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MATERIALS TECHNOLOGY ASSESSMENT FOR STIRLING ENGINES

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SUMMARY

A materials technology assessment for the Stirling engine was undertaken by staff members of the NASA Lewis Research Center and the Army Materials and Mechanics Research Center. The purpose of this paper is to summarize the findings to date and to identify key components where materials research and development are needed.

For the improved (metal) Stirling engine, the heater head is considered the most critical component. Primary areas of research and development needed include mechanical property data under Stirling engine operating conditions; compatibility, permeation, and effects on mechanical properties of high pressure hydrogen; and the substitution of less strategic alloys for those currently used in prototype automotive Stirling engines. For the advanced (ceramic) engine, the air preheater is considered the most critical component. Temperature and time requirements far exceed available test data on ceramic materials such as silicon carbide and silicon nitride. The heater head is also a critical component and time, temperature, and environmental effects must be characterized for candidate ceramics under operating conditions proposed for the advanced Stirling engine. Attention must also be directed to the fabrication of components from candidate ceramic materials and component reliability must be demonstrated.

INTRODUCTION

The Stirling engine is under development for potential automotive use (ref. 1). Two stages of engine development are being sponsored by the Department of Energy as a part of the Heat Engine Highway Vehicles Systems Program. The first of these is the improved Stirling engine, which is defined

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as a relatively near-term improved version of present configuration, limited by current technology. The second stage of engine development is the advanced Stirling engine, which is defined as a longer-term future version of an engine which embodies advantages afforded by major technological advances. More detailed definitions and explanations of these two stages of engine development have been given previously (ref. 2). A materials technology assessment of high temperature components for the improved and advanced Stirling engines is being conducted under the Heat Engine Highway Vehicles Systems Program. The objectives of this study are to assess the current state-of-the-art of metals and ceramics that are potential candidate materials for hot components in both the improved and the advanced Stirling engines; identify materials research, development, and testing required to support the development of automotive Stirling engines; and recommend materials technology programs to assure material readiness concurrent with the engine system development programs.

The study is being conducted by personnel from the NASA Lewis Research Center and the Army Materials and Mechanics Research Center. Over a 4-month time period, the study group has visited several companies currently involved in development of Stirling engines and companies involved in the development and production of ceramic materials. Knowledge gained from these contacts plus literature surveys form the basis for our conclusions and recommentations outlined in this report.

The high temperature components evaluated in this assessment included the air preheater, burner, heater head, regenerator, cylinder, and piston. Materials for the more critical components in the improved and advanced engines will be emphasized in this paper.

THE STIRLING ENGINE

The Stirling engine offers potential as a possible substitute for the automotive internal combustion engine to meet the anticipated requirements of high fuel economy and low emissions in the late 1980's time period (ref. 3). The automotive Stirling engine is an external combustion engine which uses cyclic flow of a confined working fluid (in this case, hydrogen) to transform heat energy into work. The working fluid is allowed to expand at high temperatures, while at low temperatures the working fluid is compressed. A key component in the system is a regenerator which stores a large portion of the heat energy remaining in the working fluid after expansion and returns the heat energy to the working fluid after compression. A schematic representation of a Stirling engine shown in figure 1 is similar to the configuration shown previously for automotive applications (ref. 4). Figure 1 draws attention to those components that experience high operating temperatures in order to achieve these requirements of the Stirling cycle. These include the air preheater, burner, heater head, regenerator, cylinder, and piston. For the improved engine, the air preheater will employ a ceramic material such as lithium aluminum silicate or aluminum silicate. The remaining components will employ iron-base or cobalt-base superalloys, stainless steels, and other heat resistant alloys. For the advanced engine, ceramics such as silicon carbide and silicon nitride are considered to be potential candidates for most of the high temperature components.

MATERIALS FOR THE IMPROVED (METAL) ENGINE

Estimated operating conditions of time, temperature, pressure, and environment for the improved Stirling engine, are shown in figure 2 for each of the high temperature components considered in this assessment. It is assumed that the minimum life of the engine will be 3500 hours, involving approximately 20 000 cycles of startup and shutdown of the automobile (ref. 3). All components will, of course, experience this time requirement. Current estimates of operating temperatures (ref. 5) in the hot components of the engine range from a high of 1150° C (2100° F) on the hot side of the air-preheater to 260° C (500° F) on the air intake side of this heat exchanger. The burner wall is estimated to operate at 980° C (1800° F) while those components in contact with hydrogen, including the heater head, regenerator, cylinder, and piston, will experience an operating temperature of about 760° C (1400° F). The peak operating pressure of the hydrogen working fluid is estimated to be 25 MPa (3600 psi), with normal operating pressure slightly lower, near 21 MPa (3000 psi). The heater head, regenerator, cylinder, and piston will experience these high operating pressures. Environmental conditions imposed upon the hot components of the Stirling engine will include the hydrogen working fluid which will be the primary reactive atmosphere in contact with the regenerator (including housing), cylinder, and piston. The air preheater and the burner will experience an oxidation/corrosion environment of incoming air and combustion gas effluent. The heater head tubes contain the reactive hydrogen working fluid on the inside while the outside of the tubes are exposed to the corrosive combustion gas effluent. Based upon the estimated operating conditions of time, temperature, pressure, and environments in automotive Stirling engine applications, plus the high heat flux imposed upon the tubes, the heater head is considered to be the most critical component in the improved Stirling engine from a materials viewpoint. The primary emphasis of this report for the improved engine will focus on possible candidate alloys for the heater head tubes and some of the materials problems that may be encountered during operation of the engine.

The heater head for a prototype automotive Stirling engine is currently fabricated from an iron-base alloy, N-155 (ref. 6). The major alloying elements in N-155 and other typical iron-base high temperature alloys are listed in figure 3, where the range in composition of candidate heater head alloys is indicated. Iron content is noted to range from near 30 percent for N-155 and S-590 to as high as 68 percent in 19-9DL. Typical of all candidate alloys are the major alloy additions of nickel and chromium, with some alloys also containing additions of cobalt and the refractory metals columbium, molybdenum, and tungsten. The use of N-155 in the heater head is of major concern because of the high cost of the major alloying elements and also because most of these alloying additions are considered to be strategic materials from a domestic availability viewpoint.

Candidate alloys listed in figure 3 were chosen from iron-base superalloys that possess a rupture stress in air at 760° C (1400° F) that is near the operating stress estimated for current prototype automotive Stirling engines. The operating stress was estimated as 55 MPa (8 ksi) based on the operating conditions listed in figure 2 and the current tube dimensions in prototype heater heads employed on the Stirling engine. The ratio of stress for 3500 hour rupture life for several candidate alloys to the heater head tube operating stress is compared in figure 4 with alloy raw material costs on a relative basis where the commonly used 316 stainless steel raw material cost is arbitrarily set equal to one. It should be noted that while N-155, a current heater head material, has adequate strength the raw material cost of this alloy is very high.

Alloys such as A286, 19-9DL, and W545 as well as other alloys not shown here have much lower raw material costs while still meeting the estimated strength requirements of the heater tubes. The comparison shown in figure 4 suggests that lower cost iron-base superalloys can be substituted for N-155. A slightly lower stress requirement would also allow utilization of stainless steels for the heater head application. It should be further noted that mechanical property data under proposed operating conditions of environments, temperature, and pressure in the Stirling heater head tubes are not available. For example, rupture data in high pressure hydrogen at temperatures near 760° C have not been determined for alloys under consideration for the heater head tubes application. Other properties such as fabricability, hydrogen compatibility, and corrosion resistance must be determined for these alloys before they can be substituted for the N-155 in the heater tubes.

The use of strategic materials such as cobalt, chromium, nickel, and some of the refractory metals is also of major concern when a highly alloyed iron-base alloy such as N-155 is considered for use in automotive applications. The amounts of the major alloying elements in the iron-base superalloys that the United States imports are shown in figure 5 along with the major foreign sources for each element. As indicated, cobalt and chromium imports exceed 90 percent and are imported primarily from the countries outside the Western Hemisphere. Nickel imports are near 75 percent, where Canada is the major foreign source. The United States imports less than half the required amount of the refractory metals columbium and tungsten while molybdenum is exported. About one-third of the United States iron consumption is supplied by foreign sources. Cobalt is useful to illustrate the severity of the problem when strategic materials are considered for use on a large volume basis such as automobiles. The use of N-155 (which contains 20 percent cobalt) in the heater tubes and Haynes 25 (a 50-percent cobalt base alloy) in the cylinder walls and regenerator housings in current prototype Stirling engines (ref. 2) would challenge the United States cobalt metal market. For example, the production of 300 000 engines would require the total annual consumption of cobalt metal by the United States based on 1976 figures. In addition, the production of 2 000 000 engines would require the total world production of cobalt per year, again based on the latest available figures. Obviously, cobalt usage at these levels in the high volume production of automobile engines would not be feasible. Thus, the supply of strategic materials must be a major factor in considering which alloys should be used in Stirling engine applications.

The use of hydrogen at the high temperatures and high pressures required in the Stirling engine imposes several material problems, listed in figure 6, that must be addressed in selecting alloys for the heater head as well as for other components that come in contact with hydrogen. Chemical incompatibility, which involves the reaction between hydrogen and an alloying element, can lead to embrittlement of the alloy. For example, a reaction between hydrogen and carbon, which is normally added to most iron-base superalloys, can result in the formation of methane bubbles followed by embrittlement (ref. 8). A second concern involving hydrogen is permeation through the heater head tube walls leading to loss of hydrogen. The relatively high hydrogen permeability (refs. 9 and 10) of iron-base superalloys at the temperature (760° C) and pressure (25 MPa) being considered for the improved Stirling engine suggests that a very limited operational life could be expected before hydrogen recharging would be required. At full power, time between charges would probably be less than 10 hours based on permeability of hydrogen through an uncoated, nonoxidized tube. This is, of course, an unacceptable situation for the average motorist. Degradation of high temperature properties in high pressure hydrogen is a third area of consideration in selecting materials for the heater head (refs. 11 and 12). Dislocation enhanced movement of hydrogen to stress concentrated areas can lead to loss in ductility, reduction in strength, and reduction in rupture life.

CONCLUSIONS - IMPROVED (METAL) ENGINE

Based on the information available to date, the heater head is considered to be the most critical component in the improved (metal) engine from a materials viewpoint. The combination of time, temperature, pressure, and environment involved in the Stirling engine imposes stringent requirements for alloys to be used in the heater head. Mechanical property data such as rupture life are required for candidate alloys under the anticipated operating conditions of environment and pressure in the Stirling engine. Calculated permeation rates of hydrogen indicate that barrier coatings will be required for the heater head tubes. Hydrogen compatibility, permeation, and effects on properties need to be measured on candidate uncoated and coated alloys. The use of strategic materials can be reduced from current prototype engine consumption and must be considered as a primary design factor for automotive applications. Based on available mechanical property data, lower cost alloys can be substituted for N-155 and still meet current estimated stress requirements in the heater head of the Stirling engine.

MATERIALS FOR THE ADVANCED (CERAMIC) ENGINE

The advanced Stirling engine estimated operating conditions of time, temperature, pressure, and environment are shown in figure 7 for each of the high temperature components considered in this assessment. Again, it is assumed that the minimum life of the engine will be 3500 hours, involving approximately 20 000 cycles of startup and shutdown of the automobile. All components will experience this time requirement. Current estimates of operating temperatures (ref. 5) in the hot components of the engine range from a high of 1480° C (2700° F) on the hot side of the air preheater to 300° C (570° F) on the air intake side of this heat exchanger. The burner wall is estimated to operate at 1340° C (2450° F) while those components in contact with hydrogen, including the heater head, regenerator, cylinder, and piston, will experience an operating temperature of about 1090° C (2000° F). The peak operating pressure of the hydrogen working fluid is estimated to be 27 MPa (3900 psi), with normal operating pressure slightly lower, 21 MPa (3000 psi). The heater head, regenerator, cylinder, and piston will experience these high operating pressures. Environmental conditions imposed upon the hot components of the Stirling engine will include the hydrogen working fluid and the air/combustion gases in the same areas as described previously for the improved engine.

It should be emphasized that the aforementioned operating conditions for the advanced Stirling engine are preliminary estimates and may be subject to revision as the advanced engine design is refined. Based on the current estimated conditions, the air preheater is considered to be the most critical component because of the high temperature (1480° C) proposed, which may exceed the long time high temperature capabilities of candidate ceramic materials. The heater head is also a critical component because of the high pressure - high temperature hydrogen working fluid to be contained and the high temperature combustion gases on the exterior of the heater head.

Primary candidate materials for the advanced Stirling engine include silicon carbide and silicon nitride. Newer materials such as sialons may also gain in importance as more is learned about their processing and properties. Several forms of silicon carbide and silicon nitride are available as shown in figure 8 and offer potential for many of the high temperature components in the advanced Stirling engine. Silicon carbide can be produced by such processes as siliconizing, hot pressing, α sintering, and chemical vapor deposition. Silicon nitride is produced by reaction sintering, hot pressing, and sintering. Because of its good high temperature capabilities, silicon carbide is considered a candidate material for such components as the air preheater, heater head, regenerator, cylinder, and piston. The high estimated operating temperature of the air preheater (1480° C) in the advanced Stirling engine may preclude the use of silicon nitride; however, it is considered a viable candiate material for the remaining listed components in figure 8.

It should be noted that there is very little mechanical property data, environmental data, nor long-term stability data for these candidate ceramic materials under operating conditions proposed for the advanced Stirling engine. The effects of test temperature on the short time flexural strengths of silicon carbide and silicon nitride produced by various methods are shown in figure 9. Because of the large data scatter characteristic of these materials the curves should be taken only as an indication of the strengths of the ceramic materials and not as reliable strength values for design purposes. It is interesting to note that α sintered SiC exhibits a slight increase in strength with increase in test temperature up to about 1540° C (2800° F), while reaction sintered silicon nitride exhibits only a slight decrease in strength as test temperature increases to about 1370° C (2500° F). The remaining materials processed by various techniques exhibit a rapid drop in strength at higher test temperatures, but still may be considered for most components.

CONCLUSIONS - ADVANCED (CERAMIC) ENGINE

Results of the survey to date indicate that, while ceramic materials such as silicon carbide and silicon nitride are potential candiates for application in the advanced Stirling engine, there is a paucity of data on these materials under estimated operating conditions of the engine. Because of the high temperature of the air preheater, this component is considered to be the most critical from a materials viewpoint. Long-term stability data at the air preheater temperature and long-term mechanical property data under the operating conditions of the heater head are needed. Environmental effects (hydrogen and combustion gases) must be evaluated. Low cost fabrication technology must be developed for the various ceramic components where ceramics will be utilized in the advanced Stirling engine.

CONCLUDING REMARKS

This materials technology assessment for the Stirling engines has focused on the hot components of the engines where the imposed operating conditions will severely challenge current materials technology. In order for the automotive industry to be able to consider the Stirling engine as a viable alternative to the internal combustion engine by the late 1980's, considerable materials research and development will be required. It is anticipated that industry, the academic community, and government will be involved in a cooperative effort to meet the materials needs of the improved and advanced Stirling engines. For the improved (metal) engine, this effort will concentrate on economical materials and processing techniques, while for the advanced (ceramic) engine, attention will be given to material property characterization as well as engineering design data.

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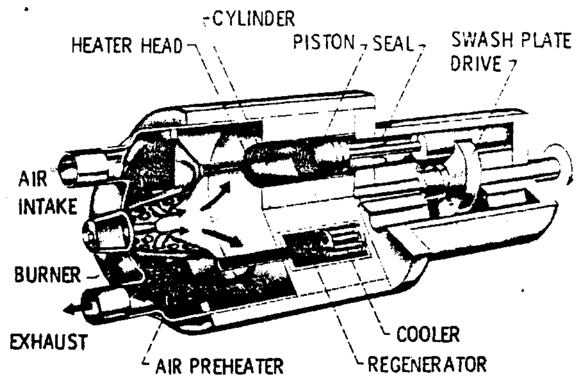

Figure 1. - Schematic representation of the Stirling engine identifying high temperature components.

COMPONENT	TIME hr (CYCLES)	TEMPERATURE, °C	(°F)	PRESSURE (PEAK) MPa (psi)	ENVIRONMENT
HEATER HEAD	3500 (20,000)	760	(1400)	25 (3600)	HYDROGEN COMBUSTION GASES
REGENERATOR	3500 (20,000)	760	(1400)	25 (3600)	HYDROGEN
CYLINDER	3500 (20,000)	760	(1400)	25 (3600)	HYDROGEN
AIR PREHEATER	3500 (20,000)	1150/260	(2100/500)	AMBIENT	AIR COMBUSTION GASES
BURNER	3500 (20,000)	980	(1800)	----------	AIR COMBUSTION GASES
PISTON	3500 (20,000)	760	(1400)	25 (3600)	HYDROGEN

Figure 2. - Estimated operating conditions for the improved (metal) engine (ref. 5).

ALLOY DESIGNATION	MAJOR ALLOYING ELEMENTS, % Fe	Ni	Cr	Co	Cb-Mo-W
S590	27	20	21	20	12
N155	31	20	21	20	7
RA330	43	35	19	--	--
A286	55	25	15	--	1
19-9DL	66	10	20	--	4

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Figure 3. - Compositions of typical candidate heater head iron-base alloys.

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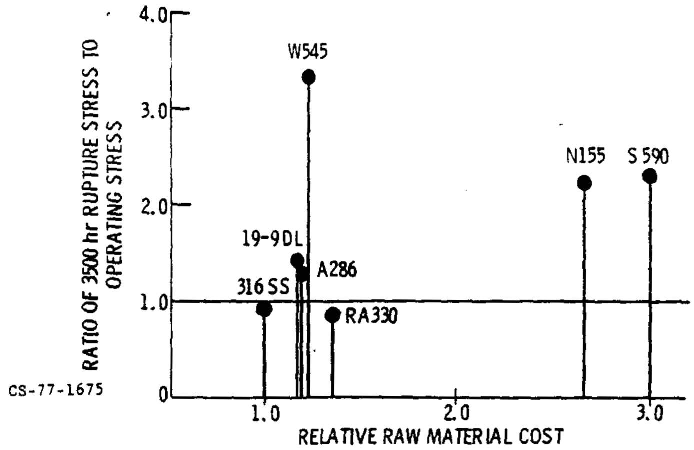

Figure 4. - Comparison of 3500 hour rupture stress to operating stress ratio to relative raw material cost of alloys based on cost of 316 stainless steel.

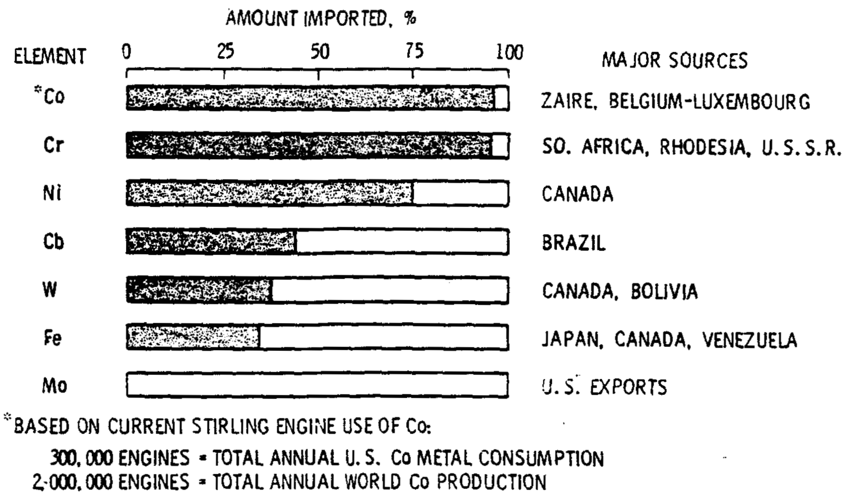

Figure 5. - Sources of strategic raw materials and the amount imported by the United States (ref. 7).

- COMPATIBILITY - EMBRITTLEMENT
- PERMEATION - HYDROGEN LOSS
- DEGRADATION - DUCTILITY, STRENGTH AND RUPTURE LIFE REDUCTION

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Figure 6. - Potential material problems encountered with use of hydrogen at high temperatures and high pressures.

E-9356

COMPONENT	TIME hr (CYCLES)	TEMPERATURE, ^{0}C	(^{0}F)	PRESSURE (PEAK) MPa (psi)	ENVIRONMENT
AIR PREHEATER	3500 (20, 000)	1480/300	(2700/570)	AMBIENT	AIR COMBUSTION GASES
HEATER HEAD	3500 (20, 000)	1090	(2000)	27 (3900)	HYDROGEN COMBUSTION GASES
BURNER	3500 (20, 000)	1340	(2450)	----------	AIR COMBUSTION GASES
REGENERATOR	3500 (20, 000)	1090	(2000)	27 (3900)	HYDROGEN
CYLINDER	3500 (20, 000)	1090	(2000)	27 (3900)	HYDROGEN
PISTON	3500 (20, 000)	1090	(2000)	27 (3900)	HYDROGEN

Figure 7. - Estimated operating conditions for the advanced (ceramic) engine.

MATERIAL	PROCESS	POTENTIAL APPLICATION
SiC	SILICONIZED CVD HOT PRESSED α SINTERED	AIR PREHEATER HEATER HEAD REGENERATOR CYLINDER PISTON
Si_3N_4	REACTION SINTERED HOT PRESSED SINTERED	HEATER HEAD REGENERATOR CYLINDER PISTON

CS-77-1670

Figure 8. - Candidate ceramics for the advanced Stirling engine.

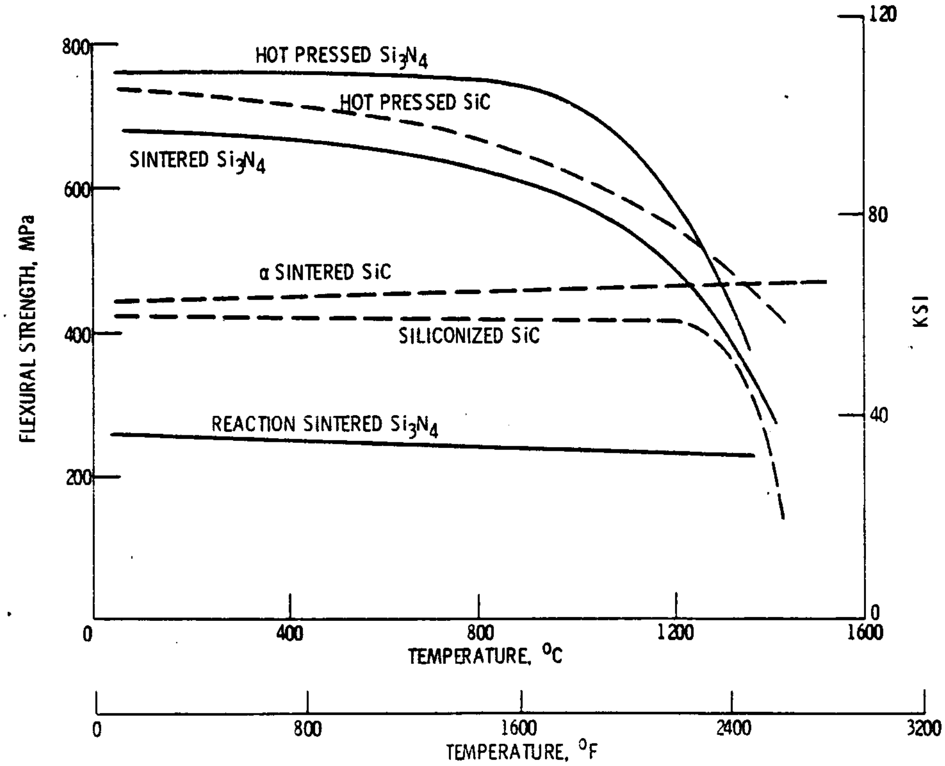

Figure 9. - Effect of test temperature on strength of candidate ceramics processed by different methods.

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16. Abstract

A materials technology assessment of high temperature components in the improved (metal) and advanced (ceramic) Stirling engines was undertaken. The objectives of the assessment were to evaluate the current state-of-the-art of metals and ceramics, identify materials research and development required to support the development of automotive Stirling engines, and to recommend materials technology programs to assure material readiness concurrent with engine system development programs. The report identifies the most critical component for each engine and a discussion of some of the material problem areas is presented.

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