NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
GAS TURBINE AND
JET ENGINE FUELS

PROGRESS REPORT NO. 4

NAVY CONTRACT N 600 (19)-58219

NOVEMBER, 1962

PHILLIPS PETROLEUM COMPANY

RESEARCH AND DEVELOPMENT DEPARTMENT

BARTLESVILLE, OKLAHOMA
SUMMARY

The fourth bimonthly period under Navy Contract N600 (19)-58219 has been spent continuing the study of the effects of sulfur in jet fuels on the durability of jet engine "hot section" components. The effort during this period has involved evaluation of the tensile strengths of Udimet 500, Waspalloy, Haynes Alloy 25, Hastelloy R-235 and René 41 simulated turbine inlet guide vanes following 12 hours exposure to sulfur-free exhaust gases at 2000 F in the Phillips 2-Inch Research Combustor. The results of these "after exposure" tensile tests, when compared to the "before exposure" values, showed that: (1) Hastelloy R-235 and Waspalloy were unaffected in tensile strength by exposure, (2) Udimet 500 and René 41 decreased significantly in tensile strength during exposure, (3) tensile results on Haynes Alloy 25 are in doubt due to possible premature fracture believed attributable to a toolmark inadvertently placed in the reduced cross section area of the specimen (a repeat test is planned), (4) all alloys showed a marked loss in ductility after exposure - Hastelloy R-235 suffering the least, Waspalloy the most, (5) no correlation between tensile loss and metal loss was observed.

Some time was also spent during this period reviewing certain recent literature on the oxidation of SO$_2$ to SO$_3$. This has indicated that: (1) very little SO$_2$ is converted to SO$_3$ at temperatures typical of those existing in jet engine combustion and turbine sections, (2) the oxidation of SO$_2$ to SO$_3$ is catalyzed quite markedly by the oxides of chromium and iron, both of which are plentiful in jet engines - this is significant only below about 1700 F, (3) significant conversion of SO$_2$ to SO$_3$ might occur in lower temperature zones such as tailpipes and (idle) afterburners, suggesting the possibility of greater sulfur attack on these components than on "hot section" components, (4) sulfur corrosion of combustor liners and turbine blades would not appear to be attributable to SO$_3$. 

I. INTRODUCTION

The fourth bimonthly period under Navy Contract N600 (19)-58219 has been spent continuing the study of the effects of sulfur in jet fuels on the durability of engine "hot section" components. The effort during this period has involved evaluation of the tensile strengths of Udimet 500, Waspalloy, Haynes Alloy 25, Hastelloy R-235 and René 41 simulated turbine inlet guide vanes following 12 hours exposure to sulfur-free exhaust gases at 2000°F in the Phillips 2-Inch Research Combustor. Metal loss data on these specimens have previously been reported in Progress Report No. 3 (3) and tensile strength data before exposure were reported in Progress Report No. 2 (2).

In addition to the test work mentioned above some time has been spent during this reporting period reviewing several recent publications on sulfur chemistry and its role in corrosion and deposits and the implications of the information reported in these papers on the present work. The more salient points will be discussed herein.

II. TEST METHODS AND APPARATUS

The Phillips 2-Inch Research Combustor and associated equipment used in preparing the combustion gas-exposed simulated turbine inlet guide vane specimens have been described in previous reports (1)(2)(3). No attempt will be made to describe this apparatus here. This combustor was operated
under conditions simulating sea level takeoff and low altitude cruise
\((P = 350 \text{ in Hg abs}, V = 100 \text{ f.p.s.}, \text{IAT} = 700 \ F, F/A = 0.020)\) of a 12:1 compression ratio turbojet. These conditions resulted in exhaust gas temperature (turbine inlet temperature) of approximately 2000 \(F\). Simulated turbine inlet guide vanes of the configuration shown in Figure 1 were placed at a position approximately six inches down stream from the combustor section. The duration of exposure of the pair of specimens was twelve hours whereupon they were removed and evaluated for loss of metal. These data were reported previously (3).

Unexposed specimens of each alloy were fabricated into the shape shown in Figure 2 and their tensile strengths determined using an Instron Model TTC testing machine operated at a crosshead travel of 0.1 inch per minute. Gage length was one inch. Tensile data on these unexposed samples were also reported previously (2). During the current reporting period the specimens subjected to 12 hours exposure in the combustor tests (using the isoparaffinic base fuel only) have been fabricated into the same shape illustrated in Figure 2 and their tensile strengths determined by exactly the same procedure using the same testing machine. These data afford an estimate of the loss in tensile strength of these alloys during 12 hours exposure to the exhaust gases derived from burning of the sulfur-free base fuel. Future testing will duplicate these runs using the same base fuel contaminated with 1.0 per cent sulfur for evaluation of the effect of sulfur on tensile strength as well as metal loss.

III. DISCUSSION OF EXPERIMENTAL RESULTS

The results of tensile tests on the simulated turbine guide vane specimens before and after 12 hours exposure in the combustor operating on a JP-5 type isoparaffinic base fuel are shown in the tabulation below and in
the stress-strain curves of Figures 3, 4, 5, 6, and 7:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tensile Strength Before Exposure, psi</th>
<th>Tensile Strength After 12 Hr. Exposure (Base Fuel), psi</th>
<th>Change in Tensile Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Udimet 500</td>
<td>158,380</td>
<td>125,425</td>
<td>-30,955</td>
</tr>
<tr>
<td>Waspalloy</td>
<td>120,650</td>
<td>124,415</td>
<td>+3,765</td>
</tr>
<tr>
<td>Haynes Alloy 25</td>
<td>146,750</td>
<td>117,135</td>
<td>-29,615</td>
</tr>
<tr>
<td>Hastelloy R-235</td>
<td>130,300</td>
<td>128,470</td>
<td>-4,830</td>
</tr>
<tr>
<td>René 41</td>
<td>136,000</td>
<td>119,400</td>
<td>-16,600</td>
</tr>
</tbody>
</table>

The loss in tensile strength observed for Hastelloy R-235 and the gain for Waspalloy are not believed to be significant when compared to the error which can reasonably be expected. The magnitude of the tensile losses for Udimet 500, Haynes Alloy 25 and René 41 are significant, however. The "after exposure" value obtained on Haynes Alloy 25 is, however, subject to doubt since there are indications that failure occurred at a point coinciding with a toolmark inadvertently placed on the specimen within the reduced section. A second specimen will be available following photomicrographic examination and will be used to run a check test on the "after exposure" tensile value for this alloy.

In addition to changes in tensile strength it will be observed from Figures 3, 4, 5, 6, and 7 that all of the alloys suffered a marked loss in ductility after 12 hours exposure in the combustor, as shown by the fact that all specimens failed at much lower strains than before exposure - Hastelloy R-235 suffering the least loss in ductility and Waspalloy the most (Haynes Alloy 25 is indicated as least ductile but, as pointed out above, this test is subject to doubt). Of interest also is the fact that, in general, the after exposure curves followed the "before exposure" curves within the elastic range. One explanation of the decrease in ductility with loss in strength would seem
to lie in the possibility of intergranular oxidation during exposure in the combustor. It would seem that these oxides might bestow little overall change in strength during elastic deformation, but be able to withstand plastic deformation, thus resulting in early failure in terms of both strain and stress. This is purely speculation at this time, of course, but further metallurgical examinations will be carried out in the future in an attempt to establish just what did occur in service. At any rate, it does appear at this time that two of the superalloys, Udimet 500 and René 41, were degraded in tensile strength during 12 hours exposure to 2000 F oxygen-rich exhaust gases.

Consideration has been given to a possible correlation between tensile strength losses and the metal losses reported in Progress Report No. 3 (3). No relationship was found to exist.

IV. DISCUSSION OF RECENT PUBLICATIONS ON SULFUR CHEMISTRY AND ITS ROLE IN CORROSION

As previously mentioned some time has been spent during the present reporting period reviewing recent literature in the field of sulfur chemistry and sulfur corrosion. The main objective of this review was to attempt to establish from the literature whether or not oxidation of fuel sulfur contaminants to form sulfur trioxide (as opposed to formation of sulfur dioxide) occurs to a sufficient extent under conditions existing in jet engine combustion systems to be considered as a significant source of corrosion.

Two recent, extensive reviews, (4)(5), which cover the subject in detail, regard those reactions resulting in the formation of SO$_3$ as most important from the corrosion standpoint. As pointed out in these and many other papers, SO$_3$ will readily combine with any water vapor that may be present to form sulfuric acid, which is, of course, very strongly corrosive.
This effect could be of some significance in jet aircraft operating with water injection or through very moist atmospheres, assuming that SO₃ is present under typical jet engine operating conditions.

Levy and Merryman (6) have shown data on the effect of temperature upon the equilibrium conversion of SO₂ and SO₃ which indicates that very little SO₃ is formed at temperatures typical of those existing in jet engine combustion and turbine sections under cruising conditions. These data are shown graphically in Figure 8 wherein it may be seen that conversion of SO₂ to SO₃ is very slight above 1700 F. In earlier work conducted by this laboratory under Navy contract, combustion liner wall temperatures of 1800 F and above were observed under conditions simulating sea level take-off and low altitude cruise, of a 12:1 compression ratio engine, thus indicating that normal jet engine "hot section" temperatures are above the level at which SO₃ is produced.

Levy and Merryman (6) have also shown data from the literature on the conversion of SO₂ to SO₃ in the presence of several catalysts including Cr₂O₃ and Fe₂O₃ - two oxides which are present in jet combustion systems. These data are shown in Figure 9. Each catalyst seems to have an optimum temperature range in which it is most effective in converting SO₂ to SO₃. At low temperatures platinum is the most effective catalyst for oxidizing SO₂. A comparison of platinum with V₂O₅ shows the latter to be considerably less effective below 860 F, but at increasing temperatures the V₂O₅ catalyst passes through a maximum SO₂ conversion value (about 960 F) and at still higher temperatures, the V₂O₅ gradually approaches platinum in effectiveness. Similar curves are observed for the balance of the catalysts, all curves approaching the platinum curve at higher temperatures. However, the quantity of catalyst present is also important and since large quantities of iron and
chromium oxides are encountered in gas turbines it would appear that the 70 and 80 per cent conversion value could make these oxides important catalysts in the oxidation of SO$_2$ to SO$_3$ at 1000 to 1200 F. Again, however, it should be noted that an extrapolation of these data to typical turbine combustor and turbine inlet temperatures would indicate that little SO$_3$ is formed in these locations. However, it should be observed that considerable oxidation of SO$_2$ to SO$_3$, catalyzed most likely by oxides of the typical turbine alloying metals, could take place in lower temperature zones such as exist in jet engine tailpipes or possibly afterburners. One might then expect to observe more severe sulfur attack of these downstream components than "hot section" components. In any event, the oxidation of SO$_2$ to SO$_3$ is favored by low temperatures rather than high temperatures. It would, therefore, appear that sulfur corrosion observed to occur on combustor liners and turbine components is not attributable to SO$_3$.

V. CONCLUSIONS

Tensile strength tests conducted on simulated turbine inlet guide vane specimens following 12 hours exposure to sulfur-free exhaust gases at 2000 F in the Phillips 2-Inch Research Combustor have shown the following:

1. Hastelloy R-235 and Waspalloy appeared to be unaffected in tensile strength by exposure in the combustor.

2. Udimet 500 and Rene 41 decreased significantly in tensile strength during exposure.

3. Tensile results on Haynes Alloy 25 are in doubt due to possible premature fracture believed attributable to a toolmark inadvertently placed in the reduced cross section area of the specimen. A repeat test is planned.
4. All alloys showed a marked loss in ductility following exposure as shown by the fact that failures occurred at considerably lower strain values - Hastelloy R-235 suffering the least loss, Waspalloy the most. It is speculated that this loss in ductility may be attributable to intergranular oxidation. Attempts will be made to prove or disprove this speculation in future work.

5. No correlation between tensile loss and metal loss was observed. A review of recent literature on the oxidation of SO$_2$ to SO$_3$ has indicated the following:

1. Only very little SO$_2$ is converted to SO$_3$ at temperatures typical of those existing in jet engine combustion and turbine sections.

2. The oxidation of SO$_2$ to SO$_3$ is catalyzed quite markedly by the oxides of chromium and iron, both of which are should be present in jet engines. Again, this is significant only at temperatures below about 1700°F.

3. It appears that considerable conversion of SO$_2$ to SO$_3$, catalyzed most likely by oxides of the typical turbine alloying metals, could take place in lower temperature zones such as tailpipes and (idle) afterburners. This suggests that greater attack by sulfur might be expected on these components than "hot section" components.

4. Sulfur corrosion observed to occur on combustor liners and turbine components would not appear to be attributable to SO$_3$.

VI. OUTLINE OF PROJECTED WORK

It is planned to conduct further metallurgical examinations of the 12 hour exposed (simulated) turbine guide vane specimens during the coming reporting periods. Additionally, upon the completion of major test facility
modifications currently in progress, it is planned to extend the six hour metal durability tests on the superalloys operated with 1.0 per cent sulfur fuel on to 12 hours total duration. These combustor tests will be followed by metallurgical and mechanical properties tests as was done in the case of the tests using the sulfur-free fuel.
REFERENCES


HOLDING MAT'L: 310 SS; STRIP MAT'L.: VARIOUS TURBINE BLADING ALLOYS
SCALE: 1" = 1"

TWO 1/2" X 2 3/8" X 16 GA. TEST STRIPS PLACED IN HOLDER DURING EACH TEST

FIGURE 1
SPECIMEN HOLDER FOR PHILLIPS 2-INCH COMBUSTOR SIMULATED TURBINE INLET GUIDE VANE DURABILITY TESTS
NOTE: TENSILE SPECIMENS TO BE FABRICATED FROM 1/2 X 2 3/8 X 16 GAGE
NEW AND EXPOSED CORROSION TEST STRIPS FROM 2-INCH COMBUSTOR TESTS.

FIGURE 2
TENSILE TEST CONFIGURATION FOR TURBINE INLET GUIDE VANE
CORROSION SPECIMENS
Figure 3
Stress-strain curve for Udimet 500 before and after 12 hours exposure to sulfur-free exhaust gas @ 2000F.
FIGURE 4
STRESS-STRAIN CURVE FOR WASPALLOY BEFORE AND AFTER 12 HOURS EXPOSURE TO SULFUR-FREE EXHAUST GAS @ 2000°F

CROSSHEAD RATE = 0.1 IN/MIN
TEMP. = 70°F
MAT'L. = WASPALLOY

○ BEFORE EXPOSURE
△ AFTER 12 HR EXPOSURE @ 2000°F - BASE FUEL

T.S. (EXPOSED) = 124,415 PSI
T.S. (UNEXPOSED) = 120,850 PSI

STRAIN, %
0 20 40 60 80 100
0 20,000 40,000 60,000 80,000 100,000 120,000 140,000 160,000
STRESS, PSI
**Figure 5**

Stress-strain curve for Haynes Alloy 25 before and after 12 hours exposure to sulfur-free exhaust gas @ 2000°F.
CROSSHEAD RATE = 0.1 IN/ MIN
TEMP. = 70 F
MAT'L. = HASTELLOY R-235

○ BEFORE EXPOSURE
△ AFTER 12 HR. EXPOSURE
2000°F - BASE FUEL

T.S. (EXPOSED) = 125,470 PSI
T.S. (UNEXPOSED) = 130,300 PSI

FIGURE 6
STRESS- STRAIN CURVE FOR HASTELLOY R-235 BEFORE AND AFTER 12 HOURS EXPOSURE TO SULFUR-FREE EXHAUST GAS @ 2000°F
CROSSHEAD RATE = 0.1 IN/ MIN  
TEMP. = 70 F  
MAT'L. = RENE 41.  
  ○ BEFORE EXPOSURE  
  ▲ AFTER 12 HR EXPOSURE  
2000F - BASE FUEL  
T.S. (EXPOSED) = 119,400 PSI  
  - T.S. (UNEXPOSED) = 136,000 PSI

FIGURE 7
STRESS- STRAIN CURVE FOR RENE 41 BEFORE AND AFTER 12 HOURS EXPOSURE TO SULFUR- FREE EXHAUST GAS @ 2000F
FIGURE 8
EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONVERSION OF SO₂ TO SO₃ (6)
FIGURE 9
CONVERSION OF SO₂ TO SO₃ IN THE PRESENCE OF SEVERAL CATALYSTS (6)

NOTE: DASH LINE EXTRAPOLATION ADDED BY PRESENT AUTHOR.