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EVALUATION OF CANDIDATE STIRLING ENGINE HEATER TUBE ALLOYS AFTER 3500 HOURS EXPOSURE TO HIGH PRESSURE DOPED HYDROGEN OR HELIUM

John A. Misencik and Robert H. Titran
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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SUMMARY

Sixteen commercial tubing alloys were endurance tested in a diesel-fuel fired Stirling engine simulator materials test rig. The objective of the tests were to evaluate the endurance limits of sixteen alloys (up to 3500 hr at 15 MPa pressure at 820° C) and select one alloy for further testing at a higher pressure of 21 MPa. During exposure, two sets of each alloy in the form of thin-wall tubing, "hairpin tubes" were pressurized -- one with hydrogen doped with 1.0 vol % CO_2 and the other with helium. The alloys tested were: iron-base N-155, A-286, Incoloy 800, 19-9DL, CG-27, W-545, 12RN72, 253MA, Sanicro 31H and Sanicro 32; nickel-base Inconel 601, Inconel 625, Inconel 718, Inconel 750 and Pyromet 901; and cobalt-base HS-188.

The iron-nickel alloys CG-27 and Pyromet 901 exhibited superior oxidation/corrosion resistance to the diesel-fuel combustion products and surpassed the design criterias' 3500 hr creep-rupture endurance life. Three other alloys, Inconel 625, W-545, and 12RN72, which are considered to have performed well, had creep-rupture failures after 2856, 2777, and 1598 hr, respectively. Hydrogen permeability coefficients determined after 250 hr of rig exposure show that Pyromet 901 had the lowest ϕ value, 0.064×10^{-6} $cm^2/sec\ MPa^{1/2}$. The next five hairpin tubes, CG-27, Inconel 601, Inconel 718(wd), Inconel 750, and 12RN72(cw) all had ϕ values below 0.2×10^{-6} more than a decade lower than the design criteria. Based upon its measured high strength and low hydrogen permeation, CG-27 was selected for 3500 hr endurance testing at 21 MPa gas pressure and 820° C.

The results of the high pressure, 21 MPa, CG-27 endurance test demonstrated that the 1.0 vol % CO_2 dopant is an effective deterrent to hydrogen permeation. The 21 MPa hydrogen gas pressure apparent permeability coefficient at 820° C approached 0.1×10^{-6} $cm^2/sec\ MPa^{1/2}$ after 500 hr, the same as the 15 MPa test. Even at this higher gas pressure and comparable permeation rate, CG-27 passed the 3500 hr endurance test without creep-rupture failures. It is concluded that the CG-27 alloy, in the form of thin wall tubing is suitable for Stirling engine applications at 820° C and gas pressures up to 21 MPa.

INTRODUCTION

The work described in this report was conducted as part of the continuing supporting research and technology activities under the DOE-NASA Stirling Engine Highway Vehicle Systems Program (ref. 1). To achieve maximum efficiency in the Stirling Engine, hydrogen is used as the working fluid and operating temperatures are high, near 870° C in some proposed engine designs. In current prototype engines, N-155, an alloy containing 20 percent cobalt is used for the heater head tubing. Because of the strategic nature of cobalt (greater than 90 percent import dependence by the United States), its limited availability compared to the mass market needs for proposed automotive Stirling engine applications, and high-cost, alloys containing cobalt cannot be considered for automotive applications (ref. 2).

Planned automotive applications of the Stirling engine require cyclic on off operation with resulting temperatures of the heater head tubes ranging from room temperature to near 900° C (ref. 3). In addition, speed of the automobile is controlled by pressure variation of the hydrogen working fluid contained in the heater head tubes. Pressure normally ranges between 2 and 15 MPa with an average pressure near 7 MPa based on a 50 percent urban/50 percent highway driving cycle.

Two Stirling engine simulator rigs have been fabricated and are being used at NASA LeRC to evaluate candidate Stirling engine heater tube alloys under simulated conditions of cyclic temperatures, hydrogen pressure, and diesel-fuel combustion gas environment. To date, five endurance runs (refs. 4 and 5) and two hydrogen dopant studies (refs. 6 and 7) have been completed using the NASA LeRC Stirling engine simulator test rigs. The first was an endurance run for 1000 hr at 760° C and 21 MPa hydrogen pressure, using pure and commercial hydrogen (ref. 4), the second was an endurance run for 535 hr at 860° C and 21 MPa hydrogen pressure, using commercial hydrogen. The third was an endurance run for 1000 hr at 820° C and 21 MPa hydrogen pressure, using commercial hydrogen (ref. 5), the fourth was an endurance run for 3500 hr at 820° C and 15 MPa hydrogen pressure, using hydrogen doped with 1.0 vol % carbon dioxide, and the fifth was an endurance run for 3500 hr at 820° C and 21 MPa hydrogen pressure using the best alloy from the previous 3500 hr run. This was also conducted using hydrogen doped with 1.0 vol % carbon dioxide. The results of the fourth and fifth endurance runs (3500 hr) will be discussed in this report.

The purpose of this investigation was three-fold: (1) to rank the candidate Stirling engine heater tube alloys according to their endurance limits in the Stirling engine simulator rig at 820° C and 15 MPa pressure; (2) to rank candidate heater tube alloys as to their ability to contain hydrogen at 820° C; and (3) to select and endurance test the best alloy at 21.6 MPa hydrogen pressure and 820° C temperature.

The alloys evaluated included N-155, and 15 other candidate heater tube alloys under conditions of cyclic temperature, pressure, and environment (hydrogen and combustion products) that simulate the actual operation of a Stirling powered highway vehicle. The alloys tested included 10 iron-base alloys, N-155, A-286, Incoloy 800, 19-9DL, CG-27, W-545, 12RN72, 253MA, Sanicro 31H, and Sanicro 32; five nickel-base alloys Inconel 601, Inconel 625, Inconel 718, Inconel 750 and Pyromet 901; and one cobalt-base alloy HS-188. The iron-base and nickel-base alloys are considered possible candidates for the Stirling engine heater tubes. Six of the alloys were evaluated previously in endurance runs at 760°, 820°, and 860° C. These alloys were N-155, A-286, Incoloy 800, 19-9DL, Inconel 718 and HS-188. The results obtained in these endurance runs are reported in references 4 and 5.

EXPERIMENTAL PROCEDURES

Materials

The alloys used in this study were obtained commercially in the form of tubing. Two sizes were studied, one with an outside diameter of 4.8 mm and inside diameter of 3.2 mm, and the second with an outside diameter of 4.5 mm and an inside diameter of 3.0 mm (the size used in current prototype engines). The 4.8 mm tubing included the following alloys: N-155, A-286, Incoloy 800, 19-9DL, CG-27, W-545, Inconel 718, Inconel 601, and HS-188. The 4.5 mm tubing included the following alloys: 12RN72, 253MA, Sanicro 31H, Sanicro 32, Inconel 625, Inconel 750, and Pyromet 901. 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. A second lot of Inconel 718 (Inconel 718(a)) in the seamless version and an as-cold worked seamless version of the 12RN72(cw) were also tested.

Chemical analysis of the tube product as reported by the fabricator or determined at NASA LeRC are listed in table I. Ten of the alloys are iron-base superalloys with substantial amounts of chromium and nickel. The iron-base alloys are: N-155, A-286, Incoloy 800, 19-9DL, CG-27, W-545, 12RN72, 253MA, Sanicro 31H, and Sanicro 32. Five of the alloys are nickel base alloys, and include Inconel 601, Inconel 625, Inconel 718 , Inconel 750, and Pyromet 901. One alloy, HS-188, is cobalt-based. Average grain size of the heater tubes ranged from 7 μm for HS-188, to 61 μm for W-545 and are reported in table I. Prior to the endurance runs, several of the alloys were heat treated to increase their grain size and thus hopefully improve the elevated temperature creep-rupture properties. The alloy, heat treatment and grain size are as follows:

Alloy	Solution treatment	Atmosphere time	Cooling	Grain size, μm
N-155	1204° C	Vacuum 10 min	Fce.	17
A-286	1148° C	Vacuum 10 min	Fce.	54
Incoloy 800	1121° C	Vacuum 1 hr	Fce.	46
19-9DL	1204° C	Vacuum 10 min	Fce.-He	25

The microstructure of the tubes before the endurance run are shown in figures 1(a) to (r). The limited supply of some tubes prevented obtaining microstructures of them before exposure to the endurance testing. The microstructure of these tubes were obtained from the cold end of the "hairpin" after endurance testing.

The tubing alloys were evaluated in the Stirling engine materials test rig in the form of a "hairpin" as shown in figure 2. Each leg of the "hairpin" was 30.5 cm long with 2.5 cm between legs. Four of these "hairpins" were attached in series to a copper header with internal passages and external tubes and valves for filling the four "hairpins." The copper header and attached tubes comprised a module. The module is shown in figure 3. The "hairpins" were attached to the copper header with gas-tight mechanical connectors. A pressure transducer is located adjacent to the thermocouple plug at the top of the module. A thermocouple is also attached to the pressure transducer. When one tube failed during the test, the pressure in the remaining three tubes of that module was also lost. Before installation in the rig, each assembled module was leak checked to 10 MPa by pressurizing with helium and submersion in water. The modules were previously proof tested to 30 MPa by pressurizing with an organic solvent. Little difficulty was experienced in achieving leak proof modules.

Hydrogen doped with 1.0 vol % carbon dioxide (CO_2) was used in both endurance tests. Analyses of the hydrogen used in the endurance run at 15 MPa are shown in table II. The hydrogen analyses for the endurance run at 21.6 MPa with CG-27 are also shown in table II. The modules were refilled every five hr during the initial 100 hr cycles of the endurance tests, due to the rapid permeation of hydrogen through the tube walls at 820° C. During the latter part of the endurance test, when the hydrogen permeation was substantially reduced, the modules were refilled with hydrogen once every week, which averaged 50 hr of testing. The modules pressurized with helium were repressurized only after "hairpin" replacement following a tube failure.

Analyses of the helium used in the test runs revealed no detectable amounts of oxygen.

Stirling Engine Simulator Rig

The Stirling engine simulator rigs used in this program were designed and fabricated at the Lewis Research Center; they consist primarily of a combustion gas heating chamber and auxiliary heating, control and gas management systems. A schematic of the heating chamber is shown in figure 4. A detailed description of the rigs and their operation is given in reference 4.

An endurance run consisted of a series of 5-hr cycles to obtain the required exposure time of 3500 hr at 820° C. A typical heating cycle was made up of a 6 to 10 min preheat to get to the operating temperatures, a 5-hr hold at temperature, followed by a cool down to near room temperature. The cool down time between cycles in the furnace was 1 hr or longer. After cool down to about 25° C the modules containing hydrogen were vented, pressure transducers rezeroed and refilled. The modules containing helium did not require refilling after each cycle: they were evacuated and refilled only after "hairpin" replacement following a failure or leak. After completion of the test run or after failure, the "hairpins" were removed from the modules and sectioned for tensile testing and metallographic examination.

The modules were of the modified design to eliminate a "hot-zone" at the top of the "hairpin", approximately 23 cm from the bottom bend. This modification consisted of the installation of a 10.2 long sleeve (9.5 mm diam) around each tube leg in the "hot zone". This effectively reduced the temperature variation along each "hairpin" of each module.

The temperature inside the heating chamber of the rig was determined at the start of the first 3500 hr endurance run. The profile was determined by measuring the temperature at three locations on each module. The thermocouples were fastened to each module at the bottom bend of the "hairpin" as well as at

10.2 and 22.9 cm from the bottom bend. The temperature profile determined for the two endurance runs are shown in figures 5(a) and (b). This figure shows the temperature at the top, middle and bottom locations on the module plotted against module position around the furnace. Also shown are the tube alloys at the module location at the start of the run. Figure 5(a) shows the results for Rig A. The temperatures at the top varied from 770° to 870° C, with the highest temperature (870° C) at the location of the N-155 "hairpin" and the lowest temperature at the location of the Incoloy 800 "hairpin." The maximum temperatures at the middle and bottom locations were substantially lower than those of the maximum at the top location and varied from 800° to 843° C at the bottom locations and 780° to 830° C at the middle locations. Most tubing failures occurred in the top locations of the "hairpins." Figure 5(b) shows the temperature profile for Rig B, which is quite similar to that of Rig A. The temperatures at the top varied from 780° to 854° C with the highest temperature at the module containing Inconel 625. The temperatures at the middle location varied from 805° to 838° C. At the bottom location the temperatures varied from 813° to 851° C.

Post Exposure Evaluations

Post exposure evaluation included tensile testing at room temperature and 820° C and metallography.

Tensile tests were conducted on tube specimens at room temperature and at 820° C. The tensile grips and a tensile specimen are shown in figure 6. The tensile specimens were 10.2 cm long when tested at room temperature and 17.8 cm long when tested at 820° C. A solid tool steel pin 2.5 cm long was inserted into the tube ends to prevent collapse of the tube during testing. The elongation after testing was determined from measurements of prescribed marks on the tensile specimens. All tests were conducted at a crosshead speed of 0.25 cm/min. Except where noted tests were conducted in duplicate.

Metallographic specimens were sectioned from the "hairpin" tubes taken from each module. The specimens were polished, appropriately etched and examined at magnifications of 100X and 500X.

RESULTS

Microstructure

As previously indicated the microstructure of the alloys before the endurance runs are shown in figures 1(a) to (r). The limited supply of some alloys prevented obtaining microstructures before endurance testing. The microstructures of these tubes 12RN72, 12RN72(cw), W-545, Inconel 601 and Inconel 625 were obtained from the cold end of room temperature tensile specimens after tensile testing. Note the dual grain size present in figure 1(n) for Inconel 718(wd). The small grain size area (10 μm) is in the heat-affected weld zone and the larger grains (23 μm) are in the base metal. This heat-affected weld zone was the location of the failures in the Inconel 718(wd) tubes and also in the other weld-drawn tube alloys. The microstructures of each tube from each alloy pressurized with hydrogen doped with 1.0 vol % CO_2 and each alloy pressurized with helium after rig exposure are also shown in figures 1(a) to (r).

Minor changes in microstructure were found for most alloys which included growth and coalescence of the precipitate particles in the matrix and grain boundaries. There was, however, substantial grain growth in several tubes, CG-27, 12RN72, 12RN72(cw), Inconel 718(wd), and Inconel 718(a) (table III). The largest grain growth, from 36 to 113 μm, was found in the CG-27 alloy for the tubes exposed to helium for 3500 hr as shown in figure 1(e). In general the alloys did not show major reaction to hydrogen doped with 1.0 vol % CO_2 or the helium used to pressurize the tubes. The W-545 and 19-9DL were the only alloys showing any substantial reaction to the diesel fuel fire-side environment as can be noted in figures 1(f) and (d). Figure 1(f) for W-545 shows that the fire-side of the tube was oxidized to nearly one-fourth of the wall thickness. Figure 1(d) for 19-9DL shows the wall thickness was also severely reduced during the endurance test. This is similar to that found in the 1000-hr endurance run reported in reference 5, where 50 percent of the 19-9DL tube was lost, indicating that the fire-side burner environment has caused oxidation and spalling of the tubing outside surface. Incoloy 800, 12RN72 and 12RN72(cw) show a reduced wall thickness, after exposure, however these photomicrographs are from failed tubes where the wall thickness was severely reduced by bulging during failure. W-545 and Inconel 601, showed thinner and deformed surfaces in the unexposed condition, however, unexposed metallographic specimens were obtained from the grip end of failed tensile specimens.

Hydrogen Permeability

The pressure of the gas contained in the modules, hydrogen doped with 1.0 vol % CO_2 or helium, was monitored during each of the 5-hr 820° C temperature cycles that made up the 3500 hr endurance run. The pressure in the modules that contained helium became constant after the module achieved the 820° C temperature and remained constant throughout the 5-hr cycle. However, the pressure in the modules that contained hydrogen doped with 1.0 vol % CO_2 varied from a maximum at the start of the 5-hr cycle to a low at the end of 5 hr at 820° C. The maximum pressure and the pressure at the end of the 5-hr cycle were used to calculate the hydrogen permeability coefficient, ϕ, using the equation:

$$P = P_o^{1/2} - \frac{\phi A P_s T t}{2 L V T_s}$$

where

P pressure in closed system, MPa

P_o 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, cm^3

T_s standard temperature, K

It should be noted that the Stirling materials simulator test rig, modules and tubes were not expressly designed for the measurement of permeation, but rather were designed for environmental endurance testing to determine the effects of burner and hydrogen environment on the life of tubes under pressure. Thus the permeation calculations should be considered as "apparent" permeation coefficients. Nonetheless, they are valuable in rating hydrogen (doped with 1.0 vol % CO_2) permeation rates through the 16 alloys investigated.

3500 Hr Endurance Test of 16 Alloys at 15 MPa and 820° C

The results of the calculations of permeability coefficient, ϕ for selected 5-hr cycles of the endurance run at 15 MPa are shown in table IV. These data are shown plotted in figures 7, 8, and 9 for the iron, nickel, and cobalt base alloys, respectively. In general the hydrogen doped with 1.0 vol % CO_2 resulted in lower hydrogen permeability coefficients, and thus lower hydrogen loss. All nickel-base alloys had hydrogen permeability coefficients less that 0.5×10^{-6} $cm^2/sec\ MPa^{1/2}$ after 110 hr into the 3500-hr endurance run and were all below 0.2×10^{-6} $cm^2/sec\ MPa^{1/2}$ at longer times during the 3500-hr endurance run. Only the three iron-base alloys, W-545, 19-9DL and 253MA, had hydrogen permeability coefficients above 2.5×10^{-6} $cm^2/sec\ MPa^{1/2}$ after 110 hr.

A ranking of the tested "hairpin" tubes according to their hydrogen permeability coefficient, ϕ, achieved after 250-hr exposure in the rig is given in table V. This time was chosen since it corresponds to the shortest failure time of any of the alloys tested and thus permits an equal comparison. Table V shows that the "hairpin" with the lowest hydrogen permeability coefficient is Pyromet 901 with a ϕ value of 0.064×10^{-6} $cm^2/sec\ MPa^{1/2}$. The next five alloys, CG-27, Inconel 601, Inconel 718(wd), Inconel 750 and 12RN72(cw) all had ϕ values below 0.2×10^{-6} $cm^2/sec\ MPa^{1/2}$. Note that the currently used N-155 alloy ranked number 10, i.e., nine "hairpin" tubes had lower hydrogen permeability coefficients. Only three "hairpin" tubes 253MA, W-545 and 19-9DL had ϕ values above 1.0×10^{-6} $cm^2/sec\ MPa^{1/2}$ after 250-hr exposure in the rig, 2.47, 3.80 and 5.05×10^{-6} $cm^2/sec\ MPa^{1/2}$, respectively. Thus, using the desired goal of 2.5×10^{-6} $cm^2/sec\ MPa^{1/2}$ as the maximum hydrogen permeation coefficient that could be tolerated in a commercial highway vehicle, only two "hairpin" tubes, W-545 and 19-9DL, failed to meet this criteria.

3500 Hr Endurance Test of CG-27 at 21 MPa and 820° C

The calculated hydrogen permeability coefficient, ϕ, for selected 5-hr cycles of the endurance run at 21 MPa pressure, are shown in table VI. This shows the ϕ value varied from 3.10×10^{-6} to 0.08×10^{-6} $cm^2/sec\ MPa^{1/2}$ during the 500 hr. These data are shown plotted with the data obtained from the 3500-hr endurance run at 15 MPa (fig. 10). Note that the ϕ values for the two endurance runs are similar to the ϕ value from the run at 15 MPa falling within the scatter obtained from the five modules of the run at 21 MPa.

Tubing Lives

Many of the "hairpin" tubes did not survive the 3500-hr endurance run at 15 MPa internal pressure. The tubes that contained helium had more failures than did those that contained hydrogen due to the higher constant pressure and hence stress maintained in the helium-containing tubes, throughout each of the 5-hr cycles at 820° C. In contrast, the hydrogen pressure generally decayed with time during each 5-hr cycle. The tube rupture lives for the 3500-hr endurance at 15 MPa pressure are shown in table VII. The tube rupture lives for the 3500-hr endurance run at 21 MPa using CG-27 are shown in table VIII.

3500 hr Endurance Run of 16 Alloys at 15 MPa and at 820° C.

The results of the 3500 hr Stirling engine simulator test rig endurance run at 15 MPa and 820° C are given in table VII. After 3500 hr, no failures were noted in the "hairpin" tubes of CG-27 and Pyromet 901, regardless of the gas, either helium or doped hydrogen. Two other tubes, 12RN72 and Inconel 625 which had rupture lives in excess of 3500 hr for those which contained hydrogen, however, they did have failures in the tubes which contained helium after 1598 and 2856 hr, respectively. There were no failures in the Incoloy 800, Sanicro 31H, Inconel 601, 253MA and Sanicro 32 "hairpin" tubes that contained doped hydrogen, however, these were removed after 130, 165, 590, 2099 and 2919 hr, respectively, due to their limited lives when pressurized with helium. Note that for W-545, 12RN72(cw), and Inconel 750 the rupture lives in the "hairpin" tubes which contained hydrogen are less than those that contained helium, indicating that there may be possible hydrogen environment degradation or embrittlement. However, the results of the tensile tests did not substantiate this. It is noted that the Inconel 718(wd) and Inconel 718(a) "hairpin" had significantly different rupture lives, 514 and 1672 hr, respectively. As there is no significant difference in composition between the two tubes, the three-fold improvement in performance of the Inconel 718(a) is attributed to its being a seamless tube rather than weld-drawn as was the Inconel 718(wd).

A ranking of the 16 alloys according to the average rupture lives of the tubes that contained helium is given in table IX and shown plotted in figure 11. The two alloys CG-27 and Pyromet 901 both had rupture lives in excess of 3500 hr in either the helium containing tubes or the doped hydrogen containing tubes. The alloy with the shortest rupture life was Incoloy 800. The "hairpin" tubes pressurized with helium failed by creep-rupture in 118 hr. Note that there are eleven "hairpin" tubes ranked higher than N-155 (606 hr rupture), the alloy currently used an heater head tubes in prototype highway vehicles. CG-27, Pyromet 901, Inconel 625, W-545, Inconel 718(a), 12RN72, HS-188, 12RN72(cw), 253MA, Sanicro 32 and Inconel 750 all had rupture lives greater than 700 hr. The remaining tubes ranked lower than N-155. In descending order they are 19-9DL, Inconel 601, Inconel 718(wd), A-286, Sanicro 31H and Incoloy 800.

3500 hr Endurance test of CG-27 at 21 MPa and 820° C

The results of the 3500-hr endurance run at 21 MPa pressure for the CG-27 alloy are shown in table VIII. Ten modules were tested, five with hydrogen and five with helium. No creep-rupture failures occurred in either the doped hydrogen or helium pressurized "hairpin" when tested at 820° C. Three failures did occur, but these are attributed to high temperatures caused by a defective heat-shield and a 270° C over-temperature spike. The defective heat-shield can be seen on the module on the right side of figure 12. It has essentially eroded away during the endurance run. This loss of the heat-shield resulted in a temperature estimated to be 40° to 60° C higher than in modules with intact heat-shields. The failures in the tubes of modules 6 and 10 occurred immediately after an over-temperature malfunction in the rig at 1075 hr into the 3500-hr endurance run. During the over-temperature spike the modules were in excess of 1090° C for 6 to 10 min. No failures occurred in the remaining seven modules which ran for the full 3500 hr at 820° C and 21 MPa pressure.

Tensile Properties

Tensile properties of the unexposed tubing were determined where material availability permitted. The endurance tested, exposed, "hairpin" tubes of all alloys were sectioned for tensile testing to determine the effect of rig environment on the tensile properties. Each of the alloys had been exposed to hydrogen doped with 1.0 vol % CO_2, helium and the burner combustions products. Both room temperature and high temperature (820° C) tensile tests were conducted. The results of these tests for the two 3500-hr endurance runs are described in the following sections.

TENSILE PROPERTIES OF 15 MPa TESTED ALLOYS

Room Temperature

The room temperature tensile properties of the tubing alloys both prior to the endurance runs as well as after are presented in table X and for the 3500-hr endurance run with 16 alloys at 15 MPa and shown graphically in figure 13.

The room temperature tensile properties of the 16 alloys, prior to use in the endurance test at 15 MPa pressure are given in table X. The ultimate strengths ranged from a low of 552 MPa for Incoloy 800 to a high of 1364 MPa for CG-27. The tensile elongation for alloys were good and ranged from 14.5 percent for the high strength CG-27 to 60.3 percent for 19-9DL. Hydrogen exposure in the rig resulted in significant losses in ultimate strength for six of the "hairpin" tubes, W-545, 19-9DL, Inconel 718(a), Inconel 750, Pyromet 901, and Sanicro 32, CG-27. The greatest loss in strength occurred in the W-545 tubing, where the ultimate tensile strength was reduced from 988 MPa for the unexposed material to 254 MPa. The ultimate strength of the Inconel 750 dropped from 1197 to 553 MPa, Pyromet 901 dropped from 1221 to 591 MPa, and Sanicro 32 dropped from 598 to 347 MPa. The ultimate strength of CG-27 dropped from 1364 to 736 MPa and 19-9DL dropped from 767 to 420 MPa. Losses in ductility ranged from 38 percent for CG-27 exposed to hydrogen to 95 percent loss in ductility for Sanicro 32 exposed to hydrogen. Exposure in the rig resulted in little or no loss in ultimate strength at room temperature in four of the "hairpin" tubes; N-155, A-286, Inconel 601, and 253MA. There were, however, large losses in ductility in three of the four alloys, a 24 percent loss for N-155, 70 percent loss for A-286 and a 65 percent loss for 253MA. These losses were similar for the tubes that contained helium or hydrogen, indicating an aging effect. The ductility of the Inconel 601 improved slightly, from 40 to 45 percent. Doped hydrogen exposure in the rig resulted in a gain in ultimate tensile strength for two of the "hairpin" tubes, HS-188, Inconel 718(wd), Helium exposures showed similar gains in three "hairpin" tubes, Inconel 625, Incoloy 800 and Sanicro 32. Generally, the gains in strength were not large, however, the Inconel 718(wd) with helium improved from 875 to 956 MPa. The changes in ductility for these five "hairpin" tubes ranged from a loss of 23 percent for Incoloy 800 (in helium) to a loss of 95 percent for Sanicro 32 (in doped hydrogen).

The 820° C tensile properties of the tubing alloys both prior to the endurance runs as well as after are presented in table XI and are shown graphically in figure 14. The elevated temperature strength at 820° C ranged from 138 MPa for Sanicro 31H to 540 MPa for Inconel 718(a). The tensile elongation at 820° C ranged from 14 percent for CG-27 to 70.2 percent for Sanicro 31H.

Exposure in the rig at 15 MPa at 820° C resulted in large losses in ultimate strength for seven of the 18 "hairpin" tubes. The greatest losses in strength occurred in: W-545, -64 percent; Inconel 718(a), -45 percent; Pyromet 901, -43 percent; Inconel 718(wd), -35 percent; Inconel 750, -35 percent; CG-27, -32 percent; and 19-9DL, -30 percent. There were minor losses in strength in seven other "hairpin" tubes: N-155, A-286, Incoloy 800, 253MA, Sanicro 32, Inconel 601, and HS-188. There were slight gains in strength in two: Inconel 625, and Sanicro 31H. The absolute strength of the alloys after exposure in the rig is of importance in ranking the alloys. The "hairpin" tubes with the highest ultimate strength after rig exposure to hydrogen were CG-27 (378 MPa), Inconel 625 (342 MPa), HS-188 (342 MPa), Inconel 718(wd) (339 MPa), Inconel 718(a) (318 MPa) and Pyromet 901 (300 MPa).

There were large losses in ductility after rig exposure in four of the "hairpin" tubes: W-545, -77 percent; 19-9DL, -53 percent; Pyromet 901, -50 percent and Sanicro 31H, -28 percent. As noted previously, there were also large losses in ultimate strength in three of these four W-545, 19-9DL, and Pyromet 901. In six of the "hairpin" tubes there were gains in ductility after rig exposure. This occurred in CG-27, +207 percent; Inconel 718(wd), +205 percent; Inconel 718(a), +148 percent; N-155, +137 percent; Inconel 750, +83 percent; and A-286, +72 percent. Generally this gain in ductility at 820° C was accompanied by a decrease in ultimate tensile strength at 820° C.

TENSILE PROPERTIES OF 21 MPa TESTED CG-27

The tensile data for CG-27 prior to and after rig exposure at 21 MPa for 3500 hr at 820° C are given in table XII and are shown graphically in figure 15. The room temperature (25° C) ultimate tensile strength was 1364 MPa and the tensile elongation was 14.5 percent. The elevated temperature tensile strength (820°) was 529 MPa and the tensile elongation was 14 percent. Note that both the doped hydrogen and helium containing tubes were degraded about the same amount when tested at room temperature or 820° C, indicating an aging effect rather than an environment effect. The helium tube loss 544 MPa (40 percent) and the doped hydrogen tube loss 577 MPa (42 percent).

DISCUSSION

The results of the 3500-hr endurance run at 15 MPa pressure show that eleven of the "hairpin" tubes studied had longer lives than did the currently used N-155 (606 hr). The temperature distribution in the rigs may account for some of the alloys being stronger than N-155 since N-155 was at the highest temperature in Rig A. Two alloys, CG-27 and Pyromet 901 had no failures in 3500 hr and two other alloys Inconel 625 and W-545 had lives of 2856 and 2777 hr, respectively. The failure times for the modules of a given alloy that contained hydrogen were generally longer than those that contained helium. This is due to the constant higher pressure maintained in the helium modules. The results for Inconel 750, W-545, 12RN72(cw) and 19-9DL show that the "hairpin" tubes that contained hydrogen had earlier failures than did the tubes that contained helium. These "hairpin" tubes also had larger tensile property degradation in the modules that contained hydrogen (table XIII). These results are indications of possible hydrogen embrittlement in these materials.

Comparison of the failure times of the Inconel 718(wd) and Inconel 718(a) as shown in table VII shows that the Inconel 718(a) had substantially longer life in both hydrogen filled and helium filled tubes. The significant difference between the two tubes is the methods of fabrication, Inconel 718(wd) being weld-drawn and Inconel 718(a) being seamless. The absence of a weld fusion line in the Inconel 718(a) eliminates a high temperature fracture prone zone and thus extends the life at 820° C. The failure time improved from 514 hr for Inconel 718(wd) helium filled tubes to 1672 hr for the helium filled Inconel 718(a) seamless tubes.

The results of the two 3500-hr endurance runs again show that hydrogen permeates through the hot tube walls and must be replenished periodically, whereas helium is readily contained in the "hairpin" tubes for each 5-hr cycle at temperature of 820° C and pressures of 15 and 21.6 MPa. The rate of hydrogen permeation was found to be substantially reduced in most alloys with the use of 1.0 vol % carbon dioxide as a dopant in the hydrogen. The rate of hydrogen permeation was found not to be constant but rather is variable and is influenced by alloy composition and O_2/CO_2 content of the hydrogen used. The reduction of hydrogen permeability during the endurance test is thought to be associated with the formation of a very thin oxide film on the inside surface of the tube. The external oxide on most alloys studied was tightly adherent, however, in the 19-9DL tubes the external fire-side oxide spalled severely, thus reducing the tube wall thickness. This behavior was also found in the endurance runs previously conducted at 820° and 860° C (described in ref. 5). As would be expected 19-9DL had the highest apparent hydrogen permeability of all alloys. This is shown plotted in figure 16. In general the nickel-base alloy tubes had lower hydrogen permeability coefficients than the iron-base alloy tubes or the cobalt-base alloy tube. However, the CG-27, 12RN72 and 12RN72(cw) tubes had low hydrogen permeation coefficients, 0.13×10^{-6}, 0.18×10^{-6}, and $0.31\times^{-6}$ $cm^2/sec\ MPa^{1/2}$, respectively after 250 hr. Examination of figure 16 shows that only three "hairpin" tubes, 253MA, W-545, and 19-9DL had hydrogen permeability coefficients above 1.0×10^{-6} $cm^2/sec\ MPa^{1/2}$. Thus it can be concluded that the 1.0 vol % carbon dioxide as a dopant in the hydrogen was effective in reducing the rate of hydrogen permeation while at 820° C. In view of the very low permeability coefficients obtain using hydrogen doped with 1.0 vol % CO_2 the possibility exists that a reduced dopant level, below 1.0 vol %, may be suitable for use in a commercial vehicle. Also, it appears that the goal of a hydrogen permeability coefficient in the order of 2.5×10^{-6} $cm^2/sec\ MPa^{1/2}$ for commercial vehicles can readily be achieved with most of the alloys studied.

SUMMARY OF RESULTS

Endurance testing of sixteen tubing alloys in a diesel-fuel-fired Stirling engine simulator materials test rig for 3500 hr at 820° C while pressurized with either hydrogen doped with 1.0 vol % CO_2 or helium had the following results:

(1) The CG-27 and Pyromet 901 tubes did not fail during the 3500 hr endurance run at the 15 MPa pressure. The remaining 16 tubes, pressurized with helium failed by creep-rupture.

(2) No creep-rupture failures occurred in the CG-27 tubes when endurance test at 21.6 MPa.

(3) The 1.0 vol % CO_2 as a dopant in hydrogen was effective in reducing hydrogen permeation at 820° C.

(4) Most alloys lost hydrogen rapidly during the early 5-hr segment of the endurance test, however, only three alloys, iron-based 19-9DL, W-545, and 253MA had hydrogen permeability coefficients, ϕ, above 1.0×10^{-6} $cm^2/sec\ MPa^{1/2}$ at the end of the test.

(5) The permeability coefficients, ϕ, of the nickel-base alloys were in general, lower than those of the iron-base or cobalt-base alloys. However, three iron-based tubes CG-27, 12RN72, and 12RN72(cw) had ϕ values below 0.06×10^{-6} $cm^2/sec\ MPa^{1/2}$, lower than the nickel-base alloys.

(6) Tensile tests conducted on the rig exposed tubes showed that the CG-27 alloy has identical room temperature ultimate strength as the N-155 alloy and the 820° ultimate strength of CG-27, 360 MPa, is 100 MPa greater than the N-155.

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TABLE I. - COMPOSITION, METHOD OF FABRICATION, GRAIN SIZE, AND TUBE SIZE FOR TUBING ALLOYS

Alloy	N-155	A-286	Incoloy 800	19-9DL	CG-27	W-545	12RN72		253MA	Sanicro 31H	Sanicro 32	Inconel 601	Inconel 625	Inconel 718(wd)	Inconel 718(a)	Inconel 750	Pyromet 901	HS-188
Fabrication	Weld-drawn	Seamless	Seamless	Weld-drawn	Seamless	Seamless	a	cw	Seamless	Seamless	Seamless	Seamless	Seamless	Weld-drawn	Seamless	Seamless	Seamless	Weld-drawn
							Seamless											
Grain size, μm	17	54	46	25	36	61	10	9	21	11	19	33	16	[a](7)23	14	32	46	7
Tube size, μm	4.8	4.8	4.8	4.8	4.8	4.8	4.3	4.3	4.3	4.3	4.3	4.8	4.3	4.8	4.8	4.3	4.3	4.8
Element	Composition, wt %																	
Chromium	21.2	14.4	22.5	18.3	13.0	12.9	19.38	19.55	20.96	21.2	21.5	23.68	21.0	17.7	18.05	15.6	12.33	22
Nickel	19.9	24.7	32.6	8.76	37.8	27.7	24.05	24.36	11.5	31.7	31.9	Bal	Bal	Bal	Bal	Bal	Bal	23.1
Cobalt	19.0	------	-----	-----	------	------	------	------	------	-----	-----	-----	-----	.03	.23	------	------	Bal
Manganese	1.45	1.01	.73	1.02	<.05	1.32	1.90	1.90	.50	.65	.65	.14	.09	.05	.23	.16	.10	.67
Molybdenum	3.03	1.17	-----	1.26	5.57	1.7	1.50	1.52	1.52	-----	-----	-----	8.04	3.02	2.93	------	5.90	------
Tungsten	2.61	------	-----	1.18	------	------	------	------	------	<.05	<.05	-----	-----	-----	-------	------	------	13.9
Titanium	-----	2.12	.52	.27	2.3	2.8	.49	.48	------	.40	.40	-----	.34	1.12	1.03	2.50	2.60	------
Columbium	1.05	------	-----	[b].37	.97	------	------	------	<.05	-----	-----	-----	3.15	[b]5.18	[b]5.00	.85	------	------
Silicon	.55	.62	.33	.47	<.1	.49	.26	.26	1.82	.68	.68	.27	.51	.20	.11	.23	.19	.38
Aluminum	-----	------	.54	-----	1.66	.15	.011	.009	------	.40	.35	1.52	.33	.56	.52	.72	------	------
Carbon	.11	.06	.01	.29	.04	.026	.099	.010	.088	.07	.07	.04	.02	.04	.04	.046	.028	.11
Nitrogen	.16	------	-----	-----	------	------	.016	.015	.20	.03	.03	-----	-----	-----	-------	------	------	------
Copper	-----	.32	.03	-----	------	.001	------	------	------	-----	-----	<.05	-----	.04	.06	.07	------	------
Vanadium	-----	.026	-----	-----	------	------	------	------	------	-----	-----	-----	-----	-----	-------	------	------	------
Boron	-----	------	-----	-----	.004	.048	------	------	<.001	-----	-----	-----	-----	-----	<.002	------	.009	.003
Lanthanum	-----	------	-----	-----	------	------	------	------	------	-----	-----	-----	-----	-----	-------	------	------	.03
Iron	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal	13.56	2.88	18.8	Bal	7.79	33.49	1.79

[a]Weld zone.
[b]Cb/Ta.

TABLE II. - HYDROGEN ANALYSIS OF HYDROGEN USED IN THE TWO ENDURANCE RUNS

Test time, hr	Bottle number	Analysis, vol %						
		CO_2	O_2	N_2	A	He	CO	CH_4
Rig A - 15 MPa								
0 - 387	727506	1.05	0.002	0.075	0.018	------	------	------
387 - 720	618258	1.10	.002	.086	.018	------	------	------
720 - 1088	680925	.98	.0000	.0000	.0000	0.0000	0.0000	0.0217
1088 - 1546	573098	1.11						------
1546 - 2060	486222	.98						.0219
2060 - 2550	277027	.99						.0171
2550 - 2705	685865							
2705 - 3324	467562	.90	.0136	.0885	.0029	------	------	------
3324 - 3500	124519							
Rig B - 15 MPa								
0 - 525	727519	1.08	.003	.095	.20	------	------	------
525 - 1222	377374	1.12	.0000	.0000	.0000	------	.0000	------
1222 - 1938	643981	1.02		.017		.0000		------
1938 - 2743	376849	.91	------	------	------	------	.0298	0.0178
2743 - 3180	449089	.91	------	------	------	------	.0292	.0348
3180 - 3340	577823							
3340 - 3500	478101	.88	.0166	.123	.009	------	------	------
Rig A (CG-27 at 21 MPa)								
0 - 1045	12459	.90	same lot as 467562					
1045 - 2785	67634	1.04						
2785 - 3500	112878	1.04						

TABLE III. - GRAIN SIZE OF "HAIRPIN" TUBES BEFORE AND AFTER RIG EXPOSURE

Material	Unexposed grain size, μm	Rig exposed			
		H_2		He	
		Grain size, μm	Exposure time, hr	Grain size, μm	Exposure time, hr
N-155	17	17	[a]1725	16	[a]743
A-286	54	51	435	55	435
Incoloy 800	46	47	130	44	409
19-9DL	25	26	450	25	450
CG-27	36	107	2624	113	3500
W-545	61	64	3500	69	2895
12RN72	10	15	1068	16	1272
12RN72(cw)	9	11	1436	18	1948
253MA	21	21	2099	21	1863
Sanicro 31H	11	11	165	13	163
Sanicro 32	19	22	2919	21	1007
Inconel 601	33	38	590	34	555
Inconel 625	16	16	3500	16	3110
Inconel 718(wd)	23	28	565	27	555
Inconel 718(a)	14	16	1990	17	1450
Inconel 750	32	33	1494	31	905
Pyromet 901	46	54	3500	52	3500
HS-188	7	10	2326	10	1463

[a]Exposure time in rig; hours at 820° C.

TABLE IV. - APPARENT HYDROGEN PERMEABILITY COEFFICIENT ϕ AS A FUNCTION OF RIG EXPOSURE TIME

Rig exposure time, hr	Apparent Hydrogen permeability coefficient, ϕ, 10^{-6} cm^2/sec MPa$^{1/2}$																	
	Hairpin tube material																	
	N-155	A-286	Incoloy 800	19-9DL	CG-27	W-545	12RN72	12RN72 (cw)	253MA	Sanicro 31H	Sanicro 32	Inconel 601	Inconel 625	Inconel 718(wd)	Inconel 718(a)	Inconel 750	Pyromet 901	HS-188
5	17.96	12.93	1.57	13.47	1.63	12.43	10.70	7.59	6.56	8.74	6.86	0.46	0.68	0.49	0.42	0.31	1.03	15.39
10		6.10	1.28		1.05		4.81	.92			2.86		.63			.26		
15		3.23	1.12		.35		2.72	.65			1.96		.55			.28		
20	6.34	2.93	.88	8.98	.45	9.24	1.72	.60	4.22	3.17	1.40	.42	.50	.21	.25	.24	.19	4.97
25		2.07	.81		.25		1.35	.42			1.43		.48			.19		
35	1.85			5.48		7.52			2.95	1.50		.22		.20	.21		.12	2.17
50	1.41	1.32	.71	4.62	.21	6.78	.85	.30	2.76	.87	1.02	.24	.40	.18	.21	.24		1.58
65	1.09			4.2		6.34			2.49	.73		.13			.27		.09	1.30
75		1.13	.73		.19		.70	.26	3.37		.92		.34	.12		.22		
80	.95			3.67		5.38				.88		.16			.18		.08	1.17
95	.81			3.40		5.39			2.59	1.05		.16			.18		.08	.96
100		.93	.76		.20		.55	.28			.93		.34			.20		
110	.73			3.51		5.39				.99		.20		.08	.21		.09	.80
250	.37	.57	Removed 130	5.05	.13	3.80	.31	.18	2.47	Removed 165	.85	.15	.33	.15	.23	.18	.64	.69
500	.30	Failed 400		5.99	.14	3.99	.26	.13	1.79		.57	.16	.31	.36	.20	Failed 281	.63	.37
1000	Failed 778			Failed 525	.098	2.63	.11	.15	1.89		.60	Removed 590	.26	Failed 525			.064	.26
1500					.09	2.15	.19	Failed 1021	1.41		.56		.29		.21		.18	Failed 1415
2000					.065	Failed 1911	.095		1.31		.26		.28		Failed 1821		.30	
2500					.09		.06		Removed 2099		.31		.30				.13	
3000					.062		.085				Removed 2909		.22				.14	
3500					.14		.10						.33				.058	

TABLE V. - RANKING OF TUBES AS TO APPARENT HYDROGEN PERMEABILITY COEFFICIENT

Rank	Tube	ϕ after 250 hr
1	Pyromet 901	0.064
2	CG-27	.13
3	Inconel 601	.15
4	Inconel 718(wd)	.15
5	Inconel 750	.18
6	12RN72(cw)	.18
7	Inconel 718(a)	.23
8	12RN72	.31
9	Inconel 625	.33
10	N-155	.37
11	A-286	.57
12	HS-188	.69
13	Incoloy 800	[a].76
14	Sanicro 32	.85
15	Sanicro 31H	[b].99
16	253MA	2.47
17	W-545	3.80
18	19-9DL	5.05

[a]After 100 hr - failed at 130 hr.
[b]After 100 hr - failed at 165 hr.

TABLE VI. - APPARENT HYDROGEN PERMEABILITY COEFFICIENT - ϕ FOR CG-27 TESTED AT 21 MPa and 820° C

Exposure time, hr	ϕ, 10^{-6}, $cm^2/sec\ MPa^{1/2}$				
	Module				
	1	3	5	7	9
5	3.10	2.65	2.52	1.46	1.36
20	1.05	1.06	1.09	.66	.70
50	.71	.40	.18	.32	.41
100	.39	.26	.39	.22	.28
250	.31	.25	.27	.16	.25
[a]500	.11	.21	----	.08	.092

[a]After 500 hr pressures monitored but not recorded.

TABLE VII. - RUPTURE LIVES FOR "HAIRPIN" TUBES ENDURANCE TESTED AT 15 MPa AND 820° C FOR 3500 hr

Alloy	Environment	Rupture life, hr	Average hr
N-155	He	535, 571, 576, 743	606
	H_2	778, 955, 1209, 1535, 1725	1240
A-286	He	339, 424, 435	399
	H_2	400, 422, 435	419
Incoloy 800	He	106, 130	118
	H_2	No failures (removed - 130 hr)	[a]130
19-9DL	He	610, 640, 685, 707	601
	H_2	525, 555, 605, 720	601
CG-27	He	None in 3500 hr	[a]3500
	H_2	None in 3500 hr	[a]3500
W-545	He	2295, 2864, 2974, 2974	2777
	H_2	1911, 2834	2372
12RN72	He	1262, 1412, 1652, 1677, 1978	1598
	H_2	None in 3500 hr	[a]3500
12RN72(cw)	He	1087, 1172, 1912	1374
	H_2	1021, 1097, 1245, 1436	1200
253MA	He	1016, 1053, 1148, 1863	1273
	H_2	None in 2099 hr	[a]2099
Sanicro 31H	He	145, 163, 165	154
	H_2	None in 165 hr	[a] 165
Sanicro 32	He	680, 695, 950, 1007	878
	H_2	None in 2919 hr	[a]2919
Inconel 601	He	545, 566, 590	567
	H_2	None in 590 hr	[a]590
Inconel 625	He	2603, 3110	2856
	H_2	None in 3500 hr	[a]3500
Inconel 718(wd)	He	475, 495, 522, 536, 545	514
	H_2	525, 1005	765
Inconel 718(a)	He	1208, 1480, 1496, 1505	1672
	H_2	1821, 1990, 2040, 2040	1925
Inconel 750	He	640, 850, 899	796
	H_2	281, 715, 715	570
Pyromet 901	He	None in 3500 hr	[a]3500
	H_2	None in 3500 hr	[a]3500
HS-188	He	1252, 1410, 1445, 1463	1392
	H_2	1415, 1486, 1916, 2326	1785

[a]Module removed from test rig unruptured.

TABLE VIII. - RUPTURE LIVES FOR CG-27 ENDURANCE TESTED FOR 3500 hr, AT 21 MPa AND 820° C

Module number	Rupture life, hr	Average time, hr
Rig B[a]		
[c]1	2624, 3393	3008
6	1075, 1100, 1115	1097
8	None	-----
9	None	-----
10	1075	1075
Rig A		
1	None	[b]3500
2	None	[b]3500
3	None	[b]3500
4	None	[b]3500
5	None	[b]3500
[d]6 (6)	1075, 1100, 1115	1097
[c]7 (1)	2624, 3393	3008
8 (8)	None	[b]3500
9 (9)	None	[b]3500
[d]10 (10)	1075	1075

[a]Transferred to Rig A after 1570 hr.
[b]No creep-rupture failures.
[c]Heat shield failed while in Rig A.
[d]Failure due to 270° C over temperature spike.

TABLE IX. - RANKING OF TUBES BY RUPTURE LIVES IN 15 MPa HELIUM AT 820° C

Rank	Alloy	Average rupture life in helium tubes, hr
[a]1	CG-27	3500
[a]2	Pyromet 901	3500
3	Inconel 625	2856
4	W-545	2777
5	Inconel 718(a)	1672
6	12RN72	1598
7	HS-188	1392
8	12RN72(cw)	1374
9	253MA	1273
10	Sanicro 32	878
11	Inconel 750	796
12	N-155	606
13	19-9DL	601
14	Inconel 601	567
15	Inconel 718(wd)	514
16	A-286	399
17	Sanicro 31H	154
18	Incoloy 800	118

[a]No creep-rupture failures, ranked alphabetically.

TABLE X. - ROOM TEMPERATURE TENSILE PROPERTIES[a] OF TUBING BEFORE AND AFTER ENDURANCE TESTING AT 820° C IN EITHER 15 MPa H_2 + 1% CO_2 or He

Alloy	Rig environment	Rig exposure time, hr	0.2 percent offset yield strength, MPa	Ultimate tensile strength, MPa	Elongation, percent
N-155	Unexposed	----	480	878	45
	Helium	743	285	785	34
	Hydrogen	1725	337	761	-----
A-286	Unexposed	----	212	635	45.7
	Helium	435	225	508	13.5
	Hydrogen	422	214	476	10
Incoloy 800	Unexposed	----	181	552	39
	Helium	130	225	570	30
	Hydrogen	130	199	551	35
19-9DL	Unexposed	----	290	767	60.3
	Helium	483	312	524	-----
	Hydrogen	605	357	420	5
CG-27	Unexposed	----	899	1364	14.5
	Helium	3500	597	757	8
	Hydrogen	3500	474	736	9
W-545	Unexposed	----	508	988	32
	Helium	2974	370	[b]540	8
	Hydrogen	3500	149	254	3
12RN72[c]	Unexposed	----	----	----	-----
	Helium	1948	291	586	44
	Hydrogen	3500	275	518	25
12RN72(cw)[c]	Unexposed	----	----	----	-----
	Helium	2826	357	611	[b]26
	Hydrogen	1912	295	558	[b]28
253MA	Unexposed	----	330	731	57
	Helium	1863	355	615	20
	Hydrogen	2099	3[illegible]1	692	24
Sanicro 31H	Unexposed	----	[illegible]92	560	42
	Helium	163	235	557	25
	Hydrogen	165	239	576	42
Sanicro 32	Unexposed	----	290	598	42.8
	Helium	680	283	553	-----
	Hydrogen	2919	248	347	2
Inconel 601	Unexposed	----	291	665	40
	Helium	555	233	536	42
	Hydrogen[b]	590	241	585	45
Inconel 625	Unexposed	----	433	874	53
	Helium	2856	523	904	31
	Hydrogen	3500	515	848	-----

[a]Average of two tests except where noted.
[b]Single test.
[c]Lack of sufficient material precluded unexposed tensile testing.

TABLE X. - CONCLUDED.

Alloy	Rig environment	Rig exposure time, hr	0.2 percent offset yield strength, MPa	Ultimate tensile strength, MPa	Elongation, percent
Inconel 718(wd)	Unexposed	----	404	875	41.5
	Helium	495	610	956	29
	Hydrogen	565	558	894	25.6
Inconel 718(a)	Unexposed	----	543	984	44.5
	Helium	1480	394	792	22
	Hydrogen	2100	475	721	-----
Inconel 750	Unexposed	----	722	1197	23
	Helium	1060	333	838	-----
	Hydrogen	1495	355	553	-----
Pyromet 901	Unexposed	----	842	1221	22.5
	Helium	3500	729	1095	6
	Hydrogen	3500	350	591	5
HS-188	Unexposed	----	404	875	41.5
	Helium	1463	584	985	-----
	Hydrogen	2326	574	928	-----

[a]Average of two tests except where noted.
[b]Single test.
[c]Lack of sufficient material precluded unexposed tensile testing.

TABLE XI. - TENSILE PROPERTIES AT 820° C[a] OF TUBING ALLOYS BEFORE AND AFTER ENDURANCE TESTING AT 820° C IN EITHER 15 MPa H_2 + 1% CO_2 or He

Alloy	Rig environment	Rig exposure time, hr	0.2 percent offset yield strength, MPa	Ultimate tensile strength, MPa	Elongation, percent
N-155	Unexposed	----	244	296	[b]24.5
	Helium	743	163	249	57.5
	Hydrogen	1725	178	258	50
A-286	Unexposed	----	157	199	29
	Helium	435	145	176	50
	Hydrogen	435	127	174	44
Incoloy 800	Unexposed	----	91	162	62
	Helium	130	121	161	53
	Hydrogen	130	108	152	52
19-9DL	Unexposed	----	147	230	37.5
	Helium	483	115	159	16
	Hydrogen	605	154	183	10
CG-27	Unexposed	----	363	529	14
	Helium	3500	275	378	43.5
	Hydrogen	3500	233	356	30.5
W-545	Unexposed	----	398	417	20
	Helium	2974	128	147	-----
	Hydrogen	3500	142	158	4.5
12RN72[c]	Unexposed	----	----	----	-----
	Helium	1948	196	226	-----
	Hydrogen	3500	121	167	58
12RN72(cw)[c]	Unexposed	----	----	----	-----
	Helium	2826	[illegible]	178	54
	Hydrogen	1912	[illegible]24	163	56
253MA	Unexposed	----	137	190	44.8
	Helium	1863	140	157	36
	Hydrogen	2099	110	171	52
Sanicro 31H	Unexposed	----	122	138	70.2
	Helium	163	----	136	55
	Hydrogen	165	123	152	50
Sanicro 32	Unexposed	----	137	148	-----
	Helium	695	127	139	34
	Hydrogen	2919	114	137	-----
Inconel 601	Unexposed	----	149	175	52.5
	Helium	555	154	177	46
	Hydrogen[b]	590	148	170	45
Inconel 625	Unexposed	----	225	309	-----
	Helium	2856	258	348	43
	Hydrogen	3500	272	342	47

[a]Average of two tests except where noted.
[b]Single test.
[c]Lack of sufficient material precluded unexposed tensile testing.

TABLE XI. - CONCLUDED.

Alloy	Rig environment	Rig exposure time, hr	0.2 percent offset yield strength, MPa	Ultimate tensile strength, MPa	Elongation, percent
Inconel 718(wd)	Unexposed	----	464	519	[b]19
	Helium	555	375	459	42
	Hydrogen	565	233	339	58
Inconel 718(a)	Unexposed	----	526	540	25
	Helium	1480	254	302	62
	Hydrogen	2100	267	318	54
Inconel 750	Unexposed	----	399	404	21.5
	Helium	1060	130	284	40
	Hydrogen	1495	172	260	-----
Pyromet 901	Unexposed	----	451	512	24
	Helium	3500	230	289	12
	Hydrogen	3500	181	300	19
HS-188	Unexposed	----	359	397	[b]50
	Helium	1463	270	349	44
	Hydrogen	2326	305	342	43

[a]Average of two tests except where noted.
[b]Single test.
[c]Lack of sufficient material precluded unexposed tensile testing.

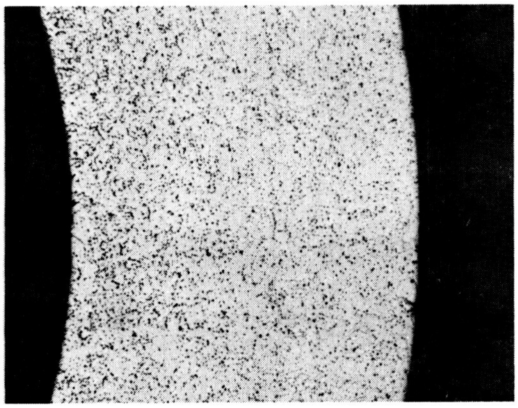
TABLE XII. - TENSILE PROPERTIES OF THE CG-27 TUBING BEFORE AND AFTER ENDURANCE TESTING FOR 3500 hr AT 21.6 MPa IN EITHER H_2 + 1% CO_2 or He at 820° C

Rig environment	Rig exposure time, hr	0.2 percent offset yield strength, MPa	Ultimate tensile strength, MPa	Elongation, percent
25° C				
Unexposed	----	899	1364	14.5
He	3500	576	820	2.8
H_2 + 1% CO_2	3500	551	787	2.3
820° C				
Unexposed	----	363	529	14
He	3500	272	355	32.9
H_2 + 1% CO_2	3500	273	346	29.5

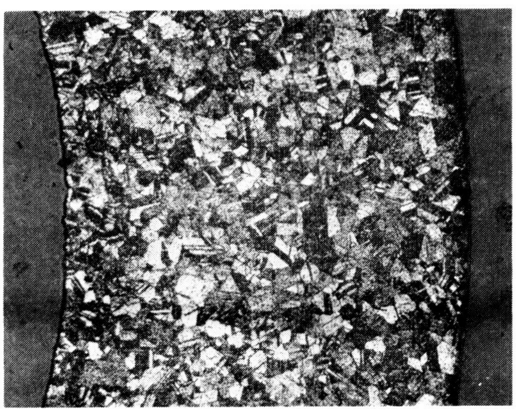
TABLE XIII. - SUMMARY OF RESULTS OF TENSILE PROPERTIES OF 820° C ENDURANCE TESTED TUBES IN EITHER H_2 + 1% CO_2 or He

Alloy	Rig environment	Average rupture time, hr	Permeability coefficient, ¢, after 250 hr exposure x 10^{-6} cm^2/sec MPa	Tensile property change as percent of as-received properties							
				15 MPa - 820° C				21 MPa - 820° C			
				Ultimate strength		Elongation percent		Ultimate strength		Elongation percent	
				RT	820° C	RT	820° C	RT	820° C	RT	820° C
N-155	He	606	--------	-11	-16	-24	+135	---	---	---	----
	H_2	1240	0.37	-13	-13	(a)	+104	---	---	---	----
A-286	He	399	--------	-20	-12	-70	+72	---	---	---	----
	H_2	419	.57	-25	-14	-78	+52	---	---	---	----
Incoloy 800	He	118	--------	+3	-0.01	-23	-14	---	---	---	----
	H_2	[c]130R	.76 (100 hr)	-0.1	.06	-56	-16	---	---	---	----
19-9DL	He	601	--------	-32	-31	(a)	-31	---	---	---	----
	H_2	601	5.05	-45	-20	-92	-47	---	---	---	----
CG-27	He	[c]3500R	--------	-44	-28	-45	204	-40	-33	-81	+135
	H_2	3500R	.13	-46	-33	-38	118	-42	-35	-84	+111
W-545	He	2777	--------	-45	-64	-75	(a)	---	---	---	----
	H_2	2372	3.80	-74	-38	-91	-78	---	---	---	----
12RN72	He	1598	--------	(b)	(b)	(b)	(b)	---	---	---	----
	H_2	[c]3500R	.31	(b)	(b)	(b)	(b)	---	---	---	----
12RN72(cw)	He	1374	--------	(b)	(b)	(b)	(b)	---	---	---	----
	H_2	1200	.18	(b)	(b)	(b)	(b)	---	---	---	----
253MA	He	1273	--------	-16	-17	-65	-20	---	---	---	----
	H_2	[c]2099R	2.47	-5	-10	-58	+16	---	---	---	----
Sanicro 31H	He	154	--------	-.5	-1	-46	-22	---	---	---	----
	H_2	[c]165R	.99 (100 hr)	+.3	-10	(a)	-27	---	---	---	----
Sanicro 32	He	878	--------	-7	(a)	(a)	(a)	---	---	---	----
	H_2	[c]2919R	.85	-42	-7	-95	(a)	---	---	---	----
Inconel 601		567	--------	-19	+1	+5	16	---	---	---	----
		[c]890R	.15	-12	-3	+12.5	14				
Inconel 625	He	2856	--------	+3	+13	-41.5	(a)	---	---	---	----
	H_2	[c]3500R	.33	-3	+11	(a)	(a)	---	---	---	----
Inconel 718(wd)	He	514	--------	+9	-12	-30	+121	---	---	---	----
	H_2	765	.15	+2	-35	-38	+205	---	---	---	----
Inconel 718(a)	He	1672	--------	-20	-44	-51	+148	---	---	---	----
	H_2	1925	.23	-27	-41	(a)	+108	---	---	---	----
Inconel 750	He	796	--------	-30	-30	-73	+86	---	---	---	----
	H_2	570	.18	-54	-36	-78	(a)	---	---	---	----
Pyromet 901	He	[c]3500R	--------	-10	-44	-73	-50	---	---	---	----
	H_2	[c]3500R	.064	-52	-41	-78	-21	---	---	---	----
HS-188	He	1392	--------	-13	-12	(a)	-12	---	---	---	----
	H_2	1785	.69	-6	-16	(a)	-14	---	---	---	----

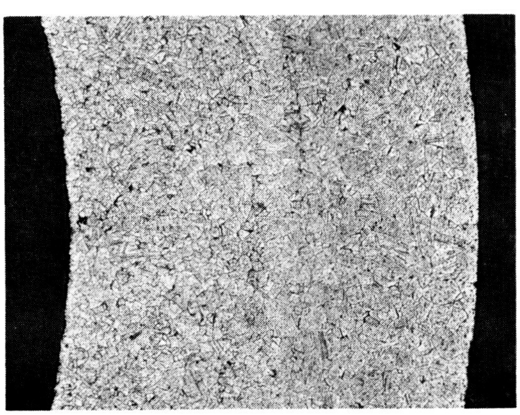
[a]Broke outside gage mark.
[b]Insufficient material for unexposed tensile test.
[c]Tube removed from rig prior to rupture.



Unexposed

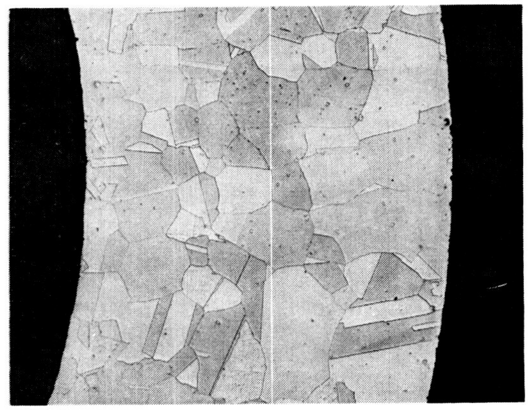


H_2 + 1% CO_2 exposed



He-exposed

(a) N-155.



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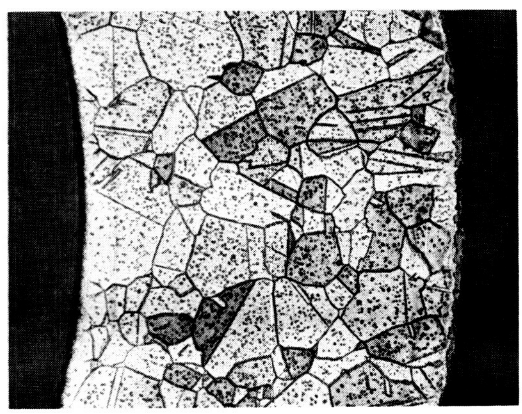
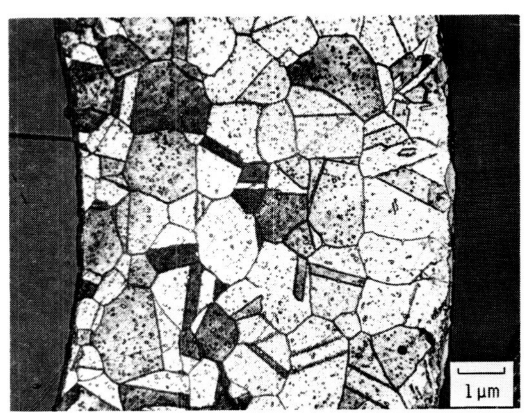


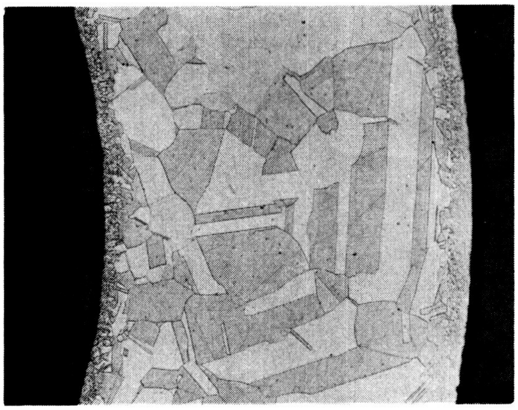
H_2 + 1% CO_2 exposed



He-exposed

(b) A-286.

Figure 1. - Microstructures of hairpin tubes before and after rig exposure.



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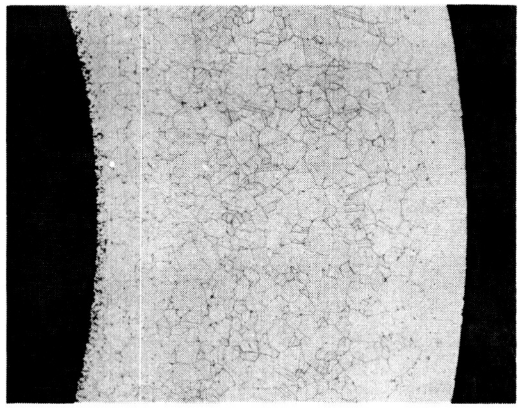
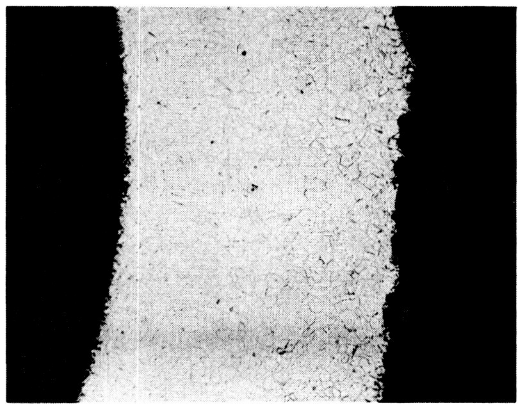
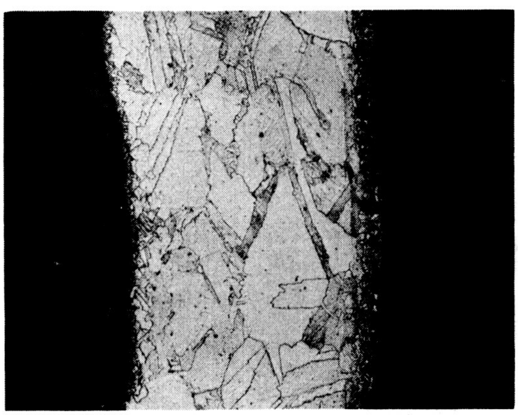


Unexposed

H_2 + 1% CO_2 exposed

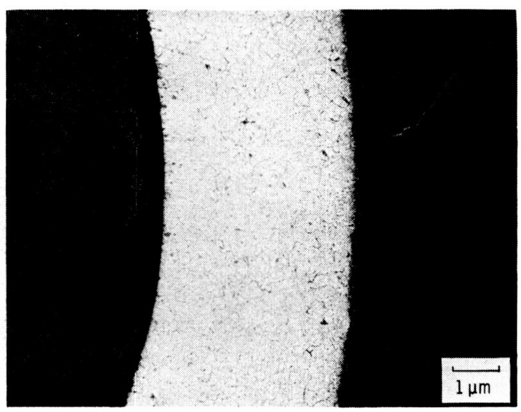


H_2 + 1% CO_2 exposed



He-exposed

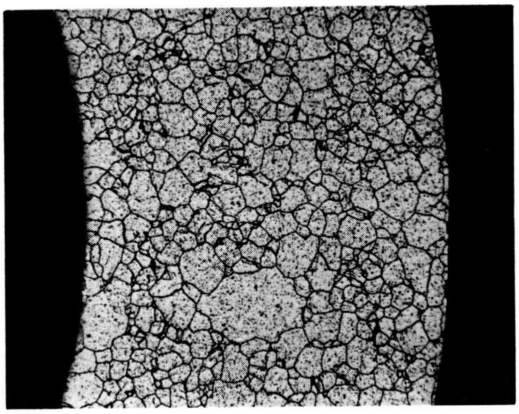
(c) Incoloy 800.



He-exposed

(d) 19-9DL

Figure 1. - Continued.



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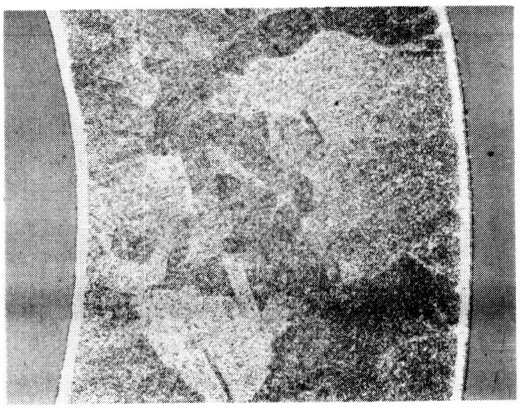
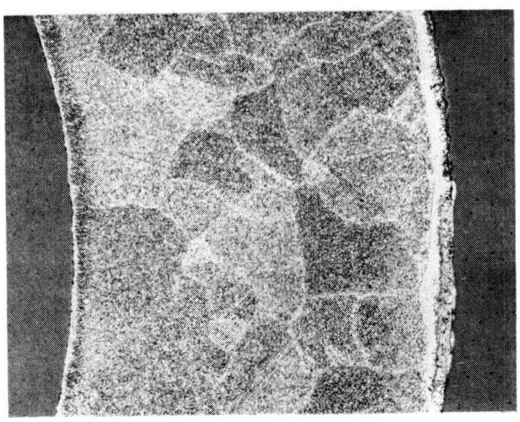
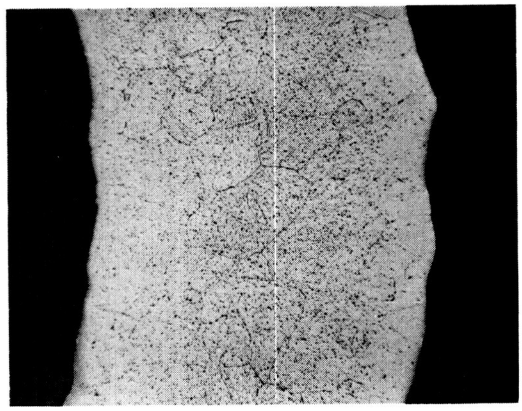


H_2 - 1% CO_2 exposed



He-exposed

(e) CG-27.



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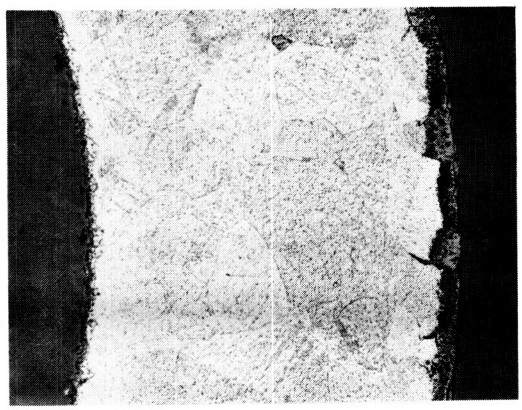
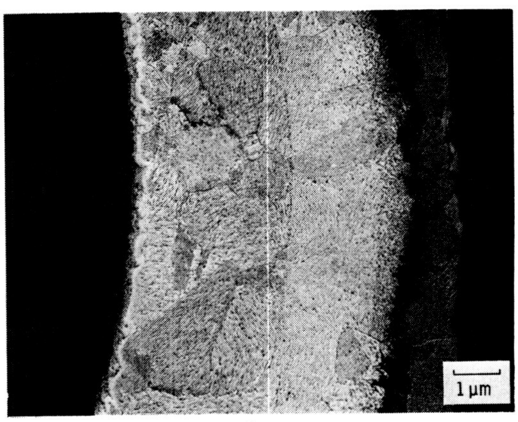


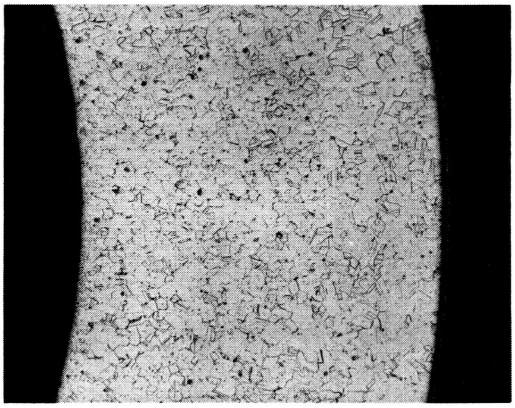
H_2 - 1% CO_2 exposed



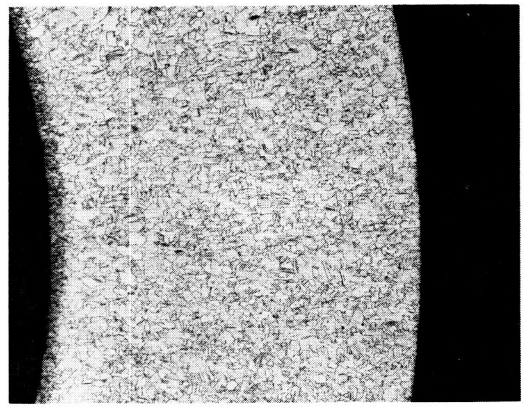
He-exposed

(f) W-545.

Figure 1. - Continued.



Unexposed



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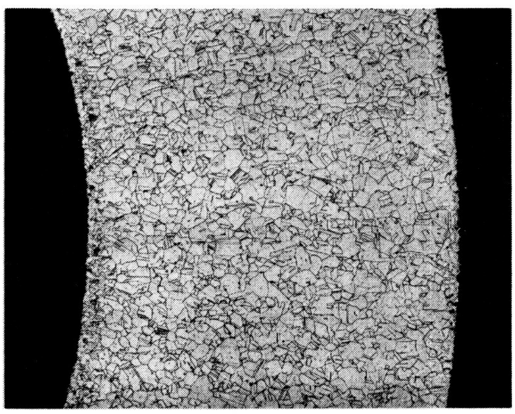
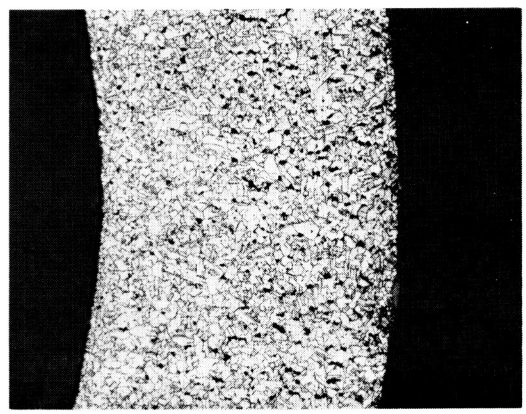
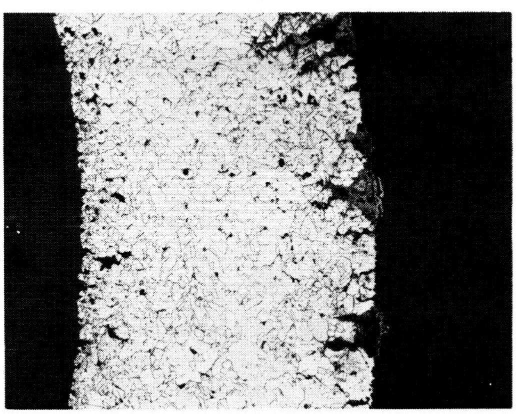


H_2 - 1% CO exposed

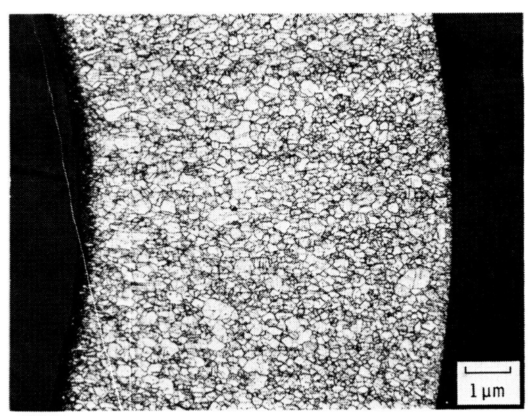


H_2 - 1% CO_2 exposed



He-exposed

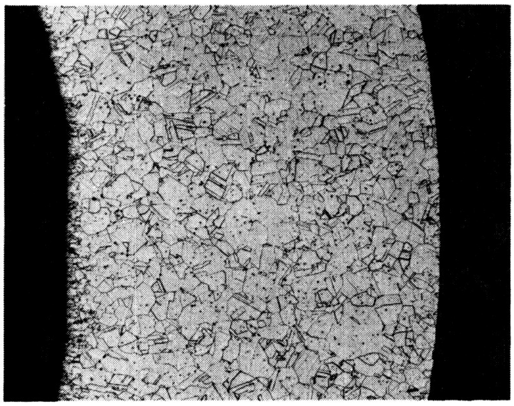
(g) 12RN72



He-exposed

(h) 12RN72(cw)

Figure 1. - Continued.



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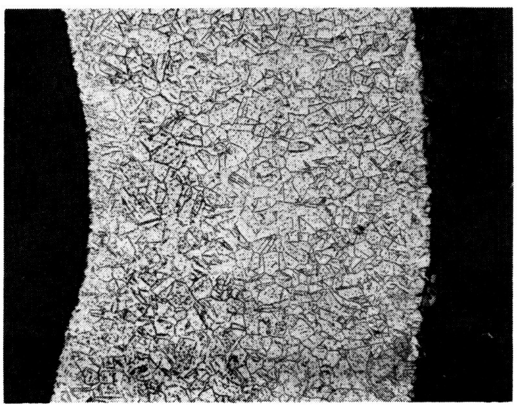
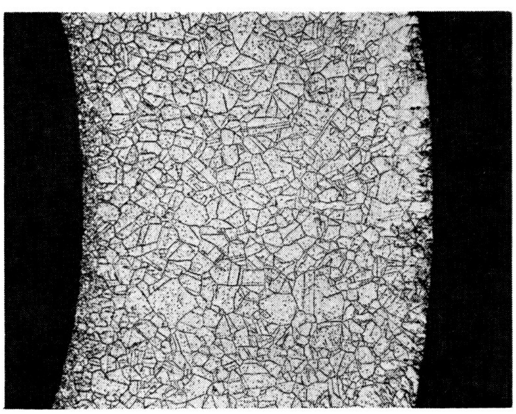
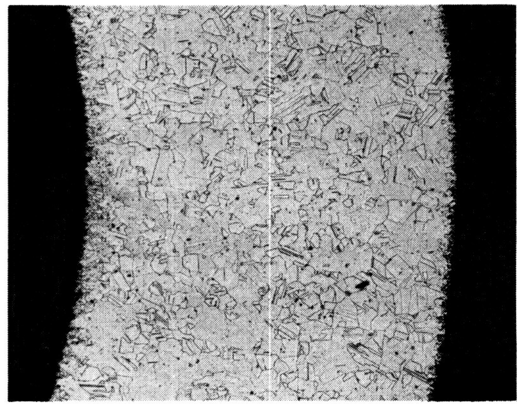


$H_2 + 1\% \ CO_2$ exposed

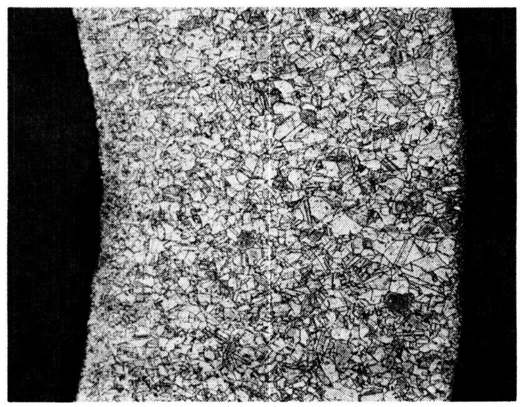


He-exposed

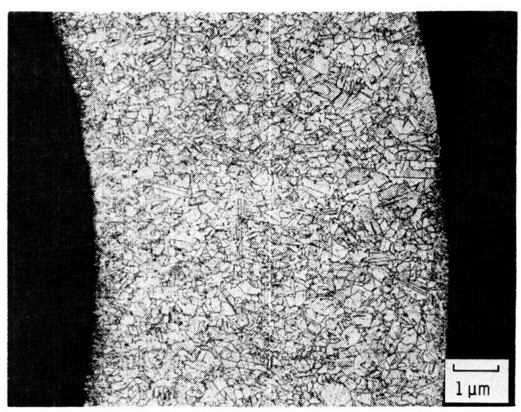
(i) 253MA



Unexposed



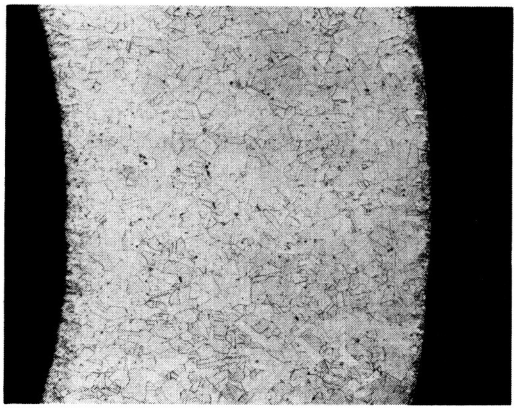
$H_2 - 1\% \ CO_2$ exposed



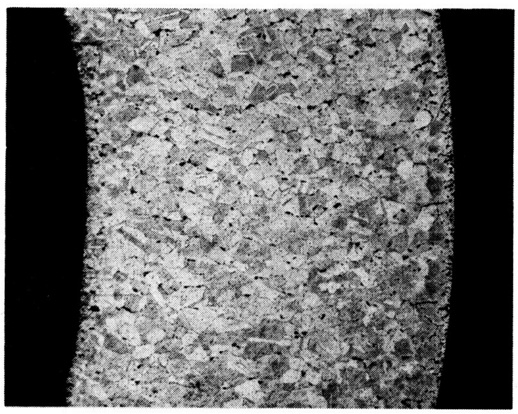
He-exposed

(j) Sanicro 31H

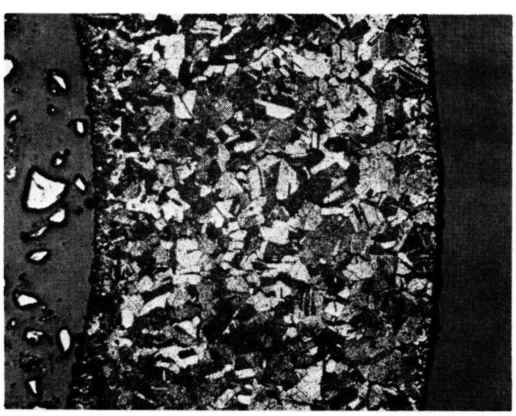
Figure 1. - Continued.



Unexposed

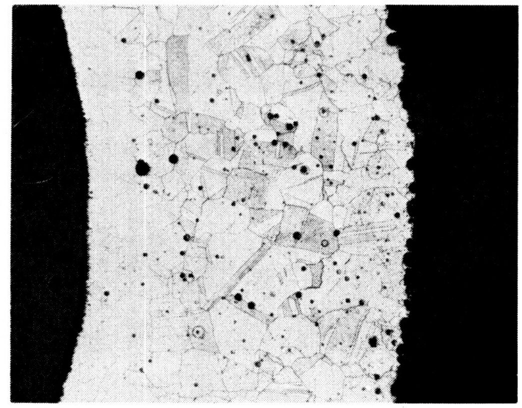


H_2 + 1% CO_2 exposed

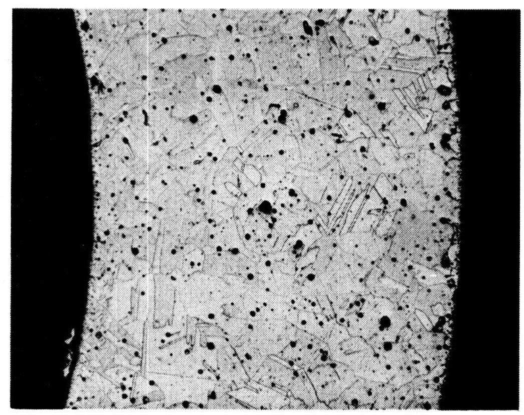


He-exposed

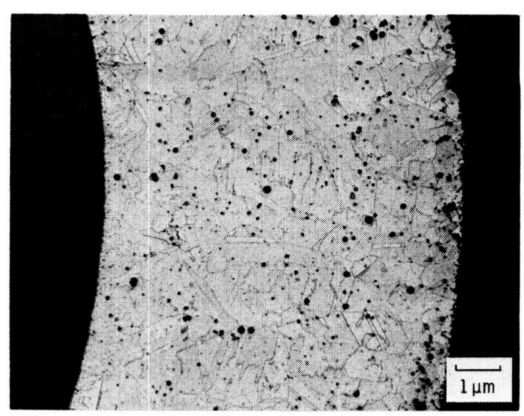
(k) Sanicro 32.



Unexposed



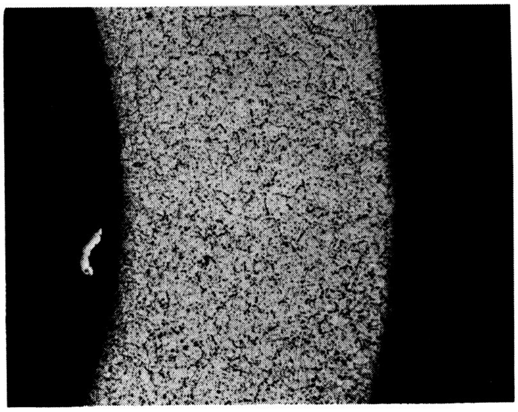
H_2 + 1% CO_2 exposed



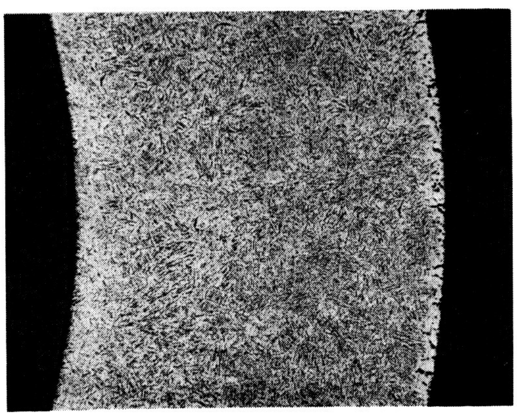
He-exposed

(l) Inconel 601.

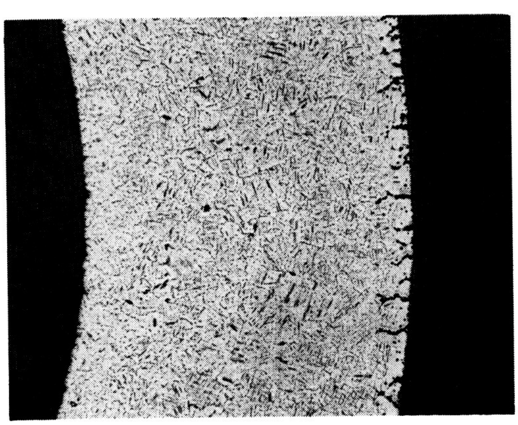
Figure 1. - Continued.



Unexposed

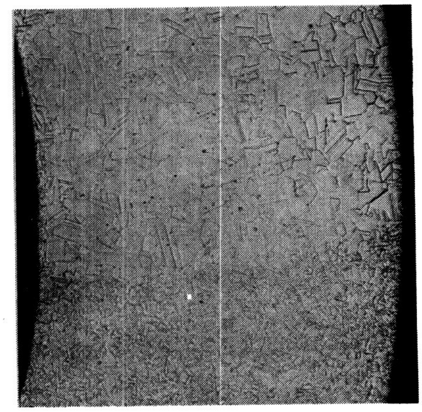


H_2 + 1% CO_2 exposed

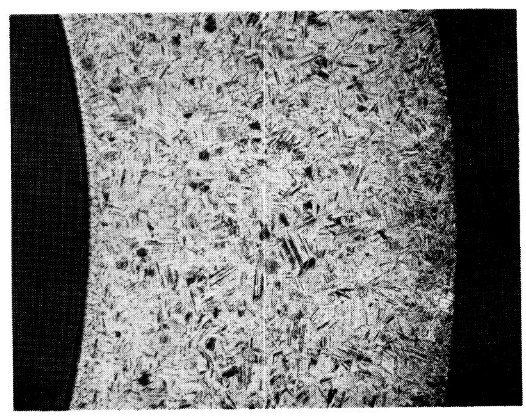


He-exposed

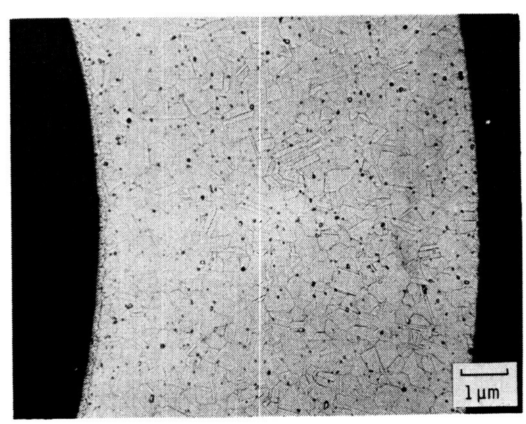
(m) Inconel 625.



Unexposed



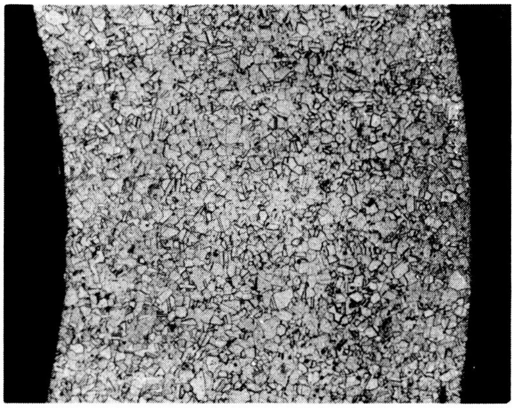
H_2 + 1% CO_2 exposed



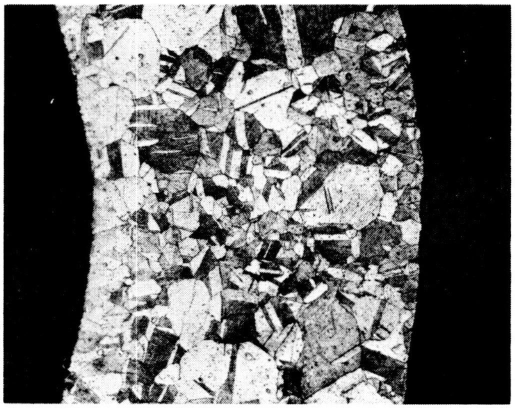
He-exposed

(n) Inconel 718(wd).

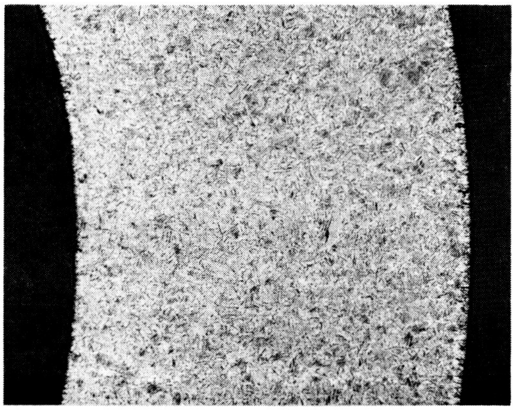
Figure 1. - Continued.



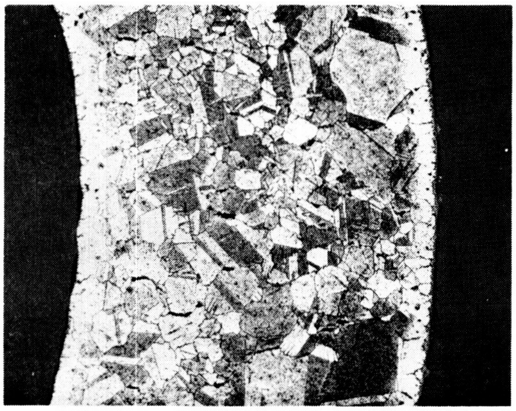
Unexposed



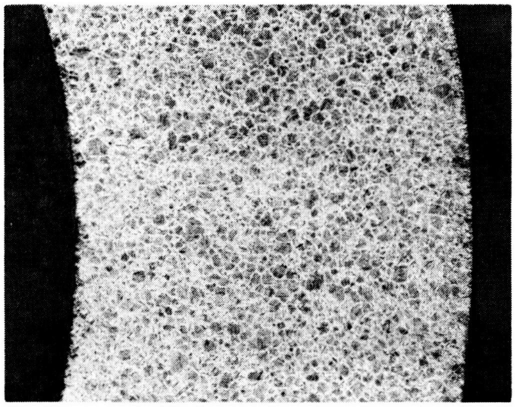
Unexposed



H_2 + 1% CO_2 exposed

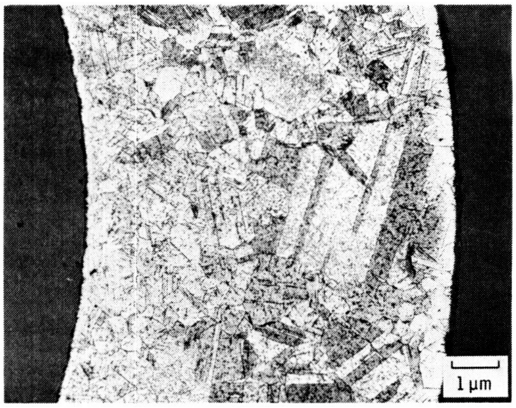


H_2 + 1% CO_2 exposed



He-exposed

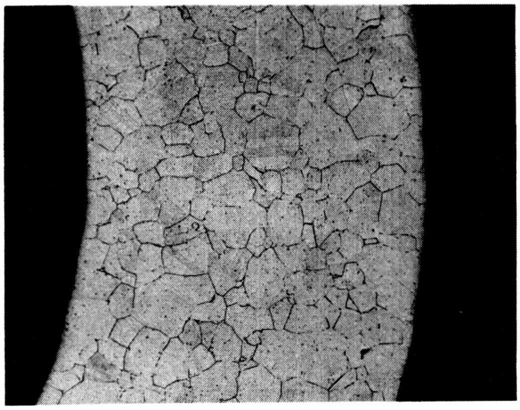
(o) Inconel 718(a).



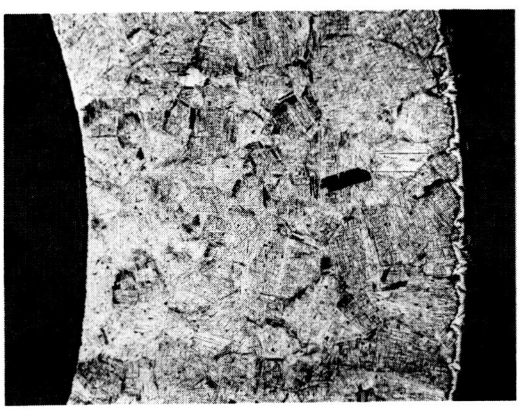
He-exposed

(p) Inconel 750.

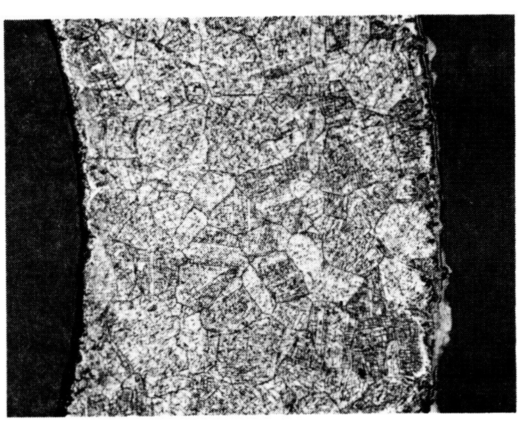
Figure 1. - Continued.



Unexposed

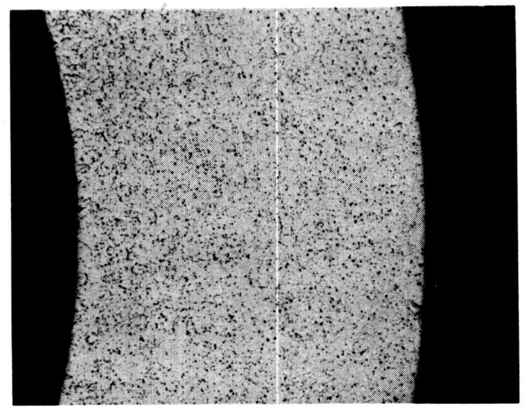


H_2 + 1% CO_2 exposed

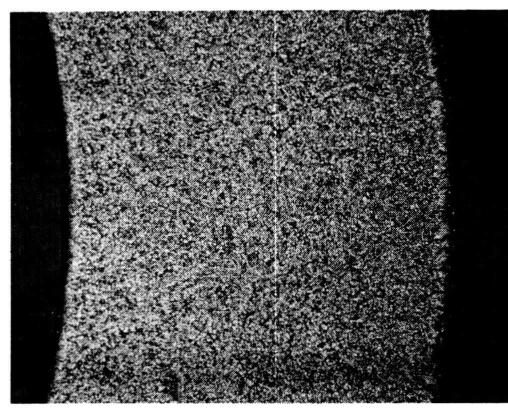


He-exposed

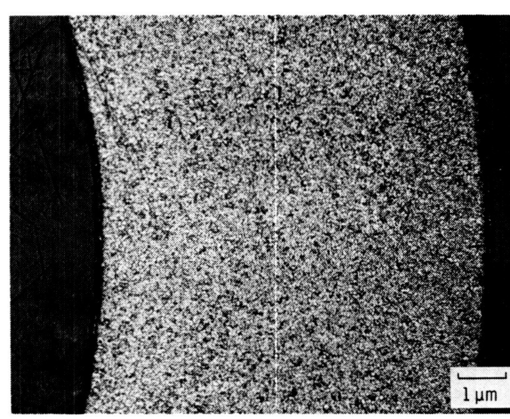
(q) Pyromet 901.



Unexposed



H_2 + 1% CO_2 exposed



He-exposed

(r) HS - 188.

Figure 1. - Concluded.

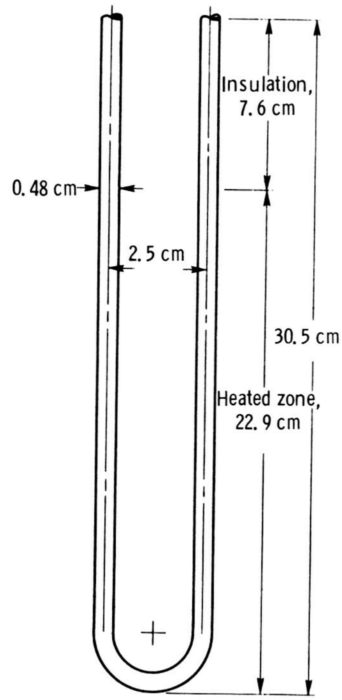


Figure 2. - Hairpin test specimen (not to scale).

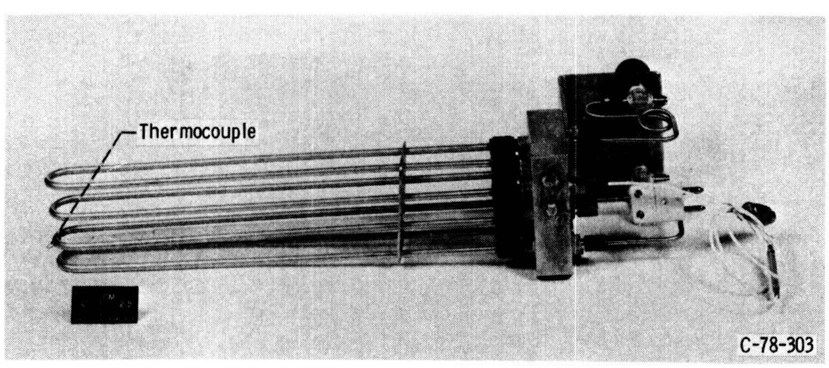


Figure 3. - Test module for Stirling engine simulator materials test rig.

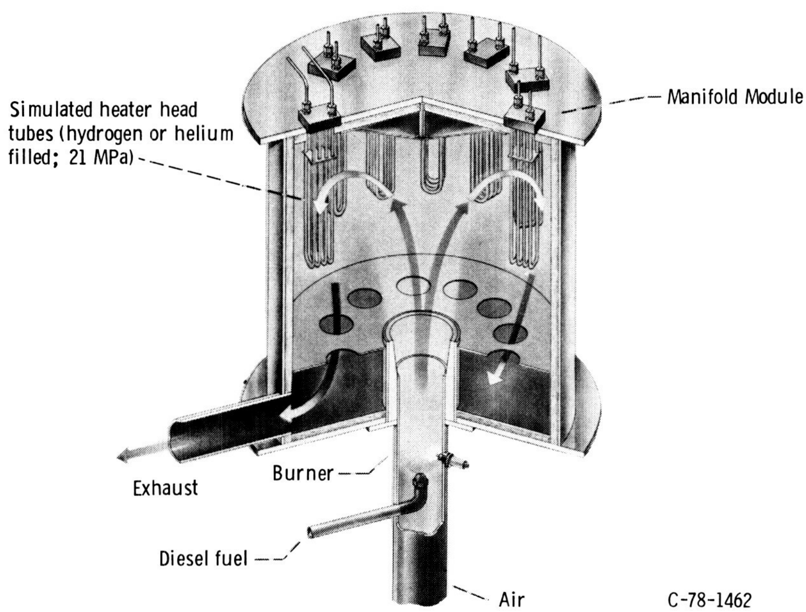


Figure 4. - Schematic representation of Stirling engine simulator materials test rig.

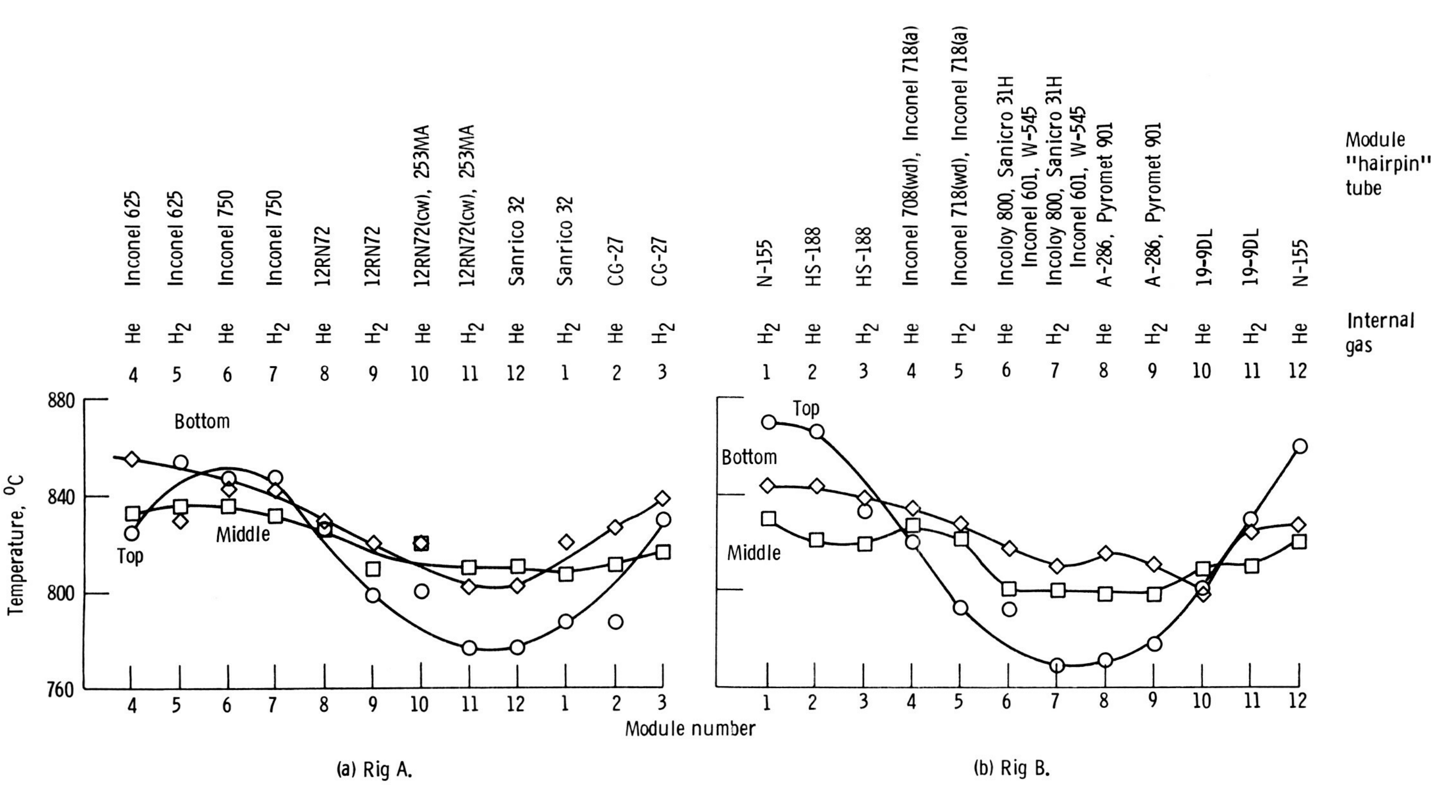


Figure 5. - Temperature profile in Stirling simulator engine test.

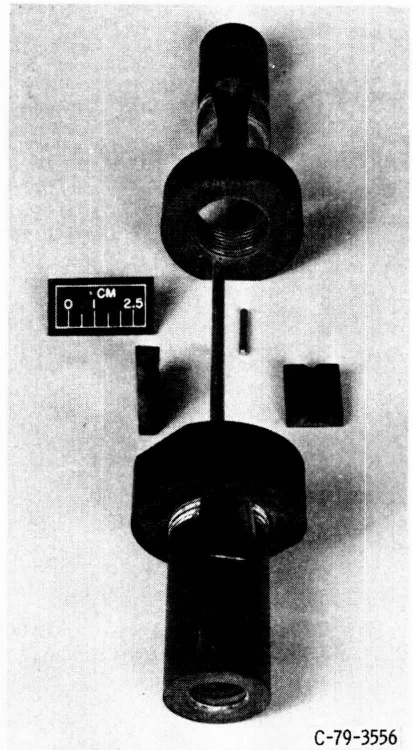


Figure 6. - Tube tensile specimen and grips.

Figure 7. - Apparent hydrogen permeability coefficient Φ versus rig exposure time for iron base alloys tested at 820° C with H_2 + 1% CO_2 at 15 MPa.

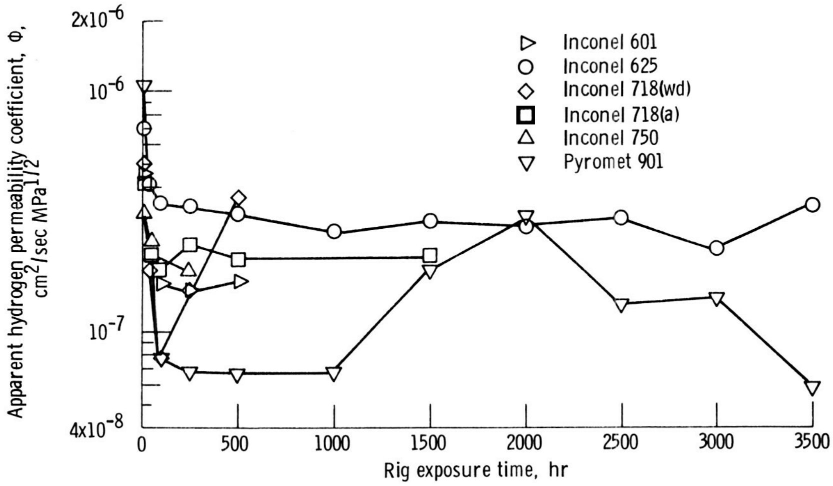


Figure 8. - Apparent hydrogen permeability coefficient Φ versus rig exposure time for nickel base alloys tested at 820^0 C with H_2 + 1% CO_2 at 15 MPa.

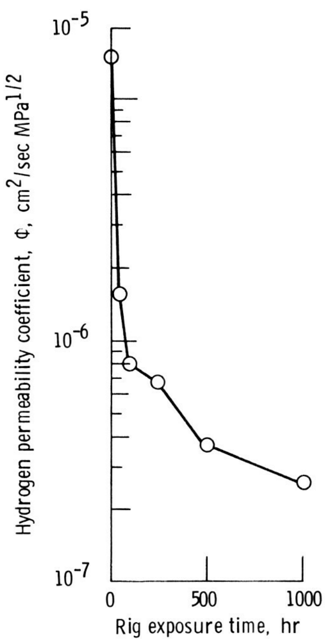


Figure 9. - Apparent hydrogen permeability coefficient Φ versus rig exposure time for cobalt-base alloy HS-188 tested at 820^0 C with H_2 + 1% CO_2 at 15 MPa.

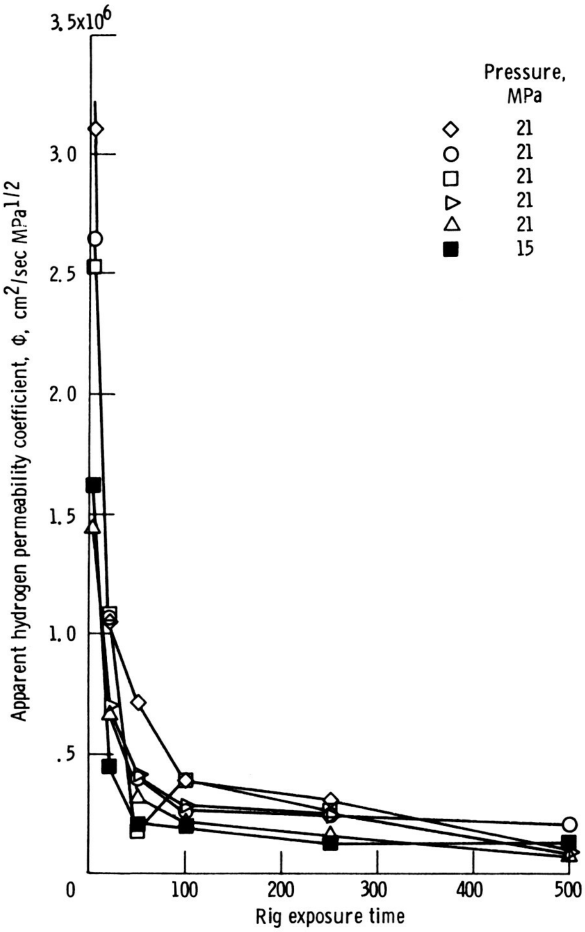


Figure 10. - Apparent hydrogen permeability coefficient for CG-27 as a function of rig exposure time. Temperature, 820^{0} C.

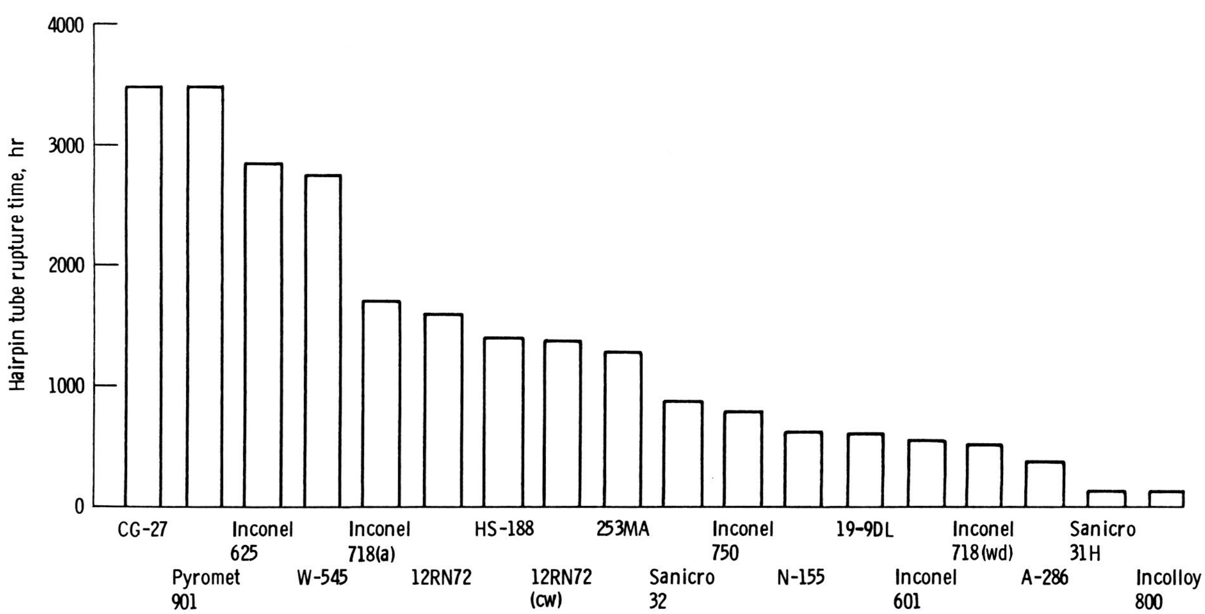


Figure 11. - Ranking of hairpin tubes according to rupture lives when pressurized with 15 MPa helium at 820^{0} C.

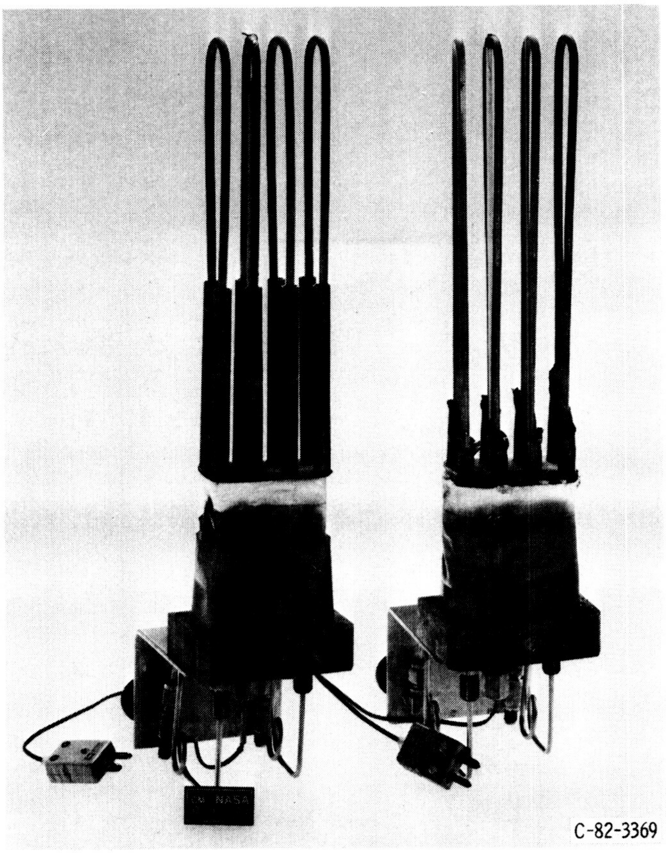


Figure 12. - Modules with normal and defective heat-shield.

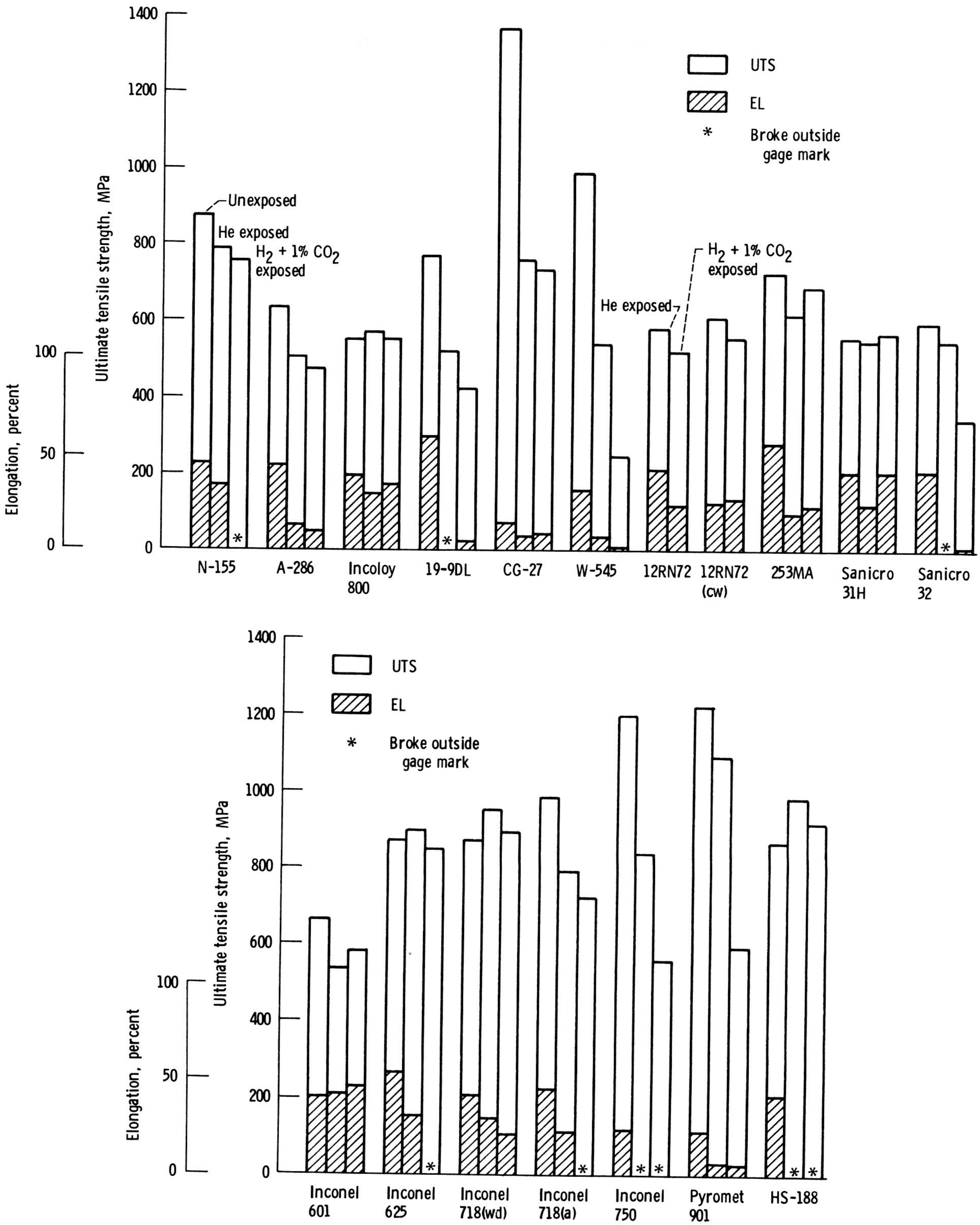
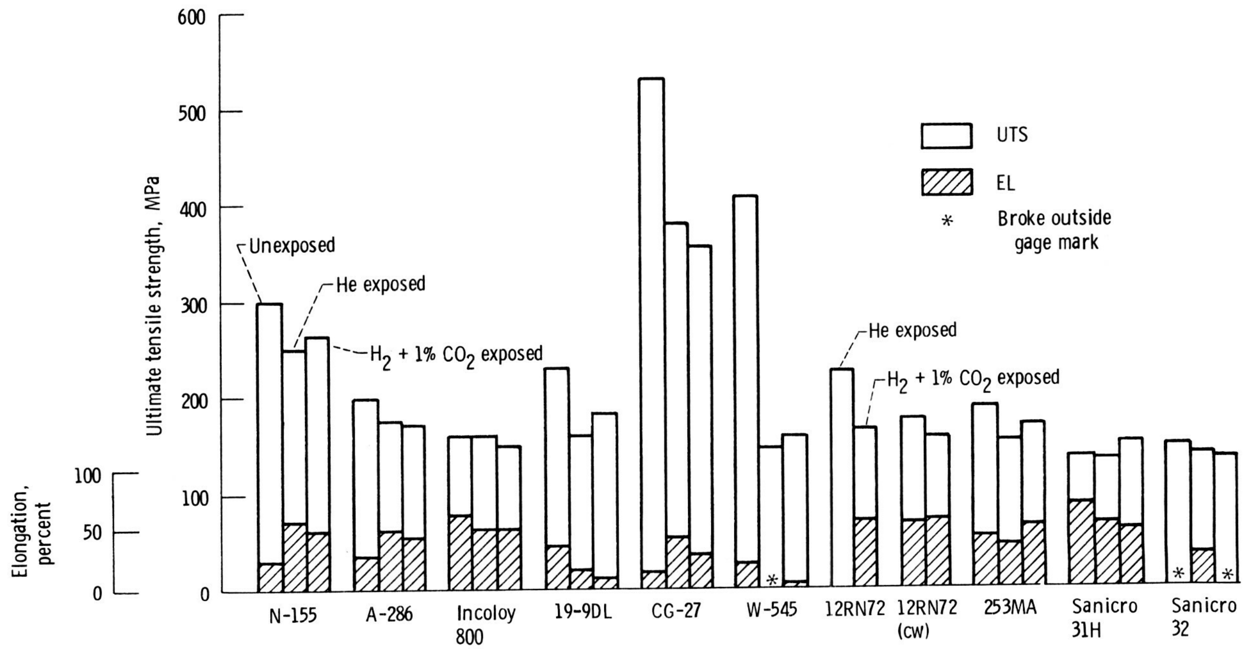


Figure 13. - Room temperature tensile properties of tubing before and after endurance testing at 820° C for 3500 hr and at 15 MPa. (No "unexposed" tensile tests were performed on 12RN72 tubes because of lack of material.)



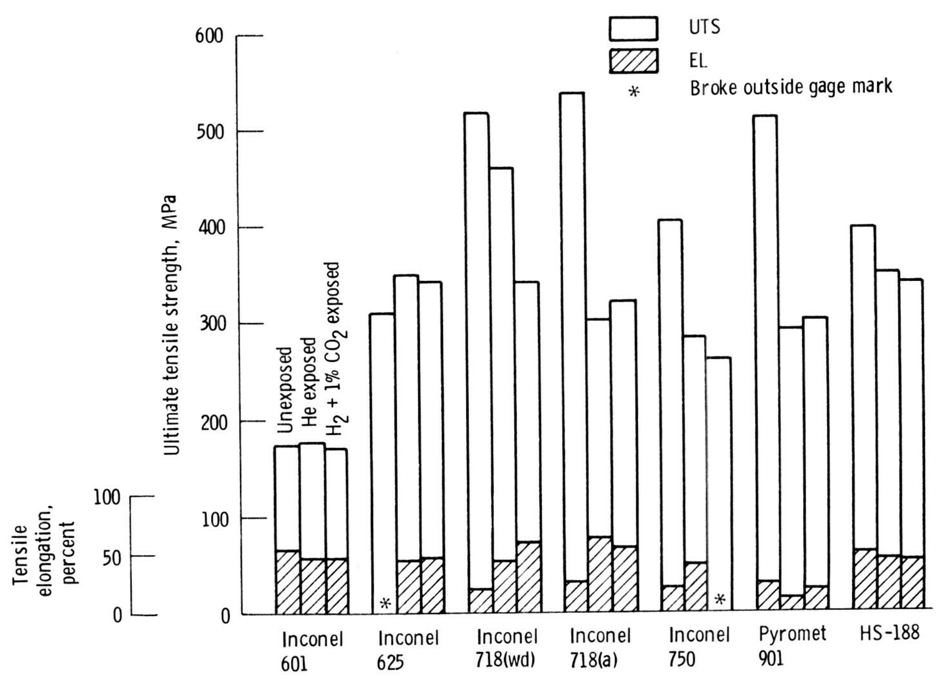


Figure 14. - 820° C tensile properties of tubing alloys before and after endurance testing at 820° C for 3500 hr and at 15 MPa. (No "exposed" tensile tests were performed on 12RN72 tubes because of lack of material.)

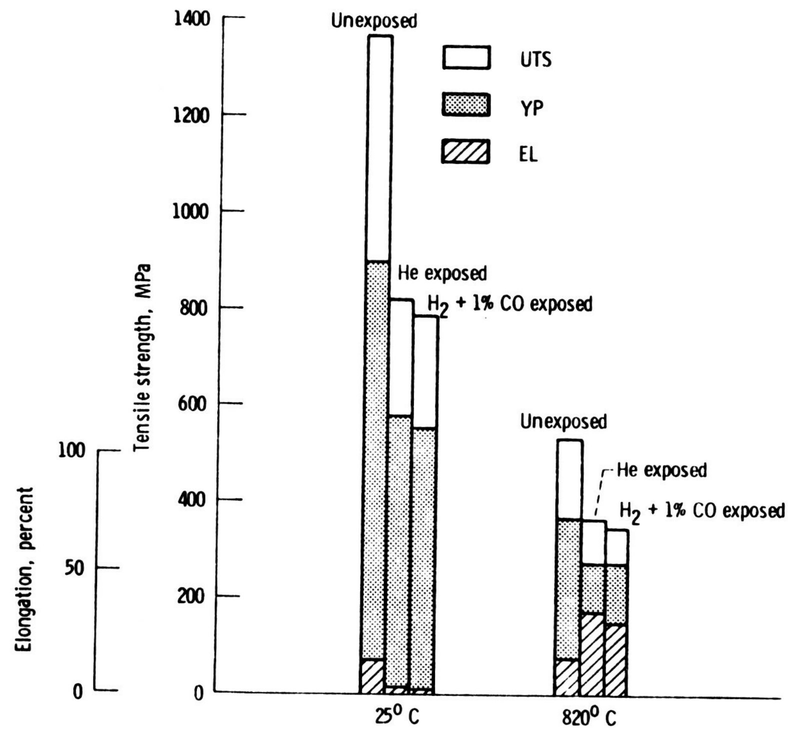


Figure 15. - Tensile properties of CG-27 before and after endurance testing for 3500 hr at 21 MPa and at 820^0 C.

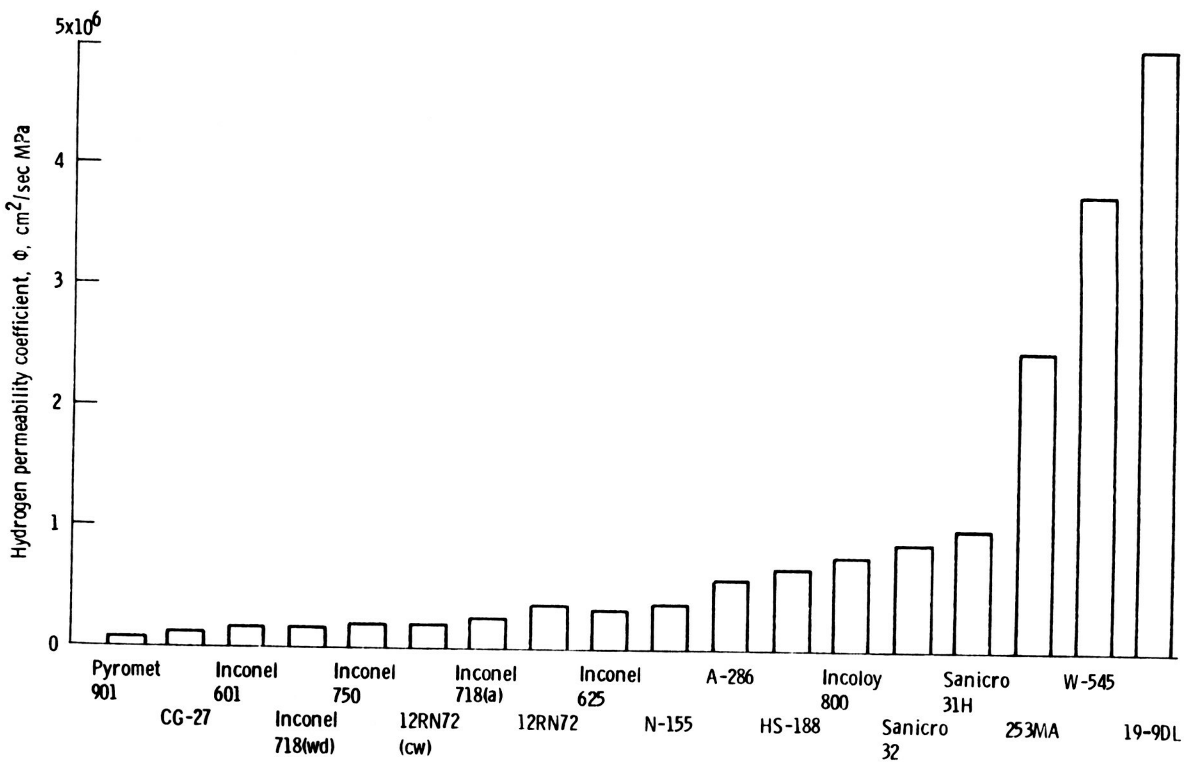


Figure 16. - Apparent hydrogen permeability coefficient at 250 hr for tubing material endurance tested at 820^0 C and 15 MPa.

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16. Abstract
The heater head tubes of current prototype automotive Stirling engines are fabricated from alloy N-155, an alloy which contains 20 percent cobalt. Because the United State imports over 90 percent of the cobalt used in this country and resource supplies could not meet the demand imposed by automotive applications of cobalt in the heater head (tubes plus cylinders and regenerator housings), it is imperative that substitute alloys free of cobalt be identified. The research described herein focused on the heater head tubes. Sixteen alloys (15 potential substitutes plus the 20 percent Co N-155 alloy) were evaluated in the form of thin wall tubing in the NASA Lewis Research Center Stirling simulator materials diesel fuel fired test rigs. Tubes filled with either hydrogen doped with 1 percent CO_2 or with helium at a gas pressure of 15 MPa and a temperature of 820° C were cyclic endurance tested for times up to 3500 hr. Results showed that two iron-nickel base superalloys, CG-27 and Pyromet 901 survived the 3500 hr endurance test. The remaining alloys failed by creep-rupture at times less than 3000 hr, however, several other alloys had superior lives to N-155. Results further showed that doping the hydrogen working fluid with 1 vol % CO_2 is an effective means of reducing hydrogen permeability through all the alloy tubes investigated.

17. Key Words (Suggested by Author(s))
Stirling engine; Permeation; Hydrogen; Rupture; Tensile

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