thermal conductivities of several classes of ceramics were measured between 25 and 1000C by the US Army as part of a ceramic gun barrel program (35). This and other work (36) (37) (38) indicate that aluminas, zirconias, carbides, nitrides, AlN, and BeO all exhibit thermal conductivity below 40 W/mK at 1200C, with silicon carbide exhibit the greatest values at elevated temperatures. The thermal conductivity of SN282 and Hexoloy SA silicon carbide are shown in Figure 8. Conductivity of SA silicon carbide decreases from ~125 W/mK at room temperature to <40W/mK at 1200C. Conductivity of SN282 decreases from ~65 to <25 W/mK at 1200C.

Silicon carbide, which exhibits the best elevated temperature thermal conductivity, can be made more electrically conductive, by the addition of titanium diboride particles (SiC/TiB₂, Hexoloy ST). Unfortunately, the thermal conductivity is a relatively low 65 W/mK (39). Liquid phase sintered silicon carbide (Hexoloy SX) exhibits less conductivity than sintered silicon carbide (35). Silicon carbide can also be modified with BeO, Y₂O₃ or La₂O₃ to increase thermal conductivity to 200 - 270 W/mK at room temperature, and to 50 W/mK at 1227C (40) (41).

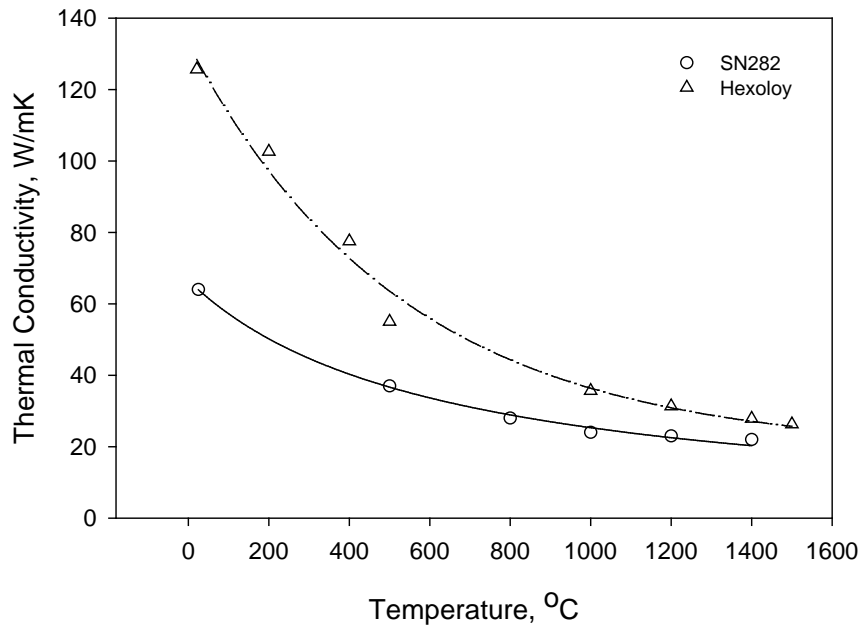


Figure 8. Thermal conductivity of Hexoloy silicon carbide and SN282 silicon nitride (manufacturer's data).

Environmental Resistance

The section on environmental effects summarizes that most ceramics would probably be stable in both the Transit and Venus Surface portions of the mission. The Si-base ceramics rely on the formation of a SiO₂ surface layer for protection. There is a possibility that the ppm-level of O₂ in the He cover gas or in vacuum may result in “active oxidation” of either ceramic, which could be serious if the source for the oxygen is continuously refreshed. Experimental verification of ceramics exposed to the entire list of environments will be required.

Fracture Toughness

Ceramics are very strong in compression (3 to 10 times the tensile strength), but sensitive to tensile loads in the presence of stress concentrations and small cracks because of very low fracture toughness. Thus all sources of cracking must be adequately controlled and proof testing of components should be pursued.

Fracture toughness as a function temperature is shown for several ceramics in Figure 9 (42). Sintered silicon carbide retains its fracture toughness (2.75 MPa√m) to >1371C. The addition of titanium diboride particles (SiC/TiB₂) not only improves electrical conductivity and machinability, but also results in larger room temperature fracture toughness due to internal residual stresses that decay at elevated temperatures (43). A commercial grade was made by Carborundum (Hexoloy ST). Another method to toughen and strength silicon carbide has been liquid phase sintering with YAG additions. Silicon carbide 20% YAG has been reported to be creep resistant (44), but can fail via slow crack growth (1300C, 480 hrs, 150 MPa, 0.05% creep strain). A commercial grade was made (Hexoloy SX)

and reported to exhibit better strength and toughness than its parent Hexoloy SA silicon carbide, and excellent creep resistance (45).

The toughness of silicon nitride tends to decrease with temperature, depending on the amount and nature of second phases present. Although SN282 exhibits lower fracture toughness than other silicon nitrides, it exhibits excellent creep resistance.

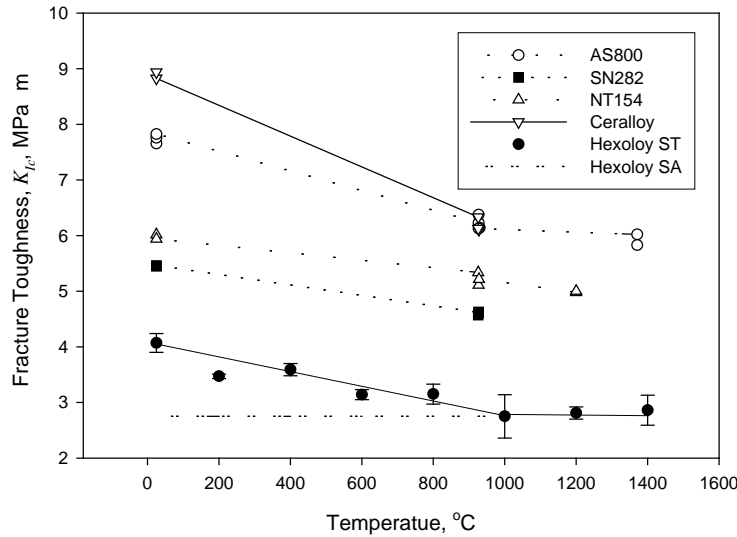


Figure 9. Fracture toughness of silicon nitrides and carbides (42), (43).

Creep

Alpha silicon carbide is very resistant to creep at ASD temperatures ($<10^{-9}$ /hr, (46)). The creep rate of SN282 is shown in Figure 10. The creep rate of silicon nitride, though significant at high stresses (<400 MPa), are low at ASD stresses (<100 MPa).

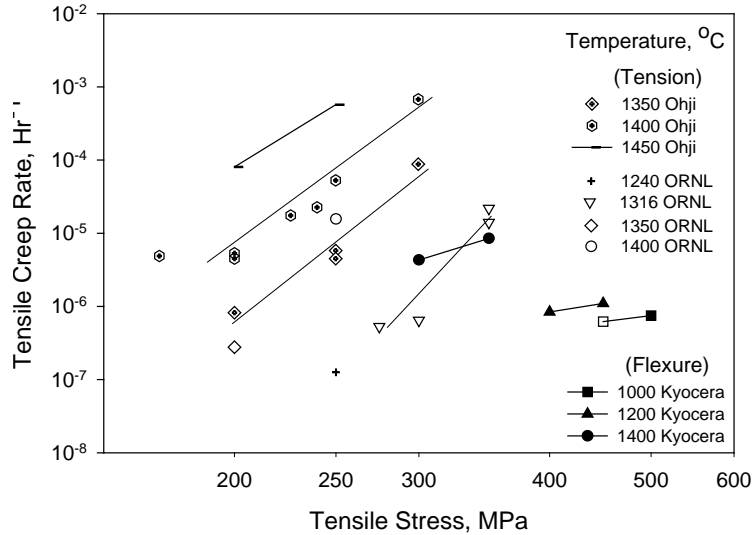


Figure 10. Creep rate for SN282 silicon nitride (47).

Stress Rupture

At lower and intermediate temperatures (1000 – 1200C) and higher stress levels, slow crack growth can dominate failure depending on the specific environment. Stress rupture levels for SN282 are shown in Figure 4. For 1250C, the stress rupture levels are excellent and substantially larger than the design stress, implying sufficient life for the Stirling stresses and temperatures. Data for SiC at 1200C is also shown in Figure 11. Older (~1980) vintages of

SiC, which were representative of limited production grades, exhibited susceptibility to static load at 1200C in air, with a nominal limit of 200 MPa (48). Govila (49) using constant stress rate testing estimated $n = 47$, similar to Quinn's results. Fractography by Quinn indicated intergranular crack growth at 1400C, but no mechanism was detected at 1000 to 1200C, with failure occurring from surface connected pores, implying oxidation attack. Preliminary testing of newer vintage SiC in air has not detected slow crack growth at 1200C and 1300C, but a slight effect at 1371°C ($n \cong 73$, (42)). Testing of new vintage SiC in relevant environments is needed.

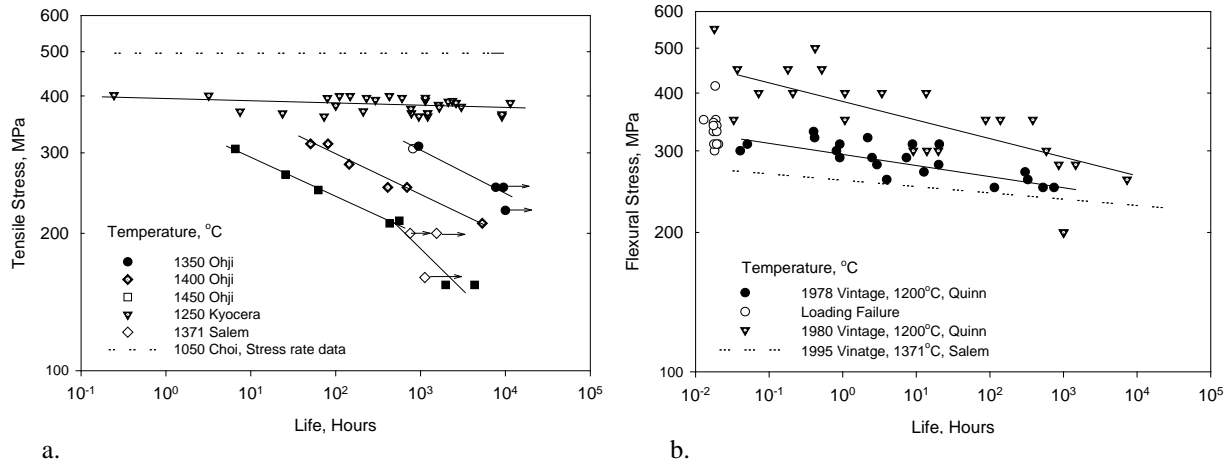


Figure 11. Stress rupture time for SN282 silicon nitride ((50), (42), (51)) and Hexoloy SA silicon carbide (52). The dashed lines represent predictions from short term, constant stress rate data.

Summary and Recommendations

Silicon carbide is a candidate for the heater head, and it possesses advantages of high creep strength, reasonably high conductivity, commercial availability and cost. Its disadvantages are very low fracture toughness, and the potential for active oxidation induced crack growth. Silicon nitrides have improved substantially and have advantages over silicon carbide in fracture toughness and perhaps oxidation resistance, but their resistance to creep is not as high. Stress rupture life is excellent. Commercial availability of high temperature nitrides is also an issue. It is very likely that adequate creep resistance in nitrides can be achieved. However, data specific to the Stirling Venus mission environments (vacuum and CO₂) is unavailable. Some of the major complications for applying ceramics in Stirling engines would be manufacturing, machining and handling of such large components. In addition, the low fracture toughness and clamping stresses require careful consideration. Although a less significant issue than mission success, the cost of a simple silicon carbide heater head is about 1/8th that of a silicon nitride head.

Table 2. Typical properties of various ceramics.

Property	Silicon Nitride	Silicon Carbide	Alumina
Flexural Strength (MPa)	250 - 800	200 - 750	250 - 500
Fracture Toughness (MPa√m)	3.5 - 12	2.5 - 5.0	2.5 - 4.0
Young's Modulus (GPa)	250 - 310	350 - 440	250 - 380
Thermal Conductivity (W/mK)	10 - 100	35 - 150	5 - 30
Thermal Expansion (10 ⁻⁶ /°K)	2 - 4	3 - 4.5	6 - 8
Bulk Density (g/cc)	2.8 - 3.2	2.5 - 3.2	3.5 - 3.7

Table 3. Limits on use temperature for relatively inert conditions.

<u>Material</u>	<u>Long term use under load, °C</u>	<u>Detectable Creep under Load, °C</u>
Silicon nitride (hot pressed)	1200	1300
Silicon nitride (reaction bonded)	1600	1700
Silicon carbide (reaction-bonded)	1400	1600
Silicon carbide (sintered)	1500	2000
Alumina (>99.5%)	1200	1400
Alumina (>95%)	900	1000

C. Refractory Metals

Refractory alloys are loosely defined as those metals that have a melting temperature above 2000C. Engineering alloys of this material class have mostly been based on Mo, Nb, Ta, W, and Re. Densities of Ta, W, and Re are very high and may be a disadvantage. Initial creep performance goals for refractory alloys are between 70 and 138 MPa at 1200C for 10000 hours. Probably the greatest deterrent of the use of refractory alloys would be their inability to resist oxidizing and corrosive environments. Research and development of coatings is a key element for potential refractory alloy application in power conversion space applications. It is also possible for spacecraft designs to control the environment around environmentally susceptible components through methods similar to encapsulation.

Mo alloys are likely the most promising of refractory alloys. In contrast to many other refractory metal counterparts, extrusion is a viable method for producing stock large enough for the envisioned heater head. Unfortunately, commercially available TZM has good creep resistance only to ~1100C. Specifically, the stress for 1 percent creep in 10,000 hours at 1100C is 120 MPa but only 21 MPa at 1200C. (53) Dispersion or precipitation strengthened Mo alloys (e.g. Mo-ODS (lanthanum oxide) or HfC-strengthened (HWM25)) are more likely to meet stress, temperature, and life requirements. High-temperature creep experiments will need to be performed as available data is scarce. Some indication does exist that the ODS alloy could approach a 103 MPa capability for 10,000 hour rupture life at 1200C. (54) HfC-strengthened Mo alloys are thought to have potential for excellent creep performance to high temperatures as well. (55)

Ta alloys have received a lot of attention in past space power programs due to their high temperature capability, high strength, and relatively good fabricability. Both solid-solution strengthened and precipitation strengthened Ta alloys are available. Ta is difficult to extrude at diameters greater than a ~10 cm due to its high melting temperature, so fabrication of Ta alloys into a Stirling engine heater head is a challenge. Advanced Ta alloys (Ta-10W, T-111, ASTAR 811C) have been evaluated for high temperature creep capability, albeit not always at temperatures and stresses of interest for the current program. Extrapolation, using a Larson-Miller approach was necessary to determine capability for a 10,000 hour mission at 1200C and a stress of at least 70 MPa. In none of the cases surveyed in the literature did either Ta-10W or T-111 meet the requirements necessary for application at 1200C and only marginally in one case for T-111 at 1100C. ASTAR 811C, however, is predicted to have excellent creep performance up to at 1200C and close to 103 MPa at 1 percent creep strain. (53) Planned experiments in support of the current program should confirm these predictions. (56) (57) (58) (59)

Tungsten has a high ductile-to-brittle transition temperature that is suppressed somewhat with the addition of Re. (60) Thus, W-25Re is a good Venus Stirling heater head candidate. Like the ASTAR 811C, predictions of creep behavior are very good up through 1200C and close to 69 MPa (for 1% creep). (53) Strengthening the W-Re alloy with HfC is expected to produce the highest creep capability of all metallic candidates. This alloy is expensive, however, and fabricability, joining, and coating of the W-Re family of alloys will also need development.

Alloys based on Nb, Re, and Pt were also considered as candidates for ASD heater head application. Nb alloys had received a lot of attention in past space power conversion studies and Re was intriguing based on its high-

temperature tensile properties. Platinum, if dispersion strengthened, was also considered since it is expected to have excellent resistance to the Venusian environment. However, all of these alloy classes do not possess adequate creep properties. Using extrapolated creep data, all Nb alloys, including FS-85 and D-43, were shown to have creep strengths at 1200C far below the 70 MPa component requirement. (61) (62) (63) (64) While high tensile strengths of Re at high temperatures are known, creep data is relatively scarce. An internal memorandum at General Electric (63) provided limited data for Re but did not include material history or microstructural information. From that data, time to rupture was expected in less than 10,000 hours at 1100 C and 70 MPa. Similarly, an oxide dispersion strengthened Pt alloy (ZGS) was also eliminated from heater head consideration as its 1200C creep strength for 1000 hour life was only 21 MPa. (65)

IV. Summary and Conclusions

This paper has addressed material selection issues for the heater head of an Advanced Stirling Duplex design for a proposed Venus lander. Material creep strength, environmental durability, fabricability, commercial availability and compatibility with working fluids were considered in this assessment. A lower risk, evolutionary advance in heater head materials is offered by nickel-base superalloy single crystals, with expected capability of approximately 1100C. However, the high temperature requirements of the Venus mission may force the selection of ceramics or refractory metals, which can operate at 1200C but are less technically mature. Monolithic ceramics based on either SiC or Si₃N₄ are especially attractive. Areas for future work have also been identified. Prime among these are the need to evaluate behavior of these candidates in the potentially corrosive Venus environment, and to generate long-term creep data on the order of 10,000 hours. Manufacturing and assembly issues, particularly with ceramics, also need careful design and development.

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