Stirling Material Technology
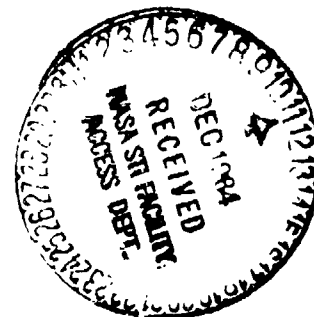
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STIRLING MATERIALS TECHNOLOGY

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SUMMARY

The Stirling engine is under investigation jointly by the Department of Energy and NASA Lewis as an alternative to the internal combustion engine for automotive applications. The most critical component from a materials viewpoint is the heater head consisting of the cylinders, heating tubes, and regenerator housing. Materials requirements for the heater head include compatibility with hydrogen, resistance to hydrogen permeation, high temperature oxidation/corrosion resistance, and high temperature creep-rupture and fatigue properties. A continuing supporting materials research and technology program has identified the wrought alloys CG-27 and 12RN72 and the cast alloys XF-818, NASAUT 4G-Al, and NASACC-1 as candidate replacements for the cobalt containing alloys used in current prototype engines. Based on this materials research program it is concluded that manufacture of the engine is feasible from low cost iron-base alloys rather than the cobalt alloys used in prototype engines.

INTRODUCTION

The Stirling engine is under investigation jointly by the Department of Energy (DOE) and the National Aeronautics and Space Administration (NASA) as an alternative to the internal combustion engine for automotive applications. The work described in this paper was conducted as a part of the supporting research and technology activities under the DOE/NASA Stirling Engine Highway Vehicle Systems program as outlined by Brogan (ref. 1). This paper reflects current and additional research and technology results from that presented at the ASM Conference on Materials for Future Energy Systems, May, 1984, Washington, D.C. (ref. 2).

The Stirling engine is an external combustion engine that offers the advantages of high fuel economy, low emissions, low noise, and low vibrations compared to current internal combustion automotive engines. A schematic representation of a prototype automotive Stirling engine is shown in figure 1. The most critical component from a materials viewpoint is the heater head consisting of the cylinders, heater tubes, and regenerator housing. The gaseous hydrogen working fluid is passed through a series of small thinwall tubes (4.5 mm od by 3 mm id) which are required for efficient heat transfer from the combustion gases to the working fluid. The hot hydrogen expands in the cylinder to drive a piston which actuates the drive system. At the opposite end of the tubes is a regenerator, which absorbs heat from the hydrogen working fluid, followed by a cooler which permits contraction of the hydrogen. This process of heating and cooling the working fluid and extracting work forms the Stirling cycle. A goal of the Automotive Stirling Engine Program is to achieve a 30 percent increase in fuel economy over internal combustion engines of similar size and vintage. To meet this goal, a working fluid of hydrogen at a maximum

E-2352

pressure of 15 MPa and a temperature of 820 °C is required. Materials requirements for the heater head include compatibility with hydrogen, resistance to hydrogen permeation, high temperature oxidation/corrosion resistance resulting from combustion products of the fuel (diesel fuel, gasoline, coal derivatives, alcohol, etc.), high temperature creep-rupture and fatigue properties that will permit operation for at least 3500 hr under conditions of cyclic hydrogen pressure (vehicle speed is controlled by working fluid pressure), and cyclic temperature changes resulting from intermittent engine starting and stopping. Current prototype engines use a cast cobalt base alloy HS-31 for the cylinders and regenerator housings and N-155, a wrought iron-base alloy with 20 percent cobalt, for the heater tubes. Because of limited availability of cobalt and its high cost, cobalt free iron-base alloys are required for the heater head.

This paper presents experimental results of research efforts aimed at meeting the materials requirements of the automotive Stirling engine. Special emphasis is placed on the heater head cylinder and regenerator housing material HS-31, the heater tube material, N-155, and potential low-cost substitutes.

PROCEDURE

A continuing supporting materials research and technology program at NASA Lewis, Mechanical Technology, Inc., United Technologies Research Center, at Ai Research Casting Company, and United Stirling AB has identified the wrought alloys CG-27 and 12RN72 and the cast alloys XF-818, NASAUT 4G-Al, and NASACC-1 as candidate replacements for the cobalt containing alloys N-155 and HS-31, respectively. Nominal composition of these candidate Stirling engine heater-head materials is given in table I. The selection of these alloys was aided by concurrent investigations of the creep-rupture behavior, cyclic fatigue failure, cyclic oxidation/corrosion resistance and hydrogen permeability. All of these properties are necessary since loss of hydrogen results in loss of the engine power system.

Table II lists the manufacturer's recommended heat treatment and when possible the ASM recommended heat treatment. Figures 2 and 3 depicts the resultant microstructure of these materials in their heat treated condition.

RESULTS AND DISCUSSION

Creep-rupture tests in air and high pressure (15 MPa) hydrogen on the unaged N-155, CG-27, and the 12RN72 alloys show (figs. 4(a) and (b)) that at 760 and 815 °C, CG-27 alloy has superior stress-rupture properties than either the N-155 or 12RN72 alloys (refs. 3 to 6). Base line data derived from the creep-rupture tests on the unaged alloys tested in air and 15 MPa hydrogen was determined to be reliable by subjecting it to a simple power relationship correlational analyses of the form:

$$\ln t_r = \ln k + n \ln \sigma \tag{1}$$

where t_r is rupture life in hours, $\ln k$ is a constant, n is the exponential stress constant, and σ is the applied stress. At 760 °C, the stresses for a 3500 hr rupture life in hydrogen are 170, 100, and 60 MPa, for CG-27, N-155, and 12RN72, respectively. At 815 °C, the corresponding stresses for a 3500 hr

rupture life in hydrogen are 105, 70, and 40 MPa, respectively. Long term aging, 3000 hr at 760 °C, in either low pressure (30 to 60 kPa) flowing argon or hydrogen did not drastically reduce the creep-rupture strength of these alloys. Figure 5 shows the effect of long time aging on 760 °C stress versus rupture-life for N-155, CG-27, and 12RN72. Generally a 10 to 15 percent loss in rupture-stress was noted after aging in either the H_2 or Ar, and is not considered to be a large enough loss to affect the 3500 hr design criteria. It is concluded that the aging cycle itself has a deleterious effect on rupture strength since similar losses were noted with each environment.

The design criteria requires the allowable stress level for 3500 hr rupture life at specific temperatures. There are many different methods (ref. 7) of analysis of creep-rupture parameters which consider both stress and temperature. A temperature-compensated analysis based on the Orowan-Sherby-Dorn method was selected for this study to determine the desired stress values. The relationship has the form:

$$\ln t_r = \ln k + n \ln \sigma + Q/RT \qquad (2)$$

where Q is the apparent activation energy for creep, R the universal gas constant, (8.314 J/K mol) and T is test temperature, K.

Using multiple linear regression analysis, apparent activation energies for creep were determined along with the various material constants. The 3500 hr rupture-life stress of the candidate tube alloys was calculated over the temperature range 700 to 900 °C and is depicted in figure 6. The present design criteria for the heater-head tube materials in the unaged condition consist of a rupture life of 3500 hr at 870 °C and at a stress of 28 MPa. At the current design maximum heater tube temperature of 870 °C, figure 6 shows that the unaged CG-27 alloy has a 3500 hr rupture stress of 45 MPa when tested in air. It is also shown that when tested in 15 MPa H_2 the rupture strength is increased to 63 MPa. This implies that CG-27 has a growth potential to approximately 920 °C with the present design concept. While the 12RN72 alloy does not meet the present high temperature stress-rupture criteria, it will be shown that it has qualities highly desirable for possible lower temperature designs.

Creep-rupture generally has never been observed as a major failure mode for prototype Stirling engine components manufactured from heavy wall castings. Fatigue has been identified as the major failure mode in the cylinder head manifold of engines (ref. 8). In 3500 hr of engine operation, the engine experiences approximately 5×10^8 cycles of high-cycle pressure variations about the mean pressure. Growth of fatigue cracks and subsequent hydrogen leakage has lead to cylinder housing failures. The fatigue design criteria for the cylinder and regenerator housing requires a safety factor of two in the stress range produced by the number of pressure cycles in 3500 hr. The present design criteria for the heater-head cast cylinder heads and regenerator housings consists of a rupture life of 3500 hr at 775 °C and a stress of 120 MPa. When a safety factor of two is applied, the design criteria fatigue stress amplitude is set at a maximum of 240 MPa at 775 °C. Figure 7(a) shows the results of fatigue tests at 800 °C for HS-31, XF-818, and the new developmental alloy NASAUT 4G-A1. Presently, at 800 °C, neither the HS-31 nor the XF-818 alloy meet the fatigue design criteria in either air or 15 MPa hydrogen. The XF-818, HS-31, and NASAUT 4G-A1 high cycle fatigue tests were conducted on smooth specimens at 800 °C, however, the NASAUT 4G-A1 alloy was tested at an

3

R ratio, $\sigma min/\sigma max$, of 0.1 at 20 Hz while the XF-818 and HS-31 were tested at an R ratio of -1.0 (fully reversed) (refs. 9 to 11).[1] These fatigue tests show that the approximate fatigue-limit (10^7 cycles) stress amplitudes are XF-818:110 MPa, HS-31:186 MPa, and NASAUT 4G-Al:250 MPa. Figure 7(b) shows the results of strain controlled fatigue test at 800 °C on the HS-31, XF-818, NASAUT 4G-Al, and NASACC-1 alloys. The NASAUT 4G-Al alloy is able to endure about 2.5 times the creep-fatigue strain of XF-818 and about 1.5 times that of HS-31 and NASACC-1. Whether or not the NASAUT 4G-Al alloy will meet the fatigue strength criterion will have to wait for further evaluation at appropriate test conditions.

Although it has been identified that the creep-rupture life of the cast component is not their limiting design criteria, an assessment of their rupture life is necessary. A creep-rupture test program similar to that for the tube materials was conducted on the cast alloys. Creep-rupture tests in air and hydrogen on the unaged, aged, and following a simulated vacuum braze cycle of 1 hr at 1150 °C were conducted on HS-31 and XF-818. The NASAUT 4G-Al and NASACC-1 alloys were not available for extensive creep-rupture testing. Figure 8 shows the results of creep-rupture tests at 760 °C for HS-31 and XF-818 in the unaged and braze cycled condition both for air and 15 MPa hydrogen (refs. 4 to 6). Creep-rupture testing in 15 MPa hydrogen had no apparent effect on the rupture-life of HS-31 and XF-818 regardless of heat treatment. Again we see, as with tube alloys, that the test environment has very little effect on the rupture-lives and that the heat treatment or aging cycle predominates. In the case of HS-31 and XF-818, the simulated braze cycle resulted in approximately a 10 percent decrease in strength. Using the temperature-compensated Weertman-Orowan-Sherby-Dorn relationship, and the results of a linear-multiple regression on available NASAUT 4G-Al and NASACC-1 rupture data, a 3500 hr rupture life design curve was constructed as shown in figure 9. All four cast alloys meet the static stress-rupture engine design criteria of 120 MPa for 3500 hr rupture life at 775 °C. Since the results of the NASAUT 4G Al and NASACC-1 are considered preliminary their projected high stress values will be verified both in air and hydrogen along with high temperature growth potential.

The oxidation/corrosion resistance of candidate Stirling engine heater head tube alloys was determined under conditions that are to be encountered in automotive applications of the Stirling engine (ref. 12). Duplicate sheet specimens were evaluated under cyclic conditions at 820 °C for 3500 hr in a Stirling engine materials simulator rig. The specimens were heated for 5 hr cycles in the combustion flame of the diesel fuel fired rig. The three heater head tube alloys N-155, CG-27, and 12RN72 exhibited differing oxidation behavior, as can be seen by the specific weight change data in figure 10. Alloy CG-27 did not exhibit any significant spalling during the 3500 hr of testing at 820 °C, oxidizing by parabolic weight gain throughout the entire test. In contrast, N-155 and 12 RN72 both spalled after 1500 hr into the test with alloy 12RN72 having a net weight loss at the end of the test. This behavior is characteristic of high temperature cyclic oxidation.

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[1]All tests with NASAUT 4G-Al to date have been on specimens produced from bars cast by directional solidification. Future tests will be run on normal cast specimens of random grain orientation to eliminate the possibility of preferred orientation effects.

Oxidation/corrosion data were fitted by least squares as described by Barrett (ref. 13) to the paralinear equation (3).

$$\frac{W}{A} = k_1^{1/2} \ t^{1/2} - k_2 t \pm SEE \tag{3}$$

where W/A is specific weight change, t is time, k_1 is an oxide growth constant comparable to parabolic oxidation scaling constant, k_2 is an oxide spalling constant, and SEE is the standard error of estimate. An oxidation attack parameter K_a (ref. 13) was derived from equation (3) and is defined in equation (4):

$$K_a = (k_1^{1/2} + 10 \ k_2) \tag{4}$$

In certain cases, as for CG-27 where scale spalling is insignificant, the k_2 term will drop out of equation (4) giving the pure parabolic oxidation/corrosion case. Oxidation/corrosion attack parameters, K_a are shown in figure 11 for the three alloys, where lower values of K_a are indicative of better oxidation resistance. The resulting oxide attack parameter, $K_a = 0.026$ for CG-27, quantitatively characterizes the oxidation behavior of this alloy and based on prior cyclic oxidation experience, CG-27 is considered to have excellent oxidation resistance. The K_a value of 0.11 for 12RN72 suggests that this alloy has good oxidation resistance under the conditions anticipated for the automotive Stirling engine.

Photomicrographs of the alloy specimens after testing are shown in figure 12. Alloy N-155 exhibits an adherent oxide scale on the specimen surface with a slight depletion zone beneath the oxide scale. Alloy CG-27 also exhibited an adherent oxide scale on the surface. Further examination of the alloy by electron microprobe techniques revealed that internal oxidation of aluminum occurred, and that a thin aluminum rich oxide layer existed next to the metal substrate, suggesting that aluminum plays a major role in the excellent oxidation behavior of this alloy. A relatively large depletion zone characterized alloy 12RN72. Electron microprobe results showed the oxide scale to be rich in chromium and iron, plus grain boundary penetration of oxygen to form chromium and titanium oxides. Based on the analysis of the oxidation weight change data, x-ray, metallographic, and electron microprobe analyses of tested specimens, CG-27 is considered the leading candidate heater head tube alloy.

Containment of the hydrogen working fluid during operation of the Stirling engine at high temperatures (870 °C), high pressures (15 MPa) and for a period of about 175 hr between refills is essential for the acceptance of the engine as an alternative to the internal combustion engine. While hydrogen readily permeates heater head tube alloys at 820 to 870 °C, it has been shown (ref. 13), that doping the working fluid with small amounts of CO or CO_2 (0.02 to 1.0 vol %) reduces hydrogen permeability by as much as two orders of magnitude and to a level that will provide an acceptable recharging frequency. Figure 13 shows the results of the final 5 hr cycle from a 100-hr cyclic permeation study at 820 °C on the N-155 alloy (ref. 13). Tubes heated externally in a diesel-fuel-fired Stirling engine simulator test rig were pressurized to 21 MPa after each 5 hr cycle. The results of this test show that the hydrogen permeation through hot tube walls can be substantially reduced using 1.0 vol % CO_2 as a dopant in the hydrogen. It has been postulated (ref. 15) that the CO_2 or O_2 in the hydrogen forms a thin adherent oxide film on the inside surface of

the tube, which, when coupled with the formation of a thick adherent oxide
layer, on the fire side of the tube, results in the noted large reductions in
hydrogen permeation. The lowest hydrogen permeation rates noted after a
3500 hr simulated engine test at 820 °C were for the highly oxidation resistant
alloys CG-27 and 12RN72. Figure 14 shows decreases in the hydrogen permeabil-
ity by as much as two orders of magnitude for both CG-27 and 12RN72 with time
(ref. 16).

CONCLUSION

Based on the materials research program in support of the automotive
Stirling engine it is concluded that manufacture of the engine is feasible
from low cost iron-base alloys rather than the cobalt alloys used in prototype
engines. In particular, heater head tubes of alloy CG-27 offer higher creep
rupture properties than N-155. This alloy is also attractive for automotive
applications since it contains the least amount of the strategic metal chromium
(ref. 14) of the alloys investigated, and is free of the strategic metal
cobalt. This is compared to the 20 percent chromium and 20 percent cobalt
contents in the N-155 alloy used in current prototype engines. The CG-27 alloy
has been selected as the tube material for current design automotive Stirling
engines. Also, the cast alloy XF-818 is currently being used in these engines.
Its castability, weldability, and creep strength make it attractive for this
use. However, fatigue resistance is in question, and continued research on the
experimental NASAUT 4G-A1 and NASACC-1 alloy is in progress. These advanced
iron-base alloys may have potential for use in future applications of the
Stirling engine where high temperature, high pressures, and cyclic conditions
are planned such as in stationary applications for domestic power systems.

REFERENCES

1. J.J. Brogan, "Highway Vehicle Systems Program Overview." Highway Vehicle
    Systems, CONF-771037, 1978, pp. 3-5.

2. R.H. Titran and J.R. Stephens, "Advanced High Temperature Materials for
    the Energy Efficient Automotive Stirling Engine." Journal of Materials
    for Energy Systems, Vol. 6, No. 2, Sept. 1984, pp. 114-121.

3. W.R. Witzke and J.R. Stephens, "Creep-Rupture Behavior of Seven Iron-Base
    Alloys After Long Term Aging at 760° in Low Pressure Hydrogen." NASA
    TM-81534, 1980.

4. R.H. Titran, "Creep-Rupture Behavior of Candidate Stirling Engine Alloys
    After Long-Term Aging at 760°C in Low-Pressure Hydrogen." NASA TM-83676,
    1984.

5. S. Bhattacharyya, "Creep-Rupture Behavior of Six Candidate Stirling
    Engine Iron-Base Superalloys in High Pressure Hydrogen, Vol. 1 - Air
    Creep-Rupture Behavior." IIT Research Inst., Chicago, IL, Report No.
    IITRI-M0601, Dec. 1984. (NASA CR-168071, 1982.)

6. S. Bhattacharyya, W. Peterman and C. Hales, "Creep-Rupture Behavior of Candidate Stirling Engine Iron Superalloys in High-Pressure Hydrogen, Vol. II - Hydrogen Creep-Rupture Behavior." IIT Research Inst., Chicago, IL, Report No. IITRI-M06116-15, June 1984. (NASA CR-174705, 1984.)

7. F. Garafalo, "Fundamentals of Creep and Creep-Rupture in Metals," Macmillan Co., NY, 1965.

8. N.P. Nightingale, "Automotive Stirling Engine Development Program - Overviw and Status Report." Proceedings of the Twentieth Automotive Technology Development Contractors' Coordination Meeting, Warrendale, PA, SAE, 1982, pp. 53-62.

9. Automotive Stirling Engine Development Program, NASA Contract No. DEN3-32.

10. Identification of a Cast Iron Alloy Containing Nonstrategic Elements, NASA Contract No. DEN3-282.

11. Cast Fe-Base Cylinder/Regenerator Housing Alloy, NASA Contract No. DEN3-234.

12. J.R. Stephens and C.A. Barrett, "Oxidation and Corrosion Resistance of Candidate Stirling Engine Heater-Head-Tube Alloys." NASA TM-83609, 1984.

13. C.A. Barrett and C.E. Lowell, "High Temperature Cyclic Oxidation Furnace Testing at NASA Lewis Research Center " Journal of Testing and Evaluation, Vol. 10, No. 6, 1982, pp. 273-278.

14. J.A. Misencik, "Evaluation of Dopants in Hydrogen to Reduce Hydrogen Permeation in Candidate Stirling Engine Heater Head Tube Alloys at 760°C and 820°C." NASA TM-82920, 1982.

15. S.R. Schuon and J.A. Misencik, "Effects of Oxide Films on Hydrogen Permeability of Candidate Stirling Engine Heater Head Tube Alloys." NASA TM-82824, 1982.

16. J.A. Misencik and R.H. Titran, "Evaluation of Candidate Stirling Engine Heater Tube Alloys after 3500 Hours Exposure to High Pressure Doped Hydrogen or Helium," NASA TM-83782, 1984.
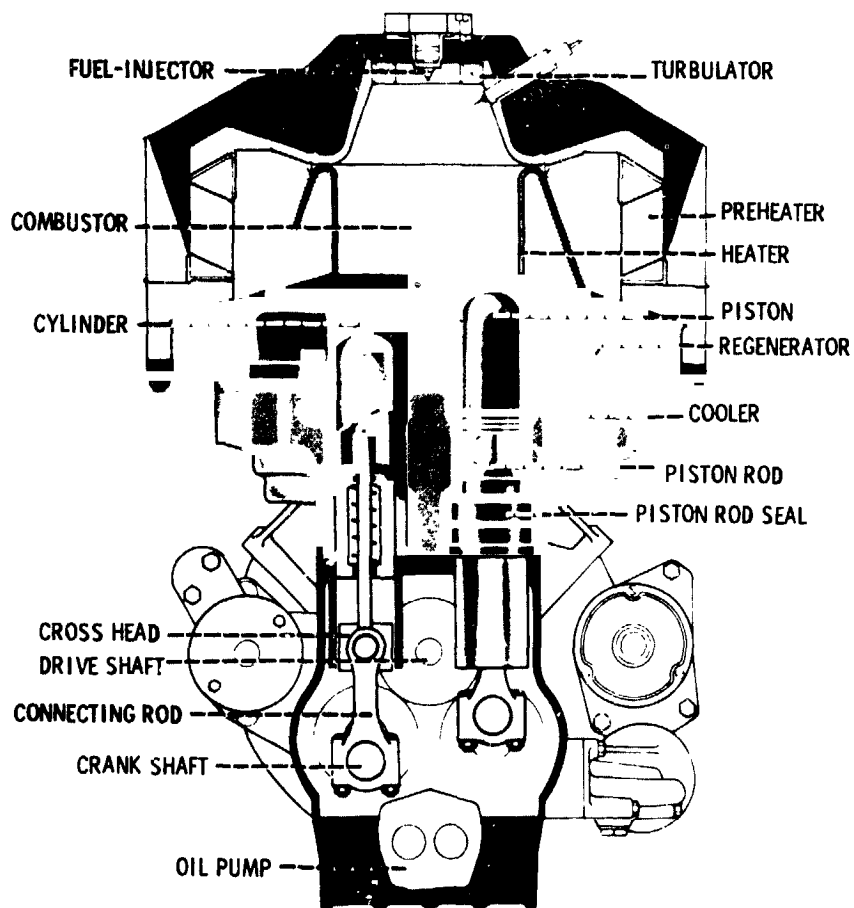
TABLE I. - NOMINAL COMPOSITION OF CANDIDATE STIRLING ENGINE HEATER-HEAD ALLOYS

Alloy	Fe	Cr	Ni	Co	Mn	Si	Mo	Cb/Ta	W	Al	Ti	C	Other
N-155	30	21	20	20	1.5	0.5	3.0	1	2.5	---	---	0.15	0.15N
CG-27	38	13	38	---	0.1	0.1	5.5	0.6	---	1.5	2.5	0.05	.01B
12RN72	52	19	25	---	1.8	0.4	1.4	---	---	---	.5	0.1	.015N
HS-31	1.5	25	10	54.5	0.5	0.5	---	---	7.5	---	---	0.5	-------
XF-818	55	18	13	----	0.1	0.3	7.5	0.4	---	---	---	0.2	0.6B
NASAUT 4G-A1	64.5	15	--	----	15	1.0	2	1.0	---	---	---	1.5	-------
NASACC-1	51.5	18	18	----	0.3	0.6	5.0	2.3	2.5	---	---	0.5	12B

TABLE II. - HEAT TREATMENT OF CANDIDATE STIRLING
ENGINE HEATER-HEAD ALLOYS

Alloy	Heat Treatment ("unaged" condition)
CG-27	Sol'n. ann. 1150 °C/10 min in vac/ fast furnace cool. Age 760 °C/ 16 hr in vac/cool to 650 °C/hold 24 hr/fast furnace cool.
12RN72	Sol'n. ann. 1175 °C/15 min in vac/ water quench.
N-155	(AMS-5532B) Sol'n. ann. 1176 °C/ rapid air cool or water quench.
HS-31	Anneal 730 °C/50 hr in vac/fast furnace cool.
XF-818	None specified (as-cast).
NASAUT 4G-A1	650 °C/100 hr in air/air cool (DS).
NASACC-1	1175 °C/2 hr in argon/fast furnace cool

FUEL-INJECTOR — TURBULATOR

COMBUSTOR — PREHEATER
— HEATER

CYLINDER — PISTON
— REGENERATOR

— COOLER

— PISTON ROD

— PISTON ROD SEAL

CROSS HEAD
DRIVE SHAFT
CONNECTING ROD
CRANK SHAFT

OIL PUMP

C-78-3145

Figure 1. - Schematic representation of automotive Stirling engine.

(a) N-155.

(b) CG-27.

(c) 12 RN 72.

Figure 2. - As heat-treated microstructures of heater head tube alloys.

(a) HS-31.

(b) XF-818.

(c) NASAUT 4G-Al.

(d) NASACC-1

Figure 3. - As heat-treated microstructures of cylinder/regenerator housing alloys.

(a) Temperature, 760° C.

(h) Temperature, 815° C.
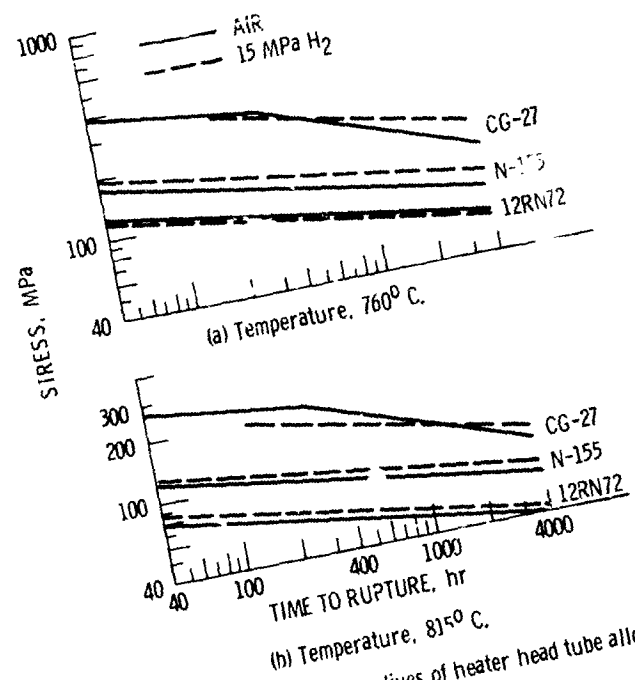
Figure 4. - Rupture lives of heater head tube alloys in air and hydrogen.
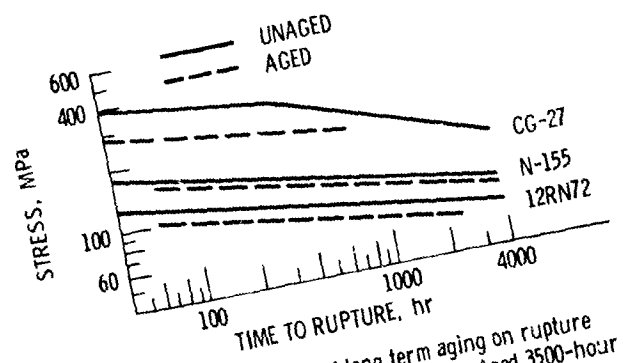
Figure 5. - Effects of long term aging on rupture lives of heater hea tube alloys. Aged 3500-hour at 760° C.
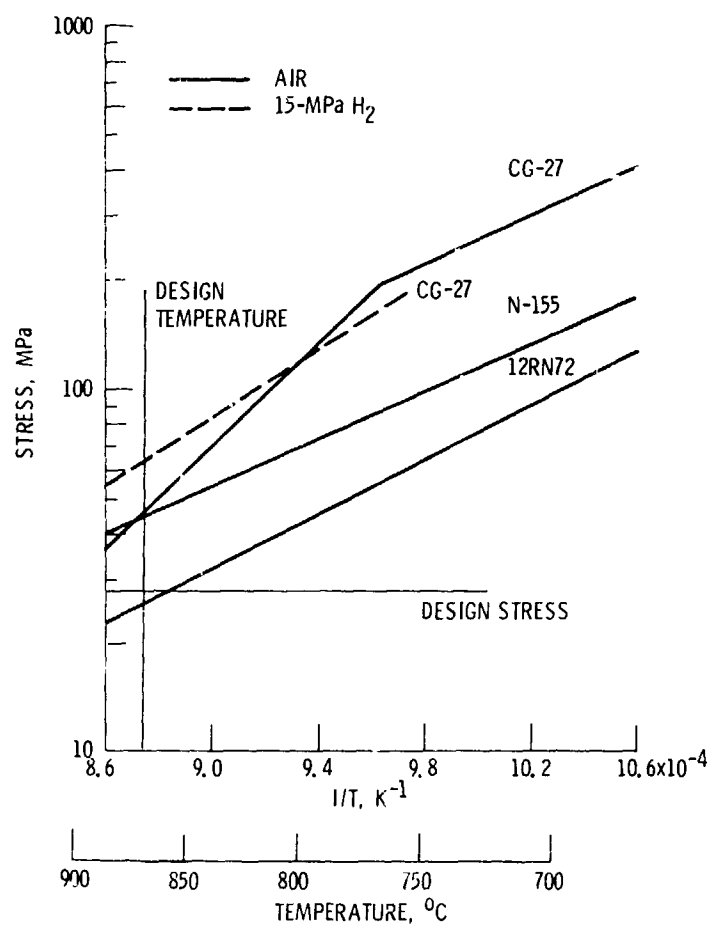
Figure 6. – Comparison of stress for 3500-hour rupture life with design criteria for heater head tubes.

(a) Stress dependence.

———— NASAUT
      4G-Al   } R = 0.1 AT 20 Hz
———— HS-31   }
———— XF-818 } R = -1.0 AT 10 Hz
-------- NASACC-1 ¦ R = -1.0 AT 25 Hz
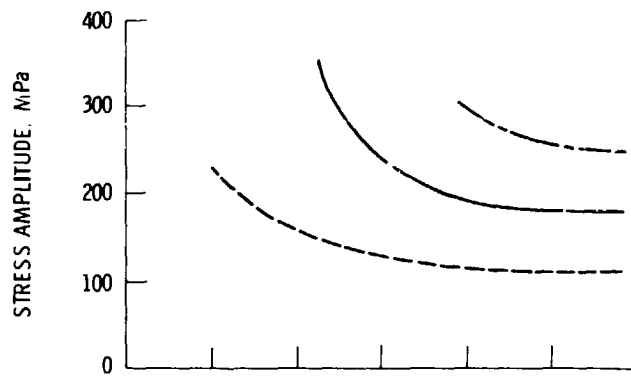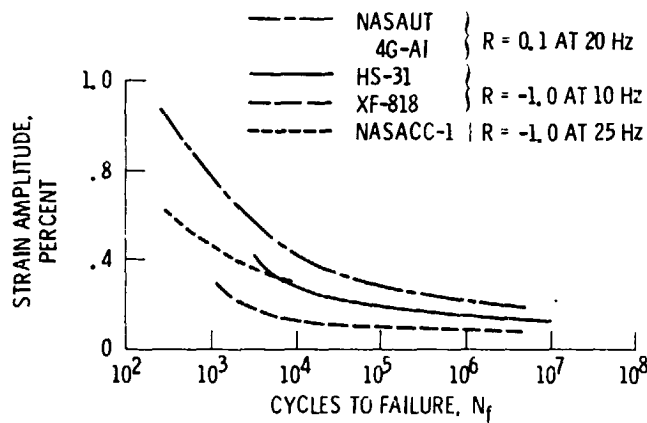
(b) Strain dependence.

Figure 7. - 800 °C fatigue resistance of cast cylinder /
regenerator housing alloys.
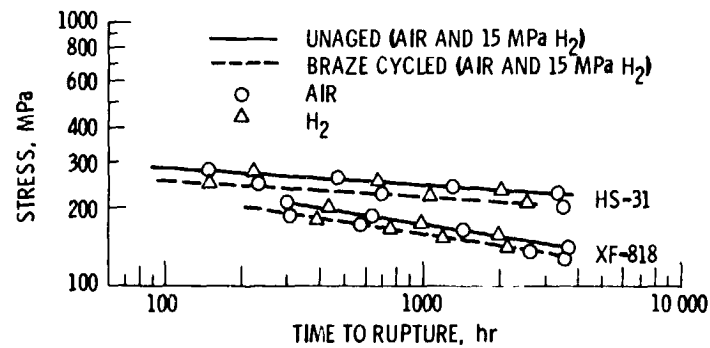
Figure 8. - Rupture lives of cast cylinder/regenerator housing
alloys at 760 °C.
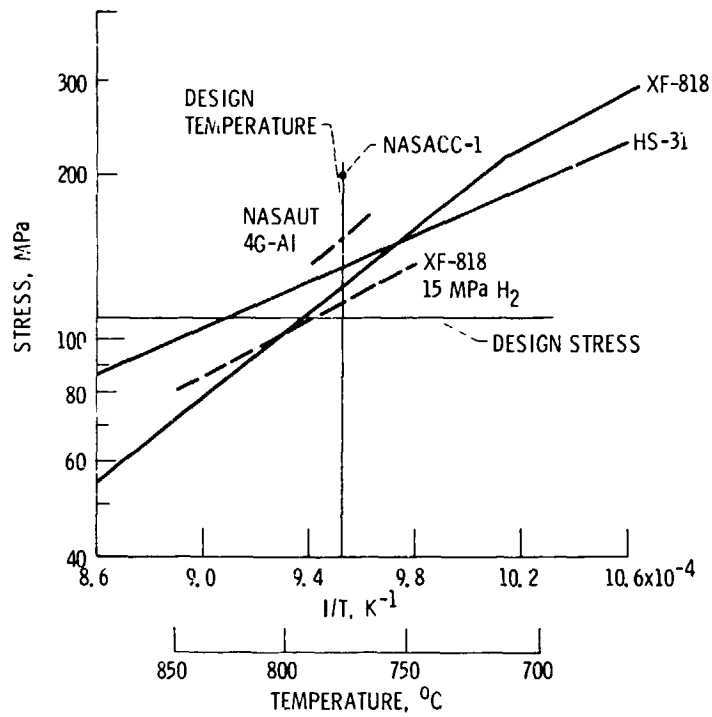
Figure 9. - Comparison of stress for 3500-hour rupture life with design criteria for heater head castings.
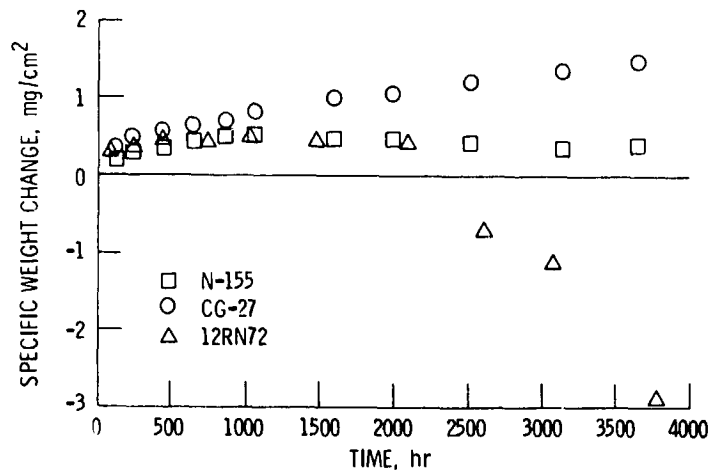
Figure 10. - Oxidation/corrosion specific weight change data for heater head tube alloys. (5-h cycles at 820 °C.)

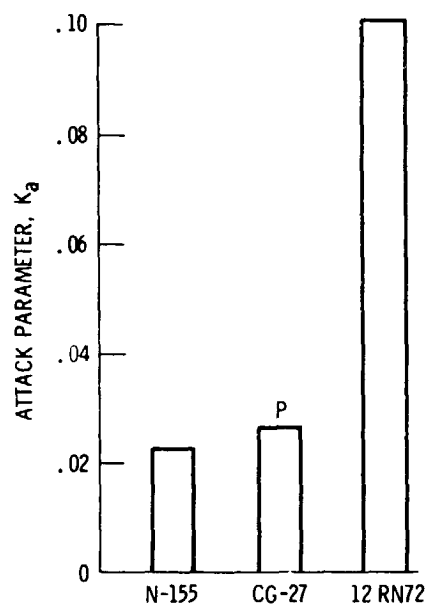Figure 11. - Oxidation /corrosion attack parameter for heater head tube alloys after 3500-hour cycle testing at 820^0 C. P - parabolic weight gain - no spalling.

(a) N-155.

(b) CG-27

(c) 12RN72.

Figure 12. - Photomicrographs of 3500 hour oxidation/corrosion heater head tube specimens showing oxide scales and depletion zones.
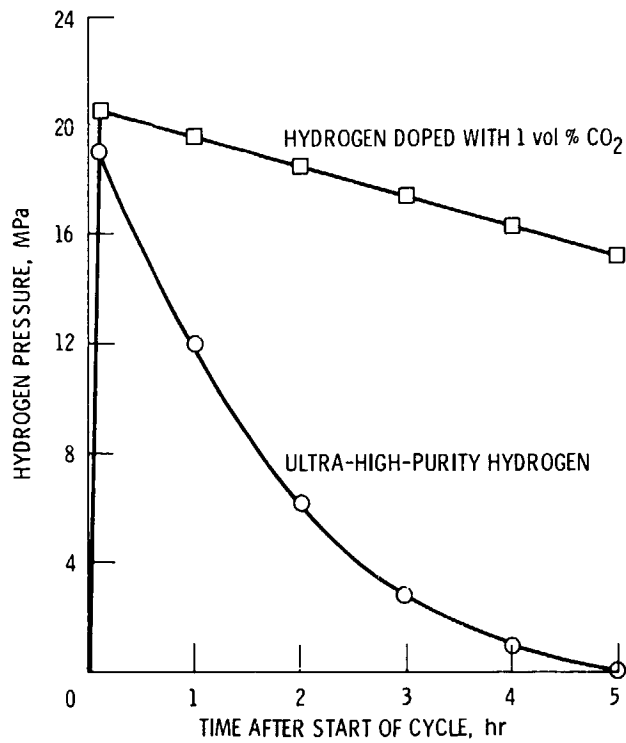
Figure 13. - Effect of doping with 1 vol % CO_2 on hydrogen loss in N-155 tubes. Final 5-hour cycle of 100-cycle run.
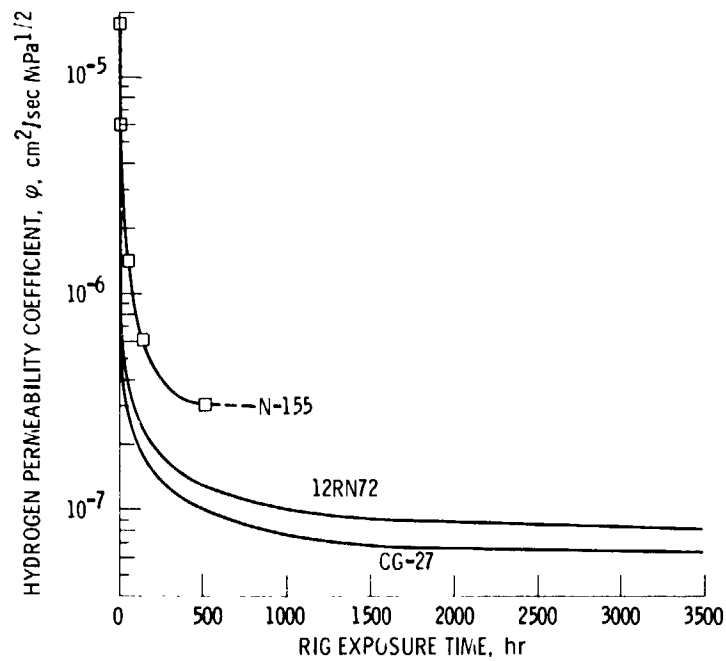

Figure 14. - Hydrogen permeability coefficient versus rig exposure time for candidate heater head tube alloys at 820 °C. Gas, H_2 + 1 vol % CO_2.