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Abstract

The automotive Stirling engine now under development by DOE/NASA as an alternative to the internal combustion engine, imposes severe materials requirements for the hot portion of the engine. Materials selected must be low cost and contain a minimum of strategic elements so that availability is not a problem. Heater head tubes contain high pressure hydrogen on the inside and are exposed to hot combustion gases on the outside surface. The cylinders and regenerator housings must be readily castable into complex shapes having varying wall thicknesses and be amenable to brazing and welding operations. Also, high strength, oxidation resistance, resistance to hydrogen permeation, cyclic operation, and long-life are required. A research program conducted by NASA Lewis focused on alloy chemistry and microstructural control to achieve the desired properties over the life of the engine. Results of alloy selection, characterization, evaluation, and actual engine testing of selected materials will be presented.

KEY WORDS: Automotive Stirling engine; Alloy chemistry; Microstructure; Creep resistance; Oxidation; Hydrogen permeation; Iron-base alloys

The Department of Energy (DOE) and NASA [1] are currently investigating the Stirling engine as an alternative power source to the internal combustion engine for automotive applications. The Stirling engine (Fig. 1) is an externally heated engine that offers the advantages of high efficiency, low pollution, low noise, and multifuel capability. Hydrogen is used as the working fluid for automotive applications in order to obtain maximum efficiency from the engine. Heat is input to the working fluid by a combustion flame impinging on the outside walls of the tubes containing the hydrogen working fluid. Current engines designed for automotive applications use tubes with a wall thickness of 0.75 mm (3.0 mm i.d. by 4.5 mm o.d.). The thin wall is required to achieve maximum heat input to the hydrogen. However, the tube material must be of sufficient strength to contain the hydrogen, which operates at high pressures and temperatures. Automotive design requirements call for a normal maximum pressure of 15 MPa, with peak pressures reaching 21 MPa during transient conditions. Tube walls are designed for an average temperature of 820 °C, with 870 °C common on the flame side. A further requirement is that the tubes operate for a period of 3500 h, which is approximately equivalent to the 160 000-km (100 000-mile) driving life of an engine.

The tubes currently are heated by direct exposure to a combustion flame fired by gasoline or diesel fuel. Alternative fuels such as alcohol and shale oil derivatives may be considered for future applications. Oxidation and corrosion resistance is one of several criteria for selecting heater-head-tube alloys to withstand the extreme operating requirements of the Stirling engine. A second criterion is the resistance of the tube material to hydrogen permeation so that hydrogen recharging of the engine is required in excess of 6 month intervals. Finally, the creep-rupture strength for 3500 h life is a determining factor in selecting a heater tube alloy. These criteria are

interrelated. For example, excessive scale spalling due to oxidation/corrosion will reduce the tube wall thickness and lead to premature failure caused by the high-pressure hydrogen rupturing the tubes or permeating rapidly through the tube walls. Prototype engines and initial models of experimental automotive engines use N-155 (Multimet) for heater head tubes. However, this iron-base alloy contains 20 percent cobalt, a costly and strategic metal. Efforts are currently under way by NASA [2-7] and the contractors on this program, Mechanical Technology Inc. (MTI) and United Stirling Sweden (USAB), to identify substitutes for N-155. The primary emphasis is on high-strength austenitic iron-base alloys although a limited number of nickel-base superalloys are under consideration. As part of the evaluation of candidate substitute alloys the oxidation and corrosion resistance has been determined for 16 alloys [8]. Hydrogen permeation coefficients have been determined for most of those alloys [9], and strength properties have been measured by creep testing in air [2] and hydrogen [10]. Further, endurance testing in a materials simulator rig and engine testing have been used to characterize selected candidate heater tube alloys [3,6,9].

The purpose of this paper is to describe the effects of alloy chemistry and microstructure on the oxidation/corrosion behavior and resistance to hydrogen permeability of candidate alloys.

Procedure

Materials

Twenty alloys (14 iron base, five nickel base, and one cobalt base) were evaluated for their oxidation and corrosion resistance, hydrogen permeability, and endurance under conditions of temperature and environment anticipated for automotive Stirling engines. The chemical compositions of the alloys are listed in Table 1. All of the alloys are commercially available except AL-EX-20, an experimental alloy supplied by Allegheny Ludlum Steel Company.

Iron-base alloys are the primary candidates for automotive Stirling engine applications because their raw material costs are lower than those for nickel-base and cobalt-base alloys. Nickel-base alloys are considered as possible candidates in the event a less expensive iron-base alloy cannot be identified that will meet all of the requirements of the Stirling engine. Cobalt-base alloys are not under consideration for automotive Stirling engine applications because of the high cost of cobalt, its limited availability, and its status as a strategic material (more than 95 percent of the cobalt used in the United States is imported). However, one cobalt-base alloy (HS-188) was included in this investigation as a comparison with the iron- and nickel-base alloys.

For oxidation testing, test coupons 1.27 by 2.54 cm, and generally 0.8 to 1.6 mm thick, with a 0.3-cm-diameter hanger hole, were cut from the alloy sheet material. For hydrogen permeability and endurance testing the alloys used in this study were obtained commercially in the form of tubing with an outside diameter of 4.5 mm and an inside diameter of 3.0 mm (the size used in current prototype engines). Four of the tubing alloys were weld-drawn and the others were seamless tubing. The weld-drawn alloys were N-155, 19-9DL, Inconel 718(wd) and HS-188.

Stirling Engine Simulator Materials Test Rig

The Stirling engine simulator rig used in this program was designed and fabricated at the NASA Lewis Research Center; it consists primarily of a combustion gas heating chamber (Fig. 2) with auxiliary heating, control, and gas management systems. The rig and its operation have been described in detail [3]. The rig was fired with natural gas for initial ignition and then with diesel fuel throughout the test run. Duplicate oxidation-corrosion test specimens were suspended by platinum wires from the hairpin turns of the tubes shown in Fig. 2. The specimens were heated to the desired 820 °C test

temperature (automotive Stirling engine temperature) by the combustion flame flowing over them. The rig was used primarily as a means of ranking candidate heater-head-tube alloys [3,6,9]. The oxidation-corrosion testing was conducted simultaneously with a 3500-h endurance and permeability run of tubing alloys. An endurance run consisted of a series of 5-h cycles to obtain the required 3500 h of test time to simulate the minimum life of an automotive engine. A typical heating cycle consisted of a 6- to 10-min preheat to get to the operating temperature, a 5-h hold at temperature, and a 1-h cooldown to near room temperature. The change in specific weight $\Delta W/A$ with time t for the oxidation coupons was fitted by least squares [11] to equation (1).

$$\frac{\Delta W}{A} = k_1^{1/2} t^{1/2} - k_2 t \pm \text{SEE} \quad (1)$$

where k_1 is an oxide growth constant comparable to a 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 [11] was derived from equation (1) and is defined as

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

The original hydrogen pressure in the tubes and the pressure at the end of a 5-h cycle were used to calculate the hydrogen permeability coefficient, ϕ , using the equation:

$$P = P_0^{1/2} - \frac{\phi A P_s T t}{2LVT_s} \quad (3)$$

where

P pressure in closed system, MPa

P_0 original pressure, MPa

A permeated area, cm^3

P_s standard pressure, MPa

T temperature of system, K

t time, sec
L membrane thickness, cm
V volume of system, cm³
T_s standard temperature, K

Results

Stirling Engine Simulator Oxidation and Corrosion Tests

Weight Change. - The alloys could be categorized into four groups on the basis of specific weight change data. Alloys in group I had excellent oxidation and corrosion resistance, and their specific weight change was positive (weight gain) throughout the 3500-h test. Group I comprised the five alloys CG-27, Incoloy 800, HS-188, N-155, and Inconel 718. Three of the alloys, CG-27, Incoloy 800, and HS-188, did not exhibit any significant spalling during testing in the Stirling engine simulator rig. Final average specific weight change (Fig. 3) ranged from 1.4 to 0.17 mg/cm² for CG-27 to Inconel 718, respectively.

A second group of alloys is considered to have relatively good oxidation and corrosion resistance under simulated Stirling engine operating conditions. The five alloys in group II in order of increasing final weight loss are RA-330, Sanicro 31H, Sanicro 32, 12RN72, and 253 MA. Final average specific weight change (Fig. 4) ranged from -0.54 to -6.0 mg/cm² for RA-330 to 253 MA, respectively.

The third group of alloys, 316 stainless steel, W-545, A-286, and Nitronic 40 is considered to have fair to poor oxidation and corrosion resistance on the basis of specific-weight-change-versus-time data. Final average specific weight change (Fig. 5) ranged from -22.8 to -41.8 mg/cm² for 316 stainless steel to Nitronic 40, respectively.

A final group of alloys, consisting of 19-9DL and AL-EX-20, exhibited catastrophic oxidation and corrosion behavior upon rig testing. Spalling

began after only a very short time into the test and excessive weight loss occurred after 500 h of cyclic testing. The tests were terminated before the 3500-h goal because of the unacceptable oxidation and corrosion resistance of these alloys.

Attack parameter K_a . - Oxidation and corrosion weight-change-versus-time data were fitted to the parabolic equation (eq. (1)). For three of the alloys, HS-188, Incoloy 800, and CG-27, where no spalling was observed, the attack parameter was calculated from equation (2) with $k_2 = 0$. The remaining 13 alloys also derived their attack parameters from equation (2) but with values of k_2 included. For alloys 19-9DL, Nitronic 40, and AL-EX-20 the $k_1^{1/2}$ term dropped out so that $K_a = 20k_2t$ was used. Figure 6 is a summary plot of calculated K_a values for the alloys. Values of K_a are plotted on a log scale in decreasing order of oxidation and corrosion resistance based on the highest values of the duplicate specimens. The attack parameter ranged from 0.011 for HS-188 to 12.49 for 19-9DL, or over three orders of magnitude. Examination of the K_a values in Fig. 6 suggested that the alloys could again be categorized into four groups. Group I comprised the alloys HS-188, Sanicro 31H, Inconel 718, Incoloy 800, N-155, CG-27, and RA-330, with K_a ranging from 0.011 for HS-188 to 0.031 for RA-330. Group II comprised the three alloys Sanicro 32, 12RN72, and 253 MA, with K_a values of 0.098, 0.110, and 0.159, respectively. Group III comprised the alloys A-286, W-545, 316 stainless steel, and Nitronic 40, with K_a ranging from 0.370 to 0.659. Group IV comprised AL-EX-20,, with a K_a of 4.68, and 19-9DL, with a K_a of 12.49. This grouping was somewhat arbitrary, but corresponded to the previous grouping based on final weight change. The only exception was for RA-330, which experienced a net weight loss and was placed in group II

(Fig. 4) but has a K_a value similar to those for the other five alloys in group I.

X-ray diffraction. - The x-ray diffraction data from the specimen surface after testing are summarized in Table 2 by rank of the alloy in decreasing X-ray intensity. In general, the most oxidation and corrosion resistant alloys formed nearly pure Cr_2O_3 as either the most or secondmost intense oxide. The Cr_2O_3 oxide is listed as a sesquioxide, $d(024) = 0.1818$ nm in Table 2. Because Fe went into solution as Fe_2O_3 , the value of d increased. As the d value approached 0.1839 nm, the oxide became essentially pure Fe_2O_3 . Chromite spinel with a_0 ranging from 0.835 to 0.840 nm also formed on most of the alloys during oxidation and corrosion testing. This chromite spinel appeared to be innocuous. Alloy A-286 showed another spinel with $a_0 = 0.830$ nm along with a lower sesquioxide with $d = 0.1813$ nm, and also NiO was formed. Alloy 19-9DL, which oxidized catastrophically, formed as its two strongest oxides a spinel with $a_0 = 0.840$ nm and the desirable oxide Cr_2O_3 with $d = 0.1821$ nm.

Metallography. - Microstructures of selected alloy specimens after the 3500-h test are shown in Fig. 7. Alloy CG-27 (Fig. 7(a)) had an adherent oxide scale on the specimen surface. Alloy Inconel 718 (Fig. 7(b)) had a thin, adherent oxide scale with a small depletion zone present in this alloy. Sanicro 32 (Fig. 7(c)) formed large voids in the depletion zone. Severe grain boundary attack occurred in W-545 (Fig. 7(d)) and resulted in almost total consumption of the alloy matrix beneath the surface oxide.

Electron microprobe analysis. - Alloy CG-27, a group I alloy, was examined because it had excellent oxidation resistance and contained the least chromium of the 16 alloys tested in the rig. The distribution of the major alloying elements and oxygen in the oxide scale and the adjacent metal substrate of CG-27 (Fig. 8) showed the surface oxide to be rich in iron,

nickel, and to a lesser extent aluminum. Beneath this oxide layer was a thin, continuous oxide layer rich in chromium and titanium. Adjacent to the chromium-rich intermediate scale was an aluminum-rich oxide next to the metal substrate, which exhibited a wide zone of internally oxidized aluminum-rich, and somewhat fewer titanium-rich, protrusions.

Metallographic results for the group III alloy W-545 (Fig. 7(d)) indicated a large surface scale consisting of a porous oxide. Results from electron microprobe analyses (Fig. 9) showed an outer oxide rich in iron, nickel, and chromium. Oxygen had penetrated uniformly into this alloy to a substantial depth. The oxide formed appeared to be rich in nickel with some chromium. Iron was depleted from this area, but discrete areas of molybdenum were observed near the surface. Aluminum and titanium did not appear to enter into the oxidation process of this alloy. The composition of W-545 is similar to that of CG-27 except for the large difference in aluminum content. This suggests that aluminum makes a major contribution to the oxidation resistance of CG-27 and that its low concentration in W-545 may explain the poor oxidation resistance of that alloy.

Stirling Engine Simulator Hydrogen Permeation and Endurance Tests

Hydrogen permeability. - Previous measurements of hydrogen permeation during cyclic testing in the simulator rig [12] indicated that hydrogen loss was rapid through the thin wall tubes of alloy N-155. Hydrogen pressure decay curves are shown in Fig. 10(a) for selected 5 h cycles in an 100 h test. It should be noted that pressure loss is rapid and is most severe for the first 5 h cycle. The slight improvement for the remaining cycles is attributed to the formation of an oxide scale on the exterior surface of the tubes. It was shown previously [13] that a thin (0.02 mm) carbide could form on the tubes internal surface in an engine presumably due to oil leaking into the heater head. This carbide layer resulted in reducing the permeability rate of

hydrogen from the engine. A program was undertaken at NASA Lewis [12] to investigate various dopants such as CO, CO₂, CH₄, etc. to form carbide or oxide surface layers on the tubes internal surfaces to act as a barrier to hydrogen permeability. The effects of 1 vol % CO₂ in hydrogen are shown in Fig. 10(b) for alloy N-155. The results suggest that the oxide that formed on the internal surfaces was effective in reducing hydrogen loss from the tubes. Hydrogen permeability coefficients were calculated from the pressure decay curves using equation (3). Permeability coefficients as a function of rig exposure time are plotted in Figs. 11 to 13 for iron, nickel, and cobalt-base alloys, respectively. For iron-base alloys, hydrogen permeability coefficients vary over two orders of magnitude while for the five nickel-base alloys a variation of about a factor of two is noted. A comparison of the hydrogen permeability coefficients after 250 h testing (since some alloys did not survive much longer) is shown in Fig. 14. In general the nickel-base alloys exhibited lower permeability coefficients than the iron-base alloys. An iron-base alloy, CG-27 was an exception to this general observation.

Endurance testing. - Endurance testing was also conducted on the tube alloys by filling with 15 MPa helium. Since helium did not permeate the tube walls, a constant pressure (stress) was maintained. This test is much more severe than actual engine operation where the mean pressure is near 4 MPa, but does provide an effective method for ranking the strengths of the alloys under simulated engine conditions. A comparison of rupture lives is shown in Fig. 15. Only CG-27 and Pyromet 901 survived the 3500 h test. It should be noted for alloy Inconel 718 that seamless tubing (Inconel 718(a)) had a much longer life than the weld-drawn tubing (Inconel 718(wd)). Cold working of 12RN72 (cw) reduced the rupture life from the standard heat treated condition.

Metallography. - Microstructures of selected alloys are shown in Fig. 16. Alloy CG-27 is shown before and after exposure. The oxide film on

both internal and exterior surfaces is evident for the hydrogen and 1 percent CO₂ containing tube (Fig. 16(a)). Alloy Inconel 625 (Fig. 16(b)) exhibited external scale cracking after cyclic exposure.

Discussion of Results

Some insight into the excellent oxidation and corrosion behavior of CG-27 can be gained from the electron microprobe results. The chromium distribution shows that CG-27 had a chromium-rich oxide layer ranging in thickness from about 3 to 4 μm . The poorer oxidation behavior of group II and III alloys was characterized by chromium-rich oxide layers about 8 μm thick (group II alloys) and from 20 to 35 μm thick (group III alloys) [8]. All 16 alloys studied herein formed Cr₂O₃ chromite spinels as their major oxides. The thin, adherent oxide formed by the group I alloys CG-27 and Incoloy 800 (not shown) is believed to be a major contributor to the oxidation resistance of these alloys.

Further comparison of the alloys characterized by electron microprobe techniques indicated that iron and nickel were present as a thin outer oxide in group I alloys. In contrast, in group II alloys and especially in group III alloys, iron and nickel were observed as thick, discrete areas of oxide that were in some cases ready to spall from the specimen. Evidently in group I alloys the iron and nickel oxides formed early in the 3500-h test, and then oxide formation of the more reactive alloying elements took over the oxidizing process. The thicker oxides and higher spalling rates in particular for group III alloys (specific weight losses of 23 to 42 mg/cm² as compared with little or no weight loss for group I alloys) suggest that iron and nickel oxides formed throughout the 3500-h test.

Particular interest was focussed on the apparent roles of the more reactive oxide-forming alloying elements aluminum and titanium contained in some of the alloys. In CG-27 internal oxidation of aluminum to a depth of

approximately 10 μm below the oxide-metal interface was evident. In addition, aluminum was present in the surface oxide, and a thin oxide layer rich in aluminum existed adjacent to the metal substrate. A similar, though not as evident, distribution of aluminum occurred in Incoloy 800. Incoloy 800 contains 0.38 wt % aluminum as compared with 1.5 wt % in CG-27. A thin, discontinuous aluminum-rich oxide layer near the oxide-metal interface and grain boundary oxides were previously noted for Sanicro 32. Titanium, at a concentration of 2.5 wt % in CG-27, appeared to be associated with aluminum in the oxide scales and as internally oxidized. In contrast, for the group III alloy W-545, which contains slightly more titanium (2.85 wt %) but much less aluminum (0.2 wt %), titanium does not preferentially oxidize.

The role of reactive elements such as yttrium, scandium, cerium, zirconium, and hafnium in improving oxide scale adherence particularly for Fe-Cr-Al, Ni-Cr-Al, and Co-Cr-Al alloys has been investigated in much detail [14-19]. The standard free energies of oxide formation of these reactive elements are more negative than those for iron, nickel, cobalt, chromium, and aluminum. Small additions (<1 at %) of these elements have been shown to dramatically improve oxide scale adherence and to reduce spalling in cyclic oxidation. The exact mechanism by which such an improvement occurs is not agreed upon by investigators in this field. For example, yttrium and scandium have been reported to increase oxide growth rates by forming rapid diffusion paths along yttria and scandia stringers [14]. Increased grain boundary transport of oxygen has been demonstrated by ^{18}O tracer studies on Ni-Cr-Al alloys with zirconium additions [15]. The resulting oxide adherence has been attributed [14,15,18] to (1) mechanical oxide pegging; (2) stress-strain accommodations at the oxide-matrix interface; (3) increased chemical bonding across the interface; and (4) a vacancy sink mechanism that precludes void formation at the oxide-metal interface, which would promote spalling.

It is postulated that for the alloys studied herein, aluminum plays a role similar to that of the reactive elements discussed previously. Aluminum has a more negative standard free energy of oxide formation than do the major alloying constituents of the candidate heater-head-tube alloys such as iron, nickel, and chromium. The internal aluminum oxidation suggests that controlling the inward oxygen diffusion plays a major role in the oxidation of CG-27 and probably Incoloy 800 [8]. Although the remaining group I alloys were not studied by electron microprobe techniques, the reactive elements niobium in N-155, niobium and aluminum in Inconel 718, and lanthanum in HS-188 probably play a role similar to that of aluminum in the two alloys that were examined. The results further suggest that although 0.4 wt % aluminum is adequate to be effective in promoting good scale adherence (Incoloy 800, Sanicro 32, Sanicro 31H, and Inconel 718), a concentration of 0.2 wt % aluminum such as exists for W-545, Fig. 9 and A-286 is insufficient to improve the oxidation behavior of these alloys. It is not clear from this study which of the previously suggested models for oxide scale adherence is to be preferred.

The factors effecting oxidation/corrosion behavior of the alloys is also important in minimizing hydrogen permeation through the tube walls. Formation of an adherent oxide film on the internal surface of the heater head tubes is required to reduce the hydrogen loss by permeation. Alloys with low oxidation/corrosion attack parameters, K_a also had low hydrogen permeability coefficients, ϕ . Results presented herein have clearly shown the importance of alloy composition, specifically the presence of the more reactive elements such as Al, Ti, and La as a key to controlling oxidation/corrosion behavior of the alloys. This, in turn, is reflected in the resulting microstructure where thin oxide layers containing the reactive

elements are desirable for long-life, low-hydrogen permeability heater head tube alloys.

Application of Results

Based on the results of these tests alloys CG-27, 12RN72, Sanicro 32, and Inconel 625 were selected for engine testing. Engine testing under accelerated conditions exceeded 2000 h or an equivalent 3300 h of urban-highway driving. Only alloy CG-27 did not fail by creep rupture in the engine test [20]. Alloy CG-27 has been selected as the heater head tube material for the automotive Stirling engine because of its good creep-rupture (endurance) strength, resistance to oxidation and corrosion, and resistance to hydrogen permeation as a result of forming a thin, tenacious oxide using CO₂ doped hydrogen.

Concluding Remarks

This study has shown that chemistry and microstructure of heater head tube alloys which develops during operation of the engine and in simulated tests play an important role in alloy selection for the automotive Stirling engine. Specifically the following features were shown to be important:

1. The presence of a sufficient amount (about 0.4 wt %) of the reactive metal aluminum in iron-base alloys leads to a microstructure characterized by a thin, adherent oxide scale rich in aluminum plus internal oxidation of aluminum which impedes inward diffusion of oxygen.

2. The thin, adherent oxide scales on both the combustion gas side and the CO₂ doped hydrogen side of the tubes act as barriers to hydrogen permeation.

3. The thin, adherent oxides characterized by no or very little spalling and metal loss lead to utilization of the full cross-sectional area of the tube alloy to provide the required strength for the 3500 hr life of an engine.

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TABLE 1 -- CHEMICAL COMPOSITION OF COMMERCIAL ALLOYS

Alloy	Composition, wt %													
	Fe	Cr	Ni	Co	Mn	Si	Mo	Nb	W	Al	Ti	C	Other	
Iron-base alloys														
N-155	30	21	20	20	1.5	0.5	3.0	1.0	2.5	---	---	0.15	0.15N	
CG-27	38	13	38	---	.1	.1	5.5	.6	---	1.5	2.5	.05	.01B	
RA-330 ^a	43	19	35	---	1.5	1.3	---	---	---	---	---	.05	---	
Sanicro 32	43	21	31	---	.6	.47	---	---	2.8	.4	.4	.89	---	
Sanicro 31H	46	21	31	---	.6	.55	---	---	---	.4	.5	.07	.02N	
Incoloy 800	46	21	32	---	.75	.5	---	---	---	.38	.38	.05	---	
12RN72	47	19	30	---	1.7	.28	1.4	---	---	---	.5	.1	.02N	
A-286	53	15	26	---	1.4	.4	1.25	---	---	.2	2.15	.05	.26V	
W-545	54	14	26	---	1.5	.4	1.5	---	---	.2	2.85	.08	.08B	
Nitronic 40 ^a	64	21	6.5	---	9.0	---	---	---	---	---	---	.04	.30N	
253 MA	66	21	11	---	.4	1.7	.04	---	---	---	---	.09	.2N	
316 Stainless steel	66	18	13	---	2.0	1.0	2.5	---	---	---	---	.08	---	
19-9DL	67	19	9	---	1.1	.6	1.2	.4	1.2	---	.3	.3	---	
AL-EX-20 ^a	70	5	1.0	---	20	.42	---	---	---	3.15	---	.02	---	
Nickel-base alloys														
Inconel 750 ^b	8	16	71	---	0.16	0.23	---	0.05	---	0.72	2.5	0.05	---	
Inconel 625 ^b	3	22	61	---	.15	.3	9.0	4.0	---	.2	0.2	0.05	---	
Inconel 601 ^b	14	23	60	---	.5	.2	---	---	---	1.4	---	.05	---	
Inconel 718	18	18	53	---	.2	.3	3.1	5.0	---	.4	.9	.04	---	
Pyromet 901 ^b	34	12	45	---	.10	.19	5.9	---	---	---	2.6	.03	---	
Cobalt-base alloys														
HS-188	1.5	22	22	40	---	---	---	---	14	---	---	0.08	0.08La	

^aEvaluated in hydrogen permeability and endurance testing only.^bEvaluated in oxidation/corrosion testing only.

TABLE 2 -- X-RAY DIFFRACTION DATA OF SPECIMEN SURFACE AFTER 3500-h TEST
 IN ORDER OF DECREASING INTENSITY
 [Values of d and a_0 are in nanometers.]

Rank	Alloy	Chromium content, wt %	1	2	3	4
1	HS-188	22	0.1818 Sesquioxide	$a_0 = 0.840$ Spinel	Mn_2O_3	0.408 (SiO_2)
2	Sanicro 31H	21	$a_0 = 0.840$	0.1819	SiO_2	$(Mn_{0.983}Fe_{0.017})_2O_3$
3	Inconel 718	18	$a_0 = 0.835$	0.1822	0.410(SiO_2)	-----
4	Inconel 800	21	$a_0 = 0.840$	0.1819	Mn_2O_3	0.409 (SiO_2)
5	N-155	21	$a_0 = 0.840$	0.1826	0.411(SiO_2)	0.272
6	CG-27	13	$a_0 = 0.835$	0.1821	0.1841 Sesquioxide	Trirutile, d = 0.330
7	RA-330	19	$a_0 = 0.840$	0.1818	Mn_2O_3	-----
8	Sanicro 32	21	$a_0 = 0.840$	0.1819	SiO_2	$(Mn_{0.983}Fe_{0.017})_2O_3$
9	12RN72	19	$a_0 = 0.840$	0.1819	$(Mn_{0.983}Fe_{0.017})_2O_3$	SiO_2
10	253 MA	21	0.1839 Sesquioxide	$a_0 = 0.835$ Spinel	SiO_2	0.1812 Sesquioxide
11	A-286	15	$a_0 = 0.830$ Spinel	0.1813	NiO	-----
12	W-545	14	$a_0 = 0.840$ Spinel	0.1849	-----	-----
13	316 Stainless steel	18	0.1842 Sesquioxide	0.1824	$a_0 = 0.845$ Spinel	Mn_2O_3
14	Nitronic 40	21	$a_0 = 0.840$ Spinel	0.1843	-----	-----
15	AL-EX-20	5	0.1839 Sesquioxide	$a_0 = 0.840$ Spinel	Mn_2O_3	-----
16	19-9DL	19	$a_0 = 0.840$ Spinel	0.1821 Sesquioxide	0.1843 Sesquioxide	-----

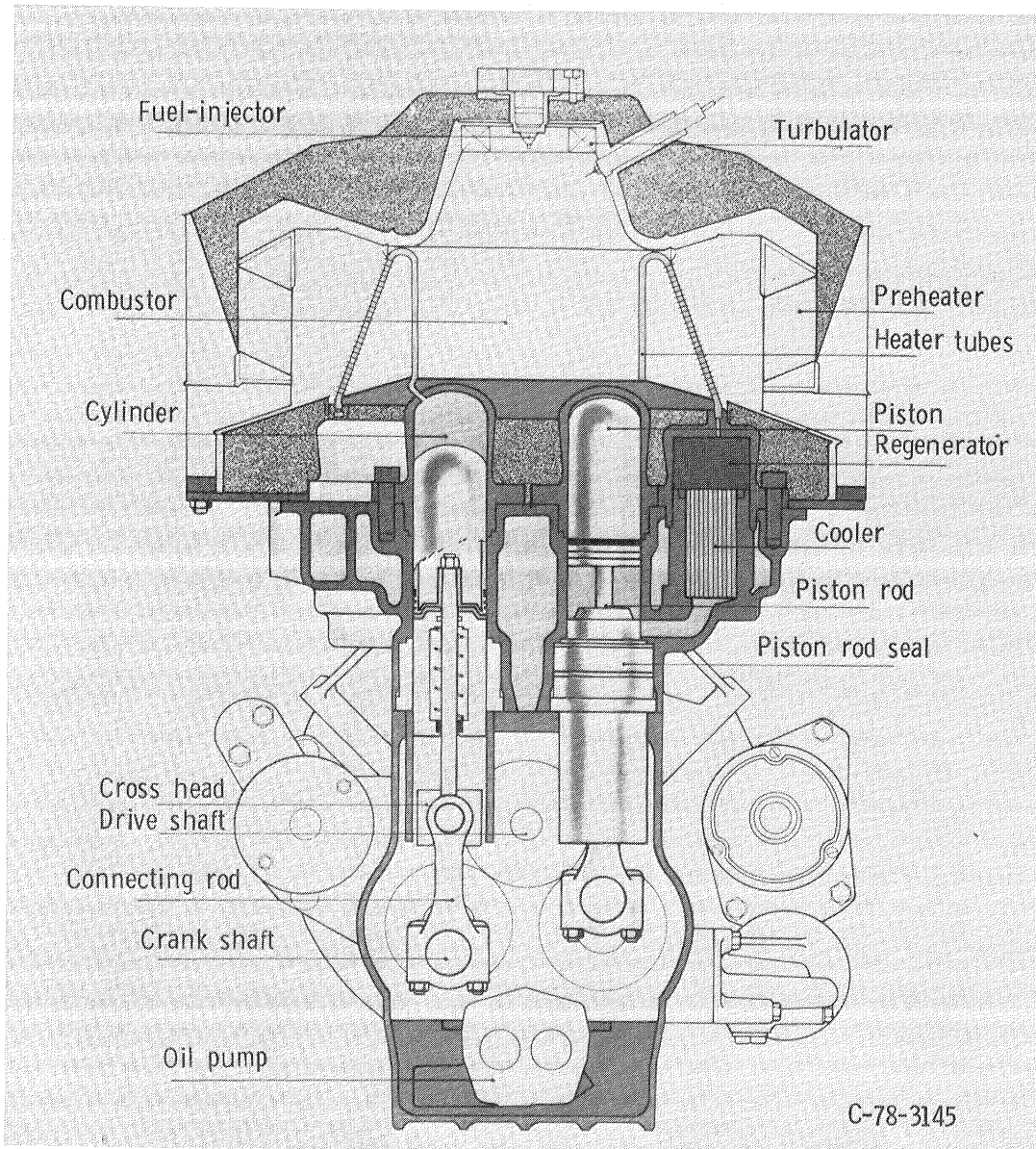


Figure 1. - Schematic representation of automotive Stirling engine.

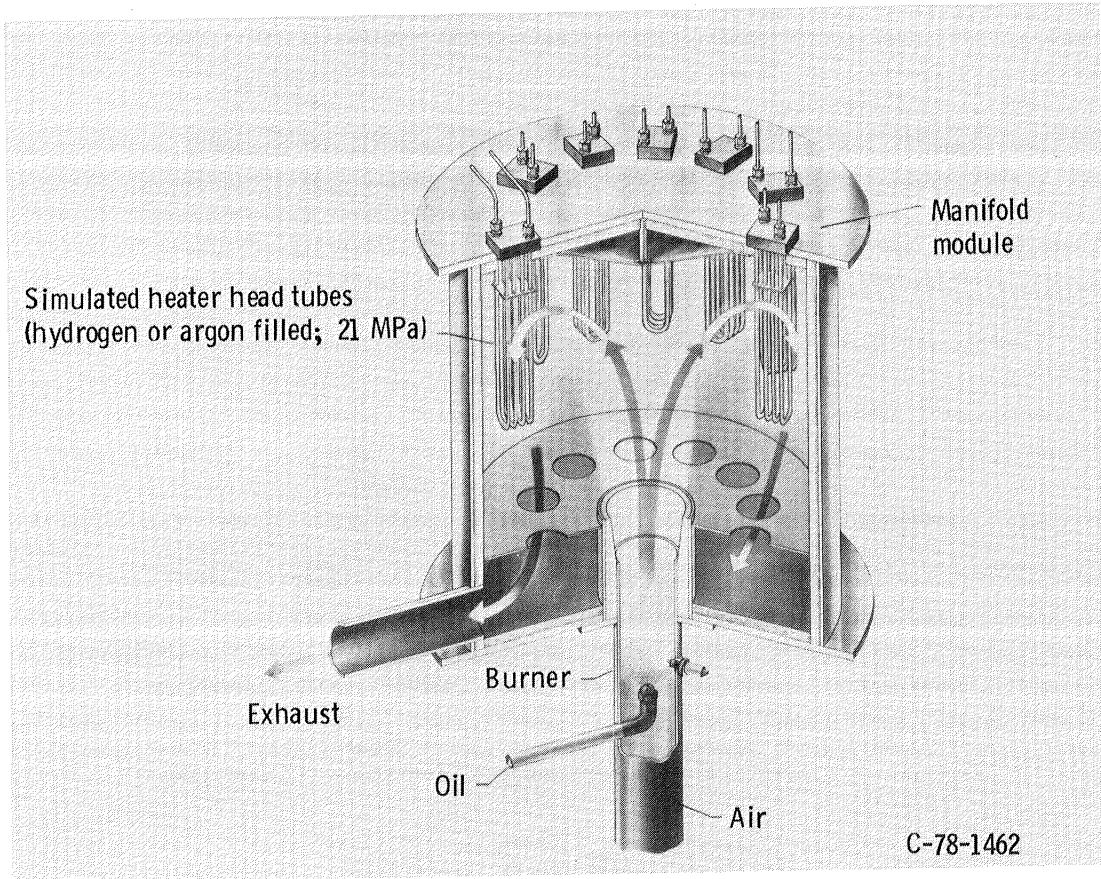


Figure 2. - Schematic representation of Stirling engine materials simulator test rig.

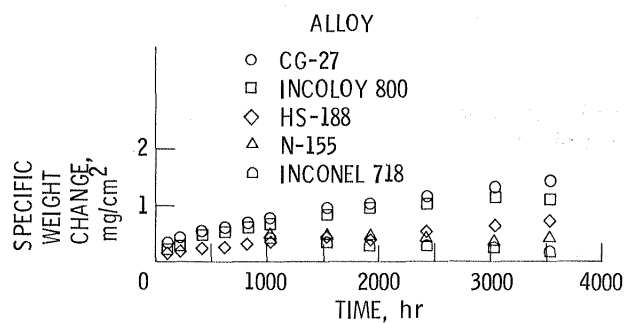


Figure 3. - Specific weight change data for group I alloys tested at 820 °C for 3500 hr.

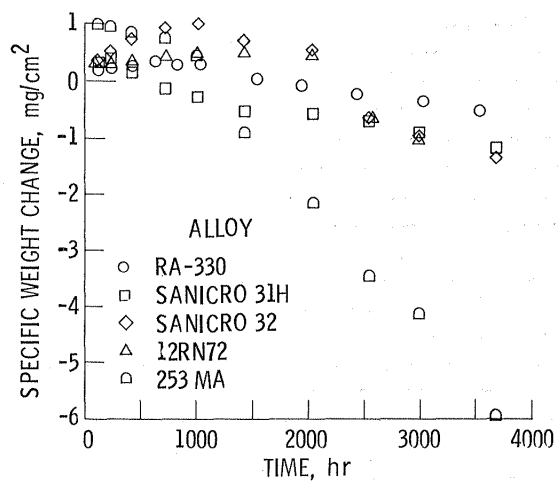


Figure 4. - Specific weight change data for group II alloys tested at 820 °C for 3500 hr.

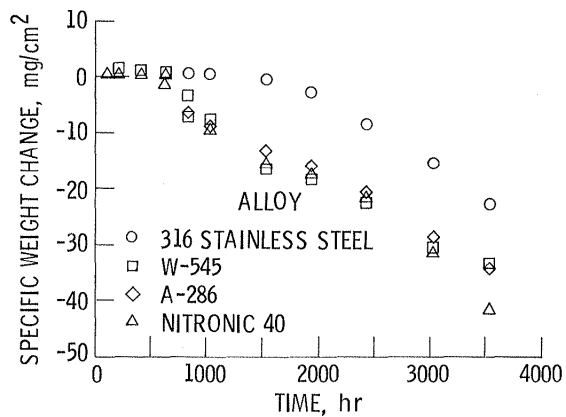


Figure 5. - Specific weight change data for group III alloys tested at 820 °C for 3500 hr.

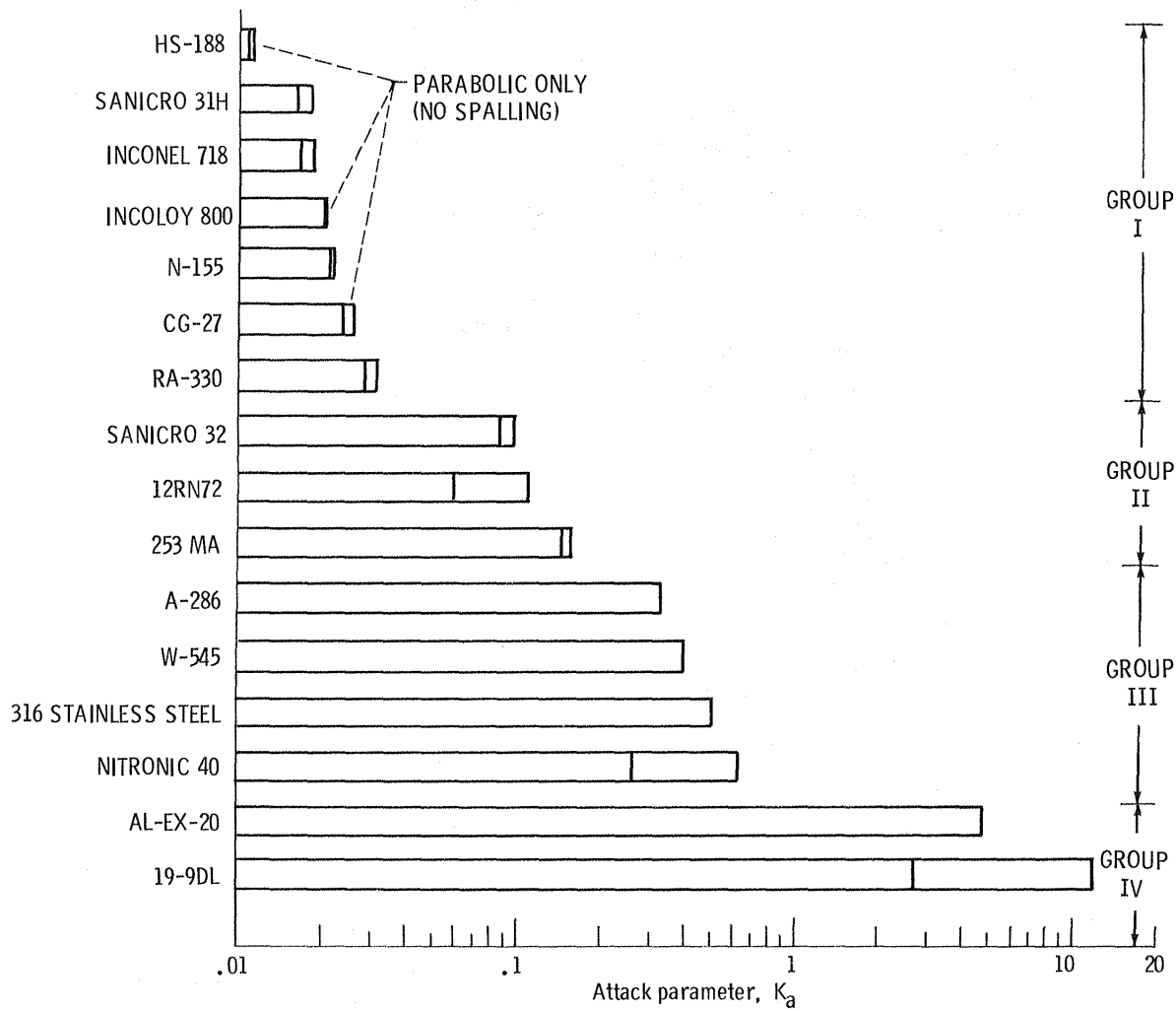
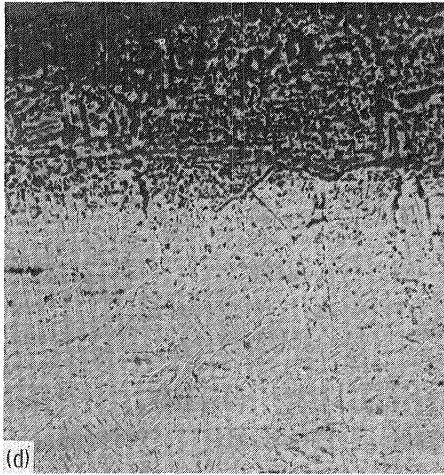
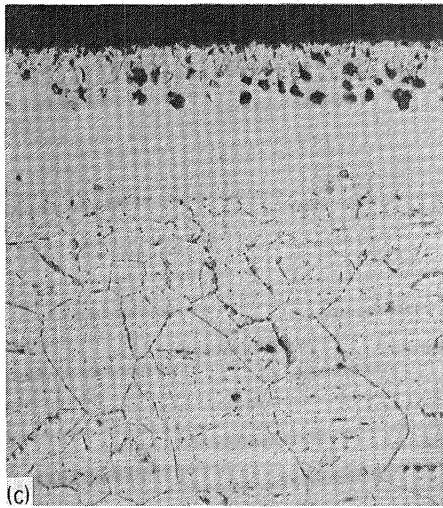
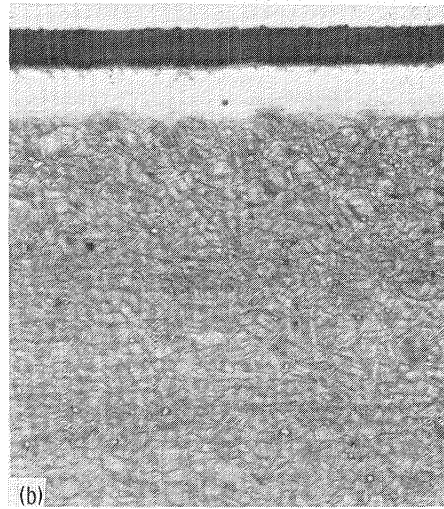


Figure 6. - Oxidation and corrosion attack parameter K_a for 3500-hr cyclic exposure in Stirling engine simulator rig. Temperature, 820°C ; cycles length, 5 hr; $K_a = k_1^{1/2} + 10k_2$. (Duplicate samples.)



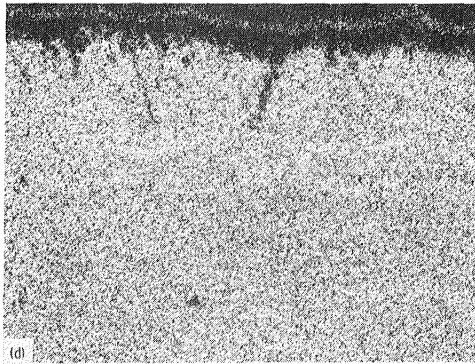
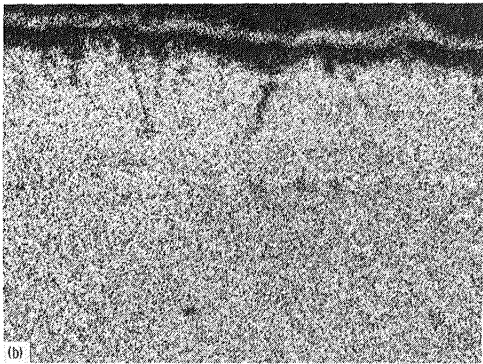
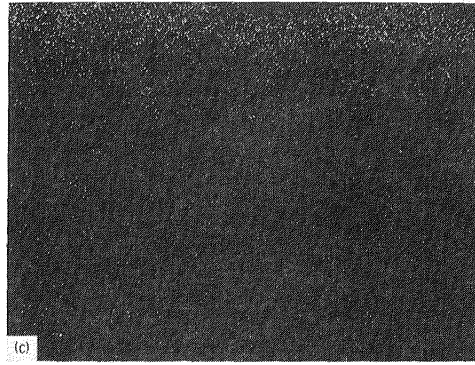
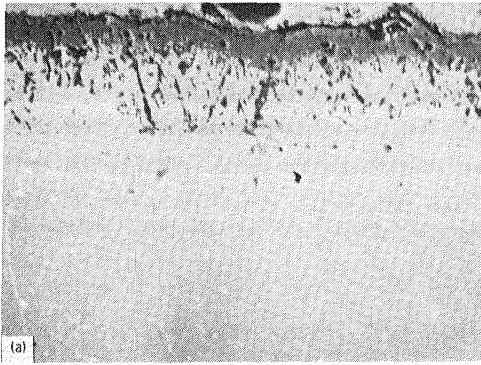
(a) CG-27.

(b) Inconel 718.

(c) Sanicro 32.

(d) W-545.

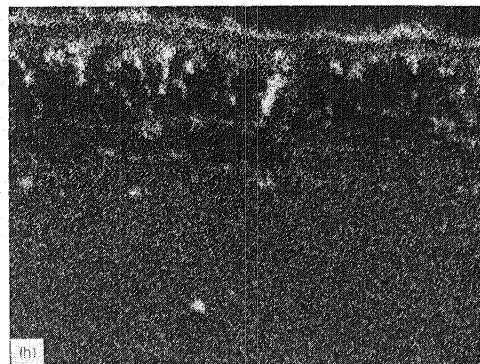
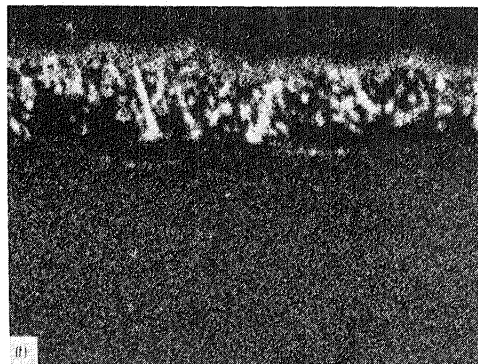
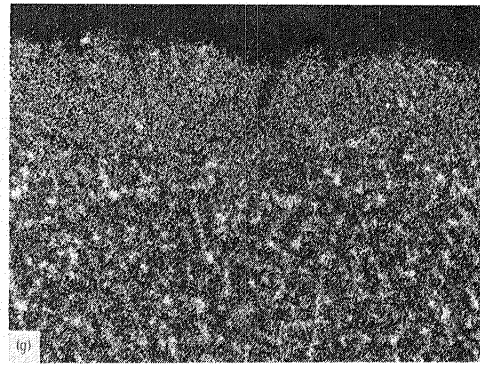
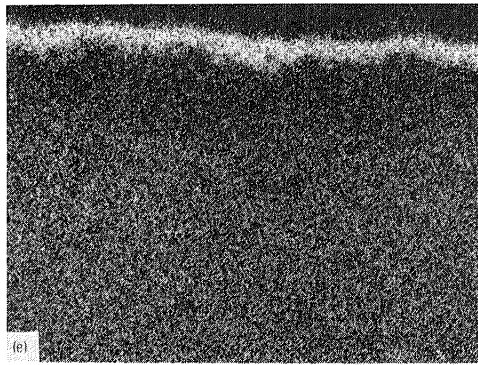
Figure 7. - Photomicrographs of selected 3500 hr oxidation and corrosion test specimens. Longitudinal view showing surface scales and depletion zones; magnification, 250.



(a) BSE.
(b) Iron.

(c) Oxygen.
(d) Nickel.

Figure 8. - Electron microprobe analyses of alloy CG-27. Magnification, 1000.



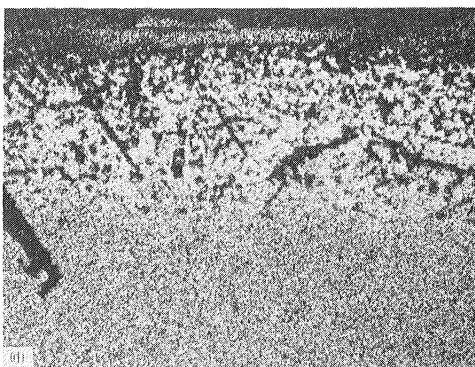
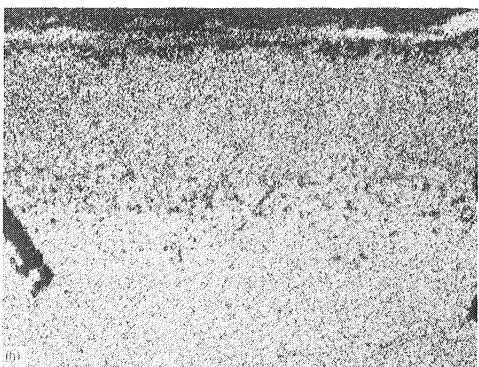
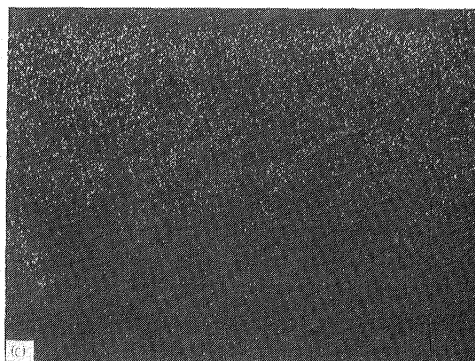
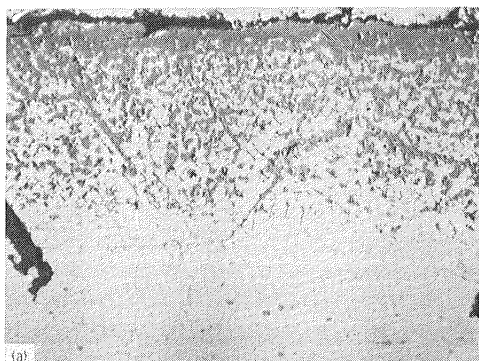
(e) Chromium.

(f) Aluminum.

(g) Molybdenum.

(h) Titanium.

Figure 8. - Concluded.



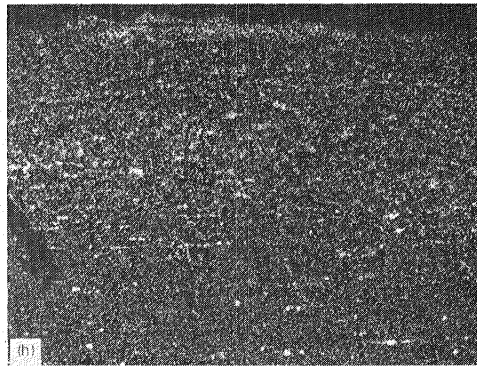
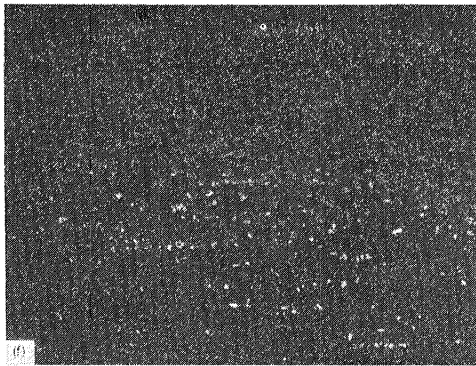
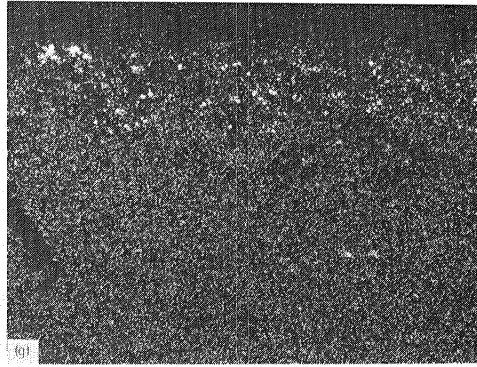
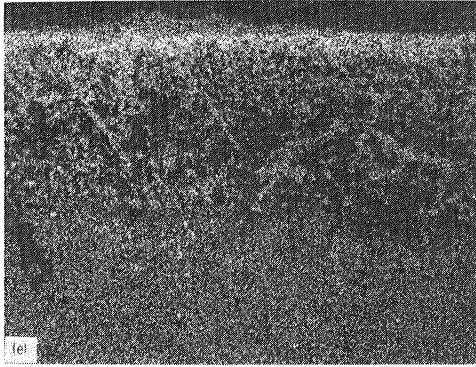
(a) BSE.

(b) Iron.

(c) Oxygen.

(d) Nickel.

Figure 9. - Electron microprobe analyses of alloy W-545. Magnification, 300.



(e) Chromium.
(f) Aluminum.

(g) Molybdenum.
(h) Titanium.

Figure 9. - Concluded.

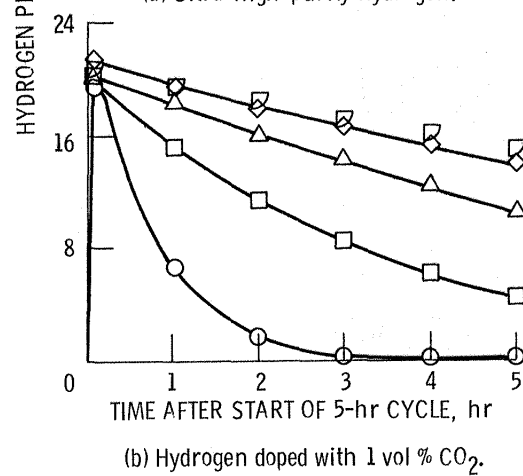
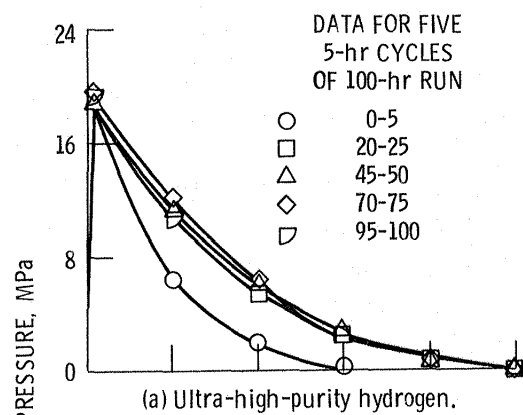


Figure 10. - Pressure decay curves for N-155 at 820 °C.

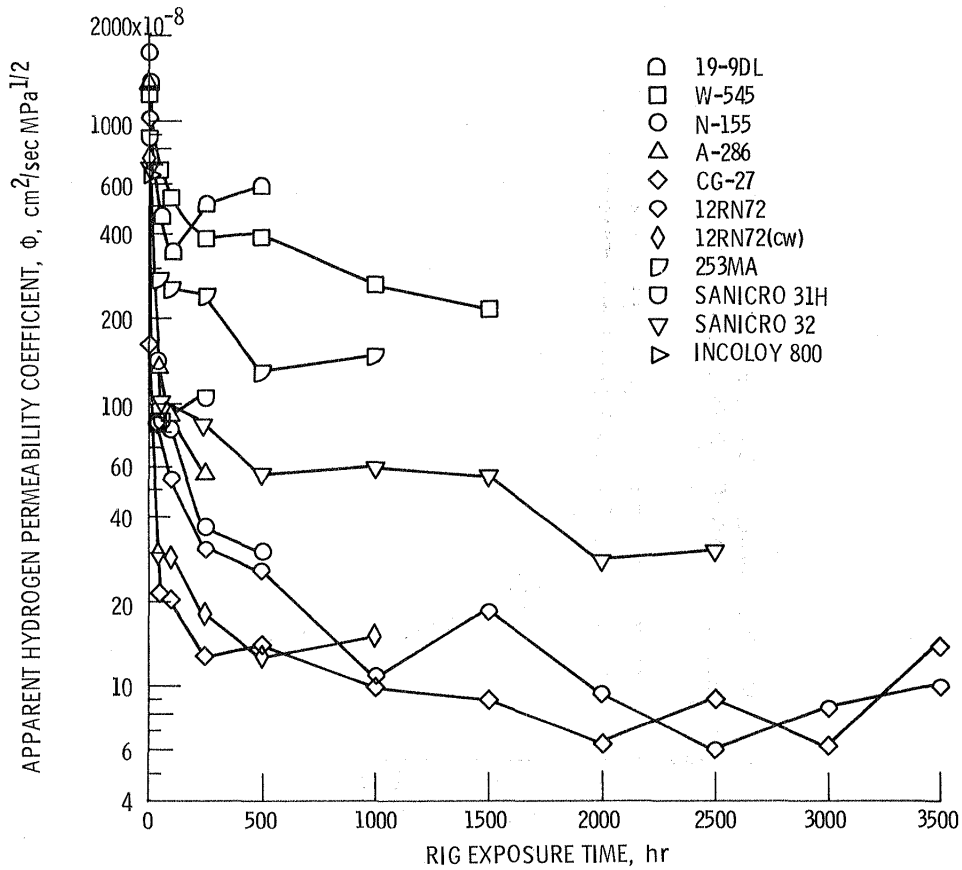


Figure 11. - Hydrogen permeability coefficient Φ versus rig exposure time for iron base alloys tested at 820 °C with $\text{H}_2 + 1\% \text{CO}_2$ at 15 MPa.

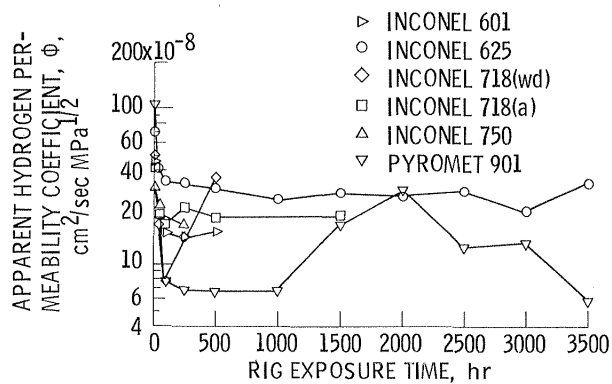


Figure 12. - Hydrogen permeability coefficient Φ versus rig exposure time for nickel base alloys tested at 820 °C with $\text{H}_2 + 1\% \text{CO}_2$ at 15 MPa.

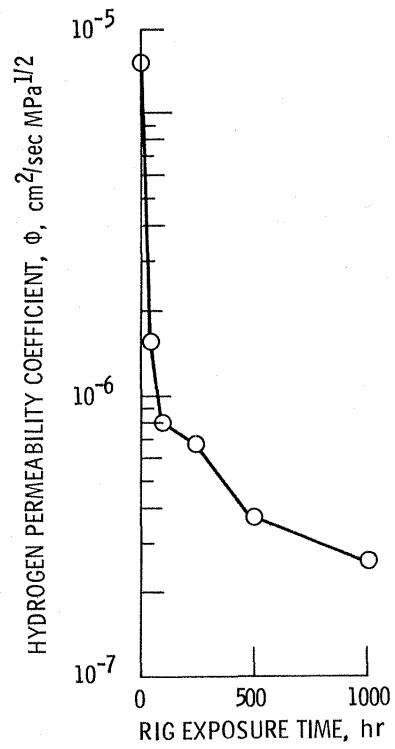


Figure 13. - Hydrogen permeability coefficient Φ versus rig exposure time for cobalt-base alloy HS-188 tested at 820 °C with H₂ + 1% CO₂ at 15 MPa.

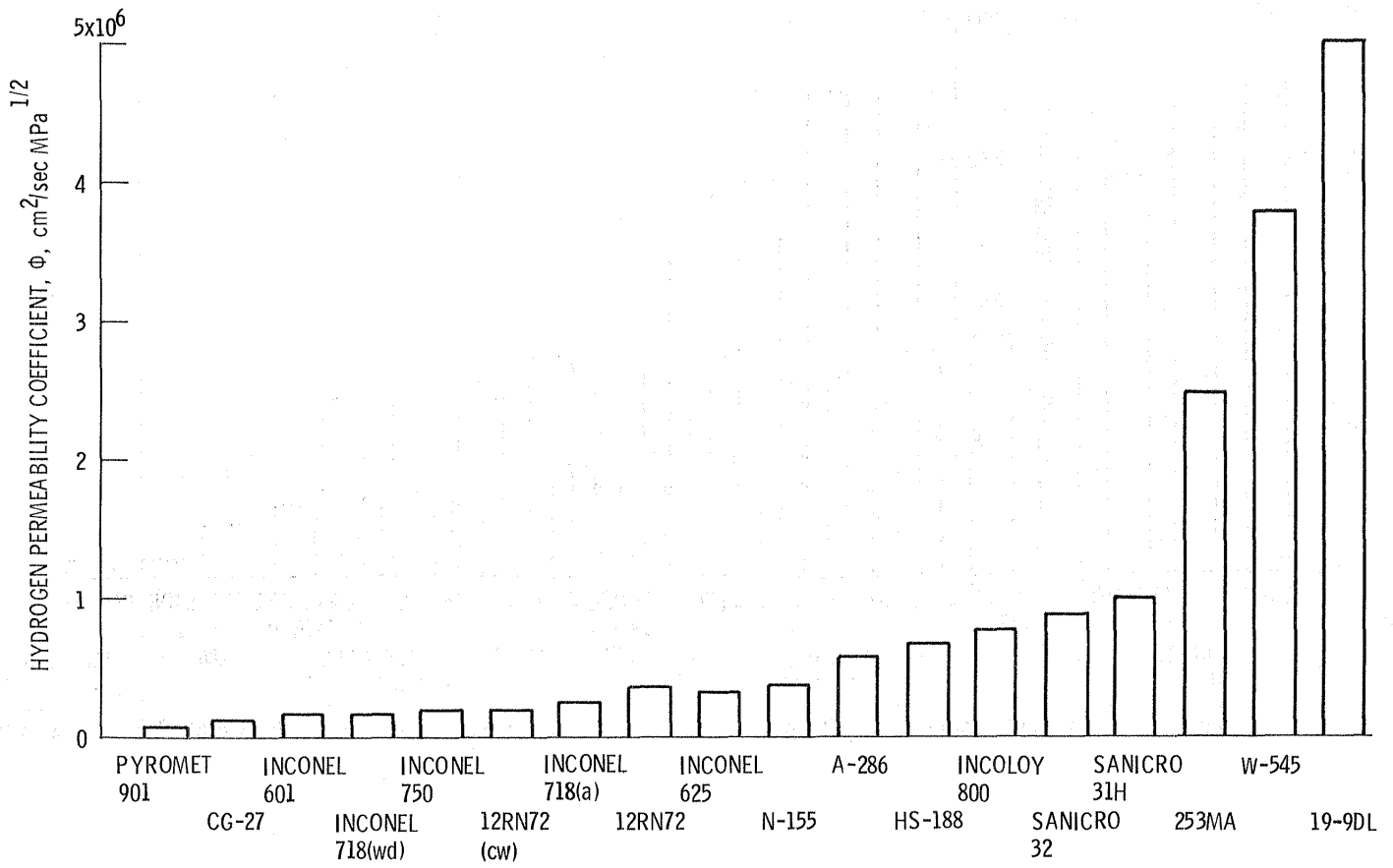


Figure 14. - Apparent hydrogen permeability coefficient at 250 hr for tubing material endurance tested at 820°C and 15 MPa.

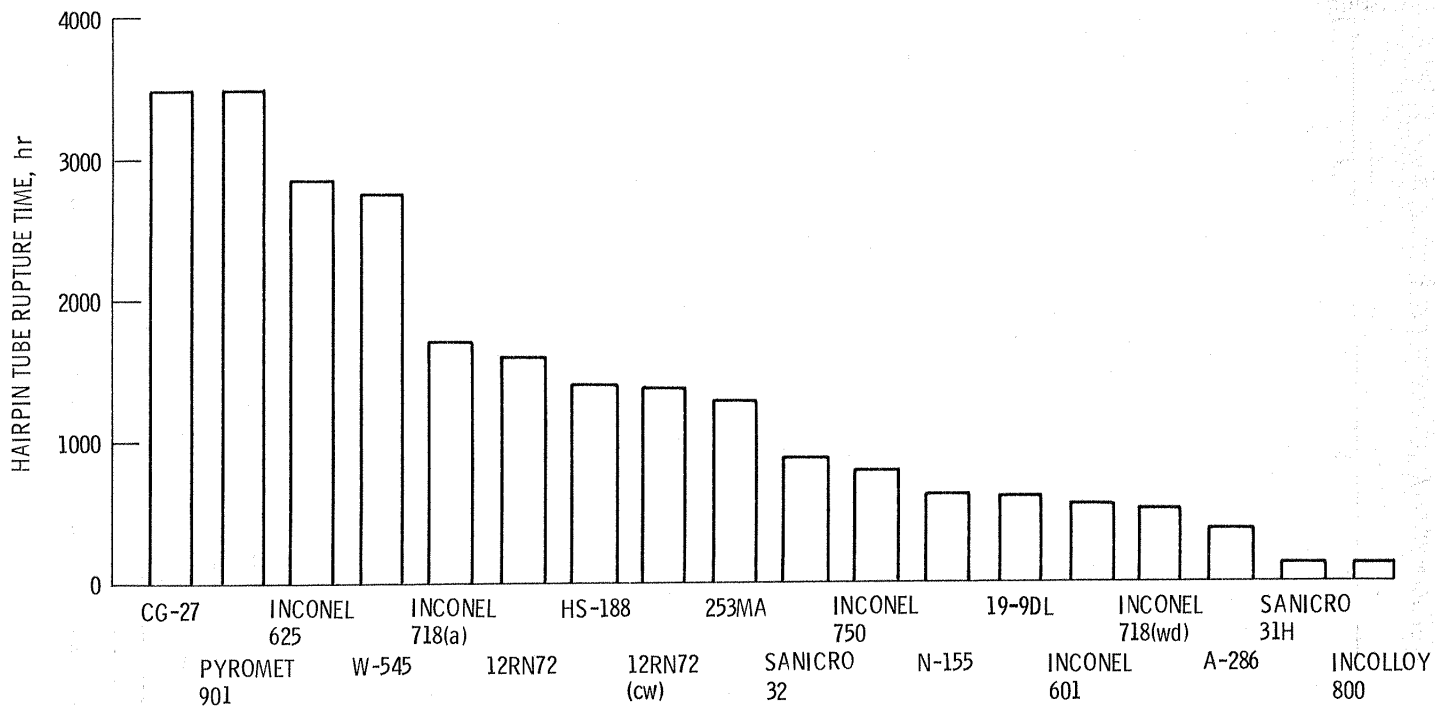
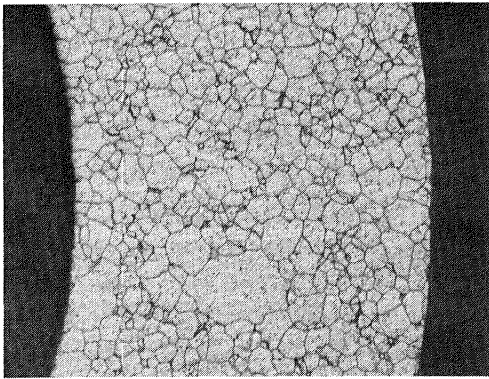
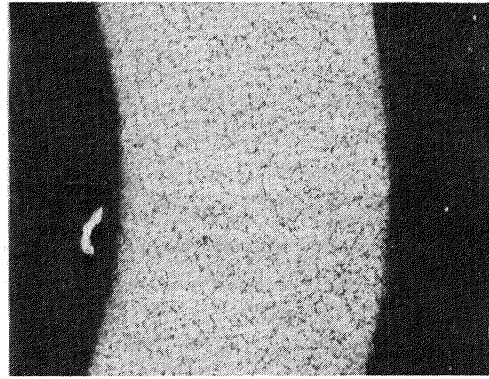


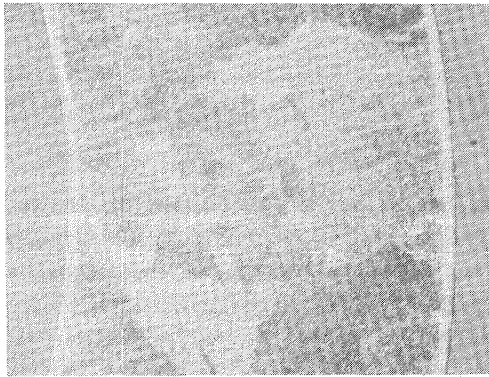
Figure 15. - Ranking of hairpin tubes according to rupture lives when pressurized with 15 MPa helium at 820 °C.



Unexposed

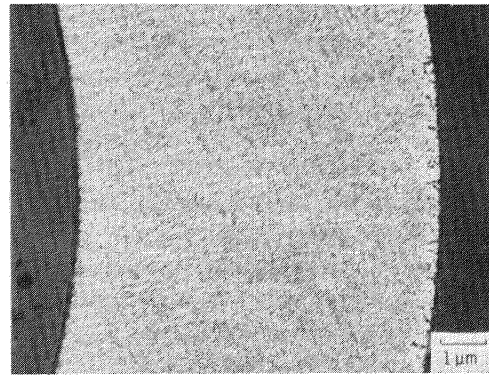


Unexposed



H₂ - 1% CO₂ exposed

(a) CG-27.



H₂ + 1% CO₂ exposed

(b) Inconel 625.

Figure 16. - Microstructures of hairpin tubes before and after rig exposure, 820 °C, 3500 h.

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16. Abstract The automotive Stirling engine now under development by DOE/NASA as an alternative to the internal combustion engine, imposes severe materials requirements for the hot portion of the engine. Materials selected must be low cost and contain a minimum of strategic elements so that availability is not a problem. Heater head tubes contain high pressure hydrogen on the inside and are exposed to hot combustion gases on the outside surface. The cylinders and regenerator housings must be readily castable into complex shapes having varying wall thicknesses and be amenable to brazing and welding operations. Also, high strength, oxidation resistance, resistance to hydrogen permeation, cyclic operation, and long-life are required. A research program conducted by NASA Lewis focused on alloy chemistry and microstructural control to achieve the desired properties over the life of the engine. Results of alloy selection, characterization, evaluation, and actual engine testing of selected materials will be presented.					
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